

CHAPTER 1

GENERAL DATA

1-0 INTRODUCTION

Almost all the procedures in the API *Technical Data Book* require pure component physical properties. This chapter provides a collection of properties for many hydrocarbons and selected nonhydrocarbons. The compounds and the properties that were selected for inclusion in this chapter are those judged most useful for petroleum refining and associated industries. Further information on physical properties may be found in the Design Institute for Physical Properties Research (DIPPR) *Data Compilation: Tables of Properties of Pure Compounds* (8). The majority of data for the compounds in this chapter were taken from the following sources (in order of priority):

1. DIPPR Compilation (8)
2. GPA 2145-94 (13)
3. API Monograph Series (1-3)
4. TRC Tables (32-34, 39-47)
5. Previous API *Technical Date Book - Petroleum Refining* (9).

Unless otherwise indicated, predictions of hydrocarbon data were made using the current Data Book procedures. Predictions of nonhydrocarbon data were made using DIPPR Compilation (8) procedures.

In addition to the pure component data tables (Sections 1C1

through 1C4), other general information is presented in this chapter. Section 1A contains a list of constants and lists of conversion factors. Section 1B is a list of letter symbols with their definitions. Section 1C enumerates the property definitions with other pertinent information on the properties in the data tables. Note that the footnote codes in the data tables indicate whether data are predicted (P), extrapolated (T), experimental (no code), or if it is unknown whether the source is predicted or experimental (S). Codes such as C, G, K, and N provide further information for experimental data points. The key for these codes follows Table 1C4. Section 1C5 is the reference key for the properties in the data tables.

For the 1994 edition, 14 hydrocarbons and five nonhydrocarbons have been added to this chapter. The API identification numbers for the compounds that were in the previous edition have not been changed. However, the added compounds were placed in the appropriate order on the physical property tables, causing a departure from numeric order in the tables. This departure is considered necessary for maintaining consistency with the numbering used in other chapters.

The data contained in Tables 1C1.1 through 1C4.12 are also available in computer readable format on tape or disk. The data are identical except that the number of significant digits may be different.

TABLE 1A1.1
FUNDAMENTAL CONSTANTS*

Basic Constants			
Name	Symbol	Value	Units
Velocity of light (vacuum)	c	2.997925×10^8	m per sec
Avogadro constant	N_A	6.02214×10^{23}	molecules per g-mole
Planck constant	h	6.6261×10^{-27}	(ergs) (sec) per molecule
Faraday constant	F	96,485.3	coulombs per mole
Absolute temperature of the "ice" point:			
0 C	T_0 C	273.15	K
32 F	T_{32} F	491.67	deg R
Pressure-volume product for 1 mole of a gas at 0 C (32 F) and zero pressure (ideal gas)	$(pV)_{T_0}^{P=0}$	2,271.11 22.4141 2.27111×10^6 359.039 5,276.42	joules per g-mole (liters) (atm) per g-mole (cu m) (Pa) per kg-mole (cu ft) (atm) per lb-mol (cu ft) (psia) per lb-mol

Derived Constants			
Name	Symbol	Value	Units
Electronic charge	$e = \frac{F}{N_A}$	1.60218×10^{-19}	coulombs
Gas constant	$R = \frac{(pV)_{T_0}^{P=0}}{T_0}$	8.3145 1.9872 1.9859 82.058 1,545.4 10.732 62.364 0.084786 0.73024 554.99 8,314.5	joules per (g-mole) (K) g-cal per (g-mole) (K) Btu per (lb-mole) (deg R) (cu cm) (atm) per (g-mole) (K) ft-lb [force] per (lb-mole) (deg R) (psia) (cu ft) per (lb-mole) (deg R) (mm Hg) (liter) per (g-mole) (K) (kg per sq cm) (liter) per (g-mole) (K) (atm) (cu ft) per (lb-mole) (deg R) (mm Hg) (cu ft) per (lb-mole) (deg R) (Pa) (cu m) per (kg-mol) (K)
Boltzmann constant	$k = \frac{R}{N_A}$	1.38066×10^{-16}	ergs per (molecule) (K)
Second radiation constant	$C_2 = \frac{hc}{k}$	1.43877	cm-deg C

Defined Constants			
Name	Symbol	Value	Units
Standard gravity	g_0	980.665 32.174	cm per sec per sec ft per sec per sec
Standard atmosphere	atm	1,013,250 14.696 101,325	dynes per sq cm psia pascals
Standard millimeter of mercury pressure	mm Hg	$\frac{1}{760}$	atm
Calorie (thermochemical)	cal	4.1840 4.1840×10^7	joules ergs
Calorie (International Steam Tables)	cal _{IT} ; I.T. cal	4.1868	joules
Liter		1,000	cu cm

CHAPTER 2

CHARACTERIZATION OF HYDROCARBONS

2-0 INTRODUCTION

For correlational purposes, it is often necessary to designate the individual hydrocarbons in the various series by numerical parameters which characterize them. Hydrocarbons are partly characterized by such physical properties as the boiling point, critical point, and the liquid density. Their molecular size and shape are simultaneously indicated by the acentric factor (10, 11). The acentric factor is useful for correlating physical and thermodynamic properties and is defined as ω

$$\omega = -\log p_r^* - 1.000 \quad (2-0.1)$$

Where:

- p_r^* = reduced vapor pressure, p^*/p_c .
- p^* = vapor pressure at $T = 0.7 T_c$, in pounds per square inch absolute.
- p_c = critical pressure, in pounds per square inch absolute.
- T = temperature, in degrees Rankine
- T_c = critical temperature, in degrees Rankine.

The acentric factor is used in hydrocarbon correlations in several chapters of this book. Accordingly, Procedure 2A1.1 is presented as a general method of estimation consistent with Procedure 5A1.10. Alternately if experimental vapor pressure data are available, the defining equation (2-0.1) should be used.

For mixtures of identifiable hydrocarbons, the acentric factor is given by the following equation:

$$\omega = \sum_{i=1}^n x_i \omega_i \quad (2-0.2)$$

Where:

- n = number of components in the mixture.
- x_i = mole fraction of component i.
- ω_i = acentric factor of component i.

This equation is an oversimplification, but it is quite satisfactory in most cases. No better substitute is currently available.

For hydrocarbon mixtures for which the composition is known, the pure-component physical

properties and acentric factors adequately characterize the system. For more complex mixtures such as petroleum fractions, it is impractical and not always possible to analyze the entire mixture to define the concentration of all the components. These undefined mixtures are usually characterized by parameters that are derived from the normal inspection tests, an ASTM D86 or D1160 distillation, and the specific gravity of the mixture. Many characterizing parameters have been proposed, but very few are generally useful.

Among the useful parameters are five different boiling points and the Watson (19) characterization factor, K. Each boiling point reduces to the normal boiling point for pure hydrocarbons and is significant for a different group of correlations. These five quantities are defined by the following equations (16):

Volumetric average boiling point:

$$VABP = \sum_{i=1}^n x_{vi} T_{bi} \quad (2-0.3)$$

Where:

- x_{vi} = volume fraction of component i.
- T_{bi} = normal boiling point of component i. Either Fahrenheit or Rankine units may be used for volumetric average boiling point, molal average boiling point, and weight average boiling point to give the same units for the average boiling point. Rankine units must be used for cubic average boiling point, however. The MABP and CABP must be in the same units to calculate mean average boiling point.

Molal average boiling point:

$$MABP = \sum_{i=1}^n x_i T_{bi} \quad (2-0.4)$$

Weight average boiling point:

$$WABP = \sum_{i=1}^n x_{wi} T_{bi} \quad (2-0.5)$$

Where:

- x_{wi} = weight fraction of component i.

Cubic average boiling point:

$$CABP = \left(\sum_{i=1}^n x_{vi} T_{bi}^{1/3} \right)^3 \quad (2-0.6)$$

Mean Average Boiling Point:

$$MeABP = \frac{MABP + CABP}{2} \quad (2-0.7)$$

Inasmuch as volume, mole, and weight fractions are not known for undefined mixtures, the boiling points are conveniently correlated in an empirical plot (Figure 2B1.2) based on the ASTM D86 distillation curve. Analytical correlations developed by Zhou (23) are also included for use on a digital computer. For high-molecular-weight fractions which are vacuum distilled by ASTM Method D1160, the results must be converted to an ASTM D86 basis before obtaining a boiling point (see Chapter 3).

The Watson characterization factor, K, is defined by the equation:

$$K = \frac{(MeABP)^{1/3}}{sp\ gr, 60\ F/60\ F} \quad (2-0.8)$$

where MeABP must be in degrees Rankine. The boiling point for the Watson characterization factor was originally taken as the molal average (19) and was later changed to the cubic average (16). Later usage (9, 21) involves the mean average, or the arithmetic average of the two earlier boiling points, as used in equation (2-0.8).

The Watson K is an approximate index of paraffinicity, with high values corresponding to high degrees of saturation. A number of Watson K-values for pure hydrocarbons are listed in Table 2A1.3. For identifiable hydrocarbon mixtures, the Watson K is given by the equation:

$$K = \sum_{i=1}^n x_{wi} K_i \quad (2-0.9)$$

where K_i is the Watson K for the component i. For petroleum fractions, equation (2-0.8) is given in nomographic form in Figure 2B6.1 where aniline point, molecular weight, and carbon-to-hydrogen ratio are also correlated.

The MeABP and specific gravity may also be used to estimate the Watson K. For high-molecular-weight petroleum fractions, thermal cracking interferes with distillations at atmospheric pressure, so it is difficult to obtain a reliable MeABP for use in the defining equation

for the Watson K. However, if the viscosity of the fraction is known at 100 F and 210 F, Figure 2B2.4 can be used to determine the molecular weight which, with gravity, defines the Watson K from Figure 2B2.2.

For heavy petroleum fractions some analytical correlations in terms of specific gravity, flash point and refractive index are proposed by Woodle (22).

The Watson characterization factor is a satisfactory approach for correlating the physical and thermal properties of paraffinic or naphthenic straight-run petroleum fractions. However, the Watson K does not accurately characterize fractions containing appreciable amounts of olefinic, diolefinc, or aromatic hydrocarbons. Examples of such fractions are catalytic cracker recycle oils, catalytic reformer streams, and hydrocarbon streams from other synthesis processes.

Molecular weight is an important input parameter for many correlations. Procedure 2B2.1 provides a method useful for both desk and computer to estimate the molecular weight of petroleum fractions, given only the mean average boiling point of the fraction and the specific gravity. This method is useful in the range of molecular weight of 70-700. An alternate, but less accurate, procedure to be used only when the mean average boiling point is unknown is given by Procedure 2B2.3. This procedure requires specific gravity and viscosity at both 100 F and 210 F to predict molecular weights from 200-800.

Acentric factors for petroleum fractions for use with analytical and generalized equations of state can be estimated by Procedure 2B3.1 which combines the Maxwell-Bonnell procedure for estimating vapor pressure with the definition of acentric factor (Equation 2-0.1). Required primary input parameters are mean average boiling point and specific gravity.

Molecular type distribution of a petroleum fraction is estimable for straight-run petroleum fractions using Procedure 2B4.1. Required input parameters are molecular weight, specific gravity, refractive index, and one value of viscosity. Molecular type analysis, using the procedures of Chapters 7 and 11 for defined mixtures rather than specialized methods for undefined mixtures, allows calculation of enthalpy, heat capacity, and viscosity of petroleum fractions. Improved accuracy is obtained, as substantiated by Riazi and Daubert (15).

Refractive index of a petroleum fraction can be

estimated by using Procedure 2B5.1. Mean average boiling point and specific gravity of the fraction are required input parameters.

Figure 2B6.1 can be used for estimating Watson K from specific gravity and mean average boiling point, molecular weight, or aniline point. This figure, although usable for estimation of molecular weight, should not be used if the mean average boiling point and specific gravity are both known where Procedure 2B2.1 is preferable.

Flash point is the lowest temperature at which application of a test flame causes the vapor of the specimen to ignite at test conditions corrected to standard pressure.

Procedure 2B7.1 can be used to predict the Pensky-Martens closed cup and Cleveland open cup flash points of petroleum fractions. The ASTM D86 10% temperature is the input parameter.

Pour point is the lowest temperature at which petroleum fraction will flow or can be poured.

The choice of pour point procedure is dictated by the available parameters in the priority order shown.

<u>Known Information</u>	<u>Equation</u>
MeABP, S, ν_{100}	2B8.1-1
MeABP, S	2B8.1-2
Cloud Point	2B14.2-1

where

S = specific gravity, 60 F/60 F

ν_{100} = kinematic viscosity at 100 F

Aniline point is the lowest temperature at which a petroleum fraction is completely miscible with an equal volume of aniline.

Procedure 2B9.1 provides a method for predicting the aniline point of petroleum fractions using the mean average boiling point, specific gravity, and Watson K factor as input parameters.

Smoke point is the height in millimeters of a flame that is produced in a lamp burning a petroleum fraction at standard conditions without causing smoking.

Procedure 2B10.1 can be used to predict the smoke point of petroleum fractions from the mean average boiling and specific gravity.

Freezing point is the temperature of a petroleum fraction at which solid crystals formed on cooling

disappear as the temperature is raised.

Procedure 2B11.1 provides a method for predicting the freezing point of petroleum fractions using the mean average boiling point and specific gravity as the input parameters.

Cloud point is the temperature of a petroleum fraction at which its solid paraffin content begins to solidify and form crystals making the fraction cloudy.

Procedure 2B12.1 provides a method for predicting the cloud point of petroleum fractions from the specific gravity and the mean average boiling point. If the cloud point is known, the pour point can be predicted by Procedure 2B14.2.

Cetane index is the percent of cetane in a blend of cetane and alpha methyl naphthalene which has the same ignition quality as a sample of the petroleum fraction.

Procedure 2B13.1 provides a method for predicting the cetane index of petroleum fractions using API gravity and the mean average boiling point as the input parameters.

Procedure 2B14.1 provides a method for predicting the smoke point of petroleum fractions using specific gravity and aniline point as the input parameters.

Procedure 2B14.2 provides a method for predicting pour point of a petroleum fraction using cloud point as the input parameter. This procedure can also be used to predict the cloud point given the pour point.

Procedure 2B15.1 provides a method to predict the flash point of blends of petroleum fractions using the Wickey-Chittenden (20) blending model.

2-1 Petroleum Product Blending

The mixing of unfinished stocks to form more valuable end products is accomplished through a process known as product blending. Petroleum product blending remains one of the most cost effective methods available to the refiner to meet ever changing product demands. To meet these specialized demands, the refiners now have various blending procedures at their disposal. To be cost effective, blending procedures must optimize the use of blending stocks. Although it is the ultimate responsibility of the refiner to determine the recipe for the specific blend, blending procedures can provide a useful means to determine the appropriate proportions of each component in the blend.

Of the available blending procedures, most blend

properties specific to each blend stock. Blending stocks are the fractional components making up an entire product blend. Some blend quantities can be accurately estimated from linear blending models. Properties that blend linearly can be expressed as a simple linearly weighted average of each blend component's properties. This average can be on either a molar, weight, or volumetric basis, which is specific to the blend quality desired. Linear blending models can be expressed as follows:

$$P_B = \sum x_i P_i \quad (2-1.1)$$

Where:

P_B = property of the total blend

P_i = property of component i

x_i = weight, molar, or volumetric fraction of component i

Most properties do not blend linearly, however. For these properties, a somewhat more complex model is used. These models often require blending indices, or blending factors. Blending indices are empirical quantities that produce functions which then are blended. These functions can be expressed as follows:

$$I_B = \sum x_i I_i \quad (2-1.2)$$

Where:

I_B = blending index of the total blend

I_i = blending index of component i

There are numerous reports summarizing procedures for petroleum product blending. Baird (1) as well as Gary and Handwerk (3) are two that have proven to be the most helpful. Each report summarizes blending procedures, developed by various authors, for properties of interest to petroleum refining.

Presented in the following sections are procedures most commonly used for petroleum product blending. It should be noted that because almost no data are available, actual testing of each procedure was not conducted by the Data Book project of the American Petroleum Institute. Recommended procedures given are based on each equation's errors (as reported by the author) and ease of computation. When models were found that produce no distinct advantage between a pair of correlations, both or multiple correlations are given. The procedures were taken directly from the literature

sources (1,3) without evaluation.

Blending Procedures for Cloud, Pour, and Freezing Points

Two commonly used blending procedures for cloud and pour points of petroleum fractions are Reid-Allen (12) and Hu-Burns (4). The Reid-Allen procedure relates each blend stock's pour point blending index to the ASTM 50% boiling temperature and pour point. Baird suggests Reid-Allen pour point indices can be approximated using the following equation:

$$PPBI = e^{(a + b PP + c BP + d (PP)(BP))} \quad (2-1.3)$$

Where:

PPBI = pour point blending index number

PP = pour point (F)

BP = ASTM 50% boiling temperature (F)

a = 4.05334

b = 1.5657E-2

c = -4.2928E-3

d = 5.0840E-5

The ASTM distillation method was not given in the article, but is assumed to be D86. Once the blending index for each stock is determined, the index of the total blend can be found by taking a volumetric weighted average of each stock's pour point index (via eq. 2-1.2). Rearranging equation 2-1.3, the pour point of the blend can be determined, from the blend's index and mid boiling point, by the following equation:

$$PP = [ln(PPBI_B) - a - c BP] / [b + d BP] \quad (2-1.4)$$

Where:

PPBI_B = pour point blending index of total blend (from eq. 2-1.2)

One disadvantage of the Reid-Allen procedure is that the total blend's mid boiling point must be known to determine the pour point of the blend. The authors overcame this problem by suggesting the mid boiling point of the blend could be estimated by volumetrically averaging the 50% boiling temperatures of each blend stock. Out of a total of 90 blends, Reid-Allen reported pour point predictions within 5 F for over 90% of all cases tested. The method is applicable to any number of components.

The Hu-Burns method for petroleum product blending uses a different approach in modeling pour and cloud points of blends. The general form of the Hu-Burns model does not require a blending index value for prediction of properties specific to the blended product. The general form of the Hu-Burns equation is as follows:

$$T_B^{1/k} = \sum x_{v_i} (T_i)^{1/k} \quad (2-1.5)$$

Where:

- T_B = pour or cloud point of the total blend (R)
- T_i = pour or cloud point of component i (R)
- x_{v_i} = volume fraction of component I
- k = constant specific to a given refinery

The value of the constant k is specific to a given refinery and should, under most circumstances, be found by a trial-and-error procedure from experimental data. For best results, Hu-Burns recommends determining the constant from experimental data. However, if insufficient data exists, the authors reported that a value of k=0.08 for pour point and k=0.05 for cloud point gave the best results on an industry wide basis. For most practical applications, the value of the constant k ranges from 0.04 to 0.15 for both pour and cloud point blending procedures.

The Hu-Burns blending model gives very large blending numbers. Hu-Burns accounted for this problem by developing a blending index. According to Baird, pour and cloud points with a value of 140 F were arbitrarily assigned an index value of 10,000. With 140 F taken as the upper limit, the index covers the practical range of pour and cloud points of distillate fuel blends and components.

A cloud and pour point index curve is provided in the Hu-Burns article for various values of k. The Hu-Burns blending index procedure is similar to that of the Reid-Allen procedure. The blending index from each component (read from the curve) is volumetrically averaged to obtain the total blend's index. The blended product's property is then obtained from the curve.

When using a general value of k=0.08 for pour point blending, Hu-Burns found 94% of 97 total blends were predicted within 5 F of laboratory test data. For cloud point blending and k=0.05, errors were noticeably more

significant with less than 60% falling within 4 F. As mentioned above, the recommended procedure for each property should include a customized value of k. Hu-Burns evaluated the accuracy of the procedure using customized values of k for 5 different refineries. Their findings were as follows:

	<u>Percent within ASTM Repeatability</u>			
	ASTM Repeatability (F)	ASTM Reproducibility (F)	General Value for k	Customized Value for k
Cloud Point	4	8	57	85
Pour Point	5	10	94	97

Very little research has been conducted for blending freezing points. Maurin (8) proposes a method for weight blending of freezing points. However, there are not any data or test results for the model. Therefore, this correlation should be used with caution.

Blending Procedures for Flash Points

Other blending procedures in addition to Procedure 2B15.1 exist for flash point. The Wickey-Chittenden model is recommended because of its ease, accuracy, and vast acceptance by the industry. Hu-Burns (4), Thiele (17), Chevron (2), and Maurin (8) offer alternative blending methods for flash point. The petroleum refiner is advised to consult these articles to determine which procedure works best for a given refining process.

Blending Procedures for Aniline Point

Baird (1), reporting on work conducted by Unzelman (18) and Jackman (6), indicates aniline points of stocks blend linearly by volume. The observation is based on 53 blends. The study found an average deviation of 0.22 F for the 53 blends. These reports suggest equation 2-1.1 is adequate for blending aniline points.

Work conducted by Chevron (2) contradicts this

theory and suggests blending indices are more appropriate for aniline point prediction. Chevron proposes calculating an aniline point blending index from the following equation:

$$APBI = e^{(0.003652 AP)} \quad (2-1.8)$$

Where:

APBI = aniline point blending index

AP = aniline point (F)

Once the aniline point blending index is calculated for each blend stock, the volumetric average is then computed to determine the index of the total blend (via equation 2-1.2). The aniline point of the blend is then found from its blending index by the following equation:

$$AP = 273.823 \ln (APBI_B) \quad (2-1.9)$$

Where:

APBI_B = aniline point blending index for total
blend (from equation 2-1.2)

Use these equations with caution.

NOTE: A report documenting the basis upon which the material in this chapter was selected has been published by the American Petroleum Institute as Documentation Report No. 2-98 and is available from Global Engineering Documents.

PROCEDURE 2A1.1

ACENTRIC FACTORS OF PETROLEUM FRACTIONS

Discussion

The acentric factor defined by equation (2-0.1) is a useful characterizing parameter for several prediction methods. The following equation is used to estimate the acentric factor of pure hydrocarbons.

$$\omega = \frac{\ln p_r^{*'} - 5.92714 + 6.09648/T_r + 1.28862 \ln T_r - 0.169347T_r^6}{15.2518 - 15.6875/T_r - 13.4721 \ln T_R + 0.43577T_r^6} \quad (2A1.1-1)$$

Where:

- ω = acentric factor.
- $p_r^{*'} =$ reduced vapor pressure at the reduced temperature, p^*/p_c .
- p^* = vapor pressure at T , in pounds per square inch absolute.
- p_c = critical pressure, in pounds per square inch absolute.
- T_r = reduced temperature, T/T_c .
- T = temperature, in degrees Rankine.
- T_c = critical temperature, in degrees Rankine.

Procedure

Step 1: To determine the acentric factor for a hydrocarbon that is not listed in Table 2A1.3, first obtain the critical temperature and pressure from Chapter 1 or predict the latter values from methods of Chapter 4.

Step 2: If the normal boiling point is available from chapter 1, set T equal to the normal boiling point and p^* equal to 14.7 psia. If the normal boiling point is not available, predict the vapor pressure at a reduced temperature of 0.7 by the methods of Chapter 5.

Step 3: Use Equation (2A1.1-1) or its equivalent, Figure 1A1.2, to estimate the acentric factor.

COMMENTS ON PROCEDURE 2A1.1**Purpose**

Procedure 2A1.1 is a general method for obtaining the acentric factors of pure hydrocarbons for use in the correlations of other chapters. Use this procedure for pure hydrocarbons which are not listed in Table 2A1.3 or in Chapter 1. For undefined hydrocarbon mixtures, use Procedure 2B3.1.

Reliability

The reliability of the acentric factors calculated with this procedure is a direct function of the reliability of the input critical properties and vapor pressures. Large discrepancies can be detected by comparison with the values in Table 2A1.3. Equation 2A1.1-1 can reproduce the values in Table 2A1.3 with an average deviation of 1.3% when the normal boiling point is used.

Special Comments

Because reliable normal boiling point temperatures are usually available, this point is generally used. However, other vapor pressure data in the same temperature range may be used.

For mixtures of identifiable hydrocarbons, the acentric factor, ω , is given by the following equation:

$$\omega = \sum_{i=1}^n x_i \omega_i \quad (2A1.1-2)$$

Where:

n = number of components in the mixture.

x_i = mole fraction of component i .

ω_i = acentric factor of component i .

This equation is an oversimplification, but it is quite satisfactory in most cases. No better substitute is currently available.

Literature Source

Lee, B. I., Kesler, M. G., *AICHE J.* **21** 510 (1975).

Example

Calculate the acentric factor of 1-butene.

From Chapter 1, $T_c = 295.6$ F, $p_c = 583$ pounds per square inch absolute, and the boiling point is 20.7 F. The reduced vapor pressure at the boiling point is $14.7/583 = 0.0252$, and the corresponding reduced temperature is $\frac{20.7 + 459.7}{295.6 + 459.7} = 0.636$.

$$\begin{aligned} \omega &= \frac{\ln(0.0252) - 5.92714 + 6.09648/0.636 + 1.28862 \ln(0.636) - 0.169347(0.636)^6}{15.2518 - 15.6875/0.636 - 13.4721 \ln(0.636) + 0.43577(0.636)^6} \\ &= \frac{-0.6168}{-3.2884} = 0.188 \end{aligned}$$

The value listed in Table 2A1.2, which was derived from data at $T_r = 0.7$, is 0.1867. Alternatively, using Figure 2A1.2,

$$T_r = 0.636, \ln P_r^* = -3.6809$$

$$\omega = 0.19$$

COMMENTS ON PROCEDURE 2B1.1

Purpose

The various average boiling points which are used to characterize petroleum fractions are correlated in Figure 2B1.2 with the ASTM D86 distillation properties of the fraction. If these boiling points are required for mixtures (or portions of a mixture) for which the composition is known, use the defining equations (2-0.3) through (2-0.7) given in the introduction.

Reliability

The reliability is unknown.

Notation

The relationships between the various average boiling points given in Figure 2B1.2 for petroleum fractions are analogous to those defined by equations (2-0.3) through (2-0.7) for mixtures of identifiable hydrocarbons.

Special Comments

If the available distillation data are not from ASTM Method D86, they must be converted by the methods of Chapter 3 to calculate the volumetric average boiling point.

Literature Sources

This figure was developed by Smith and Watson, *Ind. Eng. Chem.* **29** 1408 (1937). Equations (2B1.1-1) through (2B1.1-8) were developed by P. Zhou, *Int. Chem. Eng.*, **24**(4), 731-741 (1984).

Example

Determine the molal average boiling point, weight average boiling point, cubic average boiling point, and mean average boiling point of a petroleum fraction having the following ASTM D86 distillation properties:

Distillation, percent by volume	10	30	50	70	90
Temperature, degrees Fahrenheit	149	230	282	325	371

$$VABP = \frac{149 + 230 + 282 + 325 + 371}{5} = 271 \text{ F}$$

$$\text{Slope} = \frac{371 - 149}{80} = 2.78 \frac{\text{Fahrenheit degrees}}{\text{percent distilled}}$$

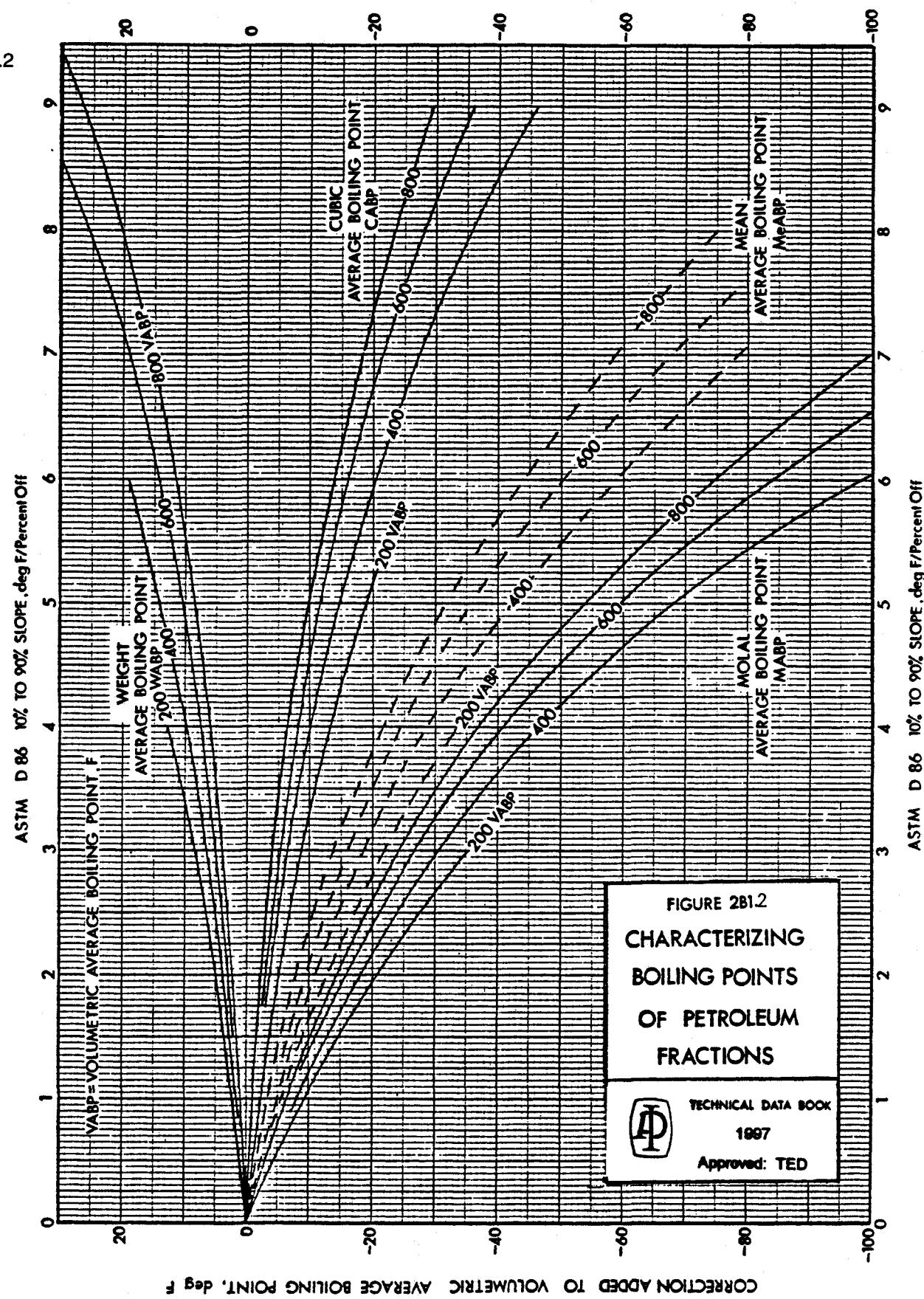
Using Figure 2B1.2, the average boiling points are calculated from the volumetric average boiling point by first reading the boiling point corrections from the figure and then calculating the various average boiling points from the VABP.

$$\begin{array}{ll} MABP = 271 - 30 = 241 \text{ F} & CABP = 271 - 7 = 264 \text{ F} \\ WABP = 271 + 7 = 278 \text{ F} & MeABP = 271 - 19 = 252 \text{ F} \end{array}$$

Alternately, using equations (2B1.1-1) through (2B1.1-8), the average boiling points are:

$$\begin{array}{ll} MABP = 240.6 \text{ F} & CABP = 264.0 \text{ F} \\ WABP = 278.3 \text{ F} & MeABP = 252.1 \text{ F} \end{array}$$

2B1.2



PROCEDURE 2B2.1**MOLECULAR WEIGHT OF PETROLEUM FRACTIONS****Discussion**

The following equation is used to estimate the molecular weight of petroleum fractions.

$$M = 20.486 [\exp(1.165 \times 10^{-4} T_b - 7.78712S + 1.1582 \times 10^{-3} T_b S)] T_b^{1.26007} S^{4.98308} \quad (2B2.1-1)$$

Where:

M = molecular weight of petroleum fraction.

T_b = mean average boiling point of petroleum fraction in degrees Rankine.

S = specific gravity, 60 F/60 F.

Procedure

Step 1: Obtain the specific gravity of the petroleum fraction.

Step 2: Obtain the mean average boiling point from Figure 2B1.2.

Step 3: Calculate the molecular weight using equation (2B2.1-1).

Alternately Figure 2B2.2, the equivalent of equation (2B2.1-1) in terms of Watson characterization factor and API gravity, can be used with slightly lower accuracy.

Where:

$$\text{API gravity} = \frac{141.5}{S} - 131.5$$

$$K = T_b^{1/3}/S$$

COMMENTS ON PROCEDURE 2B2.1**Purpose**

The purpose of this procedure is to predict the molecular weight of petroleum fractions from specific gravity and mean average boiling point, both of which are usually available.

Limitations

Equation (2B2.1-1) was evaluated over the following range of molecular weight, mean average boiling point, and gravities:

Range of Data	
Molecular weight	70–700
Boiling point, degrees Fahrenheit	90–1050
API gravity	14.4–93.1
Specific gravity	0.63–0.97

The equation may be safely extrapolated to a boiling point of 1500 F.

Reliability

The equation reproduced experimental values of molecular weight to within an average error of 3.4 percent when $M < 300$ and 4.7 percent for $M > 300$ when tested against 635 data points.

Literature Sources

The equation is a 1986 modification of a correlation developed by M. R. Riazi, "Prediction of Thermophysical Properties of Petroleum Fractions," Ph.D. Thesis, Department of Chemical Engineering, The Pennsylvania State University, University Park, Pa., 1979.

Special Comment

For heavy fractions or if the mean average boiling point is not available, Procedure 2B2.3 should be used.

Example

Determine the molecular weight of a petroleum fraction having a specific gravity (60 F/60 F) of 0.8160 and the following ASTM D86 distillation properties:

Distillation, percent by volume	10	30	50	70	90
Temperature, degrees Fahrenheit	227	276	340	413	509

Using Procedure 2B1.1 the volume average boiling point is 353 F, the 10–90 slope is 3.53, and the correction from Figure 2B1.2 is –24 F. The mean average boiling point is then $353 - 24 = 329$ F (788.67 R).

Using equation (2B2.1-1), the molecular weight is:

$$\begin{aligned} M &= 20.486 \exp(1.165 \times 10^{-4} \times 788.67 - 7.78712 \times 0.8160 + 1.1582 \times 10^{-3} \times 788.67 \\ &\quad \times 0.8160)(788.67)^{1.26007} (0.816)^{4.98308} \\ &= 134 \end{aligned}$$

An experimental value is 137.0.

Alternately using Figure 2B2.2:

$$K = (788.69)^{1/3}/0.8160 = 11.32$$

$$\text{API gravity} = \frac{141.5}{0.8160} - 131.5 = 41.9$$

$$M = 140$$

COMMENTS ON PROCEDURE 2B2.3**Purpose**

This procedure is used to determine molecular weight of a high-boiling petroleum fraction when viscosities at 100 F and 210 F are known. The molecular weight can be used with Figure 2B6.1 to estimate the Watson characterization factor for the fraction.

Limitations

The viscosities at 100 F and 210 F do not characterize petroleum fractions as well as an ASTM distillation; thus, when a choice exists, use Procedure 2B2.1 instead of this procedure for estimating molecular weights.

Use this procedure only for petroleum fractions as erroneous values may be obtained for synthetic hydrocarbon mixtures, for which it was not designed.

Use this equation in the molecular weight range of 200 to 800.

Reliability

Molecular weights obtained from this procedure differ by an average of 2.7 percent from experimental data. For the few data points for which both Procedure 2B2.1 and 2B2.3 could be used to estimate molecular weights, the predictions differed by 8.5 percent.

Special Comments

For petroleum fractions for which specific gravity is not available, the following equation can be used to estimate the specific gravity.

$$S = 0.7717 \nu_{100}^{0.1157} \nu_{210}^{-0.1616} \quad (2B2.3-2)$$

This equation is also shown in Figure 2B2.5 in terms of API gravity. If predicted values of specific gravity from equation 2B2.3-2 are used instead of experimental values, errors in equation (2B2.3-1) increase from 2.7 to 3.5 percent.

Literature Source

Riazi, M. R., private communication (1985).

Example

Determine the molecular weight and Watson *K* for an oil having an API gravity of 22.5 and kinematic viscosities of 55.1 centistokes at 100 F and 5.87 centistokes at 210 F.

$$S = \frac{141.5}{22.5 + 131.5} = 0.9188$$

A. Using equation (2B2.3-1).

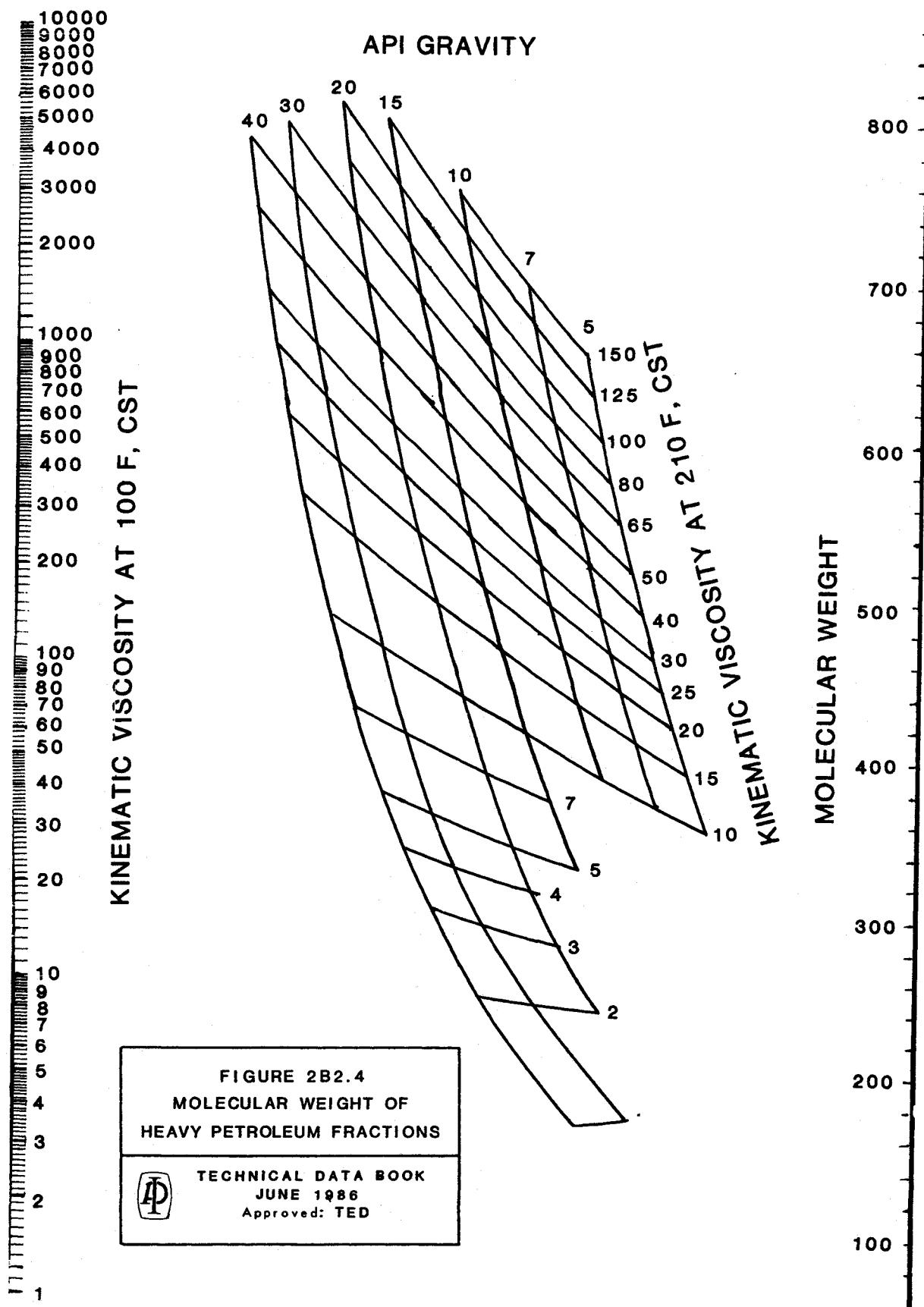
$$M = 223.56(55.1)^{(-1.2435 + 1.1228 \times 0.9188)} (5.87)^{(3.4758 - 3.038 \times 0.9188)} (0.9188)^{-0.6665} \\ = 340$$

An experimental molecular weight is 349.

B. Using Figure 2B2.4, the molecular weight is about 332.

C. Assuming the API gravity is unknown, use of equation (2B2.3-2) gives *S* = 0.9219 and an API gravity of 22.0. Figure 2B2.5 also would yield an API gravity of 22.

Using a value of molecular weight of 340 and API gravity in Figure 2B6.1, the Watson *K* is 11.58.



COMMENTS ON PROCEDURE 2B3.1

Purpose

The purpose of this procedure is to calculate the acentric factor of petroleum fractions for use in the correlations of other chapters. The method uses a reliable correlation for vapor pressure and the defining equation for acentric factor.

Limitations

Procedure 5A1.19, when used by itself to determine vapor pressures, is strictly applicable only to pure hydrocarbons and narrow-boiling petroleum fractions. However, when the procedure is used in conjunction with equation (2-0.1) to calculate acentric factor, it is also applicable to wide-boiling petroleum fractions.

Special Comment

Procedure 2A1.1 should be used to calculate the acentric factor of pure hydrocarbons.

Example

Determine the acentric factor of a petroleum fraction having a specific gravity (60 F/60 F) of 0.8160 and the following ASTM D86 distillation properties:

Distillation, percent by volume	10	30	50	70	90
Temperature, degrees Fahrenheit	227	276	340	413	509

Correcting the calculated VABP using Figure 2B1.2, the mean average boiling point = 329.0 F. Using equation (2-0.8) the Watson K is 11.32. Using Procedure 4D3.1, the pseudocritical temperature is calculated to be 683.7 F. Since the reduced temperature is 0.7, the temperature for which the vapor pressure is determined is

$$\begin{aligned} T &= 0.7(683.7 + 459.7) \\ &= 800.4 \text{ R} \\ &= 340.7 \text{ F} \end{aligned}$$

From Procedure 5A1.19, the vapor pressure at 340.7 F is 897 mm Hg. By Procedure 4D4.1, the pseudocritical pressure is 400 pounds per square inch absolute.

By definition, equation (2-0.1), the acentric factor is:

$$\omega = -\log_{10} \frac{(897)(14.7)}{(400)(760)} - 1.00 = 0.363$$

PROCEDURE 2B4.1
MOLECULAR TYPE COMPOSITION OF PETROLEUM FRACTIONS

Discussion

Equations 2B4.1-1 through 2B4.1-3 are used to predict the fractional composition of paraffins, naphthenes, and aromatics contained in both light and heavy petroleum fractions. Viscosity, specific gravity, and refractive index of the desired fraction are used as input parameters.

$$x_p = a + b(R_i) + c(VG) \quad (2B4.1-1)$$

$$x_n = d + e(R_i) + f(VG) \quad (2B4.1-2)$$

$$x_a = g + h(R_i) + i(VG) \quad (2B4.1-3)$$

Where:

a, b, c, \dots, i = constants varying with molecular weight range as given below.

Constants Molecular weight range	Light Fractions 70-200	Heavy Fractions 200-600
a	-13.359	+2.5737
b	+14.4591	+1.0133
c	-1.41344	-3.573
d	+23.9825	+2.464
e	-23.333	-3.6701
f	+0.81517	+1.96312
g	-9.6235	-4.0377
h	+8.8739	+2.6568
i	+0.59827	+1.60988

x_p, x_n, x_a = mole fraction of paraffins, naphthenes, and aromatics, respectively.

R_i = refractivity intercept as given by equation (2B4.1-4).

VG = viscosity gravity constant (VGC) as given by equations 2B4.1-5 for heavy fractions or viscosity gravity function (VGF) as given by equations 2B4.1-6 for light fractions.

$$R_i = n - \frac{d}{2} \quad (2B4.1-4)$$

Where:

n = refractive index at 68 F and 1 atmosphere.

d = liquid density at 68 F and 1 atmosphere in grams per cubic centimeter.

$$VGC = \frac{10S - 1.0752 \log (V_{100} - 38)}{10 - \log (V_{100} - 38)} \quad (2B4.1-5.1)$$

or

$$VGC = \frac{S - 0.24 - 0.022 \log (V_{210} - 35.5)}{0.755} \quad (2B4.1-5.2)$$

Where:

S = specific gravity at 60 F/60 F.

V = Saybolt universal viscosity at 100 or 210 F, in Saybolt universal seconds.

Note: For interconversion of viscosity units see Chapter 11.

$$VGF = -1.816 + 3.484S - 0.1156 \ln \nu_{100} \quad (2B4.1-6.1)$$

or

$$VGF = -1.948 + 3.535S - 0.1613 \ln \nu_{210} \quad (2B4.1-6.2)$$

Where:

ν = kinematic viscosity at 100 or 210 F, centistokes.

Step 1: Obtain the specific gravity (60 F/60 F), density at 68 F (20 C),, and refractive index at 68 F (20 C) of the fraction. Estimate the refractive index, if unknown, from Procedure 2B5.1. Estimate the density, if unknown, from methods of Chapter 6 or from equation (2B4.1-10) if appropriate.

Step 2: Estimate the molecular weight, if unknown, from Procedure 2B2.1 or Figure 2B2.2 to establish whether the fraction is light or heavy.

Step 3: Obtain the correct viscosities to use equations (2B4.1-5) or (2B4.1-6) as appropriate. If experimental values are unknown, use the methods of Chapter 11 for estimation.

Step 4: Calculate VGC or VGF as appropriate and calculate R_i from equations (2B4.1-4) through (2B4.1-6).

Step 5: Calculate the mole fraction of paraffins, naphthenes, and aromatics from equations (2B4.1-1) through (2B4.1-3) respectively. The sum must equal 1.00.

COMMENTS ON PROCEDURE 2B4.1**Purpose**

Equations are given for calculating the molecular type distribution of straight run petroleum fractions.

Limitations

This procedure was evaluated with petroleum fraction data having the following ranges of molecular weight, refractivity intercept, viscosity gravity constant or viscosity gravity function, and composition.

	Range of Data	
	Light fraction	Heavy fraction
Molecular weight	78-214	233-571
R_i	1.04-1.08	1.04-1.06
VGC or VGF	0.57-1.52	0.79-0.98
x_p	0.02-0.93	0.10-0.81
x_n	0.02-0.46	0.13-0.64
x_a	0.01-0.93	0.0-0.31

The method may be used for petroleum fractions of molecular weight as low as 70. However, it should not be used outside the range of evaluated data.

Reliability

For the 85 light petroleum fractions tested, average deviations for x_p and x_n are 0.04 and 0.06 mole fraction, respectively. For the 72 heavy fractions evaluated, average deviations of 0.02 and 0.04 mole fraction occurred for x_p and x_n , respectively.

Special Comments

A. For highly aromatic fractions where detailed knowledge of aromatic types is required, the following equation is proposed to estimate monoaromatic content of the fraction

$$x_{ma} = -62.8245 + 59.90816R_i - 0.0248335m \quad (2B4.1-7)$$

Where:

R_i = refractivity intercept as given by equation (2B4.1-4).

x_{ma} = mole fraction of monoaromatics.

m = a factor given by equation (2B.4.1-8).

$$m = M(n - 1.4750) \quad (2B4.1-8)$$

in which M is the molecular weight. Equation 2B4.1-7 is applicable to fractions with molecular weights less than 250.

Mole fraction of other types of aromatics (di- and poliaromatics) can be determined by difference between x_a from equation (2B4.1-3) and x_{ma} from equation (2B4.1-7).

$$x_{pa} = x_a - x_{ma} \quad (2B4.1-9)$$

Where:

x_{pa} = mole fraction of di- and poliaromatics.

B. For petroleum fractions for which density at 68 F (20 C) needed for equation (2B4.1-4) is not available, instead of using methods of Chapter 6, it could be more convenient to obtain this property using the following equations for fractions of molecular weight greater than 300:

$$d = 2.83085M^{0.03975} I^{1.13543} \quad (2B4.1-10)$$

Where:

d = liquid density at 68 F and 1 atmosphere, in grams per cubic centimeter.

I = Huang (1) characterization parameter at 68 F.

$$= \frac{n^2 - 1}{n^2 + 2}$$

n = refractive index at 68 F and 1 atmosphere.

M = molecular weight of petroleum fraction.

Source

Riazi, M. R., "Prediction of Thermophysical Properties of Petroleum Fractions," Ph.D. Thesis, Department of Chemical Engineering, The Pennsylvania State University, University Park, Pa., 1979.

Riazi, M. R., Daubert, T. E., *Ind. Eng. Chem. Process Des. Dev.* **19** 289 (1980).

Riazi, M. R., private communication (1985).

Example

Calculate the molecular type distribution of a petroleum fraction of specific gravity 0.9046 at 60 F/60 F, a refractive index of 1.5002, a liquid density of 0.90 at 68 F, a mean average boiling point of 798 F, and a viscosity of 336 Saybolt universal seconds at 100 F.

From equation (2B2.1-1), the molecular weight is:

$$\begin{aligned} M &= 20.486 \exp(1.165 \times 10^{-4} \times 1258 - 7.78712 \times 0.9046 \\ &\quad + 1.1582 \times 10^{-3} \times 1258 \times 0.9046)(1258)^{1.26007}(0.9046)^{4.98308} \\ M &= 378 \end{aligned}$$

Thus, the fraction is heavy and the viscosity gravity constant should be used for correlation. From equation (2B4.1-5.1), the viscosity gravity constant is:

$$\begin{aligned} VGC &= \frac{(10)(0.9046) - (1.0752) \log(336 - 38)}{[10 - \log(336 - 38)]} \\ VGC &= 0.8485 \end{aligned}$$

From equation (2B4.1-4), the refractivity intercept is:

$$R_i = 1.5002 - \frac{0.90}{2} = 1.05$$

From equations (2B4.1-1), (2B4.1-2) and (2B4.1-3), using heavy fraction constants, the mole fractions are:

$$\begin{aligned} x_p &= 2.5737 + (1.0133)(1.05) - (3.573)(0.8485) \\ x_p &= 0.606 \\ x_n &= 2.464 - (3.6701)(1.05) + (1.96312)(0.8485) \\ x_n &= 0.275 \\ x_e &= -4.0377 + (2.6568)(1.05) + (1.60988)(0.8485) \\ x_e &= 0.119 \\ \Sigma x &= 1.000 \end{aligned}$$

Experimental values of x_p , x_n , and x_e are 0.59, 0.28, and 0.13, respectively.

PROCEDURE 2B5.1**REFRACTIVE INDEX OF PETROLEUM FRACTIONS****Discussion**

Equation (2B5.1-1) is to be used to predict the refractive index of petroleum fractions.

$$n = \left[\frac{1 + 2I}{1 - I} \right]^{1/2} \quad (2B5.1-1)$$

Values of I may be calculated from equation (2B5.1-2).

$$\begin{aligned} I = & 2.266 \times 10^{-2} \exp(3.905 \times 10^{-4} \text{ MeABP} + 2.468 S \\ & - 5.704 \times 10^{-4} \text{ MeABP} S) \text{ MeABP}^{0.0572} S^{-0.720} \end{aligned} \quad (2B5.1-2)$$

Where:

- n = refractive index at 68F.
- I = modified Huang characterization parameter at 68F.
- MeABP = mean average boiling point, D86, R.
- S = specific gravity, 60F/60F.

Procedure

- Step 1:* Obtain the mean average boiling point from equation (2-0.7) or Figure 2B1.2 and specific gravity of the fraction.
- Step 2:* Calculate the modified Huang characterization parameter from equation (2B5.1-2).
- Step 3:* Calculate the refractive index of the fraction from equation (2B5.1-1).

COMMENTS ON PROCEDURE 2B5.1

Purpose

The purpose of this procedure is to predict the refractive index of petroleum fractions at 68F from the mean average boiling point and specific gravity.

Limitations

Equations (2B5.1-1) and (2B5.1-2) were used to evaluate refractive index data for petroleum fractions with mean average boiling point, specific gravity, and refractive indices in the following ranges listed.

	Range of Data
Mean average boiling point, F	100 - 950
Specific gravity, 60F/60F	0.63 - 0.97
Refractive index at 68F	1.35 - 1.55

The method may also be used to predict the refractive index for pure hydrocarbons by using the normal boiling point in place of the mean average boiling point.

Reliability

Equation (2B5.1-1) reproduced experimental values for refractive index within an average absolute percent error of 0.3%.

Literature Source

Riazi, M.R., "Prediction of Thermophysical Properties of Petroleum Fractions," Ph. D. Thesis, Department of Chemical Engineering, The Pennsylvania State University, University Park, PA 1979.

Riazi, M.R., private communication (1985).

API Documentation Report API-2-98.

Example

Calculate the refractive index of a fraction at 68F with specific gravity of 0.732 and mean average boiling point of 656 R.

Using equation (2B5.1-2), the Huang parameter is:

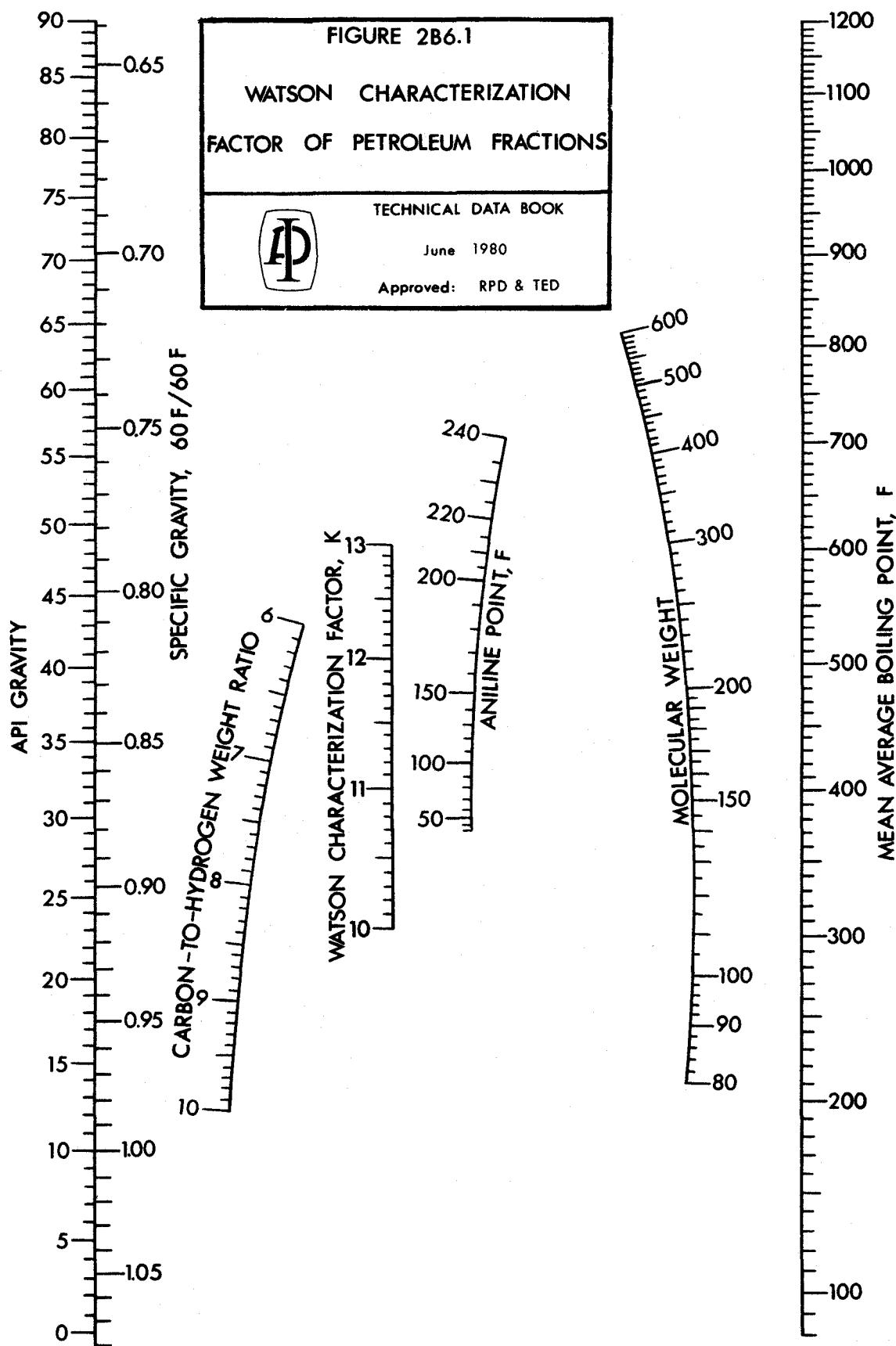
$$I = 2.266 \times 10^{-2} \exp[3.905 \times 10^{-4} (656) + 2.468 (0.732) - 5.704 \times 10^{-4} (656)(0.732)] (656)^{0.0572} (0.732)^{-0.720}$$

$$I = 0.246$$

From equation (2B5.1-1), the refractive index is:

$$n = \left[\frac{1 + 2(0.246)}{1 - 0.246} \right]^{1/2} = 1.4065$$

The experimental value for the refractive index of the fraction is 1.4074.



COMMENTS ON FIGURE 2B6.1

Purpose

The Watson characterization factor, K, of petroleum fraction which is used to estimate many other properties in subsequent chapters, has been correlated with many properties such as mean average boiling point, molecular weight, carbon-to-hydrogen weight ratio, and aniline point with either API or specific gravity. Figure 2B6.1 is provided for estimating the Watson K factor from the gravity and any one of the other properties. If the mean average boiling point and specific (or API) gravity are known, use the defining equation (2-0.8) given in the introduction for calculating the Watson K.

Please note that the prediction of properties other than Watson K using this plot will most likely be less accurate than using other specific methods given in various procedures of this chapter. For example, aniline point is much better predicted by Procedure 2B9.1 while molecular weight procedures of Section 2B2 are recommended.

Reliability

The reliability depends on the accuracy of input parameters.

Special Comments

For heavy petroleum fractions ($MW > 300$) distillation data for determination of mean average boiling point usually are not available. For such fractions molecular weight and API gravity may be used to determine Watson K from Figure 2B6.1. If molecular weight is unknown, use Procedure 2B2.3 to estimate molecular weight from kinematic viscosities at 100 F and 210 F. However, the use of API gravity with carbon-to-hydrogen weight ratio or aniline point is not recommended for determining Watson K factor.

For heavy fractions when this figure cannot be used to determine Watson K, simple correlations given by Woodle (12) in terms of API gravity, flash point, aniline point, or refractive index may be used to estimate the Watson K factor.

Literature Source

This figure was given by Winn, F. W., *Petrol. Refiner* 36[2] 157 (1957).

Example

Determine the Watson K factor of a petroleum fraction having an API gravity of 34.5, kinematic viscosity of 5.27 cSt at 100 F and 170 cSt at 210 F.

Using Procedure 2B2.3, to predict molecular weight,

$$M = 247$$

Using Figure 2B6.1, with $M = 247$ and API gravity of 34.5,

$$K = 11.85$$

Using its definition, equation (2-0.8), the Watson K is 11.89.

PROCEDURE 2B7.1**FLASH POINT OF PETROLEUM FRACTIONS****Discussion**

The following equations are used to estimate the flash point of a petroleum fraction.

For closed cup flash point:

$$FP = 0.69 T_{10\%} - 118.2 \quad (2B7.1-1)$$

For open cup flash point:

$$FP = 0.68 T_{10\%} - 109.6 \quad (2B7.1-2)$$

where:

FP = flash point, F.

$T_{10\%}$ = ASTM D86 10% temperature for petroleum fraction, F.

Procedure

Step 1: Determine the correct prediction method for the flash point type required (open or closed cup).

Step 2: Obtain the ASTM D86 10% temperature.

Step 3: Calculate the flash point using equation (2B7.1-1), or equation (2B7.1-2) depending on the flash point method to be predicted.

COMMENTS ON PROCEDURE 2B7.1

Definition and Purpose

Flash point is defined as the lowest temperature corrected to 14.7 psia (1 atm) at which application of a test flame causes the vapor of a specimen to ignite under specific conditions of testing. The purpose of this procedure is to predict Pensky-Martens Closed Cup (ASTM D93) and Cleveland Open Cup (ASTM D92) flash points of petroleum fractions from the ASTM D86 10% temperature.

Limitations

Equations (2B7.1-1) and (2B7.1-2) were evaluated over the following range of flash points and ASTM D86 10% boiling temperatures.

	Range of Data
Flash Point, F	0 - 450
ASTM D86 10% boiling temperatures, F.	150 to 850

The equations can be reasonably extrapolated beyond the tested data range to a limited extent. The flash point of a petroleum fraction should be more accurately correlated to the ASTM D86 5% boiling point as the light end determines the flash point. A lack of data prevented the development of the correlation.

Reliability

Equation (2B7.1-1) and equation (2B7.1-2) reproduced experimental values for flash point within an average absolute deviation of 9.6 and 3.2 F, respectively.

Literature Source

American Petroleum Institute, Documentation Report 2-98.

Example

Determine the open-cup flash point of a fraction having an ASTM D86 10% temperature of 403 F.

From equation (2B7.1-2)

$$FP = 0.68(403) - 109.6 = 164 \text{ F}$$

An experimental value is 165 F.

PROCEDURE 2B8.1**POUR POINT OF PETROLEUM FRACTIONS****Discussion**

The following equations are used to estimate the pour point of a petroleum fraction.

If the experimental kinematic viscosity is available:

$$PP = 753 + 136 [1 - \exp (-0.15 v_{100})] - 572 S + 0.0512 v_{100} + 0.139 MeABP \quad (2B8.1-1)$$

If the kinematic viscosity is not available:

$$PP = 3.85 \times 10^{-8} MeABP^{5.49} 10^{-(0.712MeABP^{0.315}+0.133S)} + 1.4 \quad (2B8.1-2)$$

If only the cloud point is known, pour point may be predicted using Procedure 2B14.2.

Where:

- PP = pour point of petroleum fraction, R.
- v_{100} = kinematic viscosity at 100 F, cSt.
- S = specific gravity, 60F/60F.
- MeABP = mean average boiling point, D86, R.

Procedure

Step 1: Obtain the specific gravity, mean average boiling point, and kinematic viscosity at 100 F (if available) of the petroleum fraction.

Step 2: Use equation (2B8.1-1) to calculate the pour point if kinematic viscosity data are available. When experimental viscosity data are not available, use equation (2B8.1-2).

COMMENTS ON PROCEDURE 2B8.1

2B8.1

Definition and Purpose

The pour point of a petroleum fraction is the lowest temperature at which it will flow or can be poured. The pour point is obtained experimentally using ASTM Procedure D97. The purpose of this procedure is to predict the pour point of petroleum fractions from specific gravity (60F/60F), mean average boiling point, and kinematic viscosity at 100 F.

Limitations

Equations (2B8.1-1) and (2B8.1-2) were evaluated over the following ranges.

Pour point, R	420 to 590
Mean average boiling point, R	800 to 1500
Kinematic viscosity, cSt	2 to 960
Specific gravity, (60F/60F)	0.8 to 1.0

Equations (2B8.1-1) and (2B8.1-2) may be reasonably extrapolated to a limited extent.

Reliability

Equation (2B8.1-1) reproduced experimental values of pour point to within an average deviation of 6.9 R for 280 data points. Kinematic viscosity data should not be estimated when using equation (2B8.1-1). If viscosity data are not available use equation (2B8.1-2). Equation (2B8.1-2) reproduced experimental values of pour point to within an average deviation of 9.9 R for 428 data points.

Literature Source

American Petroleum Institute, Documentation Report API-2-98.

Example

Determine the pour point of a of a petroleum fraction with mean average boiling point of 972 R, specific gravity of 0.839, and kinematic viscosity at 100 F of 3 cSt.

From equation (2B8.1-1)

$$\begin{aligned} PP &= 753 + 136(1 - \exp[-0.15(3)]) - 572(0.839) + (0.0512)3 + 0.139(972) \\ PP &= 458 \text{ R} \end{aligned}$$

An experimental pour point of the fraction is 455 R.

PROCEDURE 2B9.1**ANILINE POINT OF PETROLEUM FRACTIONS****Discussion**

The following equation is used to estimate the aniline point of a petroleum fraction.

$$AP = -1253.7 - 0.139 \text{ MeABP} + 107.8 \text{ K} + 868.7 \text{ S} \quad (2B9.1-1)$$

Where:

AP	= aniline point of petroleum fraction, R.
MeABP	= mean average boiling point, R.
S	= specific gravity, 60F/60F.
K	= Watson K factor.

Procedure

Step 1: Obtain the the mean average boiling point and specific gravity.

Step 2: Obtain the Watson K of the petroleum fraction; if unknown calculate from Equation (2-0.8).

Step 3: Calculate the aniline point using Equation (2B9.1-1).

COMMENTS ON PROCEDURE 2B9.1

Definition and Purpose

The aniline point is the lowest temperature at which a petroleum fraction is completely miscible with an equal volume of distilled aniline. ASTM Procedure D611 is used to determine experimental aniline points. The purpose of this procedure is to predict the aniline point of a petroleum fraction from mean average boiling point, specific gravity, and the Watson K factor.

Limitations

Equation (2B9.1-1) was evaluated over the following data ranges.

	Range of Data
Mean average boiling point, F	200 to 1100
Specific gravity, 60F/60F	0.7 to 1.0
Aniline point, F	100 to 240

Reliability

The equation reproduced experimental values of aniline point to within an average deviation of 4.2 R for 343 data points having a mean average boiling point less than 750 F. Including data with mean average boiling points greater than 750 F, the equation reproduced experimental values of aniline point within an average deviation of 4.7 R for 475 data points. The equation should be used with caution when estimating pure compound aniline points and petroleum fractions with a mean average boiling point greater than 750 degrees Fahrenheit.

Aniline point can also be easily estimated using Figure 2B6.1, with an average deviation of 8.6 F for 48 data points.

Literature Source

American Petroleum Institute, Documentation Report API-2-98.

Example

Determine the aniline point of a petroleum fraction having a specific gravity of 0.8304 and a mean average boiling point of 570.2 F.

Using Equation (2-0.8):
$$K = \frac{(570.2 + 459.67)^{1/3}}{0.8304} = 12.16$$

Calculate the aniline point from equation (2B9.1-1).

$$\begin{aligned} AP &= -1253.7 - 0.139(570.2 + 459.67) + 107.8(12.16) + 868.7(0.8304) \\ AP &= 635.4 \text{ R} \end{aligned}$$

An experimental value is 639.1 R.

PROCEDURE 2B10.1**SMOKE POINT OF PETROLEUM FRACTIONS****Discussion**

The following equation is used to estimate the smoke point of petroleum fractions.

$$\ln SP = -1.028 + 0.474 K - 0.00168 \text{ MeABP} \quad (2\text{B}10.1-1)$$

Where:

SP	= smoke point of petroleum fraction, mm.
MeABP	= mean average boiling point, R.
K	= Watson K factor

Procedure

Step 1: Obtain the specific gravity and mean average boiling point of the petroleum fraction.

Step 2: Obtain the Watson K factor; if not available calculate using Equation (2-0.8).

Step 3: Calculate the smoke point using Equation (2B10.1-1).

COMMENTS ON PROCEDURE 2B10.1

Definition and Purpose

The smoke point is the height in millimeters of the flame that is produced in a lamp at standard conditions without causing smoking. The purpose of this procedure is to predict the smoke point of petroleum fractions from mean average boiling point and specific gravity data. ASTM Procedure D1322 is a standard method for experimental determination.

Limitations

Equation (2B10.1-1) was evaluated over the following smoke point, specific gravity, and mean average boiling point ranges.

Range of Data	
Smoke point, mm	15 - 33
Specific gravity, 60F/60F	0.7 - 0.86
Mean average boiling point, F	200 - 550

This equation is not recommended for the unlikely case of a fraction of low specific gravity ($S < 0.8$) with a mean boiling point greater than 1000 F.

Reliability

The equation reproduced experimental values of smoke point to within an average error of 6.3 percent.

Literature Source

American Petroleum Institute, Documentation Report API-2-98.

Example

Determine the smoke point of a petroleum fraction having a specific gravity of 0.853 and a mean average boiling point of 414.5F.

Using equation (2-0.8):
$$K = \frac{(414.5 + 459.6)^{1/3}}{0.853} = 11.21$$

Calculate the smoke point from equation (2B10.1-1):

$$\ln SP = -1.028 + 0.474(11.21) - 0.00168(414.5 + 459.6) = 2.817$$

$$SP = 16.7 \text{ mm}$$

An experimental value is 17 mm.

PROCEDURE 2B11.1**FREEZING POINT OF PETROLEUM FRACTIONS****Discussion**

The following equation is used to estimate the freezing point of petroleum fractions.

$$\text{FRP} = -2390.42 + 1826 \text{ S} + 122.49 \text{ K} - 0.135 \text{ MeABP} \quad (2\text{B}11.1-1)$$

Where:

- FRP = freezing point of petroleum fraction, R.
MeABP = mean average boiling point, R.
K = Watson K factor.
S = specific gravity of petroleum fraction, 60F/60F.

Procedure

Step 1: Obtain the specific gravity and mean average boiling point of the fraction.

Step 2: Calculate the Watson K factor using Equation (2-0.8).

Step 3: Calculate the freezing point of the fraction using Equation (2B11.1-1)

COMMENTS ON PROCEDURE 2B11.1

2B11.1

Definition and Purpose

The freezing point of a petroleum fraction is the temperature at which solid crystals formed on cooling disappear as the temperature is raised. The purpose of this procedure is to predict the freezing point of petroleum fractions from the mean average boiling point and specific gravity. ASTM Procedure D2386 is a standard method for experimental determination.

Limitations

Equation (2B11.1-1) was evaluated over the following ranges of freezing points, mean average boiling points, and specific gravities.

Range of Data	
Freezing point, R	320 - 510
Specific gravity, 60F/60F	0.74 - 0.90
Mean average boiling point, R	725 - 1130

This equation (2B11.1-1) may be reasonably extrapolated beyond these ranges.

Reliability

The equation reproduced experimental values of freezing point to within 7.2 degrees Rankine.

Literature Source

American Petroleum Institute, Documentation Report API-2-98.

Example

Determine the freezing point of a petroleum fraction with a mean average boiling point of 874.5 R and specific gravity of 0.799 at 60 F.

From equation (2-0.8), the Watson K factor is as follows:

$$K = \frac{874.5^{1/3}}{0.799} = 11.97$$

From equation (2B11.1-1) the freezing point is calculated as follows:

$$FRP = -2390.42 + 1826(0.799) + 122.49(11.97) - 0.135(874.5)$$

$$FRP = 417 \text{ R}$$

An experimental value is 409 R.

PROCEDURE 2B12.1**CLOUD POINT OF PETROLEUM FRACTIONS****Discussion**

The following equation is used to estimate the cloud point of petroleum fractions.

$$\log CP = -7.41 + 5.49 \log MeABP - 0.712 MeABP^{0.315} - 0.133 S \quad (2B12.1-1)$$

Where:

- CP = cloud point of petroleum fraction, R.
MeABP = mean average boiling point, R.
S = specific gravity, 60F/60F.

Procedure

Step 1: Obtain the mean average boiling point and specific gravity.

Step 2: Calculate the cloud point using Equation (2B12.1-1).

COMMENTS ON PROCEDURE 2B12.1

2B12.1

Definition and Purpose

The cloud point of a petroleum product is the temperature at which its solid paraffin content, normally held in solution, begins to solidify and separate in tiny crystals, causing the oil to appear cloudy. The purpose of this procedure is to predict the cloud point of petroleum fractions from the specific gravity and the mean average boiling point. Procedure ASTM D97 is used to determine experimental values of cloud point.

Limitations

Equation (2B12.1-1) was evaluated with 834 points of experimental data over the following ranges of cloud point and mean average boiling point.

	Range of Data
Cloud point, R	375 to 560
Specific gravity, 60F/60F	0.77 to 0.93
Mean average boiling point, R	800 to 1225

The equation can be reasonably extrapolated beyond the tested data range.

Reliability

The equation reproduced experimental values of cloud point to within 7.4 degrees Rankine.

Literature Source

American Petroleum Institute, Documentation Report API-2-98.

Example

Determine the cloud point of a petroleum fraction having a mean average boiling point of 811.5 R and specific gravity of 0.787.

Calculate cloud point using equation (2B12.1-1)

$$\log CP = -7.41 + 5.49 \log (811.5) - 0.712(811.5)^{0.315} - 0.133(0.787) = 2.584$$

$$CP = 383.7 \text{ R}$$

The experimental value is 383.4 R.

PROCEDURE 2B13.1**CETANE INDEX OF PETROLEUM FRACTIONS****Discussion**

The following equation is used to calculate the cetane index of petroleum fractions.

$$\text{CI} = 415.26 - 7.673 \text{ API} + 0.186 \text{ MeABP} + 3.503 \text{ API log MeABP} \quad (2\text{B}13.1-1)$$
$$- 193.816 \log \text{MeABP}$$

Where:

- CI = cetane index of petroleum fraction.
API = API gravity.
MeABP = mean average boiling point, F.

Procedure

- Step 1:* Obtain the API gravity and mean average boiling point of the petroleum fraction
Step 2: Calculate the cetane index using Equation (2B13.1-1).

COMMENTS ON PROCEDURE 2B13.1**Definition and Purpose**

The cetane index is the number equal to the percentage of cetane in a blend of cetane and alpha methyl naphthalene having the same ignition quality as a sample of the petroleum fraction. The purpose of this procedure is to predict the cetane index of petroleum fractions from the API gravity and the mean average boiling point.

Limitations

Equation (2B13.1-1) was evaluated over the following ranges of API gravity and ASTM D86 mean average boiling points.

	Range of Data
API gravity	27 - 47
Mean average boiling point, F	360 - 700

The equation is not recommended for mean average boiling points < 250 F.

Reliability

The equation reproduced values of cetane index to within an average error of 2.9% for 150 data points.

Literature Source

American Petroleum Institute, Documentation Report API-2-98.

Example

Determine the cetane index of a petroleum fraction having an API gravity of 32.3 and ASTM D86 mean average boiling point of 617 F.

Using equation (2B13.1-1),

$$\begin{aligned} \text{CI} &= 415.26 - 7.673(32.3) + 0.186(617) + 3.503(32.3)\log(617) - 193.816\log(617) \\ &= 57.1 \end{aligned}$$

An experimental value is 56.

PROCEDURE 2B14.1**SMOKE POINT - ANILINE POINT INTERCORRELATION****Discussion**

The following equations are used to estimate the smoke point or aniline point of petroleum fractions.

$$SP = -3500 + 3522 S (1 + 8.234 \times 10^{-5} AP) - 3021 \ln(S) \quad (2B14.1-1)$$

$$AP = 1.214 \times 10^4 \left[\frac{SP + 3500 + 3021 \ln S}{3522S} - 1 \right] \quad (2B14.1-2)$$

Equation (2B14.1-2) is simply an algebraic rearrangement of Equation (2B14.1-1).

Where:

SP = smoke point, mm.

S = specific gravity, 60F/60F.

AP = aniline point, F.

Procedure

Step 1: Obtain the specific gravity and aniline point or smoke point of the petroleum fraction.

Step 2: Calculate the smoke point or aniline point using Equation (2B14.1-1) or (2B14.1-2), respectively.

COMMENTS ON PROCEDURE 2B14.1

Purpose

The purpose of this procedure is to predict smoke point from the specific gravity and aniline point or conversely aniline point from smoke point and specific gravity.

Limitations

Equation (2B14.1-1) was evaluated over the following data ranges of specific gravity, aniline point, and smoke point.

	Range of Data
Smoke point, mm	15 to 42
Aniline point, F	112 to 170
Specific gravity, 60F/60F	0.76 to 0.86

Reliability

The equation reproduced experimental values of smoke point to within an average absolute deviation and average absolute percent error of 1.7 mm and 7.3%, respectively. Note that Equations (2B14.1-1) and (2B14.1-2) should be used only when Procedure 2B10.1 or 2B9.1 are applicable.

Literature Source

American Petroleum Institute, Documentation Report API-2-98.

Example

Determine the smoke point of a petroleum fraction given a specific gravity of 0.839 and aniline point of 128.2 F.

Using equation (2B14.1):

$$SP = -3500 + 3522(0.839)[1 + 8.234 \times 10^{-5}(128.2)] - 3021 \ln (0.839) = 16.5 \text{ mm}$$

An experimental value is 16.7 mm.

**PROCEDURE 2B14.2
CLOUD POINT - POUR POINT INTERCORRELATION**

Discussion

The following equation is used to estimate the cloud point or pour point of petroleum fractions if the methods of Procedures 2B8.1 and 2B12.1 cannot be used.

$$\text{PP} = 0.9895 \text{ CP} + 1.4$$

(2B14.2-1)

Where:

PP = pour point, R.

CP = cloud point, R.

Procedure

Step 1: Obtain the pour point or cloud point of the petroleum fraction.

Step 2: Calculate the pour point or the cloud point of the petroleum fraction using Equation (2B14.2-1)

COMMENTS ON PROCEDURE 2B14.2

Purpose

The purpose of this procedure is to predict cloud point or pour point from the other when parameters are not available for direct prediction from Procedures 2B12.1 or 2B8.1, respectively.

Limitations

Equation (2B14.2-1) was evaluated over the following data ranges of pour points and cloud points.

Range of Data	
Cloud point, R	370 to 570
Pour point, R	370 to 570

The procedure should not be used to predict pour point unless parameters are not available to use Procedure 2B8.1. In this case use Procedure 2B12.1 to predict cloud point and then this procedure to predict pour point.

Reliability

The equation reproduced experimental values of cloud point and pour point to within an average absolute deviation of 2.2 degrees Rankine for 213 data points.

Literature Source

American Petroleum Institute, Documentation Report API-2-98.

Example

Determine the pour point of a petroleum fraction having a cloud point of 574 Rankine.

Using equation (2B14.2-1):

$$PP = 0.9895(574) + 1.4 = 569.4 \text{ R}$$

An experimental pour point value is 565 R.

PROCEDURE 2B15.1
FLASH POINT BLENDING

Discussion

The Wickey-Chittenden blending model is used to calculate the flash point of a petroleum blend. The model requires flash point indices calculated from the following equation:

$$\log \text{FBPI}_i = -6.1188 + \frac{4345.2}{(\text{FP}_i + 383.0)} \quad (2\text{B}15.1-1)$$

Where:

$$\begin{aligned} \text{FPBI}_i &= \text{flash point blending index for component } i. \\ \text{FP}_i &= \text{flash point for component } i, F \end{aligned}$$

The blend's index can be calculated by volumetrically averaging the flash point blending indices of each component using equation 2B15.1-2.

$$\text{FPBI}_B = \sum_{i=1}^n x_{v_i} \text{FPBI}_i \quad (2\text{B}15.1-2)$$

Where:

$$\begin{aligned} \text{FPBI}_B &= \text{flash point index of the total blend} \\ x_{v_i} &= \text{volumetric fraction of component I} \\ n &= \text{number of components} \end{aligned}$$

Rearranging equation (2B15.1-1), the flash point of the blend is found using equation (2B15.1-3).

$$\text{FP}_B = \frac{4345.2}{[\log(\text{FBPI}_B) + 6.1188]} - 383.0 \quad (2\text{B}15.1-3)$$

Procedure

- Step 1:* Determine the flash point and volumetric fraction for each component in the blend.
- Step 2:* Calculate the flash point blending index for each fraction from equation (2B15.1-1).
- Step 3:* Determine the total blend's index from equation (2B15.1-2).
- Step 4:* Determine the flash point of the blend from the total blend's index using equation (2B15.1-3).

COMMENTS ON PROCEDURE 2B15.1

Purpose

2B15.1

The purpose of this procedure is to predict the flash point of blends of petroleum fractions using the Wickey-Chittenden blending model.

Limitations

Wickey and Chittenden evaluated the blending procedure for binary and ternary systems, with blended flash points ranging from 78 F to 543 F. Although good results were reported for blends of components varying by as much as 345 F, the procedure is not recommended for blends of very light naphtha and asphalt. The procedure is not recommended for interblending open and closed cup flash points. Caution also should be taken with systems containing more than 3 blend components.

Reliability

The procedure reproduced values of flash points to within an average absolute deviation of 6 F for 162 blends. The authors noted, 71% of the deviations were within the reproducibility of the flash point test. No further testing was conducted by the API project staff.

Literature Source

Wickey, R. O., and Chittenden, D. H., "Flash Points of Blends Correlated," Hydrocarbon Processing and Petroleum Refiner, 42(6), 157 (1963).

Example

Determine the final blend's flash point when combining streams X and Y in the following proportions:

25% by volume of stream X with a flash point of 172 F
75% by volume of stream Y with a flash point of 325 F

Using equation (2B15.1-1) for stream X,

$$\log (FPBI_x) = -6.1188 + [4345.2/(172+383)] = 1.710$$

$$FPBI_x = 51.33$$

Similarly for stream Y,

$$FPBI_y = 1.04$$

The flash point blending index for the total blend is then calculated from equation (2B15.1-2).

$$FPBI_B = (0.25)(53.11) + (0.75)(1.04) = 13.61$$

Using equation (2B15.1-3), the flash point of the blend is,

$$FP_B = [4345.2/\log (13.61 + 6.1188)] - 383 = 216 F$$

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CHAPTER 3

PETROLEUM FRACTION DISTILLATION INTERCONVERSIONS

3.0 INTRODUCTION

ASTM and true boiling point (TBP) analytical distillations are used to define the volatility characteristics of petroleum fractions and other complex mixtures. Both are batch distillations which differ mainly in the degree of fractionation obtained during the distillation.

ASTM D86 and D1160 distillations are run in an Engler flask. No packing is employed, and reflux results only from heat losses through the neck of the flask. ASTM distillations are more widely used than TBP distillations because the former are simpler, less expensive, require less sample, and require only approximately one-tenth as much time. ASTM distillations are standardized. TBP distillations vary appreciably in procedure and apparatus.

ASTM distillation methods in use today are:

ASTM Method D86: This method is used for the distillation of motor gasolines, aviation gasolines, aviation turbine fuels, naphthas, kerosines, gas oils, distillate fuel oils, and similar petroleum products. It is carried out at atmospheric pressure. An exposed thermometer is used, and temperatures are reported without stem corrections. **ASTM D86 distillations are plotted in volume percent.**

ASTM Method D1160: This method is used for heavy petroleum products which can be vaporized partially or completely at a maximum liquid temperature of 750 F at absolute pressures down to 1 mm Hg and condensed at the pressures of the test. It is carried out at pressures between 1 mm Hg and 50 mm Hg, absolute. Temperatures are measured with a thermocouple. **ASTM D1160 distillations are plotted in volume percent.**

ASTM Method D2887: Simulated distillation (SD) by gas chromatography appears to be the most simple, reproducible, and consistent method to describe the boiling range of a hydrocarbon fraction unambiguously. This method is applicable to all petroleum fractions with a final boiling point of 1000 F or less at atmospheric pressure. The method is also limited to samples having an initial boiling point of at least 100 F. Figure 3-0.1 shows a typical relation between ASTM D86 and ASTM D2887 distillations for a petroleum fraction. **Simulated distillations are plotted in weight percent.**

ASTM Method D2892: This method is used for distillation of stabilized crude petroleum defined as having a Reid vapor pressure less than 12 psi. It employs a fractionating column of 14-18 theoretical stages operated at a reflux ratio

of 5. The method is a form of true boiling point distillation for any petroleum mixture boiling above light naphthas and mixtures with final boiling points below 750 F.

ASTM Method D3710: This method is used to determine the boiling range distribution of gasolines which do not exceed an atmospheric pressure final boiling point of 500 F. It is a gas chromatographic method otherwise similar to D2887.

In ASTM D86, D1160, and D2892 distillations there may be a residue left in the distillation equipment as well as a difference between the volume of the original charge and the sum of the distillate and residue. This difference is usually termed "loss" and is generally thought of as volatile components of the charge which have not been recondensed. For preparation of an ASTM distillation for conversion to a TBP distillation, the percent distilled at the reported temperature is the sum of the distillate collected and the loss.

When heated sufficiently hot, petroleum fractions undergo thermal cracking. Although a function of chemical composition, the amount and severity of thermal cracking increase

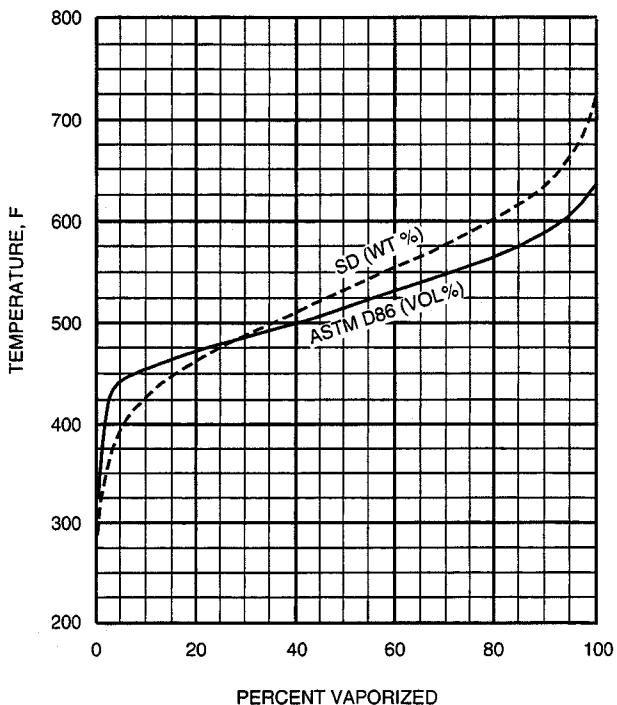
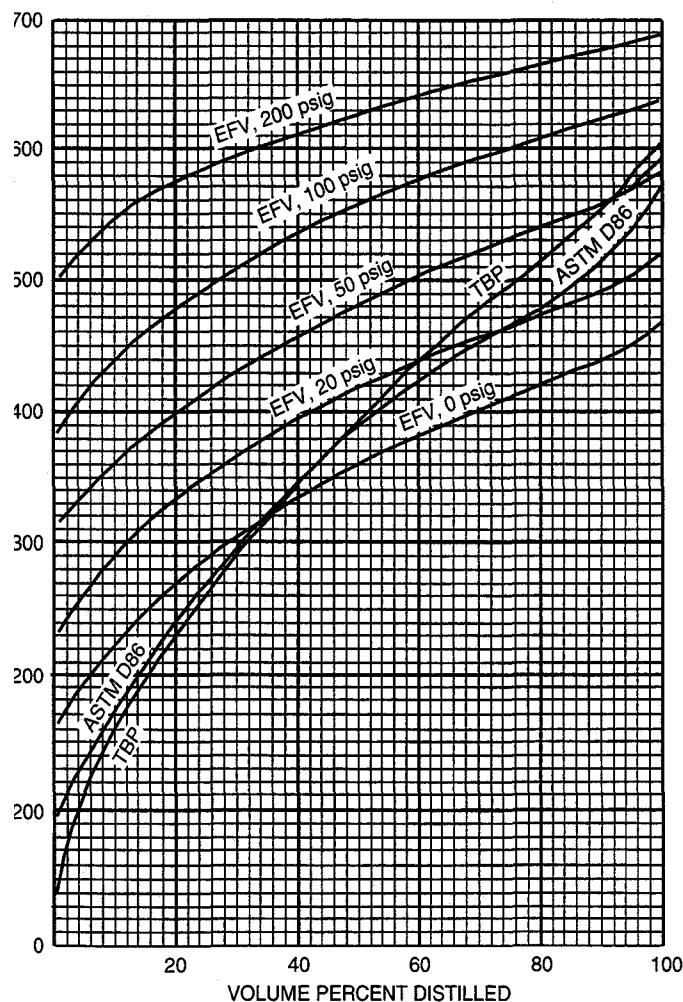


Figure 3-0.1—Typical ASTM D86 and Simulated Distillation Curves for a Petroleum Fraction

with increasing boiling point, contact time, pressure and temperature. Early editions of this chapter included a correction for cracking for observed ASTM D86 temperatures above 475 F. No correction for cracking is now recommended.

TBP distillations are performed in columns with 15 to 100 theoretical plates at relatively high reflux ratios (i.e., 5 to 1 or greater). The high degree of fractionation in these distillations gives accurate component distributions for mixtures. The lack of use of a standardized apparatus and operational procedure is a disadvantage, but the variations between various laboratories are small because a close approach to perfect separation by boiling point is usually achieved. A TBP curve is also shown in Figure 3-0.2 for comparison with an ASTM D86 distillation.



Source: Edmister and Pollock, *Chem. Eng. Progr.*, 44 905 (1948)

Figure 3-0.2—ASTM, True Boiling Point, and Equilibrium Flash Vaporization Distillation Curves for a Naphtha-Kerosine Blend

An equilibrium flash vaporization is an experiment carried out at constant pressure to determine the temperature-volume percent distilled relation. The EFV curve is a plot of temperature against percent by volume of liquid distilled, at a constant pressure. Each point on the EFV curve represents a separate equilibrium experiment. The number of equilibrium experiments needed to define all portions of the EFV curve varies with the shape of the curve. Normally, at least five such experiments are required. Figure 3-0.2 also shows the EFV curves of a naphtha-kerosine blend at atmospheric and several superatmospheric pressures compared to ASTM D86 and TBP distillations. The tedious procedures necessary to obtain experimental EFV data have made this type experiment quite rare at this time. Thus, correlations involving EFV have been eliminated from this chapter.

Users are emphatically cautioned against relying heavily on results obtained from these correlations. Because of a lack of standardization and other inherent inadequacies in the methods, the existing ASTM, TBP, and SD data on the same fractions are not sufficiently precise or consistent to develop accurate correlations. Consult the Comments on each Procedure for the accuracy of each method before use.

The correlations of this chapter were developed using data for hydrocarbon stocks and fractions which included many components and exhibited smooth distillation curves. The correlations do not apply to mixtures of few compounds with widely different boiling points.

A schematic diagram of the interconversion procedures is shown in Figure 3-0.3. Correlations are summarized in Table 3-0.4.

Correlations in this chapter are empirical in nature and are arranged according to the various pairs between ASTM, TBP, and SD relations.

Section 3A1	ASTM-TBP	(Atmospheric)
Section 3A2	ASTM-TBP	(Subatmospheric)
Section 3A3	SD-TBP-ASTM	(Atmospheric)
Section 3A4	Interconversions at Subatmospheric Pressures	

Use of Procedures

Procedures in this chapter are interconnected and are in most respects consistent. In addition, all predicted distillation curves are of the correct shape. Careful study of Figure 3-0.3 and Table 3-0.4 gives the method(s) to be used for each conversion. It should be noted that in some cases alternative paths are possible. The narrative below describes the procedures to be used in each case.

Procedure 3A1.1 (Step 1) allows interconversion between ASTM D86 and TBP distillations. Expected average errors are given in the Comments.

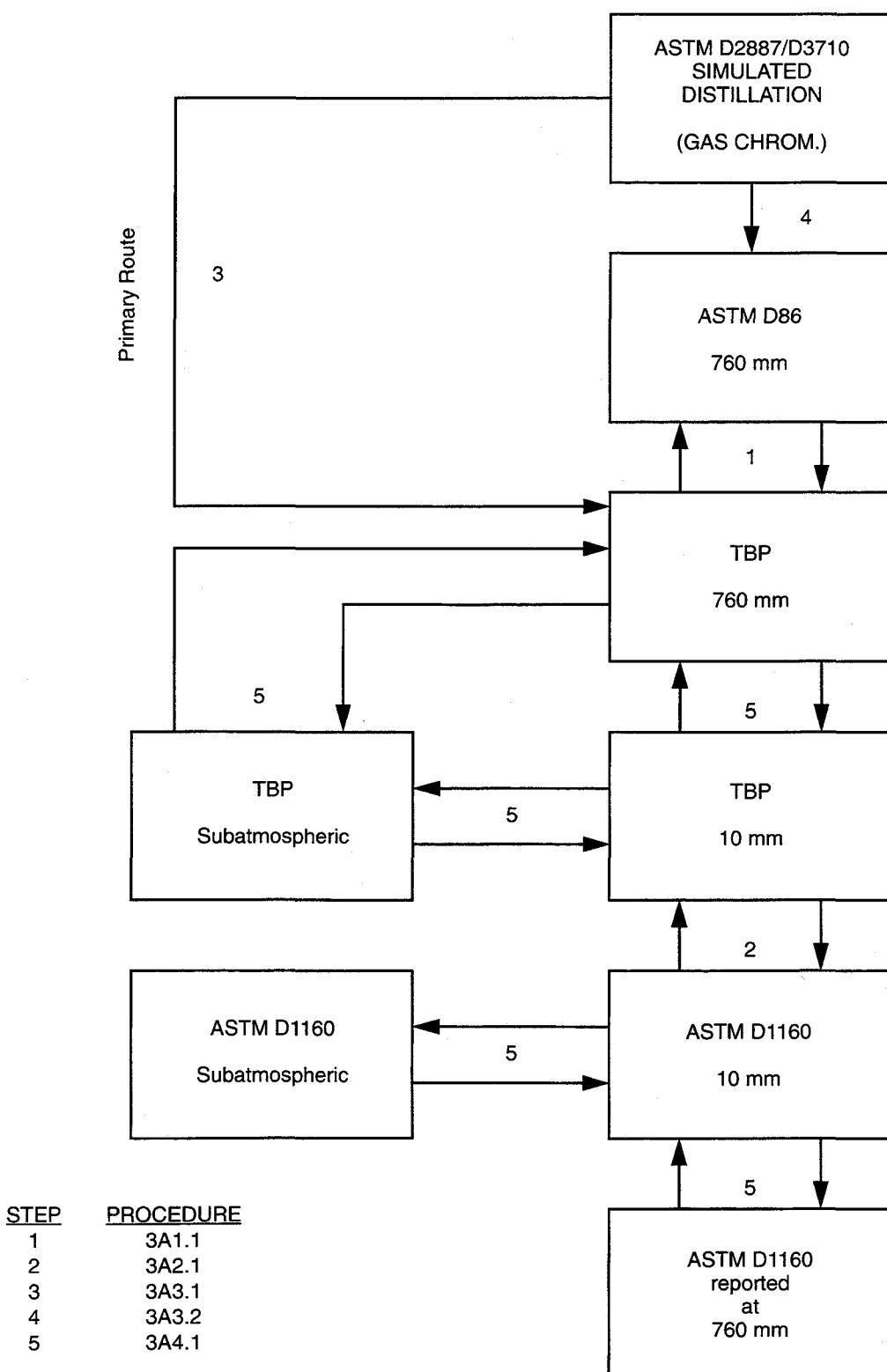


Figure 3-0.3—Distillation Conversion Routes

Procedure 3A3.1 (Step 3) allows direct interconversion of ASTM D2887 (Simulated) and TBP distillations with excellent accuracy as shown in the Comments.

Procedure 3A3.2 (Step 4) relates ASTM D2887 (Simulated) and ASTM D86 distillations with accuracy as given in the Comments. This conversion route should not be used for fractions with D86 distillation temperatures above 600 F.

The conversion of Simulated to TBP distillations can also be carried out in two steps (4 and 1) with little degradation of the prediction. See discussion in Procedure 3A3.1.

Figure 3A2.1 (Step 2) allows conversion of ASTM D1160 to TBP distillations at 10 mm mercury total pressure after which Procedure 3A4.1 (Step 5) can be used to convert the TBP to atmospheric pressure. This method is only rec-

ommended for development of a TBP distillation curve if neither an ASTM D86 or simulated distillation are available as the curve, though reasonably shaped, was not able to be verified since insufficient experimental data were available.

Equilibrium flash data, while probably more reproducible than ASTM and TBP data, are obtained using different types of apparatus and many variations in procedure. A computer method for flash calculations and estimation of equilibrium K-Values for petroleum fractions using a modified Soave-Redlich-Kwong (6) equation of state is included in Chapter 8.

NOTE: A report which documents the basis upon which the material in all editions of this chapter was selected has been published by the American Petroleum Institute as *Documentation Reports No. 3-66, No. 2,3-86, and No. 3-93*. All data used for development of prediction methods are referenced in these reports.

TABLE 3-0.4—SUMMARY OF CORRELATIONS FOR CONVERTING DISTILLATION DATA

Data Available		Data Desired		Conversion Method Steps in Fig. 3-0.3
Type	Pressure, mm Hg	Type	Pressure, mm Hg	
ASTM D2887 (SD)	760	ASTM D86	760	4
ASTM D86	760	TBP	760	1
ASTM D1160	10	TBP	10	2
ASTM D1160	10	TBP	760	2, 5
ASTM D1160	10	ASTM D86	760	2, 5, 1
TBP	10	TBP	760	5
ASTM D2887 (SD)	760	TBP	760	3
ASTM D1160	1	TBP	760	5, 2, 5
ASTM D1160	1	ASTM D86	760	5, 2, 5, 1
ASTM D1160	100	TBP	760	5, 2, 5
ASTM D1160	100	ASTM D86	760	5, 2, 5, 1

Note: All ASTM D86 temperatures at 760 mm Hg are observed values.

PROCEDURE 3A1.1

INTERCONVERSION OF ASTM D86—TBP DISTILLATIONS AT ATMOSPHERIC PRESSURE

Discussion

The following equation is used to convert an ASTM D86 distillation 50% point temperature to a true boiling point distillation 50% point temperature.

$$\text{TBP (50)} = 0.87180 (\text{ASTM D86 (50)})^{1.0258} \quad (3\text{A1.1-1})$$

Where:

TBP (50) = true boiling point distillation temperature at 50 volume percent distilled, degrees Fahrenheit.

ASTM D86 (50) = observed ASTM D86 distillation temperature at 50 volume percent distilled, degrees Fahrenheit.

To determine the difference between adjacent cut points, use the following equation:

$$Y_i = AX_i^B \quad (3\text{A1.1-2})$$

Where:

Y_i = difference in true boiling point distillation temperature between two cut points, degrees Fahrenheit.

X_i = observed difference in ASTM D86 distillation temperature between two cut points, degrees Fahrenheit.

A, B = constants varying for cut point ranges, described as follows.

i	Cut Point Range			Maximum Allowable X_i , (F)
		A	B	
1	100% - 90%	0.11798	1.6606	—
2	90% - 70%	3.0419	0.75497	100
3	70% - 50%	2.5282	0.82002	150
4	50% - 30%	3.0305	0.80076	250
5	30% - 10%	4.9004	0.71644	250
6	10% - 0%	7.4012	0.60244	100

To determine the true boiling point temperature at any percent distilled, add or subtract the proper difference(s) from the predicted 50% true boiling point temperature.

$$\begin{aligned}
 \text{TBP (0)} &= \text{TBP (50)} - Y_4 - Y_5 - Y_6 \\
 \text{TBP (10)} &= \text{TBP (50)} - Y_4 - Y_5 \\
 \text{TBP (30)} &= \text{TBP (50)} - Y_4 \\
 \text{TBP (70)} &= \text{TBP (50)} + Y_3 \\
 \text{TBP (90)} &= \text{TBP (50)} + Y_3 + Y_2 \\
 \text{TBP (100)} &= \text{TBP (50)} + Y_3 + Y_2 + Y_1
 \end{aligned} \quad (3\text{A1.1-3})$$

Procedure

Step 1: Use equation (3A1.1-1) to calculate the TBP distillation temperature at 50% distilled.

Step 2: Use equation (3A1.1-2) to calculate necessary TBP differences.

Step 3: Use equation(s) (3A1.1-3) to calculate desired TBP distillation temperatures.

To determine the ASTM D86 distillation temperatures from the TBP distillation temperatures, reverse the procedure. Thus, equation (3A1.1-1) becomes

$$(\text{ASTM D86 (50)}) = \exp \left[\frac{\ln (\text{TBP (50)} / 0.87180)}{1.0258} \right] \quad (3\text{A1.1-4})$$

Similarly, all equations (3A1.1-2) can be reversed, and all equations (3A1.1-3) can be modified by changing TBP to ASTM.

COMMENTS ON PROCEDURE 3A1.1

Purpose

The purpose of this procedure is to predict a TBP distillation at atmospheric pressure from an ASTM D86 distillation or the reverse by hand or by computer.

Limitations

Because experimental data on higher boiling fractions are quite scattered, all derivations were carried out on fractions having an ASTM 50% point temperature of 480 F and below. However, the correlation extrapolates well to fractions with ASTM 50% point temperatures up to 600 F. Care should be taken in extrapolating above this point. In addition, initial and final boiling point data are scarce and inaccurate. Thus, values for these points should be taken as rough approximations.

Reliability

Differences between the estimated and experimental TBP values at various volume % distilled points are given below.

Volume % Distilled	TBP (predicted) — TBP (experimental)	
	Average	Bias
0	21.9 F	-7.8 F
10	9.0	-1.8
30	5.7	-0.4
50	4.7	-0.1
70	5.6	1.1
90	7.1	2.3
100	4.2	4.0

Seventy-one sets of data were used in development, although fewer points were available at the 0 and 100% points. Average error is defined as the sum of the absolute values of the differences between predicted and experimental temperatures divided by the number of data points, while bias error sums the actual values of the differences.

Special Comment

This method was derived from all data available to the project and was judged to be the most appropriate form for interconversion among the various types of distillations. As additional data become available, the constants in equations (3A1.1-1 and 3A1.1-2) can easily be improved. In addition, users may wish to check the correlation with their proprietary data before using it.

Literature Source

This method was developed by the API Technical Data Book Project at The Pennsylvania State University.

Example

Estimate the atmospheric TBP distillation temperatures for a petroleum fraction having the experimental ASTM D86 distillation temperatures given in the following table. The experimental TBP temperatures are given for comparison with the predicted temperatures.

Volume percent distilled	10	30	50	70	90
ASTM D86 temperature, F	350	380	404	433	469
TBP temperature, F	321	371	409	447	491

Using equation (3A1.1-1)

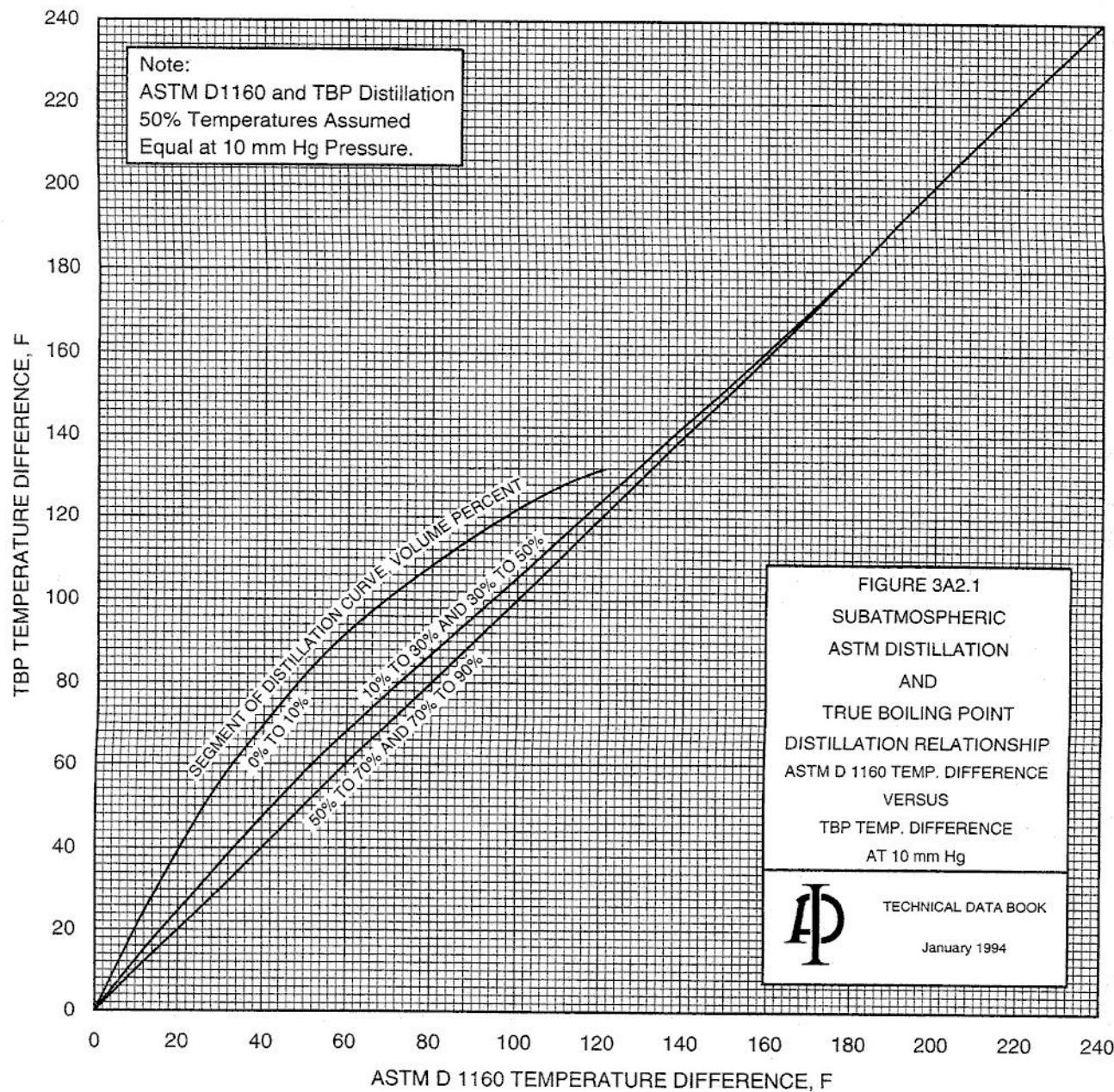
$$\begin{aligned} \text{TBP (50)} &= 0.87180 (404)^{1.0258} \\ &= 411.2 \text{ F} \end{aligned}$$

Using equation (3A1.1-2) at the 30% point

$$Y_4 = 3.0305 [X_4]^{0.80076}$$

$$\text{where } X_4 = 404 - 380 = 24 \text{ F}$$

$$\text{therefore, } Y_4 = 38.6 \text{ F}$$



COMMENTS ON FIGURE 3A2.1**Purpose**

This figure relates ASTM D 1160 and TBP distillation data at 10 mm Hg absolute pressure.

Reliability

No quantitative evaluation of the correlation could be made because of lack of data. The original reference indicates that temperatures from this method will be within 25 F of the actual values.

Special Comment

The ASTM D 1160 and TBP 50-percent points at 10 mm Hg are assumed to be equal.

Literature Source

Adapted from Edmister and Okamoto, *Petrol. Refiner* 38 [9] 271 (1959); copyrighted in 1959 by Gulf Publishing Company, Houston, Texas.

Example

Estimate the TBP curve at 10 mm Hg for a petroleum fraction having the following ASTM D 1160 distillation temperatures at 10 mm Hg:

Distillation, percent by volume	10	30	50	70	90
Temperature, deg F	300	400	475	550	650

First, from Fig. 3A2.1, find the temperature differences for each segment of the TBP curve at 10 mm Hg:

Segment of Curve (Percent by Volume)	10 mm Hg ASTM D 1160 Temperature Difference (Degrees Fahrenheit)		10 mm Hg TBP Temperature Difference (from Fig. 3A2.1) Degrees Fahrenheit
	10 to 30	30 to 50	50 to 70
10 to 30	100	75	75
30 to 50		75	
50 to 70			75
70 to 90	100		100

The TBP temperatures are then calculated. The ASTM D 1160 and TBP distillation 50-percent temperatures are assumed to be equal at 10 mm Hg absolute pressure. Here, the 50-percent temperature is 475 F:

$$\begin{aligned} \text{30-percent temperature} &= 475 - 82 = 393 \text{ F} & \text{70-percent temperature} &= 475 + 75 = 550 \text{ F} \\ \text{10-percent temperature} &= 393 - 106 = 287 \text{ F} & \text{90-percent temperature} &= 550 + 100 = 650 \text{ F} \end{aligned}$$

PROCEDURE 3A3.1

CONVERSION OF SIMULATED (ASTM D2887) TO TRUE BOILING POINT DISTILLATION AT ATMOSPHERIC PRESSURE

Discussion

The true boiling point temperature at 50 *volume* percent distilled is taken to be equal to the simulated distillation temperature at 50 *weight* percent distilled.

$$\text{TBP (50)} = \text{SD (50)} \quad (3\text{A}3.1-1)$$

Where:

TBP (50) = true boiling point temperature at 50 *volume* percent distilled, degrees Fahrenheit.

SD (50) = simulated distillation temperature at 50 *weight* percent distilled, degrees Fahrenheit.

To determine the difference between adjacent cut points, use the following equation.

$$W_i = CV_i^D \quad (3\text{A}3.1-2)$$

Where:

W_i = true boiling point temperature difference between two cut points, degrees Fahrenheit.

V_i = simulated distillation temperature difference between two cut points, degrees Fahrenheit.

C, D = constants varying for cut point ranges, described as follows.

<i>i</i>	Cut Point Range	Approximate Maximum Allowable		
		<i>C</i>	<i>D</i>	V_i , (F)
1	100% - 95%*	0.02172	1.9733	30
2	95% - 90%	0.97476	0.8723	40
3	90% - 70%	0.31531	1.2938	75
4	70% - 50%	0.19861	1.3975	75
5	50% - 30%	0.05342	1.6988	75
6	30% - 10%	0.011903	2.0253	75
7	10% - 5%	0.15779	1.4296	40

*approximate—use with care

To determine the true boiling point temperature at any percent distilled, add or subtract the proper difference(s) from the predicted 50% true boiling point temperature.

$$\begin{aligned}
 \text{TBP (5)} &= \text{TBP (50)} - W_5 - W_6 - W_7 \\
 \text{TBP (10)} &= \text{TBP (50)} - W_5 - W_6 \\
 \text{TBP (30)} &= \text{TBP (50)} - W_5 \\
 \text{TBP (70)} &= \text{TBP (50)} + W_4 \\
 \text{TBP (90)} &= \text{TBP (50)} + W_4 + W_3 \\
 \text{TBP (95)} &= \text{TBP (50)} + W_4 + W_3 + W_2 \\
 \text{TBP (100)} &= \text{TBP (50)} + W_4 + W_3 + W_2 + W_1
 \end{aligned} \quad (3\text{A}3.1-3)$$

Procedure

Step 1: Use equation (3A3.1-1) to calculate the TBP at the 50% distilled point.

Step 2: Use equation (3A3.1-2) to calculate necessary TBP differences.

Step 3: Use equation(s) (3A3.1-3) to calculate desired TBP temperatures.

COMMENTS ON PROCEDURE 3A3.1**Purpose**

The purpose of this procedure is to predict a TBP distillation at atmospheric pressure from a simulated distillation by hand or by computer.

Limitations

Data sets with TBP 50% points between 250 and 700 F were used in deriving this correlation. Although the correlation extrapolates well, use of the resulting temperature-% distilled data outside the limits is not encouraged. Also, as final boiling point data are not generally accurate, values for these points should only be taken as rough approximations.

Reliability

Differences between the predicted and experimental TBP temperatures at various % distilled points are given below.

% Distilled	TBP (predicted) — TBP (experimental)	
	Average	Bias
5	21.7 F	2.1 F
10	19.7	0.2
30	12.3	1.0
50	9.6	0.6
70	11.0	-1.4
90	12.6	-1.4
95	12.1	-2.6
100	8.1	-8.0

Twenty-one data sets were used in development of this procedure, except at the 100% point where only 8 sets were available. The initial boiling point is not included, as the data scatter is so great that the correlation is meaningless.

Special Comment

This method was derived from all data available to the project and was judged to be the most appropriate form for interconversion among various types of distillations. As additional data become available, the constants in equations (3A3.1-2) can easily be improved. In addition, users may wish to check the correlation with their proprietary data before using it.

A two step procedure giving essentially equivalent results for materials with TBP temperatures below 600 F consists of step 4 followed by step 1 of Figure 3-0.3. The table below shows an error analysis, carried out on 19 sets of data for which ASTM D86, TBP, and SD were available, which confirms this conclusion. This method should be limited to fractions boiling below 600 F.

**Conversion of Simulated to TBP Distillation
Comparison of Two-Step Procedure with One-Step Procedure—Error Analysis**

% Distilled	Data Points	Conversion of SD to ASTM D86 by Step 4 followed by Conversion of Calculated ASTM D86 to TBP by Step 1		Conversion of SD to TBP by Step 3	
		Errors, F	Errors, F	Errors, F	Errors, F
0	18	32.3	-29.0	-	-
10	19	12.2	-9.2	19.7	0.2
30	19	8.4	-2.7	12.3	1.0
50	19	7.4	0.3	9.6	0.6
70	19	9.0	2.3	11.0	-1.4
90	19	11.3	3.0	12.6	-1.4
100	8	5.6	4.5	8.1	-8.0

Literature Source

This method was developed by the API Technical Data Book Project at The Pennsylvania State University.

Example

Estimate the atmospheric TBP distillation temperatures for a petroleum fraction having an experimental simulated distillation as given in the following table. Experimental TBP temperatures are given for comparison with the calculated temperatures.

% distilled	5	10	30	50	70	90	95
SD temperature, F	293	305	324	336	344	359	369
TBP temperature, F	321	322	326	332	337	345	348

Using equation (3A3.1-1)

$$\text{TBP (50)} = \text{SD (50)} = 336 \text{ F}$$

Using equation (3A3.1-2) at the 30% point

$$W_5 = 0.05342[V_5]^{1.6988}$$

$$\text{where } V_5 = 336 - 324 = 12$$

$$\text{therefore } W_5 = 3.6 \text{ F}$$

Using equation (3A3.1-3) at the 30% point

$$\begin{aligned} \text{TBP (30)} &= \text{TBP} - W_5 \\ &= 336 - 3.6 = 332.4 \text{ F} \end{aligned}$$

Similarly, using equations (3A3.1-2) and (3A3.1-3) at other cut points

$$W_2 = 7.3 \text{ F} \quad \text{TBP (95)} = 350.1 + 7.3 = 357.4 \text{ F}$$

$$W_3 = 10.5 \text{ F} \quad \text{TBP (90)} = 339.6 + 10.5 = 350.1 \text{ F}$$

$$W_4 = 3.6 \text{ F} \quad \text{TBP (70)} = 336 + 3.6 = 339.6 \text{ F}$$

$$W_6 = 4.7 \text{ F} \quad \text{TBP (10)} = 332.4 - 4.7 = 327.7 \text{ F}$$

$$W_7 = 5.5 \text{ F} \quad \text{TBP (5)} = 327.7 - 5.5 = 322.2 \text{ F}$$

PROCEDURE 3A3.2

CONVERSION OF SIMULATED (ASTM D2887) TO ASTM D86 DISTILLATION AT ATMOSPHERIC PRESSURE

Discussion

The ASTM D86 temperature at the 50 *volume* percent distilled point may be calculated from the simulated distillation temperature at the 50 *weight* percent distilled point.

$$\text{ASTM (50)} = 0.77601 (\text{SD (50)})^{1.0395} \quad (3\text{A3.2-1})$$

Where:

ASTM (50) = ASTM D86 temperature at 50 *volume* percent distilled, degrees Fahrenheit.

SD (50) = simulated distillation temperature at 50 *weight* percent distilled, degrees Fahrenheit.

To determine the difference between adjacent cut points, use the following equation.

$$U_i = ET_i^F \quad (3\text{A3.2-2})$$

Where:

U_i = ASTM D86 distillation temperature difference between two cut points, degrees Fahrenheit.

T_i = SD temperature difference between two cut points, degrees Fahrenheit.

E, F = constants varying for cut point ranges, described as follows.

<i>i</i>	Cut Point Range			Approximate Maximum Allowable T_i , (F)
		<i>E</i>	<i>F</i>	
1	100% - 90%	2.6029	0.65962	100
2	90% - 70%	0.30785	1.2341	100
3	70% - 50%	0.14862	1.4287	100
4	50% - 30%	0.07978	1.5386	100
5	30% - 10%	0.06069	1.5176	150
6	10% - 0%	0.30470	1.1259	150

To determine the true boiling point temperature at any percent distilled, add or subtract the proper difference(s) from the predicted 50% true boiling point temperature.

$$\begin{aligned}
 \text{ASTM (0)} &= \text{ASTM (50)} - U_4 - U_5 - U_6 \\
 \text{ASTM (10)} &= \text{ASTM (50)} - U_4 - U_5 \\
 \text{ASTM (30)} &= \text{ASTM (50)} - U_4 \\
 \text{ASTM (70)} &= \text{ASTM (50)} + U_3 \\
 \text{ASTM (90)} &= \text{ASTM (50)} + U_3 + U_2 \\
 \text{ASTM (100)} &= \text{ASTM (50)} + U_3 + U_2 + U_1
 \end{aligned} \quad (3\text{A3.2-3})$$

Procedure

Step 1: Use equation (3A3.2-1) to calculate the TBP at the 50% distilled point.

Step 2: Use equation (3A3.2-2) to calculate necessary TBP differences.

Step 3: Use equation(s) (3A3.2-3) to calculate desired TBP temperatures.

COMMENTS ON PROCEDURE 3A3.2

Purpose

The purpose of this procedure is to predict ASTM D86 distillation temperature from simulated distillation data by hand or by computer.

Limitations

Data sets with ASTM D86 50% points between 150 and 600 F were used in deriving this correlation. Although the correlation extrapolates well, use of the resulting temperature-% distilled data outside the limits is not recommended. Some evidence shows errors to be significantly higher above a 600 F boiling point. As initial and final boiling point data are inaccurate, values for these points are only rough approximations and should not be used for design.

Reliability

Differences between the predicted and experimental ASTM D86 temperatures at various % distilled points are given below.

TBP (predicted) — TBP (experimental)		
% Distilled	Average	Bias
0	21.5 F	8.0 F
10	8.6	3.2
30	5.3	0.9
50	7.8	<0.1
70	4.5	-0.1
90	9.6	-1.8
100	19.5	-9.6

Approximately 125 data sets were used in development.

Special Comment

This method was derived from all data available to the project and was proven to be the most accurate form for interconversion among all types of distillations. As additional data become available, the constants in equations (3A3.2-1 and 3A3.2-2) can easily be improved. In addition, users may wish to check the correlation with their proprietary data before using it.

Literature Source

This method was developed by the API Technical Data Book Project at The Pennsylvania State University.

Example

Estimate the atmospheric ASTM D86 distillation temperature of a petroleum fraction having an experimental simulated distillation as given in the following table. Experimental ASTM D86 temperatures are given for comparison with the calculated temperatures.

% distilled	0	10	30	50	70	90	100
SD temperature, F	77	93	148	215	285	360	408
ASTM D86 temperature, F ...	104	134	163	208	269	335	390

Using equation (3A3.2-1)

$$\text{ASTM (50)} = 0.77601 (215) 1.0395 = 206.3 \text{ F}$$

Using equation (3A3.2-2) at the 30% point

$$U_4 = 0.07978 T_4^{1.5386}$$

$$\text{where } T_4 = 215 - 148 = 67$$

$$\text{therefore } U_4 = 51.5 \text{ F}$$

Using equation (3A3.2-3) at the 30% point

$$\text{ASTM (30)} = 206.3 - 51.5 = 154.8 \text{ F}$$

PROCEDURE 3A4.1**INTERCONVERSION OF DISTILLATION DATA FOR PETROLEUM FRACTIONS AT SUBATMOSPHERIC PRESSURES****Discussion**

The following procedure is recommended to convert ASTM or TBP distillation data between subatmospheric pressures (usually 1, 10, 100 mm Hg) and between subatmospheric pressures and atmospheric pressure (760 mm Hg).

Procedure**A. Data at Subatmospheric Pressure**

Step 1: Assume the Watson K of the petroleum fraction is 12, and convert the data using Procedure 5A1.19.

Step 2: Since the Watson K is set at 12, no Watson K correction is necessary.

B. Data at Atmospheric Pressure

Step 1: If the specific gravity and mean average boiling point are known or can be calculated, determine the Watson K from the defining equation (2-0.8). Otherwise assume $K = 12$.

Step 2: Follow Procedure 5A1.19.

COMMENTS ON PROCEDURE 3A4.1

Purpose

The purpose of this procedure is to convert petroleum fraction ASTM or TBP distillations from one pressure to another up to atmospheric pressure. This procedure is intended for both desk and computer use.

Limitations

Limitations are the same as given for Procedure 5A1.19.

Reliability

Reliability is the same as given for Procedure 5A1.19. If the Watson *K* is taken to be 12, larger errors will result, especially for highly aromatic fractions.

Example

Consider a 31.4° API Saudi Arabian crude for which extensive TBP data are available. Four experimental TBP distillation data points are:

Measured TBP Temperature, F	Pressure, mm Hg	Volume % Distilled	API Gravity
450	760	30	44.5
252	10	34	40.8
463	10	58	26.3
403	1	62	24.7

Interconvert these data to distillation temperatures at each of 1, 10, and 760 mm Hg pressure.

Although it is not necessary in this case, assume *K* = 12 and read results directly from Figure 5A1.20b. The measured temperature at one pressure can be converted to each of the other two pressures. The results are given below:

Pressure, mm Hg	Volume % Distilled			
	30	34	58	62
760	450*	492	742	782
10	218	252*	463*	498
1	144	175	370	403*

*Experimental values.

Each tabulation shows good consistency. In this case, note that the actual Watson *K* is calculable for the first point and could be used with the full Procedure 5A1.19. For example, for the first point:

$$K = (450 + 460)^{1/3} / [141.5 / (131.5 + 44.5)] = 12.06$$

The Watson *K* for the entire crude, assuming a MeABP of 617 F, is 11.8 and could be used as an estimate for all fractions distilled at subatmospheric pressure.

CHAPTER 4

CRITICAL PROPERTIES

4-0 INTRODUCTION

The actual experimental or true critical temperature and pressure of pure compounds and of mixtures are of importance in determining existing phase conditions and permissible operating ranges of reactors and mass transfer equipment such as distillation columns and extractors. Critical properties of pure compounds are also essential to calculate pseudocritical properties used throughout the *Technical Data Book* in the theorem of corresponding states (54) for the estimation of thermodynamic and volumetric properties of mixtures. A pseudocritical or molar average property is a calculated value that cannot be measured under any circumstances.

Critical temperatures and pressures for pure hydrocarbons and a number of nonhydrocarbons are given in Chapter 1. Critical compressibility factors are given in Chapters 1 and 2.

The Critical State of Mixtures and the Two-Phase Envelope

The conditions of equilibrium for coexisting vapor and liquid phases of a pure substance are defined on a pressure-temperature diagram by the vapor pressure curve. This curve starts at the triple point, where vapor, liquid, and solid phases are in equilibrium, and ends at the critical point. As the critical point is approached by the coexisting phases, their properties approach each other until they become identical at the critical temperature and pressure, where a single homogeneous phase is present.

In the case of homogeneous mixtures of liquids, vaporization at a constant pressure takes place over a range of temperatures instead of at the single temperature associated with the vapor pressure of pure substances. Consequently, the vaporization of multi-component liquids requires two curves on the pressure-temperature diagram to define the boiling characteristics instead of a single vapor pressure curve. To illustrate, Figure 4-0.1 shows a part of a pressure-temperature diagram for a hypothetical liquid mixture. In this diagram, the two-phase region is enclosed by the envelope $L_{PM}CT_M$ which consists of the "bubble-point" curve, $L_{PM}C$, and the "dew-point" curve, $VT_M C$. Their common point, C , is the critical point at which the coexisting liquid and vapor become a single homogeneous phase.

The significance of the bubble-point and dew-point curves may be demonstrated by following either an iso-

baric or an isothermal path across the envelope so that both bubble-point and dew-point curves are crossed. For example, the constant pressure path of Case I between points 1 and 2 in Figure 4-0.1 crosses the bubble-point curve at A . Starting at 1 in the homogeneous liquid region, increasing the temperature of the system causes no change in the state of aggregation of the mixture until the temperature corresponding to point A is reached. At this point vaporization begins, and, as the temperature is increased further, the liquid in the system decreases in quantity while the vapor phase increases. Following the same path in the reverse direction, from point 2 in the homogeneous vapor region toward point 1, no change takes place in the vapor phase until the dew-point curve is crossed at B , where condensation of vapor commences. As the temperature is reduced further, more vapor condenses until, at point A on the bubble-point curve, the system is completely liquid.

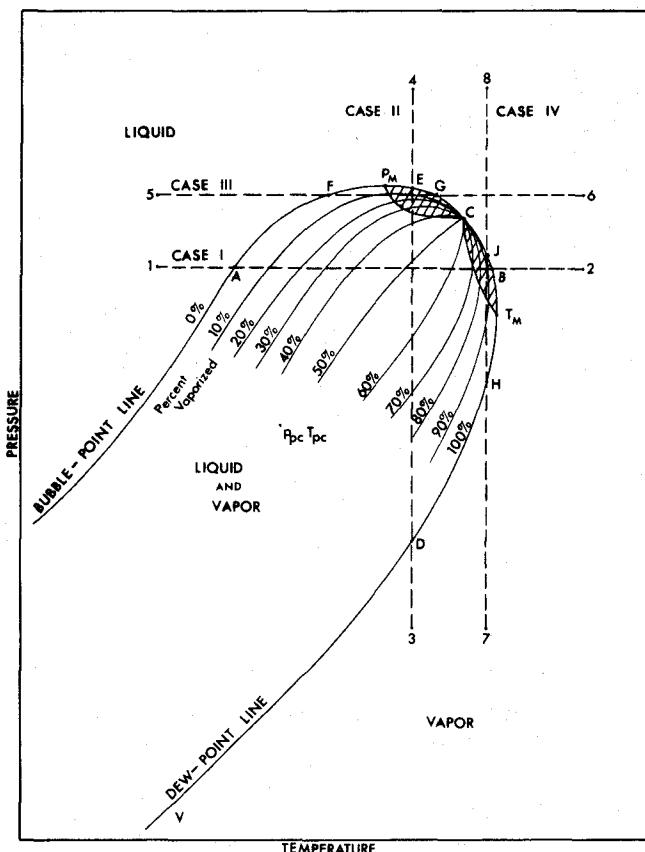


Figure 4-0.1—Pressure Temperature Diagram for a Mixture of Constant Composition Near the Critical Point

Case II shows a typical example of vaporization or condensation at constant temperature. In this case, between points 3 and *D*, the path is in the homogeneous vapor region. Between *D* on the dew-point curve and *E* on the bubble-point curve, condensation takes place with rising pressure until, at *E*, the system is entirely liquid. From *E* to point 4, the state of aggregation of the mixture is not changed by the constantly increasing pressure.

One of the important characteristics of the pressure-temperature diagrams of mixtures is that the curve defining the envelope enclosing the two-phase region can have maximum values of pressure and temperature that are not necessarily coincident with the critical point. This is illustrated in Figure 4-0.1, where a maximum pressure occurs at p_M and a maximum temperature at T_M . The maximum pressure, p_M , is frequently referred to as the cricondenbar, which is an abbreviation for the critical condensation pressure. Similarly, the maximum temperature, T_M , is known as the cricondenterm to indicate the critical condensation temperature. Etter and Kay (16), Grieves and Thodos (19), and Silverman and Thodos (54) have presented correlations for estimating these maximum values.

The points p_M and T_M on the bubble-point and dew-point curves of Figure 4-0.1 make it possible to:

1. Follow an isobaric path at a pressure higher than the critical pressure, such as Case III, which crosses the bubble-point curve twice without crossing the dew-point line.
2. Follow an isothermal path at a temperature higher than the critical temperature, such as Case IV, which crosses the dew-point curve twice without crossing the bubble-point curve.

These possibilities give rise to vaporization and condensation phenomena which differ from those of Cases I and II, whose paths are respectively at a pressure and a temperature lower than the critical pressure and temperature. In Case III, for example, the isobaric path between points 5 and 6 is at a pressure intermediate between the critical and maximum pressures and crosses the bubble-point curve at *F* and *G*. Because of this, whether the temperature rises or falls, the initial point of intersection with the bubble-point curve coincides with the beginning of vaporization for the path being followed. Inasmuch as the path must return to the homogeneous liquid phase without crossing the dew-point curve, if it is continued to the second point of intersection, it is evident that vaporization must first increase from zero, go through a maximum, and then decrease to zero again upon its second crossing of the bubble-point curve. In these circumstances, the part of the isobaric path between points *F* and *G* which lies

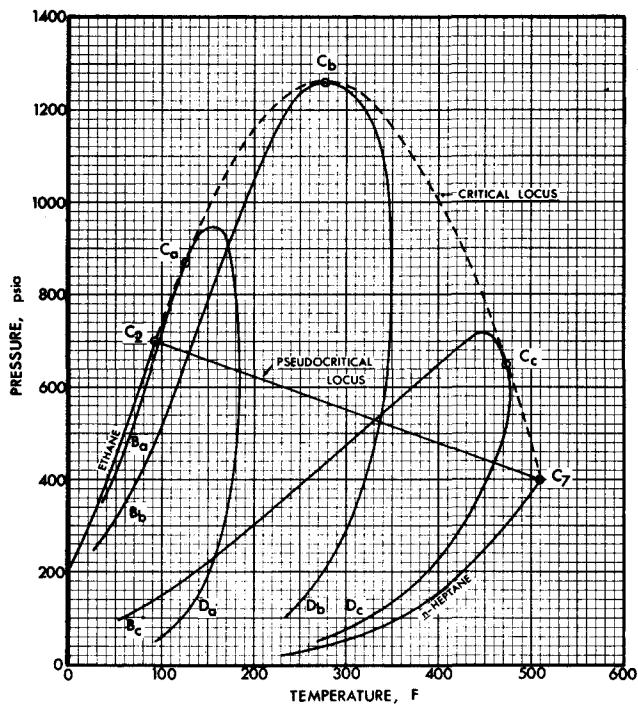
between the point of maximum vaporization and *G* involves either condensation with a rising temperature or vaporization with a falling temperature, depending upon the direction it takes. This anomalous behavior is termed "isobaric retrograde vaporization" by Sage and Lacey (60).

In Case IV, an isothermal path at a temperature between the critical temperature of the system and the maximum on the dew-point curve is taken between points 7 and 8, in the homogeneous vapor region. This path crosses the dew-point line at *H* and *J* giving rise to somewhat similar anomalous vaporization and condensation phenomena as that illustrated by Case III. Because this case is associated with the dew-point curve, Sage and Lacey refer to this anomaly as "isothermal retrograde condensation." For a more detailed discussion of the retrograde phenomena associated with the two-phase region near the critical point of mixtures, the reader is referred to Katz and Kurata (24), and Sage and Lacey.

The Critical Locus

The two-phase envelope illustrated in Figure 4-0.1 represents the pressure-temperature relationships in the critical region for a mixture having a defined composition. Any change in the composition of the mixture is reflected in changes in the curves enclosing the two-phase region. The critical temperature and pressure will change, and the maximum pressure and temperature and the slopes of the bubble-point and dew-point lines will all be different.

Figure 4-0.2 illustrates the effects of changes in composition on the shape of the two-phase envelope and its associated variables. The figure represents the pressure-temperature diagrams of Kay (26) for ethane and *n*-heptane and three mixtures in the critical region. Of the three two-phase envelopes given in Figure 4-0.2, the one indicated by the symbol C_c for the binary mixture containing 9.78 percent by weight ethane is the one that approaches most closely the diagram presented in Figure 4-0.1 for a hypothetical mixture. In those labeled C_a and C_b there are conspicuous differences in all of the variables mentioned previously. The change of position of the critical point relative to the maximum values of temperature and pressure found on the three envelopes shown is of concern here. Comparison of the three envelopes presented in Figure 4-0.2 with that of Figure 4-0.1, for example, shows that the critical point apparently can be located anywhere around the closed end of the envelope between the vicinities of *A* and *H* in Figure 4-0.1. When the mixture contains a relatively high proportion of the light component, the critical point will probably be found between points *A* and *E* in Figure



Curve	Ethane (Percent by Weight)
C ₂	100.0
C _a	90.22
C _b	50.25
C _c	9.78
C ₇	0.00

Symbols:

- C = critical point.
- B = bubble-point line.
- D = dew-point line.

Figure 4-0.2—Critical Locus for the Ethane-*n*-Heptane System and Envelopes for Three Binary Mixtures (23)

4-0.1. When the concentration of the volatile component is smaller than that of the less volatile one, the critical point will probably lie between E and H in Figure 4-0.1. One of the consequences of this variation in the relative positions of critical points, cricondenbars, and cricondentherms is that the character of the retrograde phenomena described previously varies for each case. The types of retrograde phenomena described in association with Figure 4-0.1, for example, are only two out of a total of eight possibilities described by Sage and Lacey, if the full range of compositions between light and heavy components is considered.

The broken line of Figure 4-0.2, connecting the critical point of ethane with that of *n*-heptane and drawn tangent to each composition envelope at its critical point, is known as the critical locus. On such a locus only one critical pressure occurs for each critical tem-

perature, and each critical point is associated with only one composition.

In practice, critical loci for multicomponent systems are of greater concern than are those of binary systems. The aforementioned principles developed for binary systems with the aid of Figure 4-0.2, however, can easily be shown to apply for multicomponent systems. It is only necessary to imagine one or both of the vapor pressure curves of the binary system to have been replaced by envelopes representing pressure-temperature diagrams of mixtures of fixed composition. Then each terminus of the critical locus that represents the critical point of a mixture, such as point C of Figure 4-0.1, may be considered to be the critical point of a "pseudocomponent."

As long as the pseudocomponents involved in the substitution remain unchanged in composition, the critical locus associated with them will be fixed, and the pressure-temperature envelopes of all intermediate compositions can be defined as binary mixtures of the two. In a mixture of several pure components of varying volatility, for example, the two pseudocomponents required to establish the termini of the critical locus for the mixture may be chosen so that the vapor pressure curve of the most volatile component provides the pressure-temperature relationship of one of the components of the hypothetical binary mixture. The other component needed to establish the critical locus then becomes the two-phase envelope that defines pressure-temperature relations of the multicomponent mixture consisting of all the remaining components of the mixture under consideration. This means that in a pressure-temperature diagram, such as Figure 4-0.2, the vapor pressure curve of the heavy component in the binary system is replaced by the two-phase envelope of a certain mixture of the combined heavier components considered as a pseudocomponent. At the same time, the vapor pressure curve of the light pure component continues to represent the pressure-temperature relationship for the more volatile component of the pseudo binary system used as a more tractable substitute for the entire multicomponent system considered.

Mixtures considered as pseudocomponents must have rigidly fixed compositions so that the envelopes representing the intermediate compositions can be defined as binary mixtures of the two terminal pseudocomponents. Any change of composition in the pseudocomponent mixtures obviously will displace the critical point to be used as a terminus of the critical locus for what is, in effect, a different system.

The critical locus illustrated in Figure 4-0.2 is typical of many commonly known systems. For this reason, most present methods of predicting critical temperatures and pressures of hydrocarbon mixtures pre-

suppose systems which form that type of critical locus. For convenience, this common type of critical locus is referred to in this chapter as *Type I*.

There are at least four other types of critical loci to which the available correlations for predicting critical temperatures and pressures do *not* apply. So far, two of these four reported types of critical loci are for binary systems containing methane, but these phenomena have not yet been explored sufficiently to exclude with certainty such compounds as ethane, propane, butane, and ethylene from similar behavior under analogous conditions. Kay (28) has stated that such deviant behavior exists in binary systems containing methane with *n*-hexane and higher homologs. With ethane as the common component, loci other than Type I occur only when the second component has 20 or more carbon atoms. For propane and *n*-butane, the behavior begins at higher molecular weights.

In the absence of experimental data, at least in the case of binary mixtures, it may be expected that, when the heavy component has a melting point equal to or greater than the critical temperature of the light component, the critical locus of the mixture will depart from the Type I form. Whether or not this departure continues to exist when components of intermediate volatility are added to such a binary mixture is not certain. It is suspected, however, that the presence of components of intermediate volatility tends to normalize the critical locus of a mixture whose terminal components would form an anomalous critical locus when they constitute a binary mixture. If the components of intermediate volatility are present in sufficient numbers and concentrations, the critical locus of the resulting multi-component mixture might even appear to have the Type I form.

The following are the systems known to form anomalous types of critical loci:

Type II: Methane-*n*-heptane system (6, 32). The critical locus extends from the critical point of *n*-heptane to lower temperatures and ends at a temperature below the critical temperature of methane and a pressure above the critical pressure of methane. The end of this critical locus is its intersection with another critical locus of two liquid phases and a solid phase. The methane-*n*-octane and methane-*n*-nonane systems are expected to behave similarly.

Type III: Methane-*n*-decane system (5). The critical locus extends from the critical point of *n*-decane to lower temperatures and ends at both a higher temperature and a higher pressure than the critical values for methane. This critical locus ends in a critical point which is also the terminus of a gas-liquid-solid locus. Figure 4-0.3 is the pressure-temperature diagram for this system showing the anomalous behavior described.

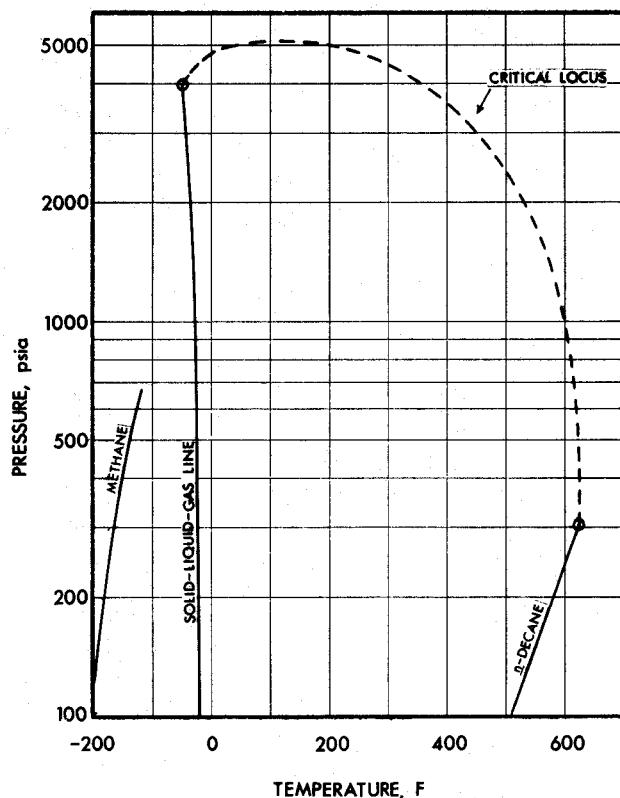


Figure 4-0.3—Critical Locus for the Methane-*n*-Decane System (52)

Analogous behavior should be expected for all binary systems containing methane and a component with a higher freezing point than *n*-decane.

Type IV: Azeotropic binary systems. Some, but not all, form critical loci with a minimum critical temperature, such as that illustrated in Figure 4-0.4 for the acetylene-ethylene system (9).

Type V: Benzene-water system (5). The gas-liquid critical locus extends from the critical point of benzene and ends at the three-phase critical end point. The three-phase critical end point is the highest temperature at which all three phases coexist; above that, the hydrocarbon rich liquid phase disappears. Experimental values for three phase critical endpoints of several hydrocarbon-water systems are tabulated in Chapter 9.

Effect of Size, Shape, and Chemical Nature of the Components on the Critical Locus

An excess critical property is defined as the difference between the value of the true critical property of a mixture and the molar average of the critical properties of the pure components. The excess property, the deviation of the critical locus from ideal mixture behav-

ior, is useful in studying trends in critical properties because difference quantities magnify the effects of the factors being studied. An increase in the excess critical properties indicates a greater nonideality of a mixture and a greater curvature of the critical locus curve.

Studies by Kay (30) have shown that excess critical properties are affected in some complex manner by differences in molecular size, molecular structure, and chemical nature of the components.

By examining a large amount of binary data, Kay (30) noted the following trends in the critical loci and excess critical properties in systems containing a common component.

P-T Critical Loci for Systems Whose Components Belong to the Same Homologous Series

Where the components of the system are about the same molecular weight, the critical locus curve approaches a straight line. (See Figure 4-0.5-a.) As the relative size difference increases, the locus curve changes to a curved line, concave downward, and a maximum pressure point appears. With further increases in the relative size difference, the maximum pressure increases and may attain a very high value relative to the critical pressures of the pure components.

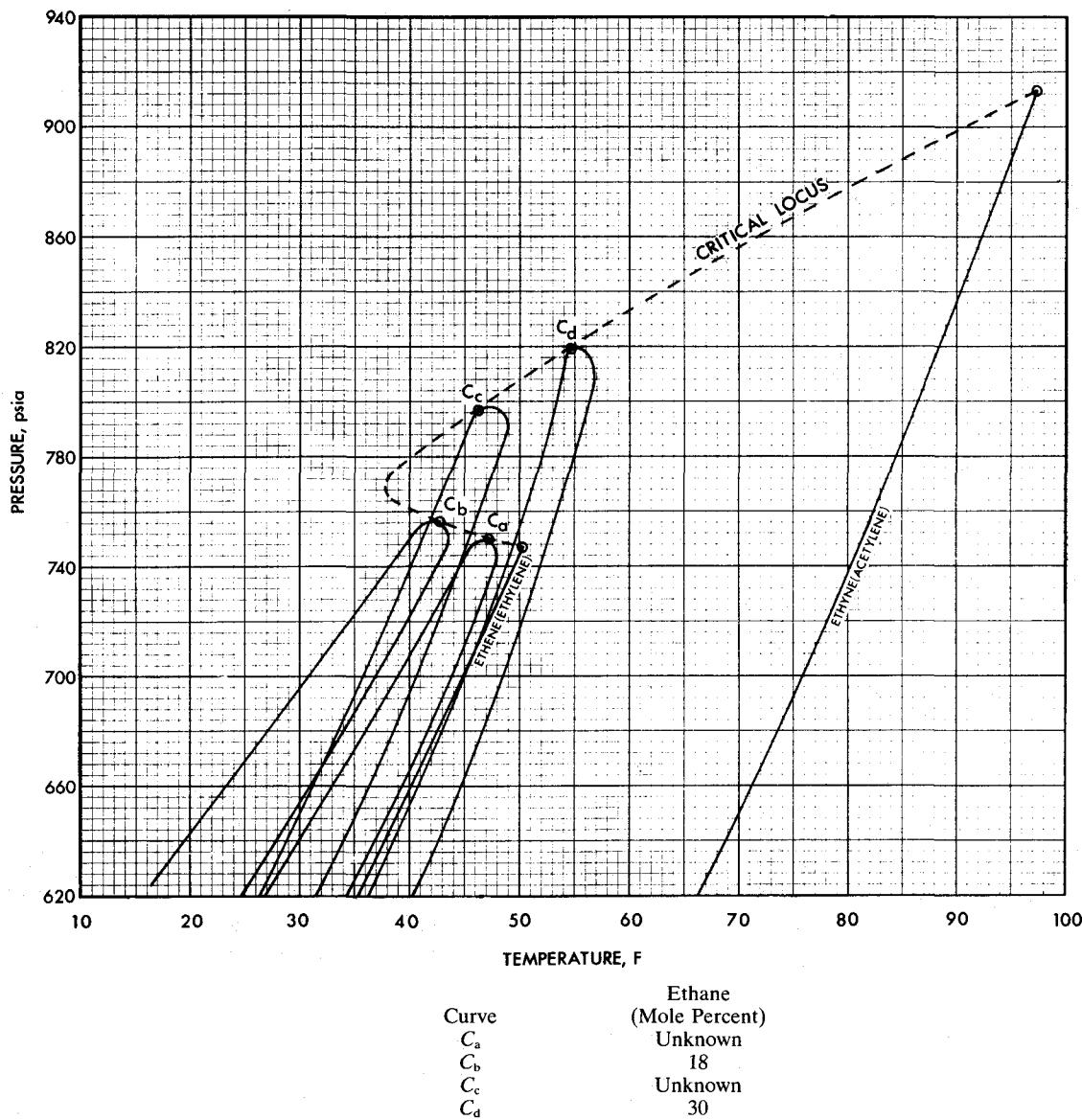


Figure 4-0.4—Critical Locus for the Ethyne-Ethene (Acetylene-Ethylene) System and Envelopes for Four Binary Mixtures (6)

P-T Critical Loci for Systems Whose Components Belong to Different Homologous Series

The trends are generally the same as homologous systems with regard to size although differences in chemical nature and molecular structure play a part that is not clearly discernible. (See Figure 4-0.5-b and -c.) Because the critical temperatures of *n*-hexane and *n*-heptane are lower than that of cyclohexane, the critical loci cross over from one side of cyclohexane to the other side as the molecular weight of the paraffin is increased. The same relation is observed in the benzene-paraffin series. However, this series is different from the cyclohexane-paraffin series because the critical locus of benzene-*n*-octane has a minimum temperature point that suggests the presence of a critical azeotrope. Approximately of the same size but belonging to completely different homologous series are *n*-hexane, cyclohexane, and benzene. (See Figure 4-0.5-d.) Therefore, differences in their loci with a common component may be considered to be due, principally, to the differences in their molecular structure and chemical nature. The same is true for *o*-xylene and ethylbenzene which have the same molecular weight but different molecular structures.

Excess Critical Temperature for Systems Whose Components Belong to the Same Homologous Series

A plot of excess critical temperature, T_c^e , as a function of composition is not necessarily symmetrical. (See Figure 4-0.6-a.) The maximum T_c^e are shifted toward the more volatile component. For a constant difference in molecular weight, the lower the molecular weight of the components, the greater the maximum T_c^e . (See Figure 4-0.7b.) As the difference in molecular weight between components increases, the maximum T_c^e is greater, the lower the average molecular weight.

Excess Critical Temperature for Systems Whose Components Belong to Different Homologous Series

The plots are asymmetrical and show the transition from a minimum T_c^e (negative) to a maximum T_c^e (positive) as the difference in the size of the components increases. (See Figure 4-0.6-b and -c.) Maximum T_c^e are approximately the same when component molecules are of the same size even though the molecular structure and/or chemical nature are different. (See Figure 4-0.6-d.) This indicates that the effect of size is greater than that of structure and chemical nature.

Excess Critical Pressure for Systems Whose Components Belong to the Same Homologous Series

The same trends as given for excess critical temperature apply. (See Figure 4-0.7-c and -d and Figure 4-0.8-c.)

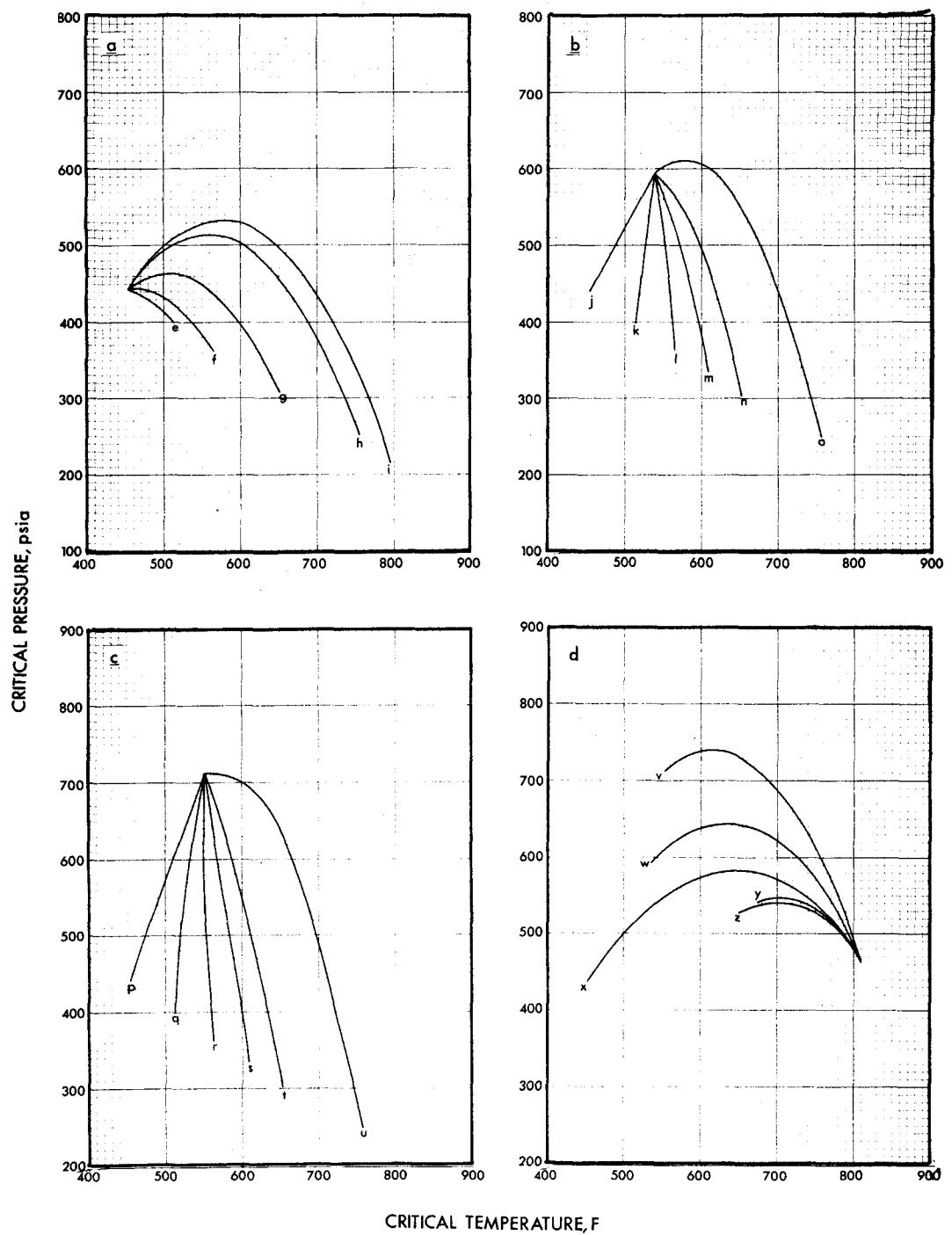
Excess Critical Pressure for Systems Whose Components Belong to Different Homologous Series

The plots are highly asymmetric for the systems of cyclohexane and benzene with *n*-paraffins. (See Figure 4-0.8-a and -b.) As the molecular weight of the paraffin decreases, the p_c^e becomes more negative and then reverses after the *n*-heptane binary to become less negative. As the size difference gets larger, the curves show a transition in which both a minimum p_c^e and a maximum p_c^e exist. Systems of *cis*-decalin with *n*-hexane, cyclohexane, and benzene exhibit a maximum p_c^e (positive). (See Figure 4-0.8-d.) The maximum p_c^e tends to shift toward the higher mole percent of the lower molecular weight component as observed in other binary systems. The maximum p_c^e value is greatest for *n*-hexane but is almost the same for benzene and cyclohexane. This is to be expected because *n*-hexane differs from *cis*-decalin in size, structure, and chemical nature, whereas benzene and cyclohexane differ from *cis*-decalin in size but have a ring structure. The difference in chemical nature between benzene and *cis*-decalin seems to be negligible. The excess critical pressures are practically the same for the physical isomers ethylbenzene and *o*-xylene.

Pseudocritical Temperature and Pressure

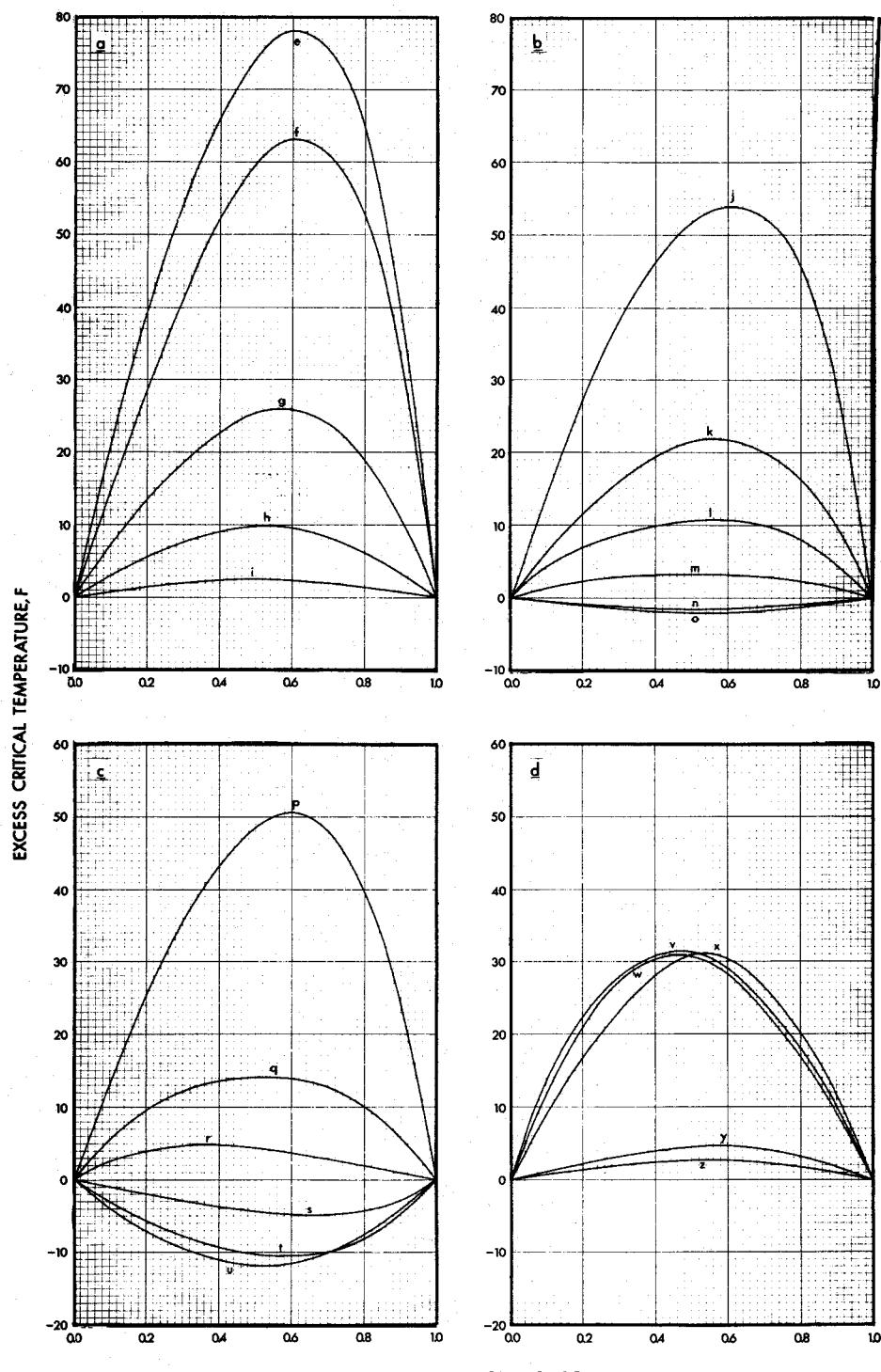
The use of the theorem of corresponding states for the correlation of the properties of hydrocarbon mixtures requires the correlating parameters known as the reduced temperature and the reduced pressure. For pure substances, these are the quotients of the temperature and pressure of interest divided by the critical temperature and the critical pressure of the pure compound. For hydrocarbon mixtures, the corresponding-states correlations apply when pseudocritical temperatures and pressures are used. The pseudocritical properties are not experimentally determined values but are obtained by Kay's empirical equation (25).

A pseudocritical property of a defined hydrocarbon mixture is the sum of the products of the mole fraction of each pure component and its respective critical property value.

*Legend*

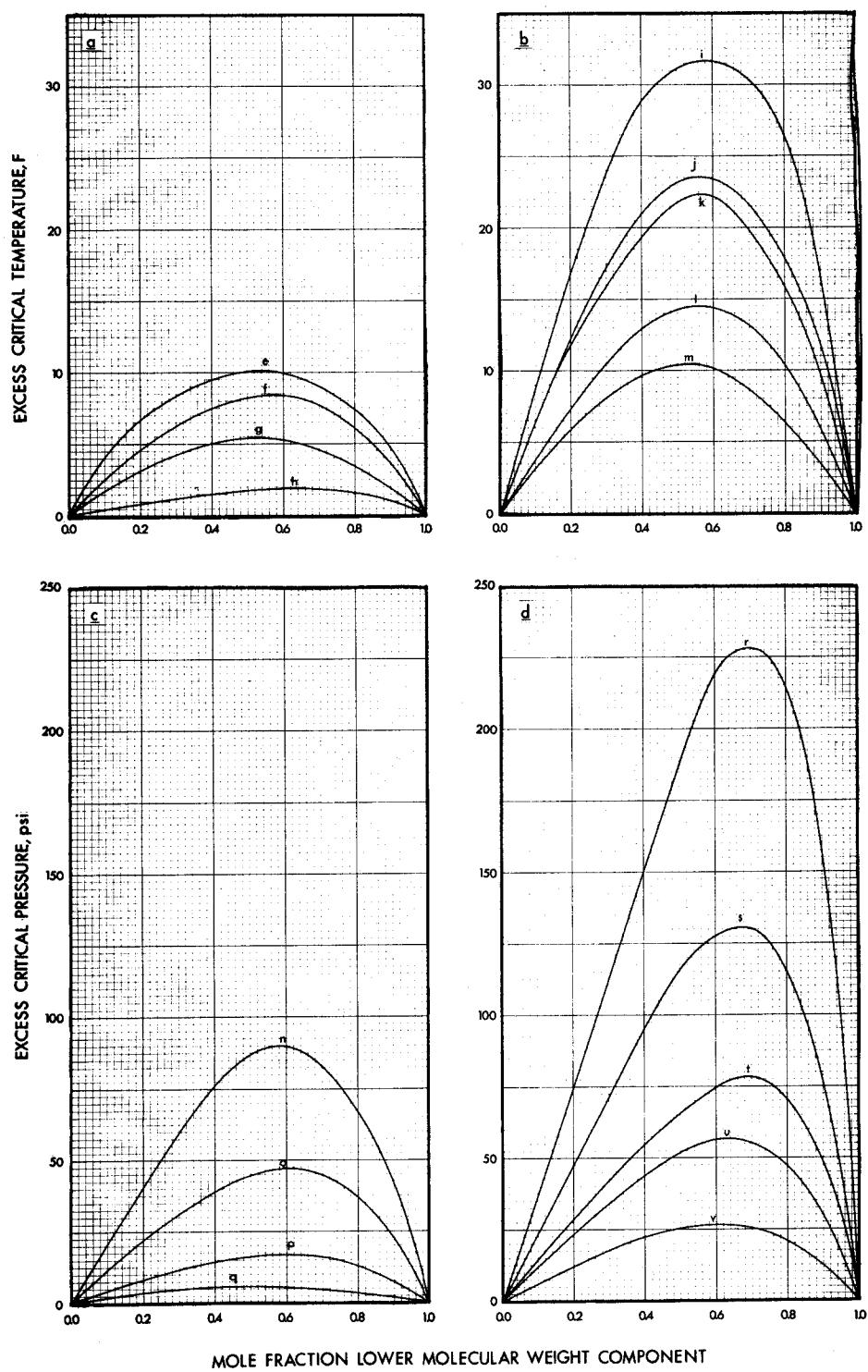
e n-hexane-n-heptane	k cyclohexane-n-heptane	q benzene-n-heptane	v cis-decalin-benzene
f n-hexane-n-octane	l cyclohexane-n-octane	r benzene-n-octane	w cis-decalin-cyclohexane
g n-hexane-n-decane	m cyclohexane-n-nonane	s benzene-n-nonane	x cis-decalin-hexane
h n-hexane-n-tridecane	n cyclohexane-n-decane	t benzene-n-decane	y cis-decalin-o-xylene
i n-hexane-n-tetradecane	o cyclohexane-n-tridecane	u benzene-n-tridecane	z cis-decalin-ethylbenzene
j cyclohexane-n-hexane	p benzene-n-hexane		

Figure 4-0.5—P-T Critical Loci of Binaries Containing a Common Component and a Representative from a Homologous Series

*Legend*

e	<i>n</i> -hexane- <i>n</i> -tetradecane	k	cyclohexane- <i>n</i> -decane	q	benzene- <i>n</i> -decane	v	<i>cis</i> -decalin-cyclohexane
f	<i>n</i> -hexane- <i>n</i> -tridecane	l	cyclohexane- <i>n</i> -nonane	r	benzene- <i>n</i> -nonane	w	<i>cis</i> -decalin-benzene
g	<i>n</i> -hexane- <i>n</i> -decane	m	cyclohexane- <i>n</i> -octane	s	benzene- <i>n</i> -octane	x	<i>cis</i> -decalin- <i>n</i> -hexane
h	<i>n</i> -hexane- <i>n</i> -octane	n	cyclohexane- <i>n</i> -heptane	t	benzene- <i>n</i> -heptane	y	<i>cis</i> -decalin-ethylbenzene
i	<i>n</i> -hexane- <i>n</i> -heptane	o	cyclohexane- <i>n</i> -hexane	u	benzene- <i>n</i> -hexane	z	<i>cis</i> -decalin- <i>o</i> -xylene
j	cyclohexane- <i>n</i> -tridecane	p	benzene- <i>n</i> -tridecane				

Figure 4-0.6—Excess Critical Temperature vs Composition for Representative Binary Systems

*Legend*

e propane-n-pentane	j n-butane-n-octane	o n-butane-n-hexane	s n-butane-n-octane
f n-butane-n-octane	k n-pentane-n-nonane	p n-hexane-n-octane	t n-pentane-n-nonane
g n-hexane-n-octane	l n-hexane-n-decane	q n-decane-n-dodecane	u n-hexane-n-decane
h n-decane-n-dodecane	m n-nonane-n-tridecane	r propane-n-heptane	v n-nonane-n-tridecane
i propane-n-heptane	n propane-n-pentane		

Figure 4-0.7—The Effect of Relative Size and Absolute Molecular Weight on the Excess Functions

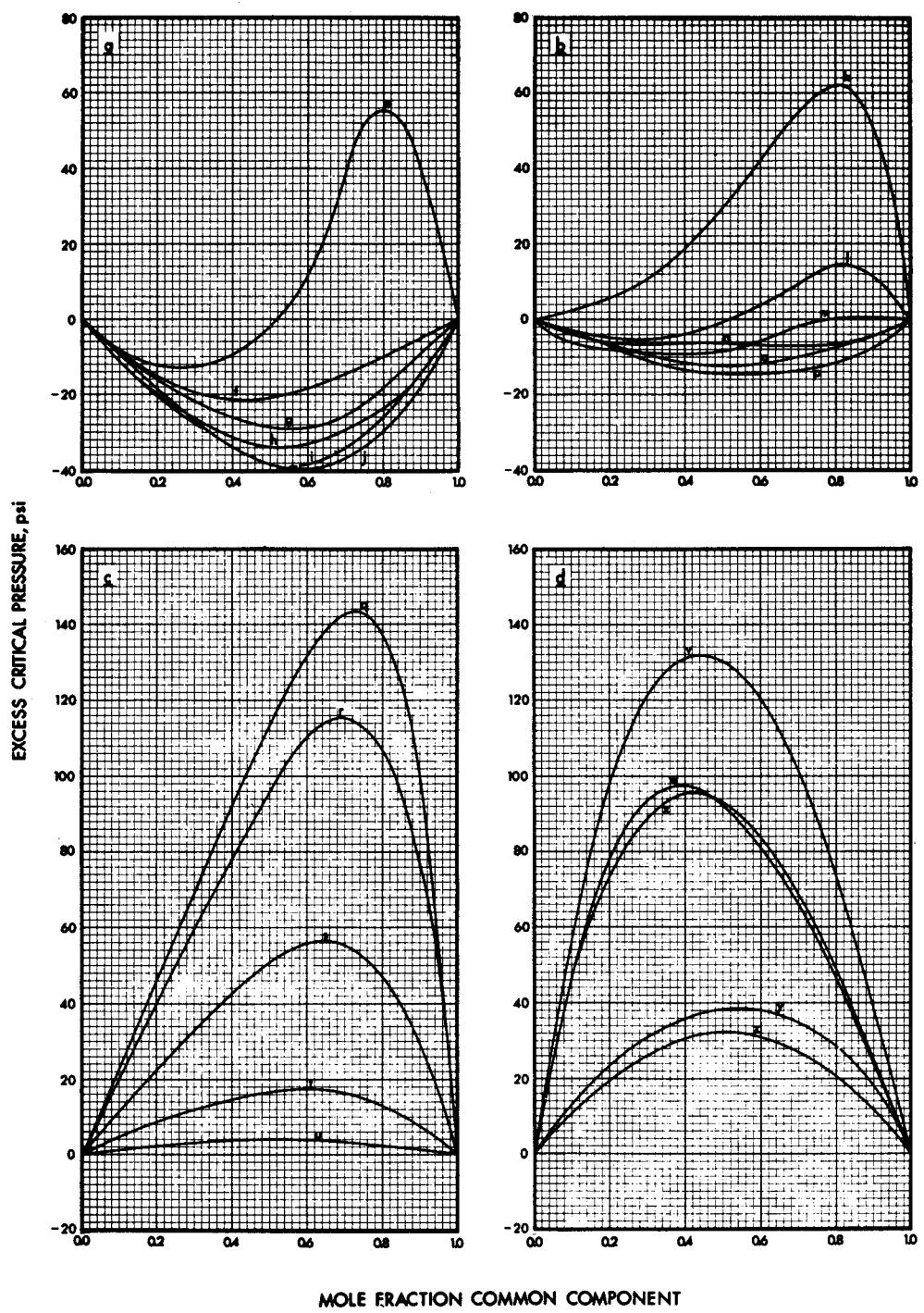


Figure 4-0.8—Excess Critical Pressure vs Composition for Representative Binary Systems

$$J_{pc} = \sum_{i=1}^n x_i J_{ci} \quad (4-0.1)$$

Where:

- J_{pc} = pseudocritical property (temperature, pressure, or volume) of the mixture.
- n = number of components in mixture.
- x_i = mole fraction of pure component i in the mixture.
- J_{ci} = critical property of pure component i .

Because of these methods of calculation, the pseudocritical temperatures and pressures are always less than the so-called true critical values of the same mixture with mixtures following a Type I locus. In Figure 4-0.1, for example, the point (p_{pc}, T_{pc}) might represent the pseudocritical temperature and pressure of the mixture whose true critical value is at point C in the same pressure-temperature diagram. For the same reason, the locus of the pseudocritical point is a straight line for the full range of composition of a mixture such as that illustrated in Figure 4-0.2.

For undefined mixtures, a pseudocritical property may be defined by a particular correlation. The pseudocritical temperature defined by Procedure 4D3.1 is an example of such a correlation.

Other rules for obtaining "pseudo" values for the critical properties are available, and some of these rules have been used in other chapters of the *Technical Data Book*. However, when the temperature or pressure is predicted by some rule other than equation (4-0.1), the resulting values are referred to as the mixture correspondence temperature and mixture correspondence pressure and are useful only in their specific procedure.

Critical Temperature

A list of experimental critical temperatures for many pure compounds is given in Chapter 1. To predict the critical temperature of other pure compounds, use Procedure 4A1.1 or Procedure 4A2.1. Procedure 4A1.1 may be more useful when all the critical properties of a compound are desired. Procedure 4A2.1 is a simple regression equation.

Procedure 4B1.1 and an optional computer method (Procedure 4B4.1) are given for calculating the true critical temperature of a defined mixture. Specific recommendations and restrictions are given for binary hydrocarbon-hydrocarbon, binary hydrocarbon-nonhydrocarbon, and multicomponent mixtures.

The true critical temperature of natural gas mixtures can be calculated from Figure 4C1.1. A natural gas contains a large amount of methane and sometimes an appreciable amount of hydrogen, helium, nitrogen, and carbon dioxide.

The method for obtaining the true critical temperature of petroleum fractions is described in Procedure 4D1.1. Pseudocritical temperatures of petroleum fractions can be estimated from Procedure 4D3.1 using specific gravity and mean average boiling point as input parameters.

The method of obtaining the true and pseudocritical temperatures of mixtures of known hydrocarbons and one or more petroleum fractions is described in Procedure 4D3.2. This method should not be used as an alternative for Procedure 4B1.1 or 4D1.1.

Critical Pressure

A list of experimental critical pressures is given in Chapter 1. To predict the critical pressure of a pure compound, use Procedure 4A1.1. This is a group contribution method and the required increments are given in Table 4A1.2.

The true critical pressure of defined mixtures may be calculated by hand from Procedure 4B2.1. The procedure is most accurate for mixtures containing only hydrocarbons. Restrictions are stated for mixtures containing methane and inorganic gases. An alternate computer method, Procedure 4B4.1, is more reliable for critical pressures.

Use Figure 4D2.1 to calculate the true critical pressure of petroleum fractions. The ASTM slope, ASTM volumetric average boiling point, and the API gravity of the fraction, all of which are needed for this method, are usually directly determined from standard inspection tests or can be calculated from standard inspection tests. Chapter 2 may be helpful when using this method.

The pseudocritical pressure of a petroleum fraction can be estimated from Procedure 4D4.1 using specific gravity and mean average boiling point as input parameters. The method for obtaining the true and pseudocritical pressure of mixtures of known hydrocarbons and one or more petroleum fractions is described in Procedure 4D4.2 and is illustrated by a numerical example. This method should not be used as an alternative for Procedure 4B2.1 or Figure 4D2.1.

Critical Volume

A list of some experimental critical volumes is given in Chapter 1. The critical volume of pure compounds may be estimated by Procedure 4A1.1 or 4A3.1. Procedure 4A1.1 may be more useful when all the critical properties of a compound are desired. However, Procedure 4A3.1 is much simpler if critical temperature and critical pressure are known.

Procedure 4B3.1 is used to predict the critical volume of a defined mixture. Procedure 4B4.1 may also be used as a computer method. No methods are recommended for the critical volume of natural gases or petroleum fractions.

A method for predicting the critical volume of petroleum fractions is given by Hall and Yarborough (22). Since few experimental data exist, this method could not be evaluated in the preparation of this chapter.

PROCEDURE 4A1.1**GROUP CONTRIBUTION METHOD FOR CALCULATING THE CRITICAL TEMPERATURE, PRESSURE AND VOLUME OF A PURE HYDROCARBON****Discussion**

The following equation is to be used to calculate the critical pressure of a pure hydrocarbon. Since the technique uses the group contribution method, the structure of the compound must be known.

$$P_c = \frac{14.5M}{(0.339 + \Sigma \Delta_p - 0.026 \Delta \text{Platt \#})^2} \quad (4A1.1-1)$$

Where:

P_c = critical pressure of pure hydrocarbon, in pounds per square inch absolute.

M = molecular weight.

$\Sigma \Delta_p$ = summation of critical pressure group contributions.

$\Delta \text{Platt \#}$ = the Platt number of any alkyl chains in the compound minus the Platt number of the *n*-alkane with the same number of carbons. The Platt number is the number of pairs of carbon atoms which are separated by three carbon-carbon bonds and is an indicator of the degree of branching in the molecule. The Platt number of an *n*-alkane is equal to the number of carbons minus three. Further discussion of the Platt number is given by Wiener, *J. Am. Chem. Soc.*, **69**, 17 (1947).

Procedures consistent with this method are given below for critical temperature and critical volume of a pure hydrocarbon. These procedures are of practically equivalent accuracy to procedures 4A2.1 and 4A3.1.

$$T_c = T_b \left[1 + \frac{1}{(1.242 + \Sigma \Delta_T - 0.023 \Delta \text{Platt \#})} \right] \quad (4A1.1-2)$$

$$V_c = 0.01602 [40 + \Sigma \Delta_v] \quad (4A1.1-3)$$

Where:

T_c = critical temperature of pure hydrocarbon, in degrees Rankine.

V_c = critical volume of compound in cubic feet per pound-mole.

T_b = boiling temperature of compound in degrees Rankine.

Procedure

Step 1: Obtain the molecular weight and boiling temperature from Chapter 1.

Step 2: Determine the structure of the compound.

Step 3: Obtain the needed group contributions from Table 4A1.2.

Step 4: Sum these group contributions to obtain $\Sigma \Delta_p$, $\Sigma \Delta_T$ or $\Sigma \Delta_v$.

Step 5: Compute the desired critical property from equation (4A1.1-1), (4A1.1-2) or (4A1.1-3).

COMMENTS ON PROCEDURE 4A1.1**Purpose**

Equations are given for calculating the critical properties of pure hydrocarbons. For many hydrocarbons, Chapter 1 lists experimental critical properties; these are to be preferred when available. However, for compounds containing 12 carbon atoms or more, including an alkyl chain, even "measured" critical properties may not be reliable, because of thermal decomposition at elevated temperatures.

Limitations

The equations are applicable to all hydrocarbon families provided the structure of the compound is known. The equation was evaluated for C₁-C₂₀ paraffins and for C₃-C₁₄ compounds for all other families. The accuracy of results for critical pressure and critical volumes of compounds with more than twelve carbons may be questionable. Maximum deviations should be expected for cycloalkanes.

Reliability

	<i>P_c</i>	<i>T_c</i>	<i>V_c</i>
Average percent deviation	2.2	0.7	3.4
Average deviation	10.2 psia	7.6 R	0.2 ft ³ /lb-mole
Maximum percent deviation	18.7	8.0	15.6
Maximum deviation	165.8 psia	98.1 R	1.4 ft ³ /lb-mole

Literature Source

Adapted from Ambrose, D., "Correlation and Estimation of Vapor-Liquid Critical Properties, I. Critical Temperatures of Organic Compounds," National Physical Laboratory, Teddington, NPL Report 92 (Sept. 1978/corrected Mar. 1980b), and Ambrose, D., "Correlation and Estimation of Vapor-Liquid Critical Properties, II. Critical Pressures and Critical Volumes of Organic Compounds," National Physical Laboratory, Teddington, NPL Report 98 (May 1979).

Examples

1. 2,2,3 Trimethylpentane

From Chapter 1, the molecular weight is 114.230 and the boiling point is 229.72 F. From Table 4A1.2, the increment contributions are:

Group #	# of occurrences	$\Sigma \Delta_p$	$\Sigma \Delta_T$	$\Sigma \Delta_v$
1	5	5(0.226)	5(0.138)	5(55.1)
2	1	0.226	0.138	55.1
3	1	0.220	0.095	47.1
4	1	0.196	0.018	38.1
The summations are:		1.772	0.941	415.8

$$\Delta \text{ Platt } \# = 8 - 5 = 3$$

From equation (4A1.1-1):

$$P_c = \frac{(14.50)(114.230)}{[0.339 + 1.772 - 3(0.026)]^2} = 400.75 \text{ psia}$$

From equation (4A1.1-2):

$$T_c = 689.39 \left[1 + \frac{1}{[1.242 + 0.941 - 0.023(3)]} \right] = 1015.50 \text{ R} = 555.83 \text{ F}$$

From equation (4A1.1-3):

$$V_c = (40 + 415.8)(0.01602) = 7.302 \text{ ft}^3/\text{lb mole} = 0.0639 \text{ cu ft per lb}$$

Experimental values are:

$$T_c = 554.63 \text{ F} \quad P_c = 395.91 \text{ psia} \quad V_c = 0.0611 \text{ cu ft per lb}$$

PROCEDURE 4A2.1**EQUATION FOR CALCULATING THE CRITICAL TEMPERATURE OF A PURE HYDROCARBON****Discussion**

The following equation is to be used to calculate the critical temperature of pure hydrocarbons. It is applicable for all families of hydrocarbons.

$$\log_{10} T_c = A + B \log_{10} (\text{sp gr}) + C \log_{10} T_b \quad (4A2.1-1)$$

Where:

T_c = critical temperature of pure hydrocarbon, in degrees Rankine.

A, B, C = empirically derived constants (specific for each family).

sp gr = specific gravity, 60 F/60 F.

T_b = normal boiling point, in degrees Rankine.

Procedure

Step 1: Obtain the normal boiling point and specific gravity of the compound from Chapter 1.

Step 2: Obtain the values of A, B, and C from Table 4A2.2.

Step 3: Calculate the critical temperature using equation (4A2.1-1).

**TABLE 4A2.2
VALUES OF COEFFICIENTS FOR EQUATION 4A2.1-1 FOR CALCULATING
CRITICAL TEMPERATURE OF A PURE HYDROCARBON**

Type Compound	A	B	C
Paraffin	1.47115	0.43684	0.56224
Naphthene.....	0.70612	-0.07165	0.81196
Olefin.....	1.18325	0.27749	0.65563
Acetylene	0.79782	0.30381	0.79987
Diolefins	0.14890	-0.39618	0.99481
Aromatic.....	1.14144	0.22732	0.66929

COMMENTS ON PROCEDURE 4A2.1

Purpose

An equation is given for predicting the critical temperature of a pure hydrocarbon. For many hydrocarbons, Chapter 1 lists experimental critical temperatures; these values are preferable when available. However, for compounds containing 12 carbon atoms or more, including an alkyl chain, even "measured" critical properties may not be reliable because of thermal decomposition at elevated temperatures.

Limitations

The equation is applicable to all hydrocarbon families. Equation (4A2.1-1) was tested, however, using only experimental boiling points and specific gravities. Estimated values of these parameters may lead to larger errors. The equation was tested using data in the range C₁-C₂₀ for paraffins and in the range C₃-C₁₄ for all other families. Higher molecular weight hydrocarbons may yield less accurate results.

Reliability

The average deviation from experimental data is about 5.0 deg F or 0.84 percent. To retain this accuracy the untruncated values of A, B, and C in Table 4A2.2 should be used. The maximum deviation expected is 100 deg F or 7 percent.

Special Comment

For naphthenes and aromatics with paraffinic side chains, use the coefficients given in Table 4A2.2 for the naphthene or aromatic. Densities for these compounds can be estimated by methods in Chapter 6.

Literature Source

Adapted from Nokay, R., *Chem. Eng.* **66** [4] 147 (1959).

Example

Calculate the critical temperature of *n*-octane.
From Chapter 1:

$$\begin{aligned}T_b &= 258.21 \text{ F} \\ \text{sp gr} &= 0.7070\end{aligned}$$

From Table 4A1.2:

$$\begin{aligned}A &= 1.47115 \\ B &= 0.43684 \\ C &= 0.56224\end{aligned}$$

$$T_b = 258.21 + 459.67 = 717.88$$

$$\log T_c = 1.47115 + 0.43684 \log_{10}(0.7068) + 0.56224 \log_{10}(717.88)$$

$$\log T_c = 1.47115 + 0.43684 (-0.1506) + 0.56224 (2.85605)$$

$$\log T_c = 3.0111$$

$$T_c = 1025.89 \text{ R} = 566.22 \text{ F}$$

The experimental value from Chapter 1 = 564.22 F.

PROCEDURE 4A3.1**EQUATION FOR CALCULATING THE CRITICAL
VOLUME OF A PURE HYDROCARBON****Discussion**

The following equations are to be used to calculate the critical volume of a pure hydrocarbon. It is applicable for all families of hydrocarbons.

$$V_c = \frac{RT_c}{p_c[3.72 + 0.26(\alpha - 7.00)]} \quad (4A3.1-1)$$

$$\alpha = 5.811 + 4.919\omega \quad (4A3.1-2)$$

Where:

V_c = critical volume of pure hydrocarbon in cubic feet per pound-mole.

R = gas constant = 10.731 (psia) (cu ft) per (lb-mole) (deg R).

T_c = critical temperature, in degrees Rankine.

p_c = critical pressure, in pounds per square inch absolute.

α = Riedel factor.

ω = acentric factor.

Procedure

Step 1: Obtain the critical pressure and critical temperature of the compound from Chapter 1.

Step 2: Obtain the acentric factor from Chapter 2 or by Procedure 2A1.1.

Step 3: Calculate α using equation (4A3.1-2).

Step 4: Calculate the critical volume using equation (4A3.1-1).

COMMENTS ON PROCEDURE 4A3.1**Purpose**

An equation is given for calculating the critical volume of a pure hydrocarbon. For many hydrocarbons, Chapter 1 lists experimental critical volumes; these are to be preferred when available. However, for compounds containing 12 carbon atoms or more, including an alkyl chain, even "measured" critical properties may not be reliable because of thermal decomposition at elevated temperatures.

Limitations

The equation is applicable to all hydrocarbon families. Equation (4A3.1-1) was tested using experimental values for the critical temperatures and critical pressures. Estimated values of these parameters may yield larger errors in the critical volume. Also, the equation was evaluated for C₃-C₁₈ paraffins and for C₃-C₁₁ for each of the other families. Heavier materials may give less accurate results.

Reliability

The average error from experimental data is about 0.24 cubic feet per pound-mole or 3.26 percent. Maximum deviation is 1.83 cubic feet per pound mole or 20 percent. This method is least reliable for cycloalkanes and aromatic compounds.

Literature Source

Adapted from Riedel, L., *Chem. Ingr.-Tech.* **26** 679 (1954).

Equation (4A3.1-2) is adapted from Riedel, L., *Chem. Ingr.-Tech.* **28** 557 (1956).

Example

Calculate the critical volume of *n*-nonane.

From Chapter 1:

$$T_c = 610.68 \text{ F}$$

$$p_c = 331.8 \text{ psia}$$

$$T_c = 610.68 + 459.7 = 1,070.35 \text{ R}$$

From Chapter 2:

$$\omega = 0.4368$$

From equation (4A3.1-2):

$$\alpha = 5.811 + (4.919)(0.4368)$$

$$\alpha = 7.960$$

By equation (4A3.1):

$$V_c = \frac{(10.731)(1,070.35)}{(332)[3.72 + 0.26(7.960 - 7.00)]}$$

$$V_c = 8.72 \text{ cu ft per lb-mole} = 0.0680 \text{ cu ft per lb}$$

The experimental value from Chapter 1 = 0.0684 cu ft per lb.

PROCEDURE 4B1.1

METHOD FOR THE CRITICAL TEMPERATURE OF A MIXTURE OF DEFINED COMPOSITION

Discussion

The Li equation (4B1.1-1) is to be used to calculate the critical temperature of a mixture of defined composition. For this purpose the critical volumes of the pure components must be known or estimated. The following equation is applicable for most hydrocarbons over the entire composition range.

$$T_{cm} = \sum_{i=1}^n \theta_i T_{ci} \quad (4B1.1-1)$$

Values of θ_i may be calculated from equation (4B1.1-2) and (4B1.1-3).

$$\theta_i = \frac{x_i V_{ci}}{V_{pc}} \quad (4B1.1-2)$$

$$V_{pc} = \sum_{i=1}^n x_i V_{ci} \quad (4B1.1-3)$$

Where:

T_{cm} = true critical temperature of mixture, in degrees Rankine.

θ_i = volumetric fraction of component i .

T_{ci} = critical temperature of component i , in degrees Rankine.

x_i = mole fraction of component i .

V_{ci} = molar critical volume of component i , in cubic feet per pound-mole.

V_{pc} = molar average critical volume, in cubic feet per pound-mole.

Procedure

Step 1: Obtain the critical temperature, critical volume, and molecular weight of each component from Chapter 1. If values of the critical temperature and critical volume are not available, they may be calculated from methods given in Section 4A of this chapter.

Step 2: Convert each critical temperature and critical volume to the units specified in the discussion.

Step 3: Compute the molar average critical volume using equation (4B1.1-3).

Step 4: Compute the volumetric fractions from equation (4B1.1-2).

Step 5: Calculate the critical temperature from equation (4B1.1-1).

COMMENTS ON PROCEDURE 4B1.1

Purpose

Procedure 4B1.1 is to be used to predict the true critical temperature of a mixture containing any number of components. It is intended for use both as a desk and a computer method.

Limitations

This procedure was evaluated using experimental critical temperatures and critical volumes. If estimated values of these parameters are used, some loss of accuracy should be expected.

A. Defined Binary Hydrocarbon-Hydrocarbon Systems

The equation is not reliable for mixtures containing more than 0.5 mole fraction methane. If the ratio of the molecular weights of the components is greater than 2.5 the expected error is increased.

B. Defined Binary Hydrocarbon-Nonhydrocarbon Systems

The procedure should not be used for mixtures containing hydrogen, more than 0.3 mole fraction carbon dioxide or carbon monoxide, or more than 0.45 mole fraction nitrogen. Procedure 4B4.1 should be used for these cases.

C. Defined Multicomponent Systems

This method has been evaluated primarily with binary data although it can be extended to higher-order systems. Very few experimental data are available for critical temperatures of multicomponent systems, but equation (4B1.1-1) has been applied to mixtures containing as many as nine components. For even higher order systems, it would be more appropriate to use either Procedure 4C1.1 for natural gases or Procedure 4D1.1 for petroleum fractions.

This procedure can be used for multicomponent systems containing a small amount of methane (0.10 to 0.15 mole fraction). At higher methane concentrations Procedure 4C1.1 for natural gases should be used.

Reliability

A. Defined Binary Hydrocarbon-Hydrocarbon Systems

Errors in the calculated critical temperature average about 0.6 percent (5.2 deg F). For non-methane mixtures the maximum deviation expected is 15 deg F. For mixtures containing more than 0.5 mole fraction methane, errors as high as 100 deg F have been obtained, with an average deviation of 5.7 percent (31 deg F).

B. Defined Binary Hydrocarbon-Nonhydrocarbon Systems

For binaries containing at least one nonhydrocarbon, the errors in the calculated critical temperatures average about 5.0 percent (36 deg F). If the procedure is used for mixtures containing hydrogen or more than 0.45 mole fraction nitrogen, absolute deviations in the range of 100 to 200 deg F should be expected. For mixtures containing in excess of 0.3 mole fraction carbon dioxide, deviations in the order of 50 deg F have been found.

C. Defined Multicomponent Systems

Average deviations in the calculated critical temperatures are 1.2 percent (8 deg F) for non-methane systems. Generally the error is higher for a system containing methane and increases as the number of components increases.

Special Comments

This procedure may be used for defined binary hydrocarbon mixtures, defined binary mixtures containing one or more nonhydrocarbons, and defined multicomponent systems. The evaluation of the Li equation with the binary hydrocarbon-hydrocarbon data was the most extensive with a data set of 1,230 points representing 135 systems. For hydrocarbon-nonhydrocarbon systems, a data set of 430 points representing 69 systems was evaluated while 235 data points representative of 35 multicomponent systems were tested in the multi-component portion of the study (see *Documentation Report No. 4-73*).

Literature Source

Adapted from Li, C. C., *Can. J. Chem. Eng.* **49** 709 (1971); Errata **50** 152 (1972).

PROCEDURE 4B2.1

METHOD FOR THE CRITICAL PRESSURE OF A MIXTURE OF DEFINED COMPOSITION

Discussion

Equation (4B2.1-1) is to be used to calculate the critical pressure of a defined mixture. For this purpose the critical pressure and critical temperature of the pure components, as well as the true critical temperature of the mixture, must be known or estimated. The equation, which is generally applicable over the entire composition range, is as follows:

$$p_{cm} = p_{pc} + p_{pc} \left[5.808 + 4.93 \left(\sum_{i=1}^n x_i \omega_i \right) \right] \left[\frac{T_{cm} - T_{pc}}{T_{pc}} \right] \quad (4B2.1-1)$$

Values for the pseudocritical temperature and pseudocritical pressure are calculated as molar average values.

$$T_{pc} = \sum_{i=1}^n x_i T_{ci} \quad (4B2.1-2)$$

$$p_{pc} = \sum_{i=1}^n x_i p_{ci} \quad (4B2.1-3)$$

Where:

p_{cm} = true critical pressure of mixture, in pounds per square inch absolute.

p_{pc} = pseudocritical pressure of mixture, in pounds per square inch absolute.

n = number of components in mixture.

x_i = mole fraction of component i .

ω_i = acentric factor of component i .

T_{cm} = true critical temperature of mixture, in degrees Rankine.

T_{pc} = pseudocritical temperature of mixture, in degrees Rankine.

T_{ci} = critical temperature of component i , in degrees Rankine.

p_{ci} = critical pressure of component i , in pounds per square inch absolute.

Procedure

Step 1: Obtain the critical temperature and critical pressure of each component from Chapter 1. Obtain the values of the acentric factor of each component from Chapter 2. If values of the critical pressure and critical temperature are not available, they may be calculated from methods given in Section 4A of this chapter.

Step 2: Compute the pseudocritical temperature from equation (4B2.1-2).

Step 3: Calculate the pseudocritical pressure from equation (4B2.1-3).

Step 4: If, as is generally true, the critical temperature of the mixture is unknown, calculate it using Procedure 4B1.1 or Procedure 4B4.1.

Step 5: Calculate the true critical pressure from equation (4B2.1-1).

COMMENTS ON PROCEDURE 4B2.1

Purpose

Procedure 4B2.1 is to be used to predict the true critical pressure of a mixture containing any number of components. It is intended for use both as a desk and a computer method.

Limitations

This procedure was evaluated using the experimental critical temperature and critical pressure of each component. If estimated values of these parameters are used, errors may be higher.

A. Defined Binary Hydrocarbon-Hydrocarbon Systems

The equation should not be used for mixtures containing methane. Instead, Procedure 4B4.1 should be used.

The procedure is less reliable for mixtures of ethane and aromatics as well as mixtures of naphthalenes with higher molecular weight paraffins (C_9 and above).

B. Defined Binary Hydrocarbon-Nonhydrocarbon Systems

The procedure should not be applied for mixtures containing nonhydrocarbon gases like carbon dioxide or hydrogen. Instead, Procedure 4B4.1 is recommended.

C. Defined Multicomponent Systems

Equation (4B2.1-1) yields reasonable results for methane-free multicomponent systems. The method has been evaluated primarily with binary data, but it has been applied to mixtures containing up to eight components. For even higher order systems, it would be more appropriate to use Figure 4D2.1.

Very few experimental data are available on the critical pressures of multicomponent systems.

Reliability

A. Defined Binary Hydrocarbon-Hydrocarbon Systems

Errors in the calculated critical pressures are about 3.8 percent (30 psia) for non-methane systems. For methane-hydrocarbon mixtures the maximum deviation expected is approximately 50 percent (710 psia).

B. Defined Binary Hydrocarbon-Nonhydrocarbon Systems

For binary systems containing at least one nonhydrocarbon (inorganic gas), the average error in the calculated critical pressure is about 22 percent (760 psia).

C. Defined Multicomponent Systems

Average deviations in the calculated critical pressures are 4.6 percent (74 psia).

Special Comments

This method should not be applied to predict the critical pressure of systems containing methane or inorganic gases. A number of diagrams representing experimental data for representative methane, carbon dioxide, and hydrogen sulfide systems are given in Figure 4B2.2 to 4B2.4.

Literature Source

Adapted from Kreglewski, A. and Kay, W. B., *J. Phys. Chem.* **73** 3359 (1969).

Examples

A. Estimate the critical pressure of an ethylbenzene-*n*-octane mixture containing 30 mole percent ethylbenzene. The experimental critical temperature of this mixture is 584.4 deg F (27).

From Chapter 1:

	Ethylbenzene	<i>n</i> -Octane
Critical temperature, deg F	651.24	564.22
Critical pressure, psia	523.5	360.7

PROCEDURE 4B3.1

METHOD FOR THE CRITICAL VOLUME OF A MIXTURE OF DEFINED COMPOSITION

Discussion

The Chueh-Prausnitz equation (4B3.1-1) is to be used to calculate the critical volume of a defined mixture. For this purpose the critical volume of the pure components must be known or estimated. The equation, which is applicable over the entire composition range, is as follows:

For binaries,

$$V_{cm} = \phi_1 V_{c1} + \phi_2 V_{c2} + 2\phi_1\phi_2\nu_{12} \quad (4B3.1-1)$$

In general,

$$V_{cm} = \sum_i^n \phi_i V_{ci} + \sum_i^n \sum_j^n \phi_i \phi_j \nu_{ij} \quad (i \neq j) \quad (4B3.1-2)$$

$$\phi_i = \frac{x_i V_{ci}^{2/3}}{\sum_{i=1}^n x_i V_{ci}^{2/3}} \quad (4B3.1-3)$$

$$\nu_{ij} = \frac{V_{ij}(V_{ci} + V_{cj})}{2.0} \quad (4B3.1-4)$$

$$V_{ij} = -1.4684(\eta_{ij}) + C \quad (4B3.1-5)$$

$$\eta_{ij} = \left| \frac{V_{ci} - V_{cj}}{V_{ci} + V_{cj}} \right| \quad (4B3.1-6)$$

Where:

$C = 0.1559$ if component i or j is a nonhydrocarbon.

$C = 0$ if components i and j are hydrocarbons.

V_{cm} = true critical volume of mixture, in cubic feet per pound-mole.

V_c = molar critical volume of component i , in cubic feet per pound-mole.

n = number of components in mixture.

i, j = any two of the components.

$\nu_{ij}, V_{ij}, \eta_{ij}$ = correlation parameters.

C = empirically derived constant.

Procedure

Step 1: Obtain the critical volume and molecular weight of each component from Chapter 1. If values of the critical volume are not available, they may be calculated from methods given in Section 4A of this chapter.

Step 2: Convert each critical volume to the desired units.

Step 3: Compute the value of ϕ for each component from equation (4B3.1-3).

Step 4: Compute each η_{ij} from equation (4B3.1-6).

Step 5: Obtain the value of C and compute each V_{ij} using equation (4B3.1-5).

Step 6: Calculate the corresponding values of ν_{ij} from equation (4B3.1-4).

Step 7: Compute the critical volume from equation (4B3.1-2).

4B3.1

COMMENTS ON PROCEDURE 4B3.1

Purpose

Procedure 4B3.1 can be used to predict the true critical volume of a mixture containing any number of components. It is intended for use both as a desk and a computer method.

Limitations

This procedure was evaluated using the experimental critical volume of each pure component. If estimated values of these parameters are used, errors may be higher.

This method has been evaluated primarily with binary data although it can be extended to higher-order systems. Very few experimental data are available for critical volumes of multicomponent systems.

Reliability

Average errors in the calculated critical volume are about 8 percent (0.302 cubic ft per lb-mole) for non-methane hydrocarbon-hydrocarbon binary mixtures and 11 percent (0.176 cubic ft per lb-mole) for methane mixtures. The maximum deviation expected is approximately 40 percent.

For binary mixtures containing at least one nonhydrocarbon, the errors in the calculated critical volume are about 9 percent (0.1 cubic ft per lb-mole).

Special Comments

Although this procedure is not so accurate as the procedures for predicting other critical properties of defined mixtures, it has been included because it is the most accurate method available. Equation (4B3.1-1) was evaluated with a comparatively small data set since only a small amount of critical volume data are available. The problem is further complicated by the nonideality of most of the systems considered. For mixtures having components of similar size, shape, and chemical family, it would probably be better to use a simple molar average of the pure components as an estimate for the true critical volume. In the Chapter 6 introduction, the discussion of excess volume of mixing may offer additional guidelines.

Literature Sources

Adapted from Chueh, P. L. and Prausnitz, J. M., *AIChE Journal* **13** 1107 (1967).

Example

Estimate the critical volume of a *n*-butane-*n*-heptane mixture containing 63 mole percent *n*-butane.
From Chapter 1:

	1 <i>n</i> -Butane	2 <i>n</i> -Heptane
Critical volume, cu ft per lb	0.0704	0.0691
Molecular weight	58.12	100.20

Conversion to molar units:

$$V_{c1} = (0.0704) (58.12) = 4.09 \text{ cu ft per lb-mole}$$

$$V_{c2} = (0.0691) (100.20) = 6.92 \text{ cu ft per lb-mole}$$

From equation (4B3.1-3):

$$\begin{aligned}\theta_1 &= \frac{(0.63) (4.09)^{2/3}}{(0.63) (4.09)^{2/3} + (0.37) (6.92)^{2/3}} & \theta_2 &= \frac{(0.37) (6.92)^{2/3}}{(0.63) (4.09)^{2/3} + (0.37) (6.92)^{2/3}} \\ &= \frac{(0.63) (2.56)}{(0.63) (2.56) + (0.37) (3.63)} & &= \frac{(0.37) (3.63)}{(0.37) (3.63) + (0.63) (2.56)} \\ &= 0.546 & &= 0.454\end{aligned}$$

By equation (4B3.1-6):

$$\eta_{ij} = \left| \frac{4.09 - 6.92}{4.09 + 6.92} \right|$$

$$\eta_{ij} = 0.258$$

COMMENTS ON PROCEDURE 4B4.1

4B4.1-5

Purpose

The procedure is presented as an optional computer method to calculate the true critical properties of mixtures. The procedure is consistent with the procedure for vapor liquid equilibrium discussed in Chapter 8. Binary interaction coefficients should be calculated as described in Chapter 8.

Limitations

A. Single variable Newton iteration schemes with numerical derivatives (e.g., secant method or forward differencing) have been used successfully in the iterations on T_{cm} and V_{cm} . Multivariable methods appear to be unreliable because of undesired multiple roots.

B. Although infrequent, the following errors may be encountered and should be detected by using counters and conditional testing.

1. Iteration on T_{cm} may not converge.
2. Iteration on V_{cm} may not converge.
3. V_{cm} may converge to a value less than the excluded volume b .
4. P_{cm} may be less than zero.

Reliability

System Type	T_{cm}		P_{cm}		V_{cm}	
	% AAD	AAD(R)	% AAD	AAD[psia]	% AAD	AAD [ft ³ /lb/mole]
Methane-hydrocarbon	6.9	32.8	4.9	86.7	16.0	0.31
Hydrocarbon-hydrocarbon	0.8	6.3	2.0	13.9	9.3	0.35
Hydrocarbon-nonhydrocarbon	1.7	11.6	5.3	76.0	18.22	0.45

$$\% \text{AAD} = \frac{\sum |\text{Calc.} - \text{Exp.}| / \text{Exp.}}{\text{Number of points}} \times 100\%$$

$$\text{AAD} = \frac{\sum |\text{Calc.} - \text{Exp.}|}{\text{Number of points}}$$

This method has considerably better accuracy than the hand calculation procedures for critical pressures. The accuracy is also better than that of the hand calculation procedures for all the critical properties of asymmetric mixtures.

Special Comments

The attractive parameter "a" and any temperature dependent binary interaction coefficients (e.g., hydrogen mixtures) must be calculated in the same step as calculation of $\det Q$ because of their temperature dependence.

B. A more recent algorithm has been published by Michelsen and Heidemann. The Michelsen and Heidemann algorithm is less than twice as fast as the algorithm recommended here, however, and considerably more difficult to implement.

Literature Sources

Soave, G., "Equilibrium Constants from a Modified Redlich-Kwong Equation of State," *Chem. Eng. Science* 27, 1197 (1972).

Heidemann, R. A., Khalil, A. M., "The Calculation of Critical Points." *AIChE J.*, 26, 769 (1980).

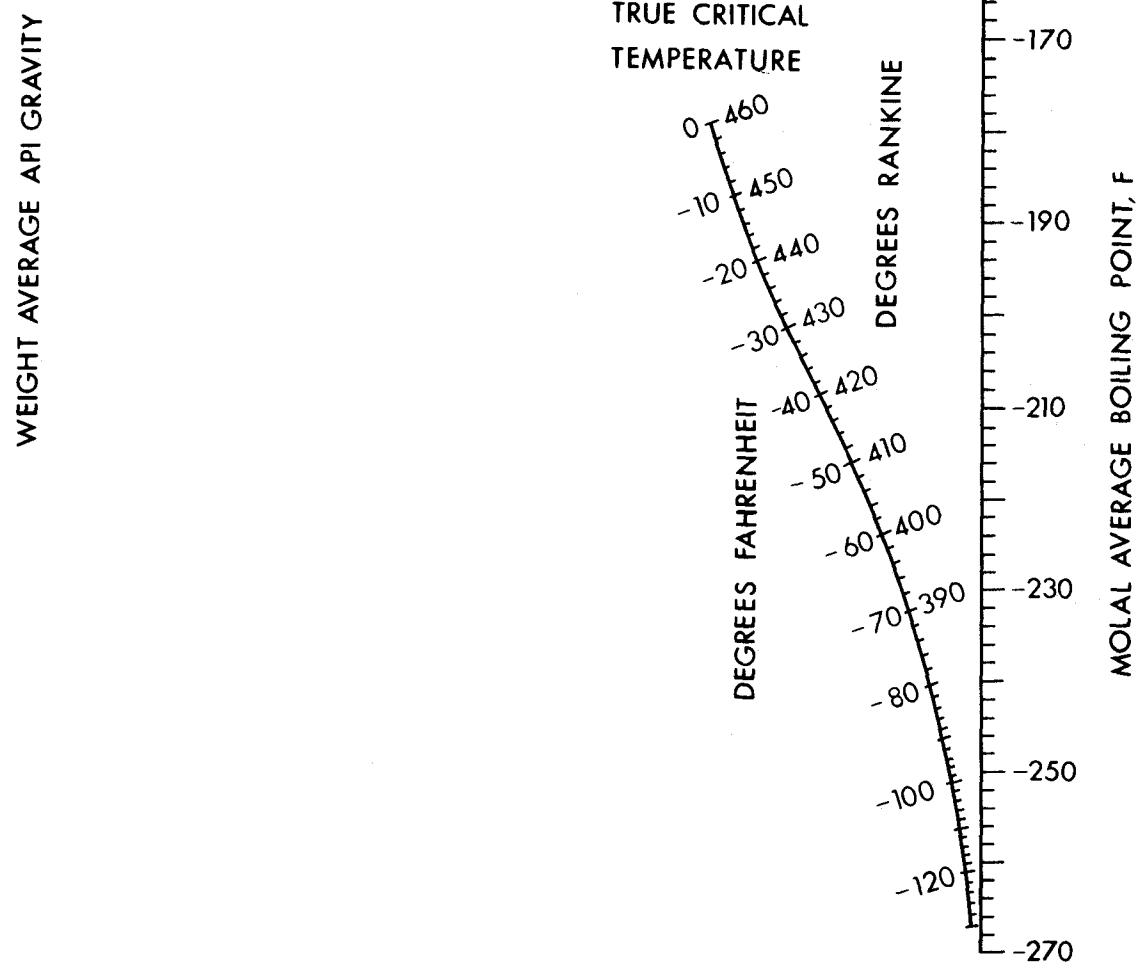
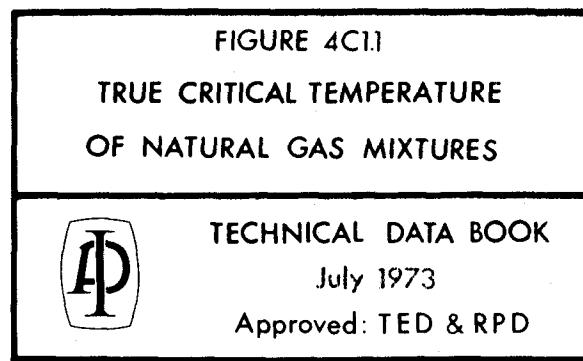
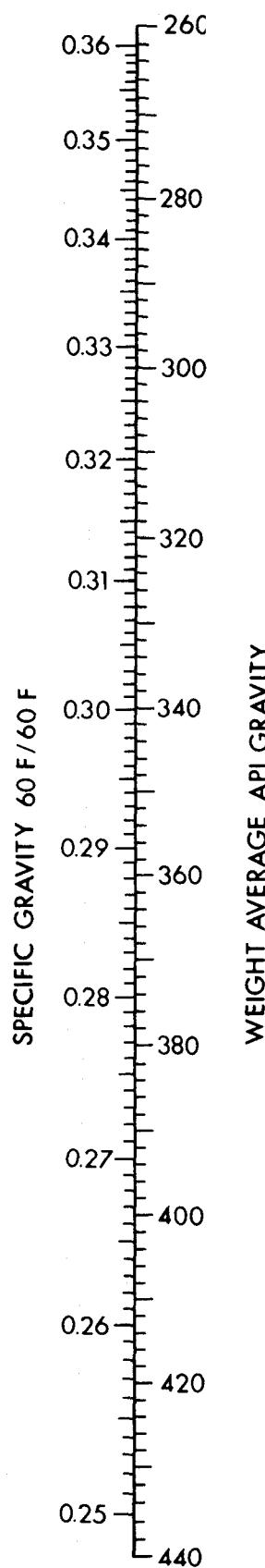
Michelsen, M. L., Heidemann, R. A., "Calculation of Critical Points from Cubic Two-Constant Equations of State." *AIChE J.*, 27, 521 (1981).

Example

Compute the critical point of a mixture of 10 mole percent methane and 90 mole percent ethane.

$$R = 10.731 \frac{\text{psia ft}^3}{\text{lbmol} \cdot R}$$

$$T_{cm} = 538.79R; P_{cm} = 770.54 \text{ psia}; V_{cm} = 2.1929 \frac{\text{ft}^3}{\text{lbmol}}$$



COMMENTS ON FIGURE 4C1.1**Purpose**

The critical temperature of a natural gas mixture in which methane is the predominant component is estimated from this figure.

Limitations

The API gravity and the molal average boiling point (MABP) must be known or estimated by methods given in Chapter 2. The method was evaluated only with experimental data for mixtures containing more than 60 mole percent methane. For mixtures of lower methane content, errors may be larger. The method should not be used for natural gas mixtures containing more than 10 mole percent nitrogen or 3 mole percent carbon dioxide.

Reliability

The average error in estimating the critical temperature of a natural gas is about one percent or ± 4 deg F. The maximum deviation expected is about 30 deg F.

Special Comments

The molal average boiling point, in degrees Fahrenheit is

$$\text{MABP} = \sum_{i=1}^n x_i T_{bi}$$

Where:

MABP = molal average boiling point, in degrees Fahrenheit.

n = number of components.

x_i = mole fraction of component i .

T_{bi} = normal boiling point of component i , in degrees Fahrenheit.

The specific gravity at 60 deg F may be converted to API gravity by using Table 6A1.1 or by rearranging equation (6-0.2) from Chapter 6.

In general, the liquid specific gravities (60 F/60 F) used in calculating the weight average for the mixture are taken from Chapter 1. For methane, ethane, carbon dioxide, and nitrogen, however, the following values must be used.

	Effective API Gravity	Effective Specific Gravity 60 F/60 F
Methane	340	0.300
Ethane	265.76	0.3562
Carbon dioxide.	41.48	0.8180
Nitrogen	43.32	0.8094

The weight fraction of each component may be obtained from the mole fraction using the following equation:

$$x_{wi} = \frac{x_i M_i}{\sum_{i=1}^n x_i M_i} \quad (4C1.1-2)$$

Where:

x_{wi} = weight fraction of component i .

M_i = molecular weight of component i .

The following equations can be used instead of Figure 4C1.1:

$$T_c = A \times \exp [B \times \text{TMBP} + C \times \text{SG} + D \times \text{SG} \times \text{TMBP}]$$

$$T_c = (\text{TMBP})^E$$

$$T_c = (\text{SG})^F$$

$$T_c = T_1 \times T_2 \times T_3$$

T_c = Critical Temperature (Rankine)

SG = Specific Gravity

TMBP = Molal Average Boiling Point (Rankine)

$$A = \exp (-5.624853)$$

$$D = 0.013200830$$

$$B = -0.01058520$$

$$E = 2.4289880$$

$$C = -1.44011260$$

$$F = -0.2998080$$

	Mole Fraction
Methane	0.868
Ethane	0.065
Propane	0.025
<i>n</i> -Butane	0.007
Nitrogen	0.034
	1.000

From Chapter 1:

	Methane	Ethane	Propane	<i>n</i> -Butane	Nitrogen
Molecular weight	16.043	30.07	44.097	58.124	28.02
Normal boiling point, deg F	-258.69	-127.48	-43.67	31.10	-320.4
API gravity	440*	213*	147.2	110.6	43.6*

The molal average boiling point is computed using equation (4C1.1-1):

$$\begin{aligned} MABP &= (0.868)(-258.69) + (0.065)(-127.48) \\ &\quad + (0.025)(-43.67) + (0.007)(31.10) + (0.034)(-320.4) \\ &= -224.5 - 8.3 - 1.1 + 0.2 - 10.9 \\ &= -244.6 \text{ F} \end{aligned}$$

The average molecular weight of the mixture is:

$$\begin{aligned} MW_m &= (0.868)(16.043) + (0.065)(30.07) + (0.025)(44.097) \\ &\quad + (0.007)(58.124) + (0.034)(28.02) \\ &= 13.93 + 1.95 + 1.10 + 0.41 + 0.95 \\ &= 18.34 \end{aligned}$$

The weight fraction of each component is calculated from equation (4C1.1-2).

$$\begin{aligned} x_{w1} &= \frac{(0.868)(16.043)}{18.34} \\ &= 0.759 \\ x_{w2} &= 0.107 \\ x_{w3} &= 0.060 \\ x_{w4} &= 0.022 \\ x_{w5} &= 0.052 \end{aligned}$$

The weight average gravity in degrees API is:

$$\begin{aligned} \text{API gravity} &= (0.759)(440) + (0.107)(213) + (0.060)(147.2) \\ &\quad + (0.022)(110.6) + (0.052)(43.6) \\ &= 370 \text{ API} \end{aligned}$$

From Figure 4C1.1,

$$T_{cm} = -84.0 \text{ F.}$$

Literature value (18) = -81.3 F.

* Taken from Special Comments.

PROCEDURE 4D1.1

METHOD FOR THE CRITICAL TEMPERATURE OF PETROLEUM FRACTIONS

Discussion

The Roess equation (4D1.1-1) is to be used to calculate the true critical temperature of a petroleum fraction. For this purpose the specific gravity and volumetric average boiling point (VABP) of the fraction must be known or estimated. The equation is as follows:

$$T_{cm} = 186.16 + 1.6667\Delta - 0.7127(10^{-3})\Delta^2 \quad (4D1.1-1)$$

$$\Delta = (\text{sp gr}) \times (\text{VABP} + 100.0) \quad (4D1.1-2)$$

Where:

T_{cm} = true critical temperature of fraction, in degrees Fahrenheit.

sp gr = specific gravity, 60 F/60 F.

VABP = volumetric average boiling point (defined in comments on Figure 2B1.1), in degrees Fahrenheit.

Procedure

Step 1: If values of VABP and specific gravity are not known, obtain these parameters from methods given in Chapter 2. The average molecular weight and an ASTM D86 distillation for the fraction should be known if these estimates are required. If a true boiling point (TBP) or ASTM D1160 distillation is given, it should be converted to an ASTM D86 distillation by the methods of Chapter 3.

Step 2: Compute the value of Δ using equation (4D1.1-2).

Step 3: Calculate the true critical temperature from equation (4D1.1-1).

COMMENTS ON PROCEDURE 4D1.1**Purpose**

An equation is given for calculating the true critical temperature of a petroleum fraction (a mixture of undefined composition). This method is intended for use both as a desk and a computer method.

Limitations

This equation was evaluated with petroleum fractions characterized by the following physical property ranges:

Critical temperature, deg F.....	550 to 1,000
Critical pressure, psia.....	250 to 700
Specific gravity, 60 F/60 F.....	0.660 to 0.975

Most of the fractions were made up by blending base stock such as: Mid-Continent straight run gasoline, cracked naphtha, Mid-Continent kerosine, Mid-Continent gas oil, naphthene base gas oil, Pennsylvania crudes, and the more recent data from North Slope fractions. If the aforementioned physical property ranges are exceeded, errors may be larger.

Reliability

Errors in the calculated critical temperatures are about one percent (± 6 deg F) using this procedure. The maximum deviation expected is 22 deg F.

Special Comments

The Edmister-Pollock chart (12) which is as accurate as equation (4D1.1-1) for predicting the critical temperature of petroleum fractions, may also be used. However, since an equation form is convenient for both desk calculation and computer usage, the Roess equation has been selected.

The critical temperature of mixtures for which other procedures of this chapter do not apply may be calculated by this procedure. However, the error may be higher than indicated under Reliability.

Literature Source

Adapted from Roess, L. C., *J. Inst. Petrol. Tech.* **22** 665 (1936).

Example

Estimate the critical temperature of the following North Slope naphtha. The specific gravity is 0.7762 at 60 F/60 F and the volumetric average boiling point is 290.4 deg F.

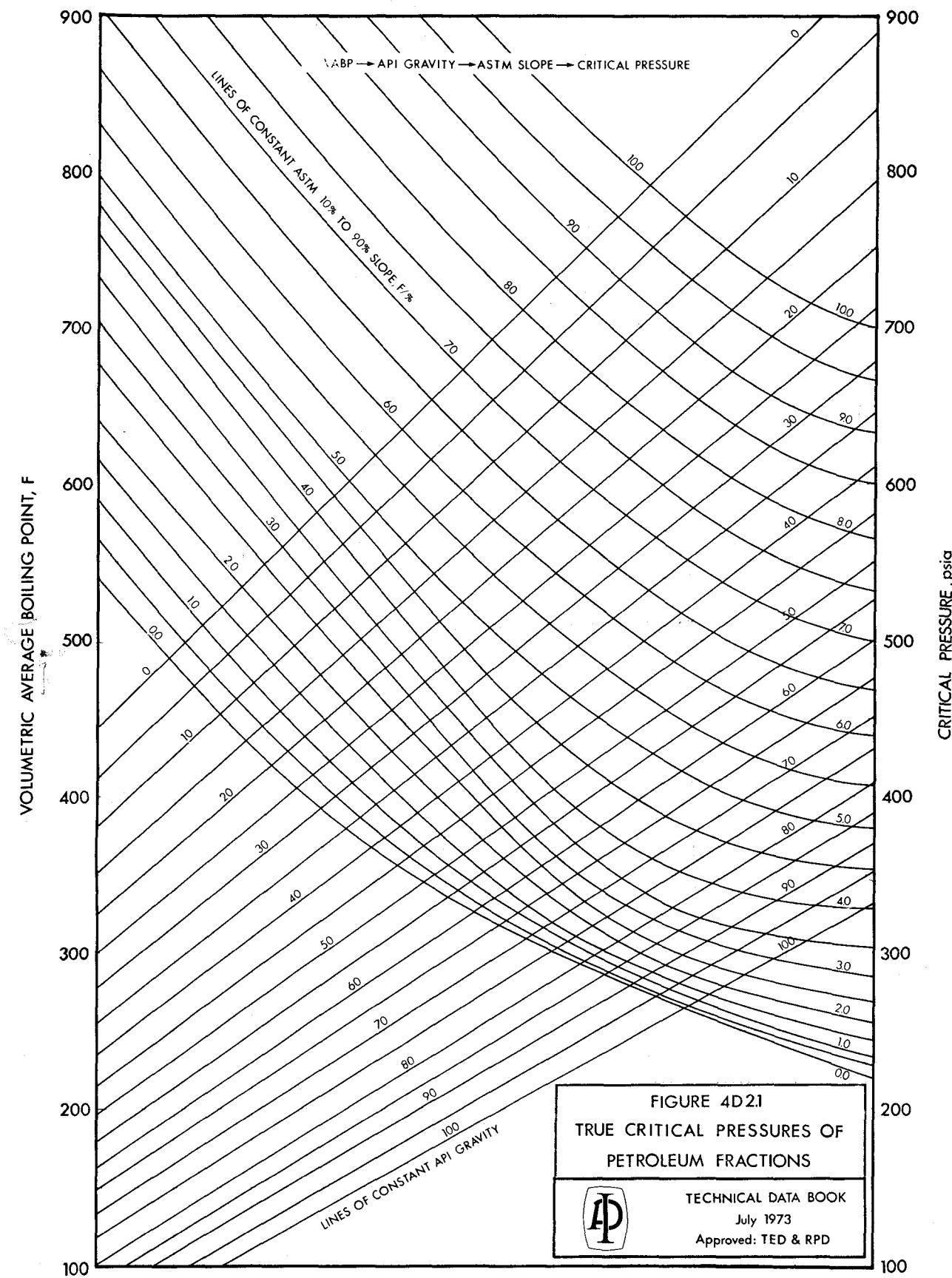
From equation (4D1.1-2):

$$\begin{aligned}\Delta &= (0.7762)(290.4 + 100.0) \\ &= 303.0\end{aligned}$$

By equation (4D1.1-1):

$$\begin{aligned}T_{cm} &= 186.16 + (1.6667)(303.0) - 0.7127(10^{-3})(303.0)^2 \\ &= 625.7 \text{ F}\end{aligned}$$

The experimental value (30) = 632.7 F.



COMMENTS ON FIGURE 4D2.1**Purpose**

The true critical pressure of a petroleum fraction is estimated from Figure 4D2.1, which relates the true critical pressure of petroleum fractions to the ASTM slope, ASTM volumetric average boiling point, and the API gravity of the fraction. This figure was developed by plotting all available data (9) for the true critical pressures of fractions, and smoothing the resulting curves.

Limitations

This method was evaluated with petroleum fraction data characterized by the following physical property ranges:

Critical temperature, deg F	550 to 1,000
Critical pressure, psia	50 to 700
Specific gravity, 60 F/60 F	0.660 to 0.975

Most of the fractions were made up by blending base stocks such as: Mid-Continent straight run gasoline, cracked naphtha, Mid-Continent gas oil, naphthalene base gas oil, Pennsylvania crudes, and the more recent data from North Slope fractions. If the aforementioned physical property ranges are exceeded, errors may be larger.

Reliability

Errors in the calculated critical pressures are about three percent (± 16 psia) using this procedure. The maximum deviation expected is 60 psia.

Special Comments

An advantage of this figure is that the correlating parameters can be determined directly from standard inspection tests. If all of the parameters are not available, they may be estimated from methods given in Chapter 2.

Figure 4D2.1 has been computerized and is listed as PPC2 of Chapter 16.

Literature Source

Adapted from Edmister, W. C., and Pollock, D. H., *Chem. Eng. Progr.* 44 905 (1948).

Example

Estimate the critical pressure of a North Slope naphtha having the following properties:

$$\begin{aligned} \text{VABP} &= 497.4 \text{ deg F} \\ \text{API gravity} &= 41.8 \\ \text{ASTM slope} &= 0.35 \text{ deg F/percent distilled} \end{aligned}$$

Locate 497.4 deg F on the left-hand vertical temperature axis. Draw a horizontal line from this point until it intersects the 41.8 deg API gravity line.

Construct a vertical line from this point of intersection until it reaches an ASTM slope value of 0.35.

A horizontal line from this point intersects the critical pressure axis at a value of 342 psia.
The experimental value (30) is 342 psia.

PROCEDURE 4D3.1

METHOD FOR THE PSEUDOCRITICAL TEMPERATURE OF PETROLEUM FRACTIONS

Discussion

Equation (4D3.1-1) is used to calculate the pseudocritical temperature of petroleum fractions. For this purpose, specific gravity and mean average boiling point must be known or estimated. The equation is as follows:

$$T_{pc} = 10.6443 [\exp(-5.1747 \times 10^{-4} T_b - 0.54444S + 3.5995 \times 10^{-4} T_b S)] \\ \times T_b^{0.81067} S^{0.53691} \quad (4D3.1-1)$$

Where:

T_{pc} = pseudocritical temperature of petroleum fraction, degrees Rankine.

T_b = mean average boiling point, degrees Rankine.

S = specific gravity, 60 F/60 F.

Equation 4D3.1-1 is also shown in Figure 4D3.2 in terms of the Watson K and API gravity.

Where:

$$\text{Watson } K = \frac{T_b^{1/3}}{S}$$

$$\text{API gravity} = \frac{141.5}{S} - 131.5$$

Procedure

Step 1: Obtain the specific gravity of the petroleum fraction.

Step 2: Obtain the mean average boiling point using Figure 2B1.2.

Step 3: Calculate the pseudocritical temperature using equation (4D3.1-1) or read it from Figure 4D3.2 after converting specific gravity to API gravity.

COMMENTS ON PROCEDURE 4D3.1

Purpose

An equation is given for calculating the pseudocritical temperature of a petroleum fraction (a mixture of undefined composition). This equation is intended as both a desk and a computer method.

Limitations

Equation (4D3.1-1) is valid over the following range of molecular weight, normal boiling point, and API gravity:

	Range of Data
Molecular weight	70–295
Normal boiling point, degrees Fahrenheit	80–650
API gravity	6.6–95.0

In Figure 4D3.2 dotted lines represent extrapolated values and should be used with caution.

Reliability

Equation (4D3.1-1) can reproduce pure hydrocarbon critical temperature data to within an average error of 0.8 percent. The correlation was not evaluated using petroleum fraction data as pseudocritical temperature is defined rather than measured.

Literature Source

Equation (4D3.1-1) is a 1985 modification of the correlation developed by M. R. Riazi, "Prediction of Thermophysical Properties of Petroleum Fractions," Ph.D. Thesis, Department of Chemical Engineering, The Pennsylvania State University, University Park, Pa., 1979.

Example

Calculate the pseudocritical temperature of a petroleum fraction with specific gravity (60 F/60 F) of 0.8160 and the following ASTM D86 distillation properties.

Distillation, percent by volume	10	30	50	70	90
Temperature, degrees Fahrenheit	227	276	340	413	509

From Figure 2B1.2, the mean average boiling point is 329 F or 789 R.

By equation (4D3.1), the pseudocritical temperature is:

$$\begin{aligned}
 T_{pc} &= 10.6443 \exp(-5.1747 \times 10^{-4} \times 789 - 0.54444 \times 0.8160 \\
 &\quad + 3.5995 \times 10^{-4} \times 789 \times 0.8160)(789)^{0.81067} (0.8160)^{0.53691} \\
 &= 1145 \text{ R}
 \end{aligned}$$

The pseudocritical temperature of this petroleum fraction is, therefore, 685 F. No experimental value is available because pseudocritical temperature is defined rather than measured. To estimate the pseudocritical temperature from Figure 4D3.2, first calculate the Watson K and API gravity.

$$\text{API gravity} = \frac{141.5}{S} - 131.5 = \frac{141.5}{0.8160} - 131.5 = 41.9$$

$$K = \frac{789^{1/3}}{0.8160} = 11.3$$

Using Figure 4D3.2:

$$T_{pc} = 1148 \text{ R} = 688 \text{ F.}$$

PROCEDURE 4D3.3

TRUE AND PSEUDOCRITICAL TEMPERATURES OF MIXTURES CONTAINING BOTH IDENTIFIED HYDROCARBONS AND PETROLEUM FRACTIONS

Discussion

This procedure estimates the true and pseudocritical temperatures of mixtures containing both identified hydrocarbons and petroleum fractions. The procedure is applicable where several of the more volatile components of a mixture are identified as pure hydrocarbons. The remainder is described as one or more petroleum fractions, each of which is characterized only by an ASTM D86 distillation curve and an API gravity.

Procedure

Step 1: Obtain the necessary input data. A mole percent analysis must be available for the entire fraction, with the unidentified portion treated as a pseudocomponent. An ASTM D86 distillation curve and the API gravity are also necessary for the unidentified portion as well as the molecular weights, which can be estimated using the methods of Chapter 2. Use the molecular weights and API gravities for the pure components that are required for the calculations from the tables in Chapter 1, but the following effective gravity values must be used for the light hydrocarbons:

	Effective API Gravity	Effective Specific Gravity 60 F/60 F
Methane.....	440	0.247
Ethane	213	0.41
Ethene (ethylene)	213	0.41

Step 2: If the available characterizing distillations differ from ASTM Method D86, convert using the methods in Chapter 3.

Step 3: For each unidentified portion, calculate the volumetric average boiling point as the weighted average of the ASTM D86 distillation temperatures after 10, 30, 50, 70, and 90 percent by volume have been distilled, $\frac{T_{10} + T_{30} + T_{50} + T_{70} + T_{90}}{5}$. Also, calculate the slope

assuming a linear distillation curve between the 10- and 90-percent points, $\frac{T_{90} - T_{10}}{90 - 10}$, in degrees Fahrenheit per percent distilled.

Step 4: Using the figures in Chapter 2, obtain the mean, molal, and cubic average boiling points for the unidentified portions.

Step 5: Using the component molecular weights and mole fractions, calculate the mixture average molecular weight. Determine all the component weight fractions by dividing the product of the molecular weight and mole fraction for the component by the mixture average molecular weight.

Step 6: Using the component weight fractions and API gravities, calculate the weight average API gravity and specific gravity for the entire mixture.

Note: Skip Steps 7 and 8 if only the true critical temperature is desired.

Step 7: Using the component weight fractions and component specific gravities, calculate the component volume fractions by dividing the quotient of the component weight fractions and specific gravities by the sum of the quotients for all components

$$x_{v_i} = \frac{x_{w_i}/\text{SpG}_i}{\sum(x_{w_i}/\text{SpG}_i)}$$

Step 8: Using the component mole fractions and volume fractions, respectively, together with the molal average and cubic average boiling points of each component (normal boiling points for pure hydrocarbons), calculate the molal and cubic average boiling points from the definitions in the Chapter 2 introduction. Calculate the mean average boiling point from its definition.

Note: Skip Step 9 if only the pseudocritical temperature is desired.

Step 9: Using the component volume fractions and the volume average boiling point of each component, calculate the volume average boiling point from the definition in Chapter 2.

4D3.3

Step 10: Calculate the true critical temperature using the volume average boiling point from Step 9 and the specific gravity for the mixture from Step 6 in Procedure 4D1.1.

Step 11: Calculate the pseudocritical temperature using the mean average boiling point from Step 8 and the specific gravity for the mixture from Step 6 in Procedure 4D3.1.

COMMENTS ON PROCEDURE 4D3.3

Purpose

True and pseudocritical temperatures of mixtures containing both identified hydrocarbons and petroleum fractions are estimated by this procedure. For the true and pseudocritical pressures of these mixtures, use Procedure 4D4.3.

Limitations

This method is limited to mixtures containing both identified hydrocarbons and petroleum fractions and is applicable only to Type I critical loci (see introduction).

Reliability

Data are not available to evaluate the reliability of this procedure.

Special Comments

The various average boiling points are defined and correlated in Chapter 2.

When ASTM D86 distillation data are used to obtain the boiling points, temperatures above 475 F must be corrected for cracking by equation (3A1.1-1).

Literature Source

The procedure was developed by Hadden, S. T., *Chem. Eng. Progr.* **44** 135 (1948).

Example

Calculate the true and pseudocritical temperature of a Conroe crude oil that is characterized by the following data:

	Mole Fraction
Methane	0.3223
Ethane	0.0424
Propane	0.0335
2-Methylpropane.....	0.0108
n-Butane	0.0148
Pentanes	0.0218
Hexane and heavier	0.5544
	1.0000

The hexane-and-heavier portion has an API gravity of 38.0, molecular weight of 172, and the following ASTM D86 distillation properties:

Distillation, percent by volume	10	30	50	70	90
Temperature, degrees Fahrenheit	234	372	478	592*	722*

From the distillation, the volumetric average boiling point is 480 F and the 10-percent to 90-percent slope is 6.10 $\frac{\text{degrees Fahrenheit}}{\text{percent distilled}}$.

From Chapter 2, Procedure 2B1.1, the mean average boiling point for the hexane-and-heavier portion is 423 F, the molal average boiling point is 386 F, and the cubic average boiling point is 457 F.

To calculate the various average properties of the entire crude oil, the following tabulation is convenient. The average boiling points of pure substances are equal to their normal boiling points.

PROCEDURE 4D4.1

METHOD FOR THE PSEUDOCRITICAL PRESSURE OF PETROLEUM FRACTIONS

Discussion

Equation (4D4.1-1) calculates the pseudocritical pressure of petroleum fractions. For this purpose, specific gravity and mean average boiling point must be known or estimated. The equation is as follows:

$$P_{pc} = 6.162 \times 10^6 [\exp(-4.725 \times 10^{-3} T_b - 4.8014S + 3.1939 \times 10^{-3} T_b S)] T_b^{-0.4844} S^{4.0846} \quad (4D4.1-1)$$

Where:

P_{pc} = pseudocritical pressure, pounds per square inch absolute.

T_b = mean average boiling point, degrees Rankine.

S = specific gravity, 60 F/60 F.

Equation 4D4.1 is also shown in Figure 4D4.2 in terms of the Watson K and API gravity where

$$\text{Watson } K = \frac{T_b^{1/3}}{S} \text{ and API gravity} = \frac{141.5}{S} - 131.5.$$

Procedure

Step 1: Obtain the specific gravity of the petroleum fraction.

Step 2: Obtain the mean average boiling point using Figure 2B1.2.

Step 3: Calculate the pseudocritical pressure using equation (4D4.1-1) or read it from Figure 4D4.2.

COMMENTS ON PROCEDURE 4D4.1**Purpose**

An equation is given for calculating the pseudocritical pressure of a petroleum fraction (a mixture of undefined composition). This equation is intended as both a desk and a computer method.

Limitations

Equation (4D4.1-1) is valid over the following range of molecular weight, normal boiling point, and API gravity:

	Range of Data
Molecular weight	70–295
Normal boiling point, degrees Fahrenheit	80–650
API gravity	6.6–95.0

In Figure 4D4.2 dotted lines represent extrapolated values and should be used with caution.

Reliability

Equation (4D4.1-1) can reproduce pure hydrocarbon critical pressure data to within an average error of 2.6 percent. The correlation could not be evaluated using petroleum fraction data because pseudocritical pressures are defined rather than measured.

Literature Source

Equation (4D4.1-1) is a 1985 modification of a correlation developed by M. R. Riazi, "Prediction of Thermophysical Properties of Petroleum Fractions," Ph.D. Thesis, Department of Chemical Engineering, The Pennsylvania State University, University Park, Pa., 1979.

Example

Calculate the pseudocritical pressure of a petroleum fraction with specific gravity (60 F/60 F) of 0.8160 and the following ASTM D86 distillation properties:

Distillation, percent by volume	10	30	50	70	90
Temperature, degrees Fahrenheit	227	276	340	413	509

From Figure 2B1.2, the mean average boiling point is 329 F or 789 R.

By equation (4D4.1-1), the pseudocritical pressure is:

$$\begin{aligned} P_{pc} &= 6.162 \times 10^6 [\exp(-4.725 \times 10^{-3} \times 789.0 - 4.8014 \times 0.8160 \\ &\quad + 3.1939 \times 10^{-3} \times 789.0 \times 0.8160)](789.0)^{-0.4844}(0.8160)^{4.08460} \\ &= 396 \text{ psia} \end{aligned}$$

To estimate the pseudocritical pressure from Figure 4D4.2 first calculate the Watson *K* and API gravity.

$$\begin{aligned} \text{API} &= \frac{141.5}{S} = -131.5 = \frac{141.5}{0.8160} - 131.5 = 41.9 \\ K &= \frac{789^{1/3}}{0.8160} = 11.3 \end{aligned}$$

Using Figure 4D4.2:

$$P_{pc} = 400 \text{ psia}$$

No experimental value is available because pseudocritical pressure is defined rather than measured.

PROCEDURE 4D4.3**TRUE AND PSEUDOCRITICAL PRESSURES OF MIXTURES CONTAINING BOTH
IDENTIFIED HYDROCARBONS AND PETROLEUM FRACTIONS****Discussion**

This procedure should be used to estimate the true and pseudocritical pressures of mixtures containing both identified hydrocarbons and petroleum fractions. For example, the procedure is applicable where several of the more volatile components of a mixture are identified as pure hydrocarbons and the remainder are described as one or more petroleum fractions, each of which is characterized only by an ASTM D86 distillation curve and an API gravity. Figure 4D4.4 is included in this procedure.

Procedure

Step 1: Obtain the true and pseudocritical temperatures of the mixture using Procedure 4D3.3. Convert these to absolute temperatures, and calculate the value of the ratio of true to pseudocritical temperatures. Retain all intermediate calculations from Procedure 4D3.3.

Step 2: Use the weighted average specific gravity and the mean average boiling point for the entire mixture in Procedure 4D4.1 to calculate the pseudocritical pressure of the mixture.

Step 3: With the pseudocritical pressure and the critical temperature ratio from Step 1, use Figure 4D4.4 or Equation 4D4.3-1 to determine the true critical pressure of the mixture.

COMMENTS ON PROCEDURE 4D4.3**Purpose**

True and pseudocritical pressures of mixtures containing both identified hydrocarbons and petroleum fractions are estimated by this procedure. For true and pseudocritical temperatures of these mixtures, use Procedure 4D3.3 (which is also required in this procedure).

Limitations

The procedure is limited to mixtures containing both identified hydrocarbons and petroleum fractions and is applicable only to Type I critical loci (see introduction).

Reliability

Data are not available to evaluate the reliability of this procedure.

The errors in true critical pressures of defined hydrocarbon mixtures estimated from Figure 4D4.4 are within an average of 5 percent for critical pressures less than 1000 pounds per square inch absolute. The magnitude of error in estimating true critical pressures above 1000 pounds per square inch absolute by this figure is unknown. Severe errors occur for methane-rich systems having critical pressures greater than 2000 pounds per square inch absolute or critical temperatures less than 100 F.

Special Comments

The various average boiling points are defined and correlated in Chapter 2. Figure 4D4.4 may be replaced by the following regression equation:

$$\log P_c = 0.050052 + 5.656282 \log (T_c/T_{pc}) - 1.001047 \log P_{pc} \quad (4D4.3-1)$$

Literature Source

The procedure was developed by Hadden, S. T., *Chem. Eng. Progr.* **44** 135 (1948).

Figure 4D4.4 was adapted with permission from the *Engineering Data Book*, Mobil Oil Company, Inc. It was based on Smith, R. L., and Watson, K. M., *Ind. Eng. Chem.* **29** 1408 (1937).

Example

Calculate the true and pseudocritical pressures of the Conroe oil of the example of Procedure 4D3.3. From this example the true critical temperature is 643 F, and the pseudocritical temperature is 530 F.

Step 1:

$$\frac{T_c}{T_{pc}} = \frac{643 + 460}{530 + 460} = \frac{1103}{990} = 1.114$$

Step 2: Using Procedure 4D4.1 or Figure 4D4.2 the pseudocritical pressure is 450 psia.

Step 3: Using Figure 4D4.4, the true critical pressure is 910 psia.

CHAPTER 5

VAPOR PRESSURE

5.0 INTRODUCTION

Vapor pressure is the pressure at which the vapor phase of a substance is in equilibrium with the liquid phase of that substance at a specified temperature. The term is commonly applied to pure substances, but it is also used occasionally with mixtures. Apart from the temperature effect, the composition of the vapor and liquid phases (when not pure) also influences the equilibrium pressure. Therefore, to use the term vapor pressure with mixtures, the composition effect must be taken into account, either by holding liquid, vapor, or overall composition constant or by focusing attention on a portion of the liquid mixture which is sufficiently close-boiling that composition changes with temperature have a negligible effect on pressure.

Specific vapor pressure correlation equations are recommended in Procedures 5A1.1 and 5A1.3. For compounds covered in this section these equations will give more accurate vapor pressures over the range specified for the particular compound than the generalized predictive procedures. The approximate average error to be expected and the range of applicability for each compound for each correlating equation deemed satisfactory are given together with the correlation coefficients in Tables 5A1.2 and 5A1.4. Procedure 5A1.1 is the primary method and is of a form that can be extrapolated slightly above the critical point when necessary. Procedure 5A1.3 is the alternate method which is constrained at the exact critical point and cannot be extrapolated higher.

The experimental vapor pressure-temperature relationships of a number of the more common hydrocarbons and a few important nonhydrocarbons are plotted directly in Figures 5A1.5 through 5A1.15. The scales of most of these figures are the logarithm of the vapor pressure and a modified reciprocal temperature scale $\frac{1}{t + 382}$, where t is temperature in degrees Fahrenheit.

An accurate generalized method of predicting pure hydrocarbon vapor pressures is given as Procedure 5A1.16. This procedure requires the critical temperature, critical pressure, and acentric factor of a hydrocarbon. A slightly less accurate alternate prediction method is given for use for pure hydrocarbons only when these critical properties are not available. This alternate method, Procedure 5A1.19, requires only the normal boiling point and the specific gravity and also is applicable to narrow-boiling petroleum fractions. The procedure, which includes Figures 5A1.20 and 5A1.21, also can be used to convert a known boiling point from one pressure to another. Table 5-0.1 gives average and bias percent errors for each family of compounds tested for Procedures 5A1.16 and 5A1.19.

The Reid vapor pressure (Rvp) is the absolute pressure exerted by a mixture (in pounds per square inch) determined at 100 F and at a feed vapor-to-liquid volume ratio of 4. (Defined and specified in ASTM Method D 323, the apparatus and procedures are standardized under the auspices of the American Society for Testing and Materials.) Frequently, the Rvp is used to characterize the volatility of gasolines and crude oils. It also provides a convenient approximation of the absolute vapor pressure of a partly vaporized sample at 100 F. Two figures which relate the Rvp and ASTM D 86 boiling characteristics to true vapor pressure over a wide range of temperatures for crude oils (Figure 5B1.2) and for gasolines and other finished petroleum products (Figure 5B1.1) are given. Procedure 5B1.3 gives a new computer method for predicting the Reid vapor pressure for both pure compounds and petroleum fractions.

NOTE: A report which documents the basis upon which the material in this chapter has been selected has been published by the American Petroleum Institute as *Documentation Report No. 5-93* available from University Microfilms International, Books and Collections, Ann Arbor, Michigan.

TABLE 5-0.1—COMPARISON OF PREDICTION METHODS

Family	No. of Cpds	Procedure 5A1.16 (Lee Kesler) Percent Error		Procedure 5A1.19 (Maxwell Bonnell) Percent Error	
		Bias	Average	Bias	Average
<i>n</i> -Alkanes	22	0.5	3.1	-0.9	3.8
Methyl alkanes	16	-0.1	1.8	0.2	1.4
Dimethyl alkanes	16	-1.2	1.5	0.1	3.0
Other branched alkanes	20	-1.3	1.6	-0.4	4.6
Cycloalkanes	4	-1.5	2.0	1.3	3.1
Sub. cyclopentanes	10	-2.9	4.0	-1.9	2.9
Sub. cyclohexanes	13	1.9	3.5	-3.5	5.4
Decalins/bicyclohexyl	3	10.6	14.7	-4.6	13.7
<i>n</i> -Alkenes	18	-0.3	2.3	-1.5	3.9
Other linear alkenes	13	-0.8	1.2	0.6	1.9
Methyl alkenes	13	-1.1	2.8	1.1	2.0
Other branched alkenes	10	1.8	3.8	0.4	1.8
Cycloalkenes	4	-2.2	3.7	-1.9	3.6
Alkadienes	13	12.7	14.5	3.9	4.5
Alkynes	8	-1.1	5.3	1.0	8.0
<i>n</i> -Alkybenzenes	14	-1.9	2.9	-0.2	1.9
Substituted alkylbenzenes	25	-0.6	3.3	1.3	1.9
Aromatics with unsaturated side chains	13	-0.5	3.4	4.7	6.0
Naphthalenes & tetralin	8	-1.9	3.7	2.0	3.3
Fused ring aromatics	6	-12.9	13.7	-16.5	17.1
Multiple aromatic rings	6	5.2	12.7	-4.0	15.6
Indene/indane	2	-6.0	6.1	3.8	4.3
Thiophene/THT	2	2.3	2.6	3.0	3.7
Nitrogen rings	5	-4.4	5.2	-4.1	10.0
Total	264				

PROCEDURE 5A1.1**CORRELATION OF THE VAPOR PRESSURE
OF PURE COMPOUNDS****Discussion**

The following equation is recommended for calculating the vapor pressure of any pure compound over the temperature range specified for the compound.

$$\ln P = A + \frac{B}{T} + C \ln T + DT^2 + \frac{E}{T^2} \quad (5A1.1-1)$$

Where:

P = vapor pressure of compound, psia.

T = temperature, degrees Rankine.

A,B,C,D,E = derived coefficients from Table 5A1.2.

Table 5A1.2 gives the coefficients for the above equation together with the applicable temperature range and the maximum and average percent errors from the comparison with experimental data carried out during regression.

Procedure

Use the coefficients from Table 5A1.2 in equation (5A1.1-1) to calculate the vapor pressure within the temperature range specified.

COMMENTS ON PROCEDURE 5A1.1**Purpose**

This procedure is to be used to calculate the vapor pressure of specific compounds as a function of temperature.

Limitations

This procedure only is valid over the temperature limits listed in Table 5A1.2. The procedure can be extrapolated slightly above the critical where noted by the limits given in Table 5A1.2.

Special Comments

The vapor pressures calculated by this procedure in the experimental data range are totally consistent with the vapor pressure plots for common compounds of Figures 5A1.5 through 5A1.13.

Errors given in the correlation coefficient tables should be noted when using this procedure.

The triple point temperature and critical temperature listed in Table 5A1.2 are taken from the 1992 version of the Chapter 1 database. Therefore, slight discrepancies may be found for some compounds.

Literature Sources

Procedure 5A1.1 is a modification of the Riedel (272) method and was developed by the project staff at The Pennsylvania State University. It has been tested by the project staff at The Pennsylvania State University and evaluated by the API Technical Data Committee.

Example

Determine the vapor pressure of *n*-octane at a temperature of 100 F.

The necessary parameters are obtained from Table 5A1.2 for *n*-octane (compound number 36).

$$\begin{aligned} A &= 76.793 \\ B &= -11700. \\ C &= -8.8309 \\ D &= 0.0000020086 \\ E &= -395420. \end{aligned}$$

and

$$T = 100 \text{ F} = 559.7 \text{ R}$$

Using equation (5A1.1-1)

$$\begin{aligned} \ln P &= -0.62159 \\ P &= 0.5371 \text{ psia} \end{aligned}$$

The experimental value listed in Chapter 1 is 0.5369 psia.

PROCEDURE 5A1.3**ALTERNATE CORRELATION OF THE VAPOR PRESSURE OF
PURE COMPOUNDS****Discussion**

The following alternative equation is recommended for calculating the vapor pressure of any pure compound over the temperature range specified for the compound. This equation should be used, where applicable, when an exact match at the critical is desired.

$$\ln P_r = aX_1 + bX_2 + cX_3 + dX_4 \quad (5A1.3-1)$$

Where:

$$X_1 \approx \frac{(1 - T_r)}{T_r} \quad (5A1.3-2)$$

$$X_2 = \frac{(1 - T_r)^{1.5}}{T_r} \quad (5A1.3-3)$$

$$X_3 = \frac{(1 - T_r)^{2.6}}{T_r} \quad (5A1.3-4)$$

$$X_4 = \frac{(1 - T_r)^5}{T_r} \quad (5A1.3-5)$$

$T_r = T/T_c$ = reduced temperature.

$P_r = P/P_c$ = reduced pressure.

T_c = critical temperature, in degrees Rankine.

P_c = critical pressure, in psia.

T = temperature, in degrees Rankine.

P = vapor pressure, of compound, in psia.

Table 5A1.4 gives the coefficients for the above equation together with the applicable temperature range and the maximum and average percent errors from the comparison with the experimental data carried out during regression. Compounds shown without coefficients had insufficient data to correlate by this method.

Procedure

Step 1: Obtain the critical temperature and pressure of the compound from Chapter 1.

Step 2: Calculate the reduced temperature and pressure at the desired conditions using the definitions above.

Step 3: Use the coefficients in Table 5A1.4 in equations (5A1.3-1) through (5A1.3-5) to calculate the vapor pressure within the range specified.

COMMENTS ON PROCEDURE 5A1.3

Purpose

This procedure is to be used to calculate the vapor pressure of specific compounds as a function of temperature.

Limitations

This procedure is valid over the temperature limits listed in Table 5A1.4. The procedure will exactly match the critical temperature and pressure used in the equation. *However, the equation cannot be extrapolated to temperatures above the critical point.*

Special Comments

The vapor pressures calculated by this procedure in the experimental data range are generally consistent with the vapor pressure plots for common compounds of Figures 5A1.5 through 5A1.15.

Errors given in the correlation coefficient tables should be noted when using this procedure.

The triple point temperature and critical temperature listed in Table 5A1.4 are taken from the 1992 version of the Chapter 1 database. Therefore, slight discrepancies may be found for some compounds.

Literature Sources

Procedure 5A1.3 is a linearized form of the Wagner (341) method developed by C. Shen-Tu (294). It has been tested by the project staff at the Pennsylvania State University and evaluated by the API Technical Data Committee.

Example

Determine the vapor pressure of *n*-octane at a temperature of 100 F.

The necessary parameters are obtained from Table 5A1.4 for *n*-octane (compound number 36).

$$\begin{aligned}a &= -8.0092 \\b &= 1.8442 \\c &= -3.2907 \\d &= -3.5457\end{aligned}$$

From Chapter 1 $T_c = 564.22$ F. The reduced temperature is

$$T_r = \frac{T}{T_c} = \frac{559.7R}{1023.9R} = 0.5466$$

Using equations (5A1.3-2) through (5A1.3-5)

$$\begin{aligned}X_1 &= 0.8295 \\X_2 &= 0.5585 \\X_3 &= 0.2340 \\X_4 &= 0.03505\end{aligned}$$

Using equation (5A1.3-1)

$$\begin{aligned}\ln P_r &= -6.5079 \\P_r &= 0.001492\end{aligned}$$

From Chapter 1, the critical pressure is 360.7 psia. Therefore, the predicted vapor pressure is

$$\begin{aligned}P &= 0.001492 \times 360.7 \text{ psia} \\&= 0.5380 \text{ psia}\end{aligned}$$

The experimental value listed in Chapter 1 is 0.5369 psia.

PROCEDURE 5A1.16
PREDICTION OF VAPOR PRESSURE OF PURE HYDROCARBONS

Discussion

The following equation is useful for estimating the vapor pressure of pure hydrocarbons (and narrow-boiling petroleum fractions) when the critical properties are known or can be estimated. When the critical properties are not available or cannot be accurately estimated, Procedure 5A1.19 should be used.

$$\ln p_r^* = (\ln p_r^*)^{(0)} + \omega (\ln p_r^*)^{(1)} \text{ at constant } T_r \quad (5A1.16-1)$$

Where:

p_r^* = reduced vapor pressure, p/p_c .

p = vapor pressure, in pounds per square inch absolute.

p_c = critical pressure, in pounds per square inch absolute.

$(\ln p_r)^{(0)}$ and $(\ln p_r)^{(1)}$ = correlation terms that are given in tabular and graphical form.

ω = acentric factor of hydrocarbon.

T_r = reduced temperature, T/T_c .

T = temperature, in degrees Rankine.

T_c = critical temperature, in degrees Rankine.

Procedure

Step 1: Obtain the critical temperature and critical pressure from Chapter 1 or, if not available, estimate values by the procedures of Chapter 4.

Step 2: Calculate the reduced temperature.

Step 3: Obtain the acentric factor of the hydrocarbon from Chapter 1 or Chapter 2.

Step 4: Obtain the correlation terms $(\ln p_r)^{(0)}$ and $(\ln p_r)^{(1)}$ by either interpolating linearly from Table 5A1.17 or, at a small sacrifice in accuracy, by reading directly from Figure 5A1.18. [Alternately use equations (5A1.16-2) and (5A1.16-3).]

Step 5: Calculate the reduced vapor pressure by using equation (5A1.16-1). The vapor pressure is obtained by multiplying the reduced vapor pressure by the critical pressure.

For computer calculations, the correlation terms which are equivalent to Table 5A1.17 are given by the following equations:

$$(\ln p_r^*)^{(0)} = 5.92714 - 6.09648/T_r - 1.28862 \ln T_r + 0.169347 T_r^6 \quad (5A1.16-2)$$

$$(\ln p_r^*)^{(1)} = 15.2518 - 15.6875/T_r - 13.4721 \ln T_r + 0.43577 T_r^6 \quad (5A1.16-3)$$

COMMENTS ON PROCEDURE 5A1.16

Purpose

Procedure 5A1.16 is presented as the best method for estimating the vapor pressure of a pure hydrocarbon which is not treated directly in Procedures 5A1.1 or 5A1.3 or Figures 5A1.5 through 5A1.15. The critical conditions and acentric factor must be known or estimated. The method can also be applied to narrow-boiling petroleum fractions. In the absence of critical data, use Procedure 5A1.19.

Limitations

Equation (5A1.16-1) is valid only for nonpolar substances. The method is restricted to reduced temperatures greater than 0.30 but below the critical point. Care should be taken not to use the equation below the freezing point.

Reliability

Equation (5A1.16-1) reproduces experimental data for pure hydrocarbons to within an average error of 3.5 percent when the critical properties are known. The method is most reliable for reduced temperatures between 0.5 and 0.95. When the critical properties and the acentric factor must be estimated the errors will be larger. The method has not been tested with petroleum fraction data.

Literature Sources

This procedure is based on the vapor pressure equations of Lee, B.I. and Kesler, M.G., *AICHE J.* 21 510 (1975).

Example

Estimate the vapor pressure of 1-butene at 208.4 F.

From Chapter 1, the critical temperature is 295.6 F and the critical pressure is 583 psia. The reduced temperature is $\frac{208.4 + 459.7}{295.6 + 459.7} = 0.885$.

From Chapter 2, the acentric factor is 0.1867. By linear interpolation from Table 5A1.17

$$-(\ln p_r^*)^{(0)} = 0.7232 \text{ and } -(\ln p_r^*)^{(1)} = 0.6197.$$

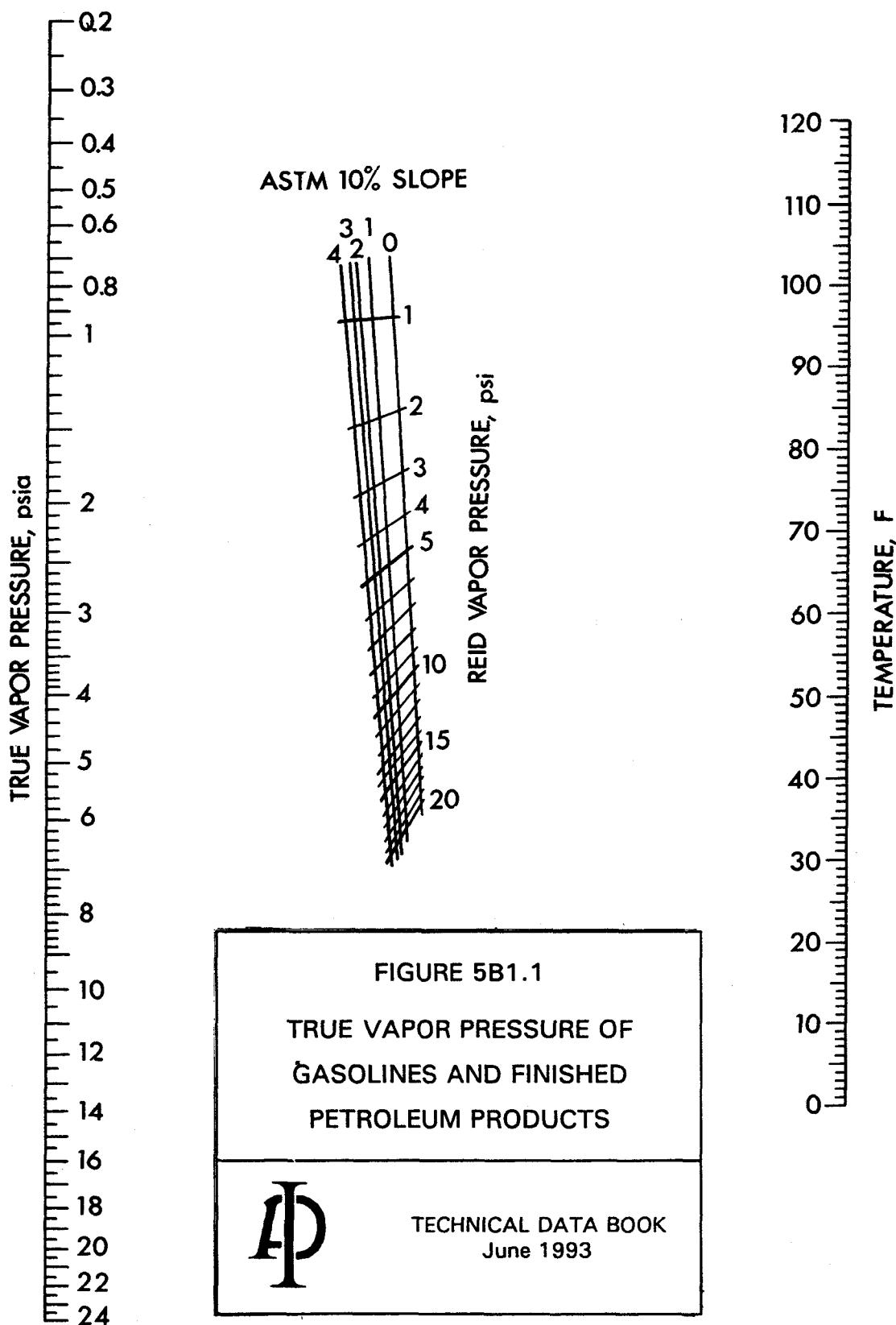
Using equation (5A1.16-1):

$$\ln p_r^* = -0.7232 + 0.1867 (-0.6197) = -0.8389$$

$$p_r^* = 0.4322$$

$$p^* = 0.4322 (583) = 252 \text{ psia}$$

The experimental value is 250 psia.



COMMENTS ON FIGURE 5B1.1

Purpose

Figure 5B1.1 is useful for estimating the true vapor pressure (tvp) of a gasoline or a finished petroleum product at normal storage temperatures. The true vapor pressure of crude oils should be determined using Figure 5B1.2.

Reliability

No estimate of the reliability of this figure is available.

Notation

Slope = slope of the ASTM D 86 distillation curve at ten percent by volume distilled = $\frac{T_{15} - T_5}{10}$, in degrees Fahrenheit per percent distilled.

Special Comments

In the absence of distillation data, the following approximate values of the ASTM ten percent slope may be used:

Motor gasoline	3	Light naphtha (9 to 14 psi Rvp)	3.5
Aviation gasoline	2	Naphtha (2 to 8 psi Rvp)	2.5

The following equation can be used instead of Figure 5B1.1:

T = temperature, in degrees Rankine.

$$S = \text{ASTM ten percent slope } \frac{\text{°F}}{\% \text{ Distilled}}$$

Reid = Reid vapor pressure, in pounds per square inch.

$$\begin{aligned} VP = & \exp \left[\left(\frac{1}{T} \right) (A + B\sqrt{S} + C \ln(\text{Reid}) + D\sqrt{S} \ln(\text{Reid}) \right. \\ & + P \times \text{Reid} + (E + G\sqrt{S} + H\sqrt{S} \ln(\text{Reid}) + O \times \text{Reid}) \times T \\ & + [ZI + ZJ\sqrt{S} + ZK \ln(\text{Reid}) + ZL\sqrt{S} \ln(\text{Reid}) \\ & \left. + ZM \times \text{Reid} + ZN (\text{Reid})^2] \right) \right]. \end{aligned}$$

$$\begin{aligned} A &= 21.36512862 & ZJ &= 2306.00561642 \\ B &= -6.7769666 & ZK &= 1097.68947465 \\ C &= -0.93213944 & ZL &= -463.19014182 \\ D &= 1.42680425 & ZM &= 65.61239475 \\ E &= -0.00568374 & ZN &= 0.13751932 \\ G &= 0.00477103 & O &= 0.00030246 \\ H &= -0.00106045 & P &= -0.29459386 \\ ZI &= -10177.78660360 \end{aligned}$$

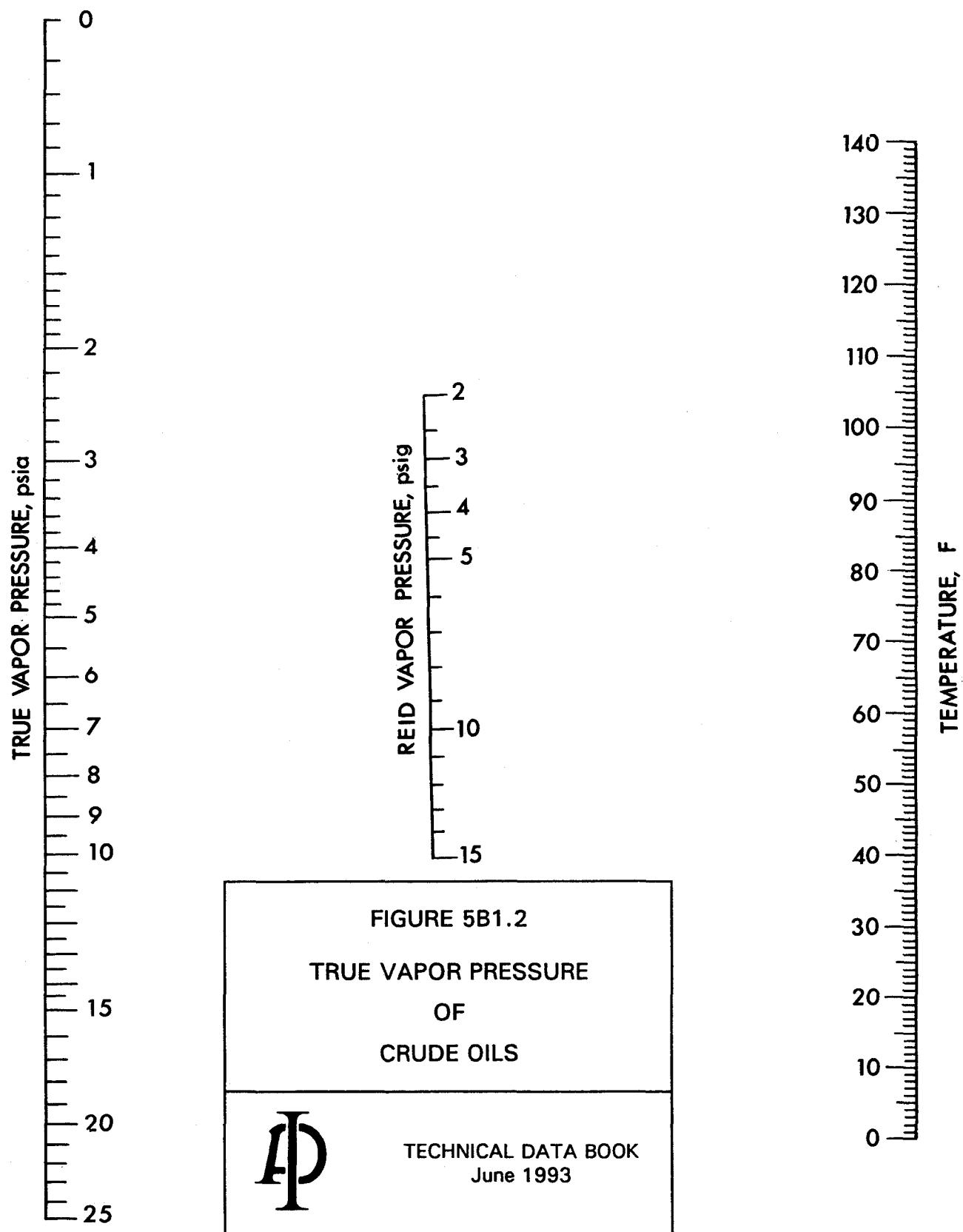
Literature Source

The figure is given in *API Bull. 2513: Evaporation Loss in the Petroleum Industry—Causes and Control*, American Petroleum Institute, New York (1959, Reaffirmed 1973). The equations were derived in API Publication 2517: "Evaporative Loss from External Floating Roof Tanks" Third edition, 1989.

Example

Estimate the tvp at 70 F of a naphtha having a ten percent ASTM slope of 3.5 and a Reid vapor pressure (Rvp) of 11 psi.

Locate the point on the grid of Figure 5B1.1 corresponding to a slope of 3.5 and Rvp of 11. A straight line extended from the 70 F point on the temperature scale through this grid point intersects the tvp scale at 6.9 psia.



COMMENTS ON FIGURE 5B1.2

Purpose

Figure 5B1.2 is useful for estimating the true vapor pressure (tvp) of a crude oil at normal storage temperatures. The true vapor pressures of gasolines and finished products should be determined using Figure 5B1.1.

Reliability

No estimate of the reliability of this figure is available.

Special Comments

The following equation can be used instead of Figure 5B1.2.

T = temperature, in degrees Rankine.

Rvp = Reid vapor pressure, in pounds per square inch.

$$\ln vp = A + B \ln (Rvp) + C (Rvp) + DT$$

$$+ \frac{\left(E + F \ln (Rvp) + G (Rvp)^4 \right)}{T}$$

$$A = 7.78511307$$

$$B = -1.08100387$$

$$C = 0.05319502$$

$$D = 0.00451316$$

$$E = -5756.85623050$$

$$F = 1104.41248797$$

$$G = -0.00068023$$

Applicable Ranges:

$$0^{\circ}\text{F} < T (\text{°F}) < 140^{\circ}\text{F} \text{ and } 2 \text{ psi} < Rvp < 15 \text{ psi}$$

Literature Source

The figure was given in *API Bull. 2513: Evaporation Loss in the Petroleum Industry—Causes and Control*, American Petroleum Institute, New York (1959, Reaffirmed 1973). Also API Publication 2517, Third Edition, February 1989.

Example

Estimate the tvp at 70 F of a crude oil having an Rvp of 6 psi.

A straight line on Figure 5B1.2 connecting the 70 F point on the temperature scale and the 6 psi Rvp point intersects the tvp scale at 4.2 psia.

PROCEDURE 5B1.3
BLENDING METHOD FOR REID VAPOR PRESSURE

Discussion

This procedure estimates the Reid vapor pressure for a blend of pure components and/or petroleum fractions. The Reid vapor pressure of each stream and the molar blending ratio must be known. The Reid vapor pressure of the blend is estimated from:

$$Rvp_b = \left(\sum_i v_i Rvp_i^\alpha \right)^{1/\alpha} \quad (5B1.3-1)$$

where:

- Rvp_b = Reid vapor pressure of the blend, psi.
- α = 1.2.
- v_i = volume fraction of stream i.
- Rvp_i = Reid vapor pressure of stream i, psi.

For a pure component, Rvp_i is taken as the pure component true vapor pressure at 100 F.

This procedure should not be used for widely dissimilar components or streams.

Procedure

Step 1: Obtain the vapor pressure of pure components at 100 F in Chapter 1 or the RVP of any stream.

Step 2: Calculate the Reid vapor pressure of the blend from Equation (5B1.3-1).

COMMENTS ON PROCEDURE 5B1.3**Purpose**

This procedure is used to estimate the Reid vapor pressure of a blend of components with known Reid vapor pressures, as defined in ASTM Procedure 323-94.

Limitations

This method is limited to pure components and petroleum fractions. It should not be used for widely dissimilar blends.

Reliability

This procedure has not been extensively tested. For applicable systems, the method is on average accurate to within 1 psi. Higher errors can be expected for mixtures of unlike components.

Example

Estimate the Reid vapor pressure of a blend that contains 7.56 gallons of tert-butyl ethyl ether (ETBE) and 92.44 gallons of isopentane.

Step 1: From Chapter 1, obtain needed data.

Step 2: Calculate the Reid vapor pressure of the blend using equation (5B1.3-1).

$$RVP_b = (0.0756(4.1478)^{1.2} + 0.9244(20.4643)^{1.2})^{1/1.2}$$

$$RVP_b = 19.2 \text{ psi}$$

An experimental Reid vapor pressure for this blend is 19.0 psi.

PROCEDURE 5B1.4

PREDICTION OF REID VAPOR PRESSURE

Discussion

This procedure predicts the Reid vapor pressure of a fully defined mixture by simulating ASTM Procedure D323-94. If it is necessary to simulate a partially undefined mixture such as a petroleum fraction or a crude oil, please see the special comments for this procedure.

The method calculates the Reid vapor pressure of the liquid sample in two steps. First, the chilled sample is saturated with air. Then, one part of the sample is mixed with four parts by volume of air at 100 F and atmospheric pressure. This mixture is then flashed at 100 F and a constant total volume. The calculated flash pressure is then corrected to obtain the Reid vapor pressure.

Procedure

- Step 1:* The input to this procedure is a liquid sample of known molar composition. For each component of the input, and for oxygen and nitrogen, obtain the molecular weight, critical temperature, critical pressure, acentric factor, Z_{RA} (a constant from Table 6A2.14), and the S_2 term from Table 8D1.3.
- Step 2:* Saturate the sample with air using Procedure 8D1.1. The flash is conducted at 33 F and 14.696 psi. The feed to the flash is 98 mole % sample and 2% bone dry air. The liquid from this flash is used for the remainder of the simulation.
- Step 3:* Use Procedure 6A3.1 to calculate the liquid density of the liquid product from Step 2 in units of pound moles per cubic foot.
- Step 4:* One cubic foot of the sample is fed to the second flash. Multiply the liquid density by one cubic foot to obtain the total pound moles that will be fed to the second flash. The pound moles of each individual component are obtained by multiplying the total pound moles by the liquid mole fractions from the first flash.
- Step 5:* Calculate the pound moles of air needed for a 4 to 1 vapor to liquid ratio at the start of the second flash. The air is fed to the flash at 100 F and 14.696 psia. From the ideal gas law, 0.0079 pound moles of nitrogen and 0.0021 pound moles of oxygen are required.
- Step 6:* Sum the pound moles of both the liquid sample from Step 4 and the vapor from Step 5 to obtain the total pound moles in the mixed feed. The mole fraction of each component in the feed is obtained by dividing the pound moles of the component by the total pound moles.
- Step 7:* Flash the mixed feed at 100 F and a constant volume of 5 ft³ using Procedure 8D1.1. Iterate on the pressure until the volumes of the two phases sums to 5 ft³. The volumes of the phases are found with a material balance calculation and appropriate density equation. For the vapor phase, calculate the density from the gas law with a compressibility factor from the flash calculation. The liquid density should be determined from Procedures 6A3.1.
- Step 8:* Subtract 14.696 psi from the flash pressure. The resulting value is the predicted Reid vapor pressure.

COMMENTS ON PROCEDURE 5B1.4

Purpose

This procedure is used to simulate ASTM Reid vapor pressure experimental procedures.

Limitations

The Reid vapor pressure experiments are highly sensitive to the presence of trapped gases and light hydrocarbons. If gases or paraffins with a carbon number less than seven are present in the mixture, the mole fractions of these light components must be accurately measured to obtain a reliable prediction.

This method does not account for water in the atmosphere because the experimental procedure does not require any correction for moisture or any record of the moisture content of the air. Further, calculations made while creating this method demonstrated that the presence of water had negligible impact on the predicted Reid vapor pressure.

Reliability

For defined mixtures, the method reproduces experimental data to an average deviation of 0.6 psi. For petroleum fractions and whole crude oils, the average deviation from experimental data is 0.8 psi.

Example A.

Simulate the Reid experiment for a mixture that is 93.57 mol % isopentane and 6.43% tert-butyl ethyl ether (ETBE). The required parameters for isopentane, ETBE, nitrogen, and oxygen are listed below.

	Molecular Weight	T _c (F)	P _c (psia)	Acentric Factor	Z _{RA}	S ₂
isopentane	72.15	369.10	490.38	0.2275	0.2718	-0.003898
ETBE	102.18	465.53	440.92	0.2957	0.2726	0.046280
oxygen	32.00	-181.43	731.44	0.0222	0.2890	0.0
nitrogen	28.01	-232.51	493.14	0.0377	0.2893	-0.011016

Use Procedure 8D1.1 to perform a flash calculation at 33 F and 14.7 psia of the sample saturated with 2% air.

Component	Mole Fraction Feed	Mole Fraction Liquid
isopentane	0.9170	0.9338
ETBE	0.0630	0.0648
oxygen	0.0042	0.0005
nitrogen	0.0158	0.0009

CHAPTER 6

DENSITY

6-0 INTRODUCTION

Liquid Systems

Density is defined as the mass of a substance contained in a unit volume and is frequently expressed in grams per milliliter or in pounds (weighed in vacuum) per cubic foot. Density is often indicated in terms of API gravity; specific gravity; and pounds (weighed in air) per gallon, per cubic foot, or per barrel. Specific gravity is the density of a liquid relative to that of water at stipulated conditions of temperature and pressure:

Specific gravity, t F/60 F

$$= \frac{\text{density of substance at } t \text{ F}}{\text{density of water at } 60 \text{ F}} \quad (6-0.1)$$

The conversion tables in this chapter, as well as the conversion factors in Chapter 1, are useful in interchanging the various density units.

The saturated liquid is understood to be a liquid in equilibrium with its own vapor.

Conversion Tables: Conversions between the more common engineering units for liquid densities are given in Table 6A1.1. The table covers the range of API gravity from 0 to 120. All weights given are weights *in air*; that is, those that would be recorded on conventional scales or balances. The table is to be used for engineering calculations only and is not meant for material transfer volume computation.

The conversion table is based on constants similar to the latest values of the National Bureau of Standards (1985).

Weight of water in air of 50 percent humidity at 60 F and 1 atmosphere:	8.32817 lb per gal
Density of standard air at 60 F and 1 atmosphere:	0.001219 g per ml
Density of brass at 60 F:	8.392950 g per ml

These values are very close to those used in calculating the ASTM-IP Petroleum Measurement Tables (reference 6a) which serve as a standard for the petroleum industry.

For conversions that are out of the range of these tables, the following equations may be used.

Specific gravity, 60 F/60 F

$$= \frac{141.5}{\text{API gravity} + 131.5} \quad (6-0.2)$$

Weight in air, in pounds per U.S. gallon at 60 F

$$= \frac{1179.8874}{\text{API gravity} + 131.5} - 0.0101578 \quad (6-0.3)$$

Weight in air, in pounds per cubic foot at 60 F

$$= 7.481 (\text{weight in air, in pounds per U.S. gallon at } 60 \text{ F}) \quad (6-0.4)$$

Weight in air, in pounds per barrel at 60 F

$$= 42 (\text{weight in air, in pounds per U.S. gallon at } 60 \text{ F}) \quad (6-0.5)$$

Pure Liquids: Specific gravities of selected saturated hydrocarbon liquids are given in Figures 6A2.1 through 6A2.12. Values for these same hydrocarbons and many other common pure compounds can be obtained analytically from Procedure 6A2.13 (the Rackett equation) or Procedure 6A2.15 (the COSTALD method). These two methods have been found to be equivalent in accuracy. The input parameters for these methods are given in Table 6A2.14.

Specific gravity data for many more hydrocarbons at 1 atmosphere pressure are presented in three nomographs. Low temperature data, -300 F to 100 F, are obtained from Figure 6A2.16. The valid temperature ranges for the compounds in this figure are presented in Table 6A2.17. The bulk of the data, however, are in the temperature range of 0 F to 400 F (the high temperature range) and are given in Figure 6A2.18 (paraffins and olefins) and Figure 6A2.20 (naphthenes and aromatics). The grid coordinates and the temperature ranges for these hydrocarbon nomographs are given in Tables 6A2.19 and 6A2.21. Extrapolations beyond these temperature ranges should not be made.

The liquid densities of compressed pure hydrocarbons may be estimated from the Lu chart, Figure 6A2.22, if one density value and the critical temperature and pressure are known. Procedure 6A2.23 provides an analytical method of estimating the density of compressed pure liquids. This method can also be used for nonhydrocarbons.

Mixtures: The densities of defined liquid mixtures at their bubble point can be predicted by either Procedure 6A3.1 (the Rackett equation) or Procedure 6A3.2 (the COSTALD method). These two methods have been found to be equivalent in accuracy. Procedure 6A3.1 requires the critical temperatures, the critical pressures,

and Z_{RA} values for all components. Procedure 6A3.2 requires the critical temperatures and two characterization parameters, V^* and ω_{SRK} , for all components. For many compounds these input parameters can be obtained from Chapter 1 and Table 6A2.14. Alternate means of estimating the parameters are suggested in the procedures. Both methods can be used for systems containing hydrocarbons and nonhydrocarbons.

For compressed liquid hydrocarbon mixtures, densities can be calculated using the Lu chart given in Procedure 6A3.3 or the alternate computer method (Tait-COSTALD) given in Procedure 6A3.4. The Lu chart method requires the critical temperatures and critical pressures of the components and a known density of the mixture. A reasonable estimate of this last value can be obtained by dividing the average molecular weight by the corresponding average molar volume of the mixture; this assumes the mixture to be an ideal solution, which is essentially true for members of a homologous series. It is also a reasonable approximation for mix-

tures of hydrocarbons of different types, provided no component is close to its critical point. The computer procedure requires the critical temperatures and COSTALD parameters for the components. It is recommended for mixtures that do not contain polar components.

The densities of liquid petroleum fractions at their saturation pressures or at pressure not far above ambient can be found from the nomograph in Figure 6A3.5 if two of three characterizing parameters (Watson K , mean average boiling point, and API gravity at 60 F) are known. Alternatively, the analytical method given in Procedure 6A3.6 may be used. To obtain the density of liquid petroleum fractions at high pressures, either Procedure 6A3.7, which incorporates Figures 6A3.8 and 6A3.9, or Procedure 6A3.10, which is an analytical method, is recommended.

For both pure liquids and mixtures, Figure 6-0.1 should be helpful in selecting the proper procedure for any particular case.

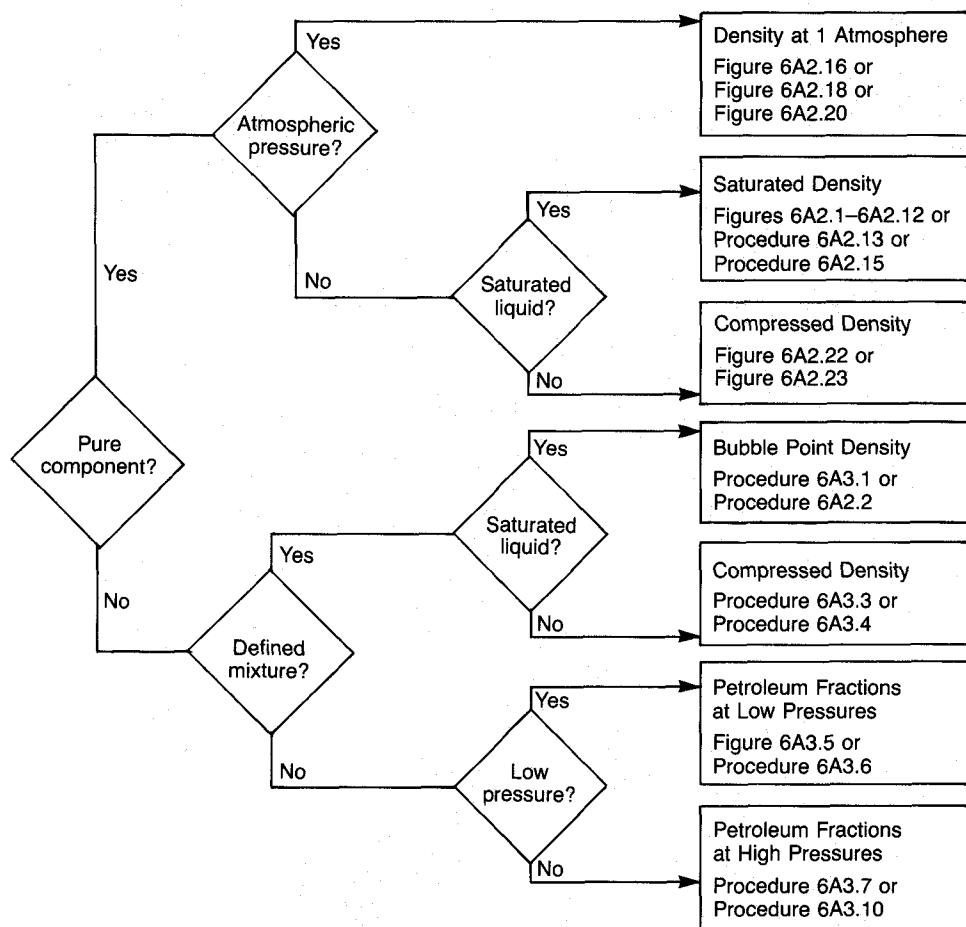


Figure 6-0.1—Liquid Density Calculation Procedures

Excess Volume of Mixing: Some of the procedures presented in this chapter, and in other chapters, assume that if a number of components are mixed, the resultant density of the mixture is a simple volumetric average of the components. In the ideal case this is correct, and for components of quite similar molecular weights and structures, this average is acceptable. As the molecular weights of the components become increasingly different, however, the volume of the resultant mixture varies somewhat from the volumetric average. This can be represented by the concept of excess molar volume, which is stated as follows:

$$V^E = V_m - \sum_{i=1}^n x_i V_i \quad (6-0.6)$$

Where:

- V^E = excess molar volume, cubic feet per pound-mole.
- V_m = actual molar volume of the mixture at given T and p , cubic feet per pound-mole.
- x_i = mole fraction of component i .
- V_i = molar volume of component i at given T and p , cubic feet per pound-mole.
- n = number of components.

This excess volume may be negative or positive depending on the components and the temperature and pressure. Apparently no simple relation exists between volume changes and chemical or physical properties. When aromatic hydrocarbons are mixed with non-aromatics or with petroleum fractions, expansion is commonly observed; but in some instances, contraction takes place. The expansion is greater when naphthenic hydrocarbons are mixed with aromatics than when aromatics are mixed with paraffins. In petroleum fractions and paraffin-paraffin systems, a contraction is generally observed, which is greatest for mixtures of components differing widely in molecular weight.

Excess volume usually increases with increasing temperature and decreases with increasing pressure. The maximum value of excess volume at any given temperature does not occur at 50 mole percent concentration, but is shifted toward the component of lowest molecular weight.

Numerous articles have appeared in the literature concerning excess volume. At this time, however, none of the theory involving excess volume is sufficiently advanced for inclusion in this chapter. The major problems appear to be that: (1) many of the correlations cannot predict both expansion and contraction; (2) very few consider the effect of pressure; (3) the correlation usually has been developed for one particular type of mixture only: paraffin-paraffin, paraffin-aromatic, and the like; and (4) some correlations that may be accept-

able contain parameters that are very difficult to estimate. Nevertheless, as an aid to the user in estimating excess volume, Table 6-0.2 and Figure 6A3.11 have been included.

Gas Systems

Gas densities are conveniently correlated using the following modification of the perfect gas law:

$$\rho = \frac{1}{V} = \frac{P}{zRT} \quad (6-0.7)$$

Where:

ρ = density, in pound-moles per cubic foot.

V = gas volume, in cubic feet per pound-mole.

P = pressure, in pounds per square inch absolute.

z = compressibility factor.

R = gas constant = 10.731 (cubic feet)(pounds per square inch absolute) per (pound-mole)(degree Rankine).

T = temperature, in degrees Rankine.

The compressibility factor, z , varies with temperature, pressure, and the nature of the substance. It is usually correlated within the framework of the simple or extended theorem of corresponding states. In the extended form, this theorem requires that any two substances having an identical value of a third parameter and in identical conditions of reduced temperature and pressure will have the same compressibility factor. Therefore, the compressibility factor behavior of all gases that conform to the extended theorem can be generalized as a function of the third parameter and reduced temperature and pressure.

Pure Gases: Procedure 6B1.1 is presented for estimating the compressibility factors of pure hydrocarbons, and it may also be used for other nonpolar gases. The procedure is based on the three-parameter corresponding states correlation of Lee and Kesler (4b), with the acentric factor, ω , as the third parameter. The Lee-Kesler correlation is a refined version of the Pitzer corresponding states method (7b), and has been used in Chapter 7 for a number of thermal properties. All these methods are internally consistent.

The compressibility factor tables for Procedure 6B1.1 are given as Tables 6B1.2 and 6B1.3. These tables have been generated from the analytical equations of Lee and Kesler. Double interpolations in reduced temperature and pressure are required for their use. Somewhat less reliable but more rapid predictions can be made from the plotted forms of the tables, Figures 6B1.4 through 6B1.7.

The alternate computer method, given as Procedure 6B1.8, uses the Lee-Kesler analytical equations directly. Since the desk method is based on tables gener-

TABLE 6-0.2
EXCESS VOLUMES FOR HYDROCARBON SYSTEMS

System	Temperature (F)	Description of Mixing	Reference
Paraffin-Paraffin			
Ethane-propane	80	Shrinkage	142a
<i>n</i> -Pentane- <i>n</i> -decane	68	Shrinkage	81a
<i>n</i> -Pentane- <i>n</i> -hexadecane	68	Shrinkage	31a,81a
<i>n</i> -Hexane- <i>n</i> -decane	68	Shrinkage	81a
<i>n</i> -Hexane- <i>n</i> -dodecane	59 to 95	Shrinkage	31a,46a
<i>n</i> -Hexane- <i>n</i> -tetradecane	77	Shrinkage	57a
<i>n</i> -Hexane- <i>n</i> -hexadecane	59 to 124	Shrinkage	31a,46a,57a,58a,81a
<i>n</i> -Hexane- <i>n</i> -tetracosane	124	Shrinkage	58a
<i>n</i> -Heptane- <i>n</i> -dodecane	59 to 95	Shrinkage	46a
<i>n</i> -Heptane- <i>n</i> -hexadecane	68 to 104	Shrinkage	31a,81a
<i>n</i> -Heptane- <i>n</i> -tetracosane	169	Shrinkage	58a
<i>n</i> -Heptane- <i>n</i> -hexatricontane	169	Shrinkage	58a
<i>n</i> -Octane- <i>n</i> -hexadecane	68 to 223	Shrinkage	31a,58a,81a
<i>n</i> -Octane- <i>n</i> -dotricontane	205 to 223	Shrinkage	58a
<i>n</i> -Octane- <i>n</i> -hexatricontane	205 to 223	Shrinkage	58a
<i>n</i> -Nonane- <i>n</i> -dexamadecane	259	Shrinkage	58a
<i>n</i> -Nonane- <i>n</i> -tetracosane	124 to 259	Shrinkage	58a
<i>n</i> -Nonane- <i>n</i> -dotricontane	205	Shrinkage	58a
<i>n</i> -Nonane- <i>n</i> -hexatricontane	205 to 259	Shrinkage	58a
<i>n</i> -Nonane- <i>n</i> -dohexacontane	259	Shrinkage	58a
<i>n</i> -Decane- <i>n</i> -dodecane	77 to 95	Shrinkage	54a
<i>n</i> -Decane- <i>n</i> -tetradecane	77 to 113	Shrinkage	54a
<i>n</i> -Decane- <i>n</i> -hexadecane	68 to 113	Shrinkage	31a,54a,81a
<i>n</i> -Dodecane- <i>n</i> -tetradecane	77 to 95	Shrinkage	54a
<i>n</i> -Dodecane- <i>n</i> -hexadecane	77 to 113	Shrinkage	54a
<i>n</i> -Tetradecane- <i>n</i> -hexadecane	77	Ideal	57a
Naphthene-Naphthene			
Cyclohexane-dicyclohexyl	68 to 104	Shrinkage	82a
Cyclohexane-dicyclohexylmethane	68 to 104	Shrinkage	82a
Cyclohexane-1,2-dicyclohexylethane	68 to 104	Shrinkage	82a
Cyclohexane-1,3-dicyclohexylpropane	68 to 104	Shrinkage	82a
Cyclohexane- <i>t</i> -butylcyclohexane	68 to 104	Shrinkage	82a
Aromatic-Aromatic			
Benzene- <i>o</i> -xylene	77 to 86	Expansion	110a,129a
Benzene- <i>m</i> -xylene	77 to 86	Expansion	110a,129a
Benzene- <i>p</i> -xylene	77	Expansion	129a
Benzene-ethylbenzene	68	Expansion	88a
Benzene-naphthalene	175	Variable ^a	17a
Benzene-biphenyl	158	Shrinkage	84a
Benzene-diphenylmethane	77 to 104	Shrinkage	34a,104a
Benzene-diphenylethane	140	Shrinkage	84a
Benzene-diphenylacetylene	140	Shrinkage	84a
Benzene-diphenyloctane	77	Ideal	84a
Toluene-ethylbenzene	68	Ideal	88a
Ethylbenzene-ethenylbenzene	68	Shrinkage	88a
Ethylbenzene- <i>o</i> -xylene	68	Shrinkage	88a
Ethylbenzene- <i>p</i> -xylene	68	Ideal	88a
Ethylbenzene- <i>n</i> -propylbenzene	68	Shrinkage	88a

TABLE 6-0.2 (Continued)

System	Temperature (F)	Description of Mixing	Reference
Aromatic-Aromatic			
Ethylbenzene-isopropylbenzene	68	Ideal	88a
Ethylbenzene-1-methyl-4-isopropylbenzene	68	Expansion	88a
Ethylbenzene- <i>t</i> -amylbenzene	68	Expansion	88a
Ethylbenzene-1,2,3,4-tetrahydronaphthalene	68	Shrinkage	88a
Paraffin-Naphthene			
<i>n</i> -Butane-cyclohexane	59 to 176	Shrinkage	24a
<i>n</i> -Hexane-cyclohexane	77	Expansion	114a
<i>n</i> -Heptane-cyclohexane	59	Expansion	124a
2,4-Dimethylpentane-cyclohexane	82	Ideal	106a
<i>n</i> -Octane-methylcyclohexane	77	Expansion	116a
2,2,4-Trimethylpentane-cyclohexane	77	Variable ^b	8a
<i>n</i> -Dodecane-bicyclohexyl	77	Shrinkage	64a
<i>n</i> -Dodecane- <i>n</i> -hexylcyclohexane	77	Shrinkage	64a
<i>n</i> -Dodecane- <i>n</i> -heptylcyclopentane	77	Ideal	64a
Paraffin-Aromatic			
<i>n</i> -Butane-benzene	59 to 176	Shrinkage	24a
<i>n</i> -Hexane-benzene	77 to 104	Expansion	34a,57a,114a
<i>n</i> -Heptane-benzene	59	Expansion	124a
2,2,4-Trimethylpentane-benzene	68 to 167	Expansion	152a
2,2,4-Trimethylpentane-toluene	82	Expansion	106a
<i>n</i> -Dodecane-benzene	77 to 104	Expansion	34a
<i>n</i> -Dodecane- <i>n</i> -hexylbenzene	77	Expansion	64a
<i>n</i> -Dodecane-phenylcyclohexane	77	Ideal	64a
<i>n</i> -Hexadecane-benzene	77	Expansion	57a
Naphthene-Aromatic			
Cyclopentane-benzene	77	Expansion	149a
Cyclopentane-toluene	77	Expansion	149a
Cyclohexane-benzene	59 to 104	Expansion	104a,114a,124a,149a
Cyclohexane-toluene	77	Expansion	149a
Cycloheptane-benzene	77	Expansion	149a
Cycloheptane-toluene	77	Expansion	149a
Cyclooctane-benzene	77	Expansion	149a
Cyclooctane-toluene	77	Expansion	149a
Petroleum Fractions			
Benzene-petroleum ether	68	Expansion	60a
Benzene-vaseline oil	68	Expansion	60a
Petroleum ether-kerosine	68	Shrinkage	60a
Petroleum ether-vaseline oil	68	Shrinkage	60a
Gasoline-kerosine	68	Shrinkage	60a
Benzol-gasoline	77	Expansion	26a
Light naphtha-heavy naphtha	77	Shrinkage	137a

^a Expansion at high benzene concentration and shrinkage at low benzene concentration.^b Expansion at low cyclohexane concentration and expansion at high cyclohexane concentration.

ated by the computer method, the accuracies of the two methods should be equivalent, except for small errors introduced by the linear interpolations.

The recommended correlations have been found to be the best available methods for general application and internal consistency. However, equations may be found in the literature that give superior accuracy for specific compounds and/or regions.

Gas Mixtures: For densities of gas mixtures, the same desk method and the same computer equations are recommended as for pure gases. However, with the possible exception of a small region in the immediate vicinity of the critical point, the true critical point should no longer be used to calculate the reduced temperature and pressure. As outlined in Procedure 6B2.1, the pseudocritical point is to be used to estimate the gas density of hydrocarbon mixtures. The pseudocritical pressure and temperature are defined as the molar average of the critical properties of the pure components. Methods for estimating the pseudocritical temperatures and pressures for mixtures of defined and undefined composition and blends of the two are given in Chapter 4.

Many equations of varying degrees of complexity have been proposed as substitutes for Kay's molar averages. Several of these result in improved accuracy, but the slight improvement does not justify the increased labor involved when calculating gas densities at the desk. Nevertheless, several alternates are noted in the Special Comments for Procedure 6B2.1. The point determined by these equations is not termed a pseudocritical point, inasmuch as this book reserves that designation for the point defined by the simple molar averaging technique. Instead, the terms *mixture correspondence temperature* and *mixture correspondence pressure* are used.

For computer calculations, the complexity of the equations for the mixture correspondence point is immaterial. Therefore, as described in Procedure 6B2.2, the somewhat more complicated "mixing rules" of Lee and Kesler (4b) have been selected for computer calculations of the mixture correspondence points. The accuracy thus obtained is generally superior to that using Kay's pseudocritical point.

For both the primary desk method (Procedure 6B2.1) and the alternate computer method (Procedure 6B2.2), an approach is outlined for estimating the gas density of mixtures of undefined composition. These approaches are simple extensions of those for defined mixtures, but no data are available to test their accuracy.

Data are not available to determine the reliability of the pseudocritical or mixture correspondence approaches for mixtures exhibiting unusual (non-Type-I) critical loci, but the accuracy of both computer and desk methods is probably worse than quoted. Fortunately, most systems of interest are Type I, but unusual behavior can occur even for hydrocarbon systems. The various critical loci are described in the Introduction to Chapter 4.

The pseudocritical temperature is lower than the true critical temperature in many common systems; thus, both liquid and vapor phases can exist at pseudo-reduced temperatures greater than unity. Under all conditions, but particularly in this region, it is necessary to know the existing phase conditions. If doubt exists, obtain the vapor-liquid equilibrium conditions for the operating temperature and pressure from Chapter 8 to determine whether the desired mixture is in the vapor, liquid, or vapor-liquid equilibrium state. In the last case, the two phases must be treated separately, and the phase compositions and amounts must first be calculated from Chapter 8.

PROCEDURE 6A2.13**SATURATED LIQUID DENSITIES OF PURE COMPONENTS****Discussion**

This procedure, using the modified Rackett equation, and Procedure 6A2.15, using the COSTALD method, are both recommended methods for the calculation of the saturated densities of pure liquids. Equation (6A2.13-1) is applicable from the triple point to the critical point.

$$\frac{1}{\rho_s} = \left(\frac{RT_c}{p_c} \right) Z_{RA} [1.0 + (1.0 - T_r)^{2/7}] \quad (6A2.13-1)$$

Where:

ρ_s = saturated liquid density at temperature T , in pound-moles per cubic foot.

R = gas constant = 10.731 (pounds per square inch absolute) (cubic feet) per (pound-mole) (degree Rankine).

T_r = reduced temperature, T/T_c .

T = temperature, in degrees Rankine.

T_c = critical temperature, in degrees Rankine.

p_c = critical pressure, in pounds per square inch absolute.

Z_{RA} = an empirically derived constant (see Table 6A2.11).

Procedure

Step 1: Obtain the critical temperature and critical pressure from Chapter 1.

Step 2: Obtain a Z_{RA} value from Table 6A2.14. If the compound is not listed in Table 6A2.14 and one or more experimental saturated liquid density values are available, calculate a Z_{RA} value from equation (6A2.13-1). If the compound is not listed in Table 6A2.14 and no experimental saturated liquid density data are available, the critical compressibility value in Chapter 2 may be used as an estimate for Z_{RA} .

Step 3: Calculate the reduced temperature and then calculate the desired density using equation (6A2.13-1).

COMMENTS ON PROCEDURE 6A2.13**Purpose**

An equation is given for calculating the saturated liquid densities of pure liquids. This equation has an accuracy comparable to the COSTALD method given in Procedure 6A2.15. Many hydrocarbons are also covered in Figures 6A2.1 through 6A2.12, which may be more convenient to use.

Limitations

The equation is generally applicable between the triple point and the critical point. When the value of Z_{RA} is not available, a Z_{RA} should be calculated from any available density data using Step 2 of the procedure. If no such data are available, Z_c may be substituted for Z_{RA} .

Reliability

The average absolute deviations from experimental data with equation (6A2.13-1) were 0.7 percent for hydrocarbons and 1.2 percent for nonhydrocarbons (32a). The equation is very sensitive to the value of Z_{RA} , particularly in the region near the critical point. If Z_c is used in place of Z_{RA} , the average absolute deviations increased to 3 percent for both the hydrocarbons and the nonhydrocarbons.

Literature Source

Adapted from Rackett, *J. Chem. Eng. Data* **15** 514 (1970) as described by Spencer and Danner, *J. Chem. Eng. Data* **17** 236 (1972). Z_{RA} values in Table 6A2.14 have been calculated by the Technical Data Book staff from experimental saturated density data or taken from Spencer and Adler, *J. Chem. Eng. Data* **23** 82 (1978).

Example

The density of saturated liquid propane at 30 F is desired.
From Chapter 1,

$$T_c = 206.01 \text{ F}$$

$$p_c = 616.3 \text{ pounds per square inch absolute}$$

$$\text{molecular weight} = 44.097$$

From Table 6A2.14, $Z_{RA} = 0.2763$.

$$T_c = 206.01 + 459.7 = 665.7 \text{ R}$$

$$T_r = \frac{30.0 + 459.7}{665.7} = 0.736$$

From equation (6A2.13-1),

$$\frac{1}{\rho_s} = \frac{(10.731)(665.7)}{(616.3)} 0.2763^{[1.0+(1.0-0.736)^{27}]}$$

$$= (11.591)(0.2763)^{[1.0+0.6835]}$$

$$= 1.3295 \text{ cubic feet per pound-mole}$$

$$\rho_s = 0.7522 \text{ pound-mole per cubic foot}$$

$$= 0.7522 \times \frac{1}{62.43} \times 44.097$$

$$= 0.5313 \text{ gram per milliliter}$$

The experimental value (30a) is 0.5315 gram per milliliter.

PROCEDURE 6A2.15**SATURATED LIQUID DENSITIES OF PURE COMPONENTS****Discussion**

This method, using the COSTALD equation, and Procedure 6A2.13, using the modified Rackett equation, are both recommended methods for the calculation of the saturated densities of pure liquids.

Equations (6A2.15-1) through (6A2.15-3) are applicable in the reduced temperature range from 0.25 to 1.0.

$$\frac{1}{\rho_s} = V^* V_R^{(0)} \left(1 - \omega_{SRK} V_R^{(0)}\right) \quad (6A2.15-1)$$

$$V_R^{(0)} = 1 + a(1 - T_r)^{1/3} + b(1 - T_r)^{2/3} + c(1 - T_r) + d(1 - T_r)^{4/3} \quad (6A2.15-2)$$

$$V_R^{(0)} = \frac{(e + fT_r + gT_r^2 + hT_r^3)}{(T_r - 1.00001)} \quad (6A2.15-3)$$

Where:

ρ_s = saturated liquid density at temperature T , in pound-moles per cubic foot.

V^* = characteristic volume, in cubic feet per pound-mole (see Table 6A2.14).

ω_{SRK} = acentric factor optimized for vapor pressure data in the Soave-Redlich-Kwong equation of state (see Table 6A2.14).

T_r = reduced temperature, T/T_c .

T = temperature, in degrees Rankine.

T_c = critical temperature, in degrees Rankine.

$a = -1.52816 \quad c = -0.81446 \quad e = -0.296123 \quad g = -0.0427258$

$b = 1.43907 \quad d = 0.190454 \quad f = 0.386914 \quad h = -0.0480645$

Procedure

Step 1: Obtain the critical temperature from Chapter 1.

Step 2: Obtain V^* and ω_{SRK} values from Table 6A2.14. If the compound is not listed in Table 6A2.14, the acentric factor ω given in Chapter 2 may be used in place of ω_{SRK} , and the critical volume given in Chapter 1 may be used in place of V^* .

Step 3: Calculate the reduced temperature and then calculate the desired density using equations (6A2.15-1) through (6A2.15-3).

COMMENTS ON PROCEDURE 6A2.15**Purpose**

Equations are given for calculating the saturated liquid densities of pure liquids. This method has an accuracy comparable to the Rackett equation given in Procedure 6A2.13. Many hydrocarbons are also covered in Figures 6A2.1 through 6A2.12, which may be more convenient to use.

Limitations

The equation is applicable in the reduced temperature range between 0.25 and 1.0. When the values of ω_{SRK} and V^* are not available, the acentric factor and the critical volume may be used in their place.

Reliability

The average absolute deviations from experimental data with this method were 0.8 percent for hydrocarbons and 2.1 percent for nonhydrocarbons (32a). Somewhat larger errors are obtained if the acentric factor and the critical volume are used in place of ω_{SRK} and V^* .

Literature Source

The COSTALD method was developed by Hankinson and Thomson, *AIChE Journal*, **25** 653 (1979). The values listed in Table 6A2.14 for ω_{SRK} and V^* have been taken from the above paper or from tabulated values obtained through personal communication with the authors.

Example

The density of saturated liquid propane at 30 F is desired.

From Chapter 1,

$$T_c = 206.01 \text{ F}$$

$$\text{molecular weight} = 44.097$$

From Table 6A2.14, $\omega_{SRK} = 0.1532$, and $V^* = 3.205$ cubic feet per pound-mole.

$$T_c = 206.01 + 459.7 = 665.7 \text{ R}$$

$$T_r = \frac{30.0 + 459.7}{665.7} = 0.736$$

Using equations (6A2.15-2) and (6A2.15-3),

$$\begin{aligned} V_R^{(0)} &= 1 + (-1.52816)(1 - 0.736)^{1/3} + (1.43907)(1 - 0.736)^{2/3} \\ &\quad + (-0.81446)(1 - 0.736) + (0.190454)(1 - 0.736)^{4/3} \\ &= 0.4291 \end{aligned}$$

$$\begin{aligned} V_R^{(8)} &= \frac{-0.296123 + (0.386914)(0.736) + (-0.0427258)(0.736)^2 + (-0.0480645)(0.736)^3}{(0.736 - 1.00001)} \\ &= 0.2033 \end{aligned}$$

From equation (6A2.15-1),

$$\frac{1}{\rho_s} = (3.205)(0.4291)[1 - (0.1532)(0.2033)]$$

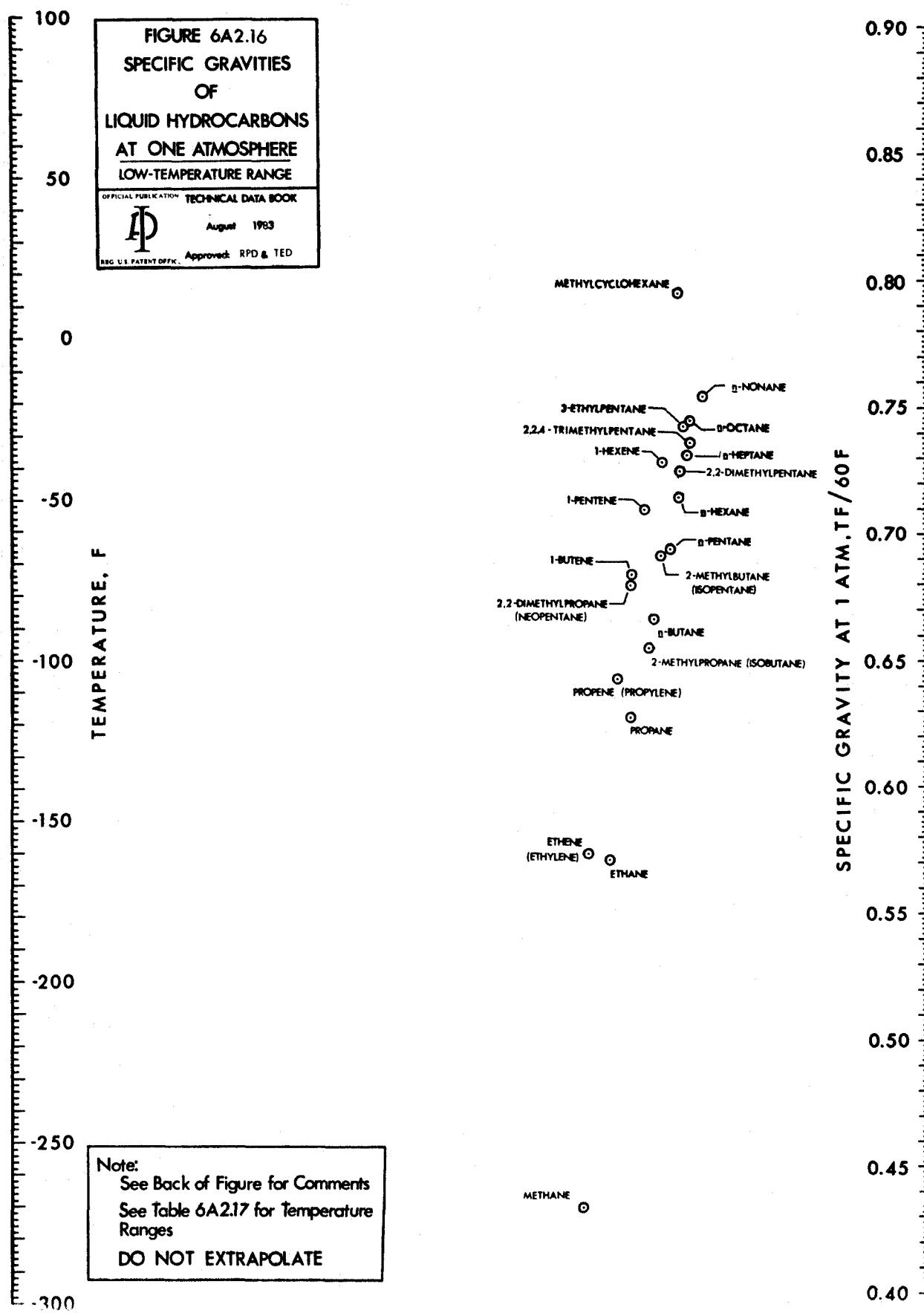
$$= 1.3325 \text{ cubic feet per pound-mole}$$

$$\rho_s = 0.7505 \text{ pound-mole per cubic foot}$$

$$= 0.7505 \times \frac{1}{62.43} \times 44.097$$

$$= 0.5301 \text{ gram per milliliter}$$

The experimental value (30a) is 0.5315 gram per milliliter.



COMMENTS ON FIGURE 6A2.16**Purpose**

Specific gravity-temperature data are presented for pure liquid hydrocarbons at 1 atmosphere pressure.

Limitations

The nomograph is valid only for liquids within the temperature ranges specified for each hydrocarbon in Table 6A2.17.

Reliability

Within the specified temperature limits, the nomograph will reproduce the experimental data with less than 1 percent error.

Literature Source

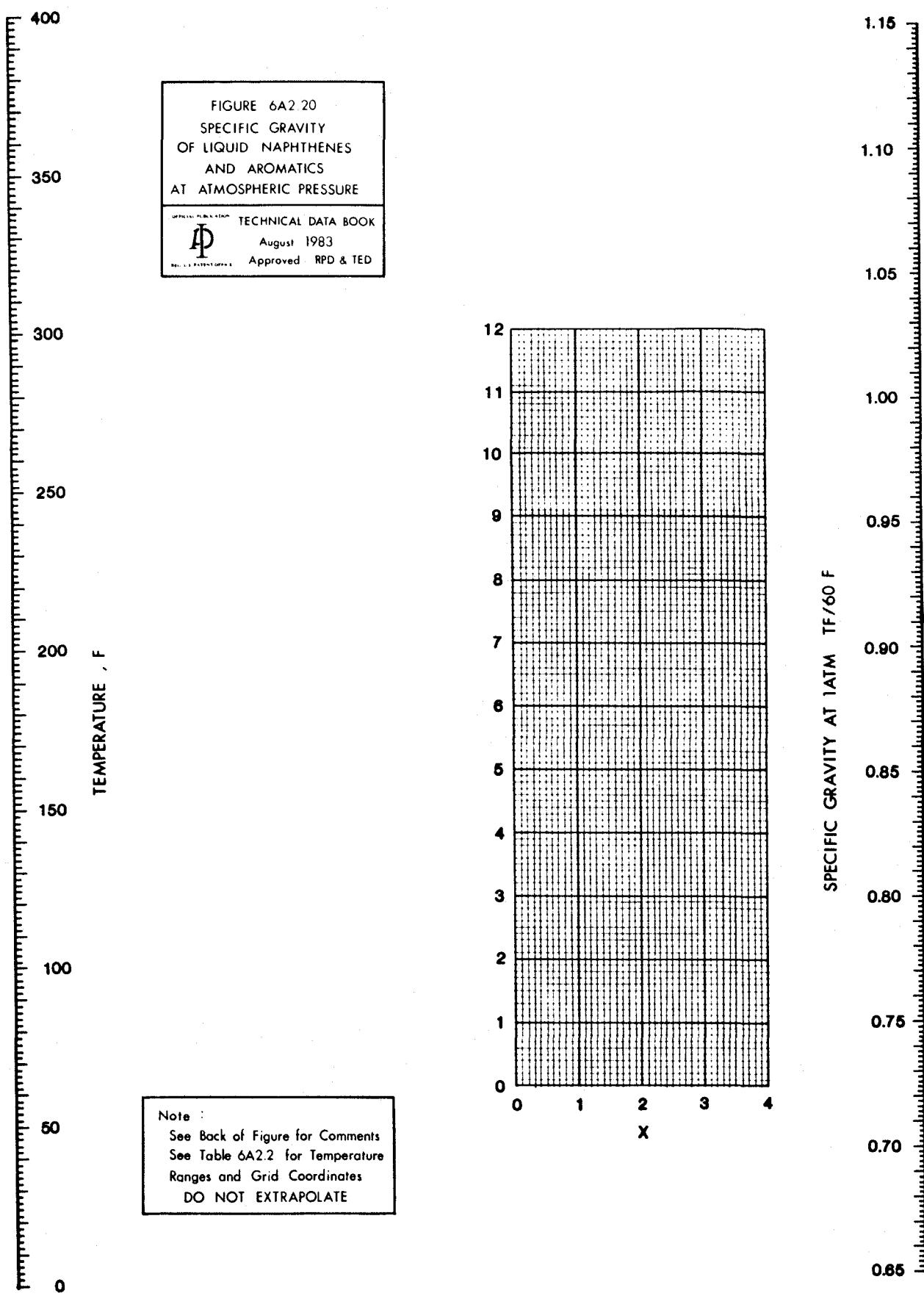
The data used in constructing the nomograph were obtained from API Research Project 44, *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*, Thermodynamics Research Center, Texas A&M University, A&M Press, College Station, Texas (loose-leaf data sheets, extant 1971).

Example

Estimate the liquid density of *n*-butane at -100 F and 1 atmosphere.

From Table 6A2.17, this temperature is determined to be within the valid range of the nomograph. The pivot point labeled *n*-butane is located on the nomograph. A straight line from -100 F on the temperature scale drawn through the pivot point intersects the specific gravity scale at 0.673.

The experimental value (1a) is 0.674.



COMMENTS ON FIGURES 6A2.18 and 6A2.20**Purpose**

Specific gravity–temperature data are presented for pure hydrocarbons at 1 atmosphere pressure.

Limitations

The nomograph is valid only within the temperature ranges specified for each compound in Tables 6A2.19 and 6A2.21.

Reliability

Within the specified temperature limits, the nomograph will reproduce the experimental data with less than 1 percent error.

Literature Sources

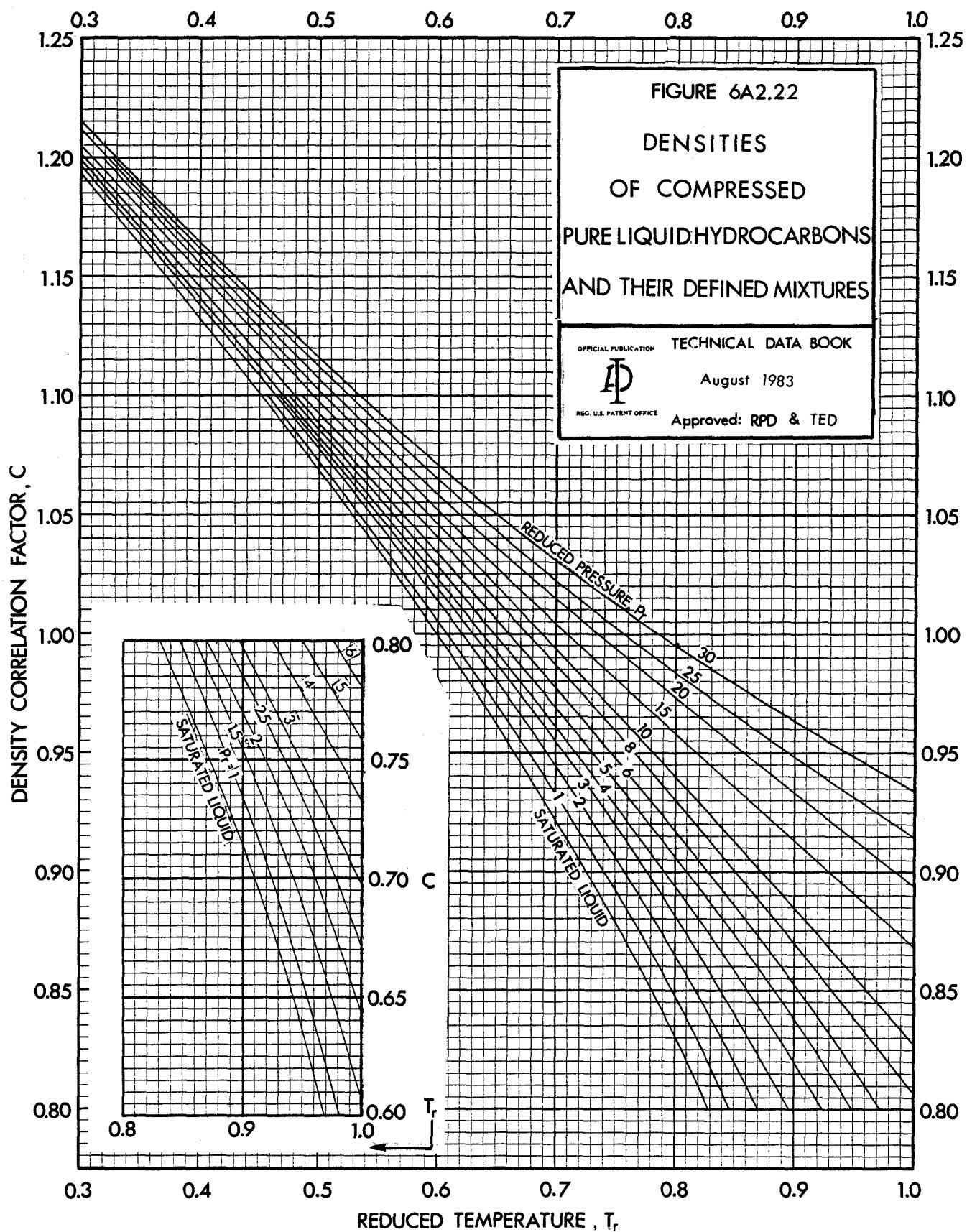
The data used in constructing the nomograph were obtained from API Research Project 44, *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*, Thermodynamics Research Center, Texas A&M University, A&M Press, College Station, Texas (loose-leaf data sheets, extant 1971). Data were also obtained from API Research Project 42, *Properties of Hydrocarbons of High Molecular Weight Synthesized by Research Project 42 of the American Petroleum Institute, 1940–66*, American Petroleum Institute, New York (1967). A small amount of data were taken from Egloff, *Physical Constants of Hydrocarbons*, Vols. I–IV, Reinhold Publishing Corp., New York (1939–53).

Example

Estimate the density of liquid benzene at 122 F and 1 atmosphere pressure.

From Table 6A2.21, 122 F is determined to be within the temperature range for this compound on the nomograph. The X and Y grid coordinates of 0.82 and 4.29 are first located on the nomograph grid (Figure 6A2.20) to locate the pivot point for benzene.

A straight line from 122 F on the temperature scale drawn through the pivot point intersects the specific gravity scale at 0.846. The experimental value is 0.8469.



COMMENTS ON FIGURE 6A2.22**Purpose**

The effect of temperature and pressure on the densities of pure liquid hydrocarbons and their defined mixtures is estimated from this figure. One input density is required. In using this figure for mixtures, follow Procedure 6A3.3.

Discussion

The correlation is based on the relationship $C_1/\rho_1 = C_2/\rho_2 = \text{constant}$, where ρ_1 and ρ_2 represent two densities and C_1 and C_2 represent the corresponding density correlation factors.

Where this relation holds, any density may be expressed as a function of one known density:

$$\rho_2 = \rho_1 \frac{C_2}{C_1} \quad (6A2.22-1)$$

Where ρ is the density in units of weight per volume.

Reliability

The average error in estimating the density of a pure hydrocarbon is 1 percent. However, errors up to 10 percent can be expected at reduced temperatures greater than 0.95.

Notation

C = an empirical density correlation factor (explained above).

T_r = reduced temperature, T/T_c .

T = temperature, in degrees Rankine.

T_c = critical temperature, in degrees Rankine.

p_r = reduced pressure, p/p_c .

p = pressure, in pounds per square inch.

p_c = critical pressure, in pounds per square inch.

Special Comment

In Figure 6A2.22, the saturation line can be considered $p_r = 0$ for interpolation. An average error of 1 percent can be expected in this case.

Literature Source

Figure adapted from Lu, *Chem. Eng.* 66 [9] 137 (1959).

Example

Estimate the liquid density of *n*-nonane at 220 F and 1000 pounds per square inch absolute.

From Chapter 1, $T_c = 610.7$ F; $p_c = 332$ pounds per square inch absolute; $\rho_{60} = 44.94$ pounds per cubic foot. The reference condition, denoted by subscript 1, is 60 F and 1 atmosphere. Therefore,

$$T_{r1} = \frac{60 + 459.7}{610.7 + 459.7} = 0.486 \quad T_{r2} = \frac{200 + 459.7}{610.7 + 459.7} = 0.635$$

$$p_{r1} = \frac{14.7}{332} = 0.0443 \quad p_{r2} = \frac{1000}{332} = 3.01$$

From Figure 6A2.22, $C_1 = 1.077$ and $C_2 = 0.998$. Using equation (6A2.22-1),

$$\rho_2 = 44.94 \frac{0.998}{1.077} = 41.64 \text{ pounds per cubic foot}$$

The experimental value (19a) is 41.11 pounds per cubic foot.

PROCEDURE 6A2.23**ANALYTICAL METHOD FOR THE DENSITIES OF COMPRESSED PURE LIQUIDS****Discussion**

The following equation is to be used to calculate densities of compressed pure liquids. It is applicable in the pressure range from the saturation pressure to 10,000 pounds per square inch absolute.

$$\frac{1}{\rho} = \frac{1}{\rho_s} \left(1 - C \ln \frac{B + p}{B + p_c} \right) \quad (6A2.23-1)$$

$$\frac{B}{p_c} = -1 + \tilde{a}(1 - T_r)^{1/3} + \tilde{b}(1 - T_r)^{2/3} + \tilde{d}(1 - T_r) + \tilde{e}(1 - T_r)^{4/3} \quad (6A2.23-2)$$

$$\tilde{e} = \exp(\tilde{f} + \tilde{g} \omega_{SRK} + \tilde{h} \omega_{SRK}^2) \quad (6A2.23-3)$$

$$C = \tilde{j} + \tilde{k} \omega_{SRK} \quad (6A2.23-4)$$

Where:

ρ = liquid density at temperature T and pressure p , in pound-moles per cubic foot.

ρ_s = saturated liquid density at temperature T , in pound-moles per cubic foot.

p = pressure, in pounds per square inch absolute.

p_s = vapor pressure at temperature T , in pounds per square inch absolute.

p_c = critical pressure, in pounds per square inch absolute.

T_r = reduced temperature, T/T_c .

T = temperature, in degrees Rankine.

T_c = critical temperature, in degrees Rankine.

ω_{SRK} = acentric factor optimized for vapor pressure data in the Soave-Redlich-Kwong equation of state (see Table 6A2.14).

$$\tilde{a} = -9.070217 \quad \tilde{d} = -135.1102 \quad \tilde{g} = 0.250047 \quad \tilde{j} = 0.0861488$$

$$\tilde{b} = 62.45326 \quad \tilde{f} = 4.79594 \quad \tilde{h} = 1.14188 \quad \tilde{k} = 0.0344483$$

Procedure

Step 1: Obtain the critical pressure and critical temperature from Chapter 1.

Step 2: Obtain ω_{SRK} from Table 6A2.14. If the compound is not included in this table, the acentric factor from Chapter 2 may be substituted for ω_{SRK} .

Step 3: Calculate the reduced temperature.

Step 4: Obtain the saturated liquid density using experimental data, or calculate it using figures or procedures given in this chapter.

Step 5: Obtain the saturation vapor pressure using experimental vapor pressure data, or calculate it using figures or procedures given in Chapter 5.

Step 6: Substitute the saturated density, reduced temperature, vapor pressure, critical pressure, and ω_{SRK} in equations (6A2.23-1) through (6A2.23-4) to obtain the liquid density at the desired temperature and pressure.

COMMENTS ON PROCEDURE 6A2.23**Purpose**

The procedure is presented as an alternate analytical method to calculate the effect of temperature and pressure on the densities of pure liquids.

Limitations

This equation was found to work well for reduced temperatures below 0.95. This method has proven satisfactory when tested against a few nonhydrocarbons.

Reliability

The average absolute deviations from experimental data were 1.2 percent for pure hydrocarbons and 2.1 percent for a set of 13 nonhydrocarbon liquids (32a).

Literature Source

The equation was developed by Thomson, Brobst, and Hankinson, *AICHE Journal* **28** 671 (1982).

Example

Estimate the liquid density of *n*-octane at 212 F and 4410 pounds per square inch absolute.
From Chapter 1,

$$T_c = 564.22 \text{ F}$$

$$p_c = 360.6 \text{ pounds per square inch absolute}$$

$$\text{molecular weight} = 114.232$$

From Table 6A2.14, $\omega_{SRK} = 0.3962$, and $Z_{RA} = 0.2569$.

$$T_r = \frac{T}{T_c} = \frac{212 + 459.7}{564.22 + 459.7} = 0.656$$

Using equation (6A2.13-1) the saturated liquid density is calculated:

$$\frac{1}{\rho_s} = \frac{(10.731)(564.22 + 459.7)}{360.6} 0.2569 \exp \left[1 + \left(1 - \frac{212 + 459.7}{564.22 + 459.7} \right)^{2/7} \right]$$

$$= 2.8742 \text{ cubic feet per pound-mole}$$

From Chapter 2, the acentric factor $\omega = 0.3962$.

Using the procedure given in Chapter 5, the saturation vapor pressure is calculated:

$$\ln p_r^* = (-2.8112) + (0.3962)(-2.95)$$

$$p_r^* = \frac{p_s}{p_c} = 0.01869$$

$$p_s = 6.74 \text{ pounds per square inch absolute}$$

Substituting into equations (6A2.23-2) through (6A2.23-4) gives

$$C = 0.086148 + (0.034483)(0.3998) = 0.099934$$

$$\tilde{\epsilon} = \exp[4.79594 + 0.250047(0.3998) + 1.14188(0.3998)^2] = 160.5$$

$$B = 360.6[-1 - 9.070217(0.344)^{1/3} + 62.45326(0.344)^{2/3} - 135.1102(0.344) + 160.5(0.344)^{4/3}] \\ = 5594.5 \text{ pounds per square inch absolute}$$

$$\frac{1}{\rho} = 2.8742 \left[1 - 0.099934 \ln \frac{(5594.5 + 4410)}{(5594.5 + 6.74)} \right]$$

$$= 2.708 \text{ cubic feet per pound-mole}$$

$$\rho = 0.3693 \text{ pound-mole per cubic foot}$$

$$= 0.3693 \times \frac{1}{62.43} \times 114.232$$

$$= 0.6758 \text{ gram per milliliter}$$

The experimental value (41a) is 0.6769 gram per milliliter.

PROCEDURE 6A3.1

DENSITIES OF DEFINED LIQUID MIXTURES AT THEIR BUBBLE POINTS

Discussion

This procedure, using the modified Rackett equation, and Procedure 6A3.2, using the COSTALD method, are both recommended methods for the calculation of the densities of defined liquid mixtures at their bubble points.

Equation (6A3.1-1) is applicable up to a reduced temperature of 0.95.

$$\frac{1}{\rho_{bp}} = R \left(\sum_{i=1}^n x_i \frac{T_{ci}}{p_{ci}} \right) Z_{RAm}^{[1 + (1 - T_r)^{2/7}]} \quad (6A3.1-1)$$

$$Z_{RAm} = \sum_{i=1}^n x_i Z_{RAi} \quad (6A3.1-2)$$

$$T_r = T/T_{mc} \quad (6A3.1-3)$$

$$T_{mc} = \sum_{i=1}^n \sum_{j=1}^n \phi_i \phi_j T_{cij} \quad (6A3.1-4)$$

$$\phi_i = \frac{x_i V_{ci}}{\sum_{j=1}^n x_j V_{cj}} \quad (6A3.1-5)$$

$$T_{cij} = \sqrt{T_i T_{cj}} (1 - k_{ij}) \quad (6A3.1-6)$$

$$k_{ij} = 1.0 - \left[\frac{\sqrt{V_{ci}^{1/3} V_{cj}^{1/3}}}{(V_{ci}^{1/3} + V_{cj}^{1/3})/2} \right]^3 \quad (6A3.1-7)$$

Where:

ρ_{bp} = liquid density at the bubble point, in pound-moles per cubic foot.

R = gas constant, 10.731 (pounds per square inch absolute) (cubic feet) per (pound-mole) (degree Rankine).

x_i = mole fraction of component *i*.

T_{ci} = critical temperature of component *i*, in degrees Rankine.

p_{ci} = critical pressure of component *i*, in pounds per square inch.

V_{ci} = critical volume of component *i*, in cubic feet per pound-mole.

Z_{RAi} = an empirically derived constant for component *i* (see Table 6A2.14).

T = temperature, in degrees Rankine.

Procedure

Step 1: Obtain the critical temperatures, critical pressures, critical volumes, and molecular weights from Chapter 1. For each component of the defined mixture obtain Z_{RAi} from Table 6A2.14. If Z_{RAi} is not available, calculate a value from equation (6A2.13-1) using any experimental density value available for component *i*. If no such data are available, the Z_{ci} value in Chapter 2 may be used as an estimate for Z_{RAi} .

Step 2: Compute the molar average Z_{RAm} using equation (6A3.1-2).

Step 3: The mixture correspondence temperature, T_{mc} , is computed using equations (6A3.1-4) through (6A3.1-7). For desk calculation purposes, a molar average critical temperature may be used.

Step 4: Compute the reduced temperature.

Step 5: Compute the bubble point density from equation (6A3.1-1).

COMMENTS ON PROCEDURE 6A3.1

Purpose

Procedure 6A3.1 is to be used to predict the density of a liquid mixture at its bubble point. This procedure has an accuracy comparable to the COSTALD method given in Procedure 6A3.2.

Special Comments

This procedure may be used to predict the density of defined mixtures containing inorganic gases such as hydrogen, hydrogen sulfide, carbon dioxide, and nitrogen. Values of Z_{RA} for inorganics are given in Table 6A2.14.

Limitations

The procedure should not be applied at reduced temperatures greater than 0.95.

The procedure should not be used for mixtures containing more than 0.5 mole fraction carbon dioxide or nitrogen, or for mixtures containing more than 0.45 mole fraction hydrogen.

Reliability

This method has been evaluated only with binary data. Errors in the calculated densities are about 2.5 percent using this method. Errors may be as high as 20 percent as the critical temperature is reached. For mixtures containing inorganics, the error is about 4 percent. As the critical region is approached, errors as high as 30 percent can be obtained. For mixtures containing more than 50 mole percent carbon dioxide or hydrogen, errors in the range of 15 to 30 percent should be expected. For systems with more than two components, no estimate of the errors is available.

If the molar average pseudocritical temperature is used for desk calculation purposes, an average error of 7 percent should be expected.

Literature Source

The equation was developed by Spencer and Danner, *J. Chem. Eng. Data* 18 230 (1973).

Example

Estimate the bubble point density of an ethane-*n*-heptane mixture at 91 F. The mixture contains 58.71 percent ethane.

Chapter 1 gives the following data for the two components:

Property	Ethane	<i>n</i> -Heptane
Critical temperature, F	90.09	512.8
Critical pressure, psia	707.8	396.8
Critical volume, cu ft per lb	0.0788	0.0691
Molecular weight	30.070	100.205

From Table 6A2.14, Z_{RA_1} (ethane) = 0.2819, and Z_{RA_2} (*n*-heptane) = 0.2610.

$$T_{c1} = 90.09 + 459.7 = 549.79 \text{ R}$$

$$T_{c2} = 512.8 + 459.7 = 972.5 \text{ R}$$

$$Z_{RA_m} = (0.5871)(0.2819) + (0.4129)(0.2610) = 0.2733$$

By equation (6A3.1-5),

$$\begin{aligned}\phi_1 &= \frac{(0.5871)(0.0788)(30.070)}{[(0.5871)(0.0788)(30.070) + (0.4129)(0.0691)(100.205)]} \\ &= 0.3273\end{aligned}$$

$$\phi_2 = 1 - \phi_1 \text{ (for binary systems)}$$

$$= 1 - 0.3273$$

$$= 0.6727$$

PROCEDURE 6A3.2

DENSITIES OF DEFINED LIQUID MIXTURES AT THEIR BUBBLE POINTS

Discussion

This procedure, using the COSTALD method, and Procedure 6A3.1, using the modified Rackett equation, are both recommended methods for calculating the density of defined liquid mixtures at their bubble points.

The following equations are applicable up to a reduced temperature of 0.95.

$$\frac{1}{\rho_{bp}} = V_m^* V_R^{(0)} (1 - \omega_{SRK,m} V_R^{(8)}) \quad (6A3.2-1)$$

$$V_m^* = (1/4) \left[\sum_{i=1}^n x_i V_i^* + 3 \left(\sum_{i=1}^n x_i V_i^{* 2/3} \right) \left(\sum_{i=1}^n x_i V_i^{* 1/3} \right) \right] \quad (6A3.2-2)$$

$$\omega_{SRK,m} = \sum_{i=1}^n x_i \omega_{SRK,i} \quad (6A3.2-3)$$

$$T_r = \frac{T}{T_{mc}} \quad (6A3.2-4)$$

$$T_{mc} = \left(\sum_{i=1}^n \sum_{j=1}^n x_i x_j V_{ij}^* T_{cij} \right) / V_m^* \quad (6A3.2-5)$$

$$V_{ij}^* T_{cij} = (V_i^* T_{ci} V_j^* T_{cj})^{1/2} \quad (6A3.2-6)$$

$$V_R^{(0)} = 1 + a(1 - T_r)^{1/3} + b(1 - T_r)^{2/3} + c(1 - T_r) + d(1 - T_r)^{4/3} \quad (6A3.2-7)$$

$$V_R^{(8)} = \frac{(e + f T_r + g T_r^2 + h T_r^3)}{(T_r - 1.00001)} \quad (6A3.2-8)$$

Where:

ρ_{bp} = liquid density at the bubble point, in pound-moles per cubic foot.

$\omega_{SRK,i}$ = acentric factor of component i optimized for vapor pressure data in the Soave-Redlich-Kwong equation of state (see Table 6A2.14).

x_i = mole fraction of component i .

V_i^* = characteristic volume, in cubic feet per pound-mole (see Table 6A2.14).

T = temperature, in degrees Rankine.

T_{ci} = critical temperature of component i , in degrees Rankine.

$a = -1.52816 \quad c = -0.81446 \quad e = -0.296123 \quad g = -0.0427258$

$b = 1.43907 \quad d = 0.190454 \quad f = 0.386914 \quad h = -0.0480645$

Procedure

Step 1: Obtain critical temperature from Chapter 1 and V^* and ω_{SRK} from Table 6A2.14. If any component of the defined mixture is not listed in Table 6A2.14, use its critical volume from Chapter 1 for V^* and the acentric factor from Chapter 2 for ω_{SRK} .

Step 2: Compute the molar average characteristic volume, V_m^* , using equation (6A3.2-2) and ω_m using equation (6A3.2-3).

Step 3: Calculate the mixture correspondence temperature of the mixture using the mixing rules given by equations (6A3.2-5) and (6A3.2-6).

Step 4: Compute the reduced temperature and substitute it into equations (6A3.2-7) and (6A3.2-8) to obtain $V_R^{(0)}$ and $V_R^{(8)}$.

Step 5: Compute the bubble point density from equation (6A3.2-1).

6A3.2

COMMENTS ON PROCEDURE 6A3.2

Purpose

Procedure 6A3.2 is to be used to predict the density of a liquid mixture at the bubble point. This procedure has an accuracy comparable to the modified Rackett method given in Procedure 6A3.1.

Special Comments

This procedure may be used to predict density of defined mixtures containing inorganics. Values of ω_{SRK} and V^* for inorganics are included in Table 6A2.14.

Limitations

The procedure should not be applied at reduced temperatures greater than 0.95. The procedure has a higher average error for mixtures containing hydrogen or carbon dioxide.

Reliability

This method has been evaluated only with binary data where the average error was about 2.4 percent. Higher errors are reported as the critical region is approached. For mixtures containing inorganics, an average error of 4 percent is reported (32a). For systems with more than two components, no estimate of the errors is available.

Literature Source

This equation was developed by Hankinson and Thomson, *AIChE Journal* **25** 653 (1979).

Example

Estimate the bubble point density of a methane-*n*-decane mixture at 160 F. The mixture contains 20 mole percent methane.

From Chapter 1, the molecular weights of the components are 16.04 for methane and 142.28 for *n*-decane, and the critical temperatures are -116.67 F for methane and 652.00 F for *n*-decane.

From Table 6A2.14, V_i^* , in cubic feet per pound-mole, is 1.592 for methane and 9.919 for *n*-decane, and $\omega_{SRK,i}$ is 0.0074 for methane and 0.4916 for *n*-decane.

Compute the molar average characteristic volume using equation (6A3.2-2).

$$\begin{aligned} V_m^* &= (1/4) \{ (0.2) (1.592) + (0.8) (9.919) + 3[(0.2) (1.592)^{2/3} + (0.8) (9.919)^{2/3}] \\ &\quad \times [(0.2) (1.592)^{1/3} + (0.8) (9.919)^{1/3}] \} \\ &= (1/4) \{ 8.254 + 3[0.2727 + 3.6932] [0.2335 + 1.7189] \} \\ &= 7.871 \text{ cubic feet per pound-mole} \end{aligned}$$

Compute $\omega_{SRK,m}$ using equation (6A3.2-3).

$$\begin{aligned} \omega_{SRK,m} &= (0.2) (0.0074) + (0.8) (0.4916) \\ &= 0.3948 \end{aligned}$$

Calculate T_{mc} using equations (6A3.2-5) and (6A3.2-6).

$$\begin{aligned} T_{c_1} &= -116.67 + 459.7 = 343.11 \text{ R} \\ T_{c_2} &= 652.00 + 459.7 = 1,111.7 \text{ R} \\ V_{12}^* T_{c_{12}} &= V_{21}^* T_{c_{21}} [(1.592) (343.11) (9.919) (1,111.7)]^{1/2} \\ &= 2454.2 \text{ (cubic feet) (degrees Rankine) per (pound-mole)} \\ T_{mc} &= [(0.2)^2 (1.592) (343.11) + (2) (0.2) (0.8) (2454.2) \\ &\quad + (0.8)^2 (9.919) (1,111.8)] / 7.871 \\ &= 999.2 \text{ R} \end{aligned}$$

Compute the reduced temperature from equation (6A3.2-4).

$$T_r = (160 + 459.7) / 999.2 = 0.620$$

PROCEDURE 6A3.3

LIQUID DENSITIES OF COMPRESSED HYDROCARBON MIXTURES OF DEFINED COMPOSITION

Discussion

The correlation is based on the relationship $C_1/\rho_1 = C_2/\rho_2 = \text{constant}$, where ρ_1 and ρ_2 represent two densities of the mixture and C_1 and C_2 represent the corresponding density correlation factors. These factors are obtained from Figure 6A2.22.

Where this relation holds, any density, ρ_2 , may be expressed as a function of one known density, ρ_1 , as shown in equation (6A2.22-1).

Procedure

Step 1: From Chapter 1, obtain the critical temperature, T_c , and the critical pressure, p_c , for each compound in the mixture. If a reference density for the mixture is not known, obtain the density at 60 F and 1 atmosphere for each component also from Chapter 1.

Step 2: Calculate the pseudocritical (molar average) temperature and pressure for the mixture. Compute the pseudoreduced temperature and pressure for the known reference point, if available, and for the desired conditions. If individual compound reference points are being used, compute the average density for the mixture at 60 F and 1 atmosphere using equation (6A3.3-1) or equation (6A3.3-2).

In terms of mole fractions,

$$\rho_1 = \frac{\sum_{i=1}^n x_i M_i}{\sum_{i=1}^n \frac{x_i M_i}{\rho_i^\circ}} \quad (6A3.3-1)$$

In terms of weight fractions,

$$\rho_1 = \frac{1.0}{\sum_{i=1}^n \frac{x_{w_i}}{\rho_i^\circ}} \quad (6A3.3-2)$$

Where:

ρ_1 = reference density of the mixture, in units of weight per volume.

ρ_i° = density of pure component i at 60 F and 1 atmosphere except for lighter hydrocarbons (see note), in units of weight per volume.

n = number of components in the mixture.

x_i = mole fraction of component i .

M_i = molecular weight of component i .

x_{w_i} = weight fraction of component i .

NOTE: For mixtures containing the lighter hydrocarbons, such as *n*-butane and those of lower molecular weight, a slightly different procedure is required. Since these hydrocarbons exist as gases at 60 F and 1 atmosphere, Chapter 1 lists the liquid density at 60 F and the equilibrium vapor pressure. Each reference density must, therefore, be converted to the same pressure (the vapor pressure of the lightest component) before computing the average density of the mixture. For methane mixtures, use Procedure 6A3.1 to calculate a reference density for the mixture. If the vapor pressure is not available, use the Procedures in Chapter 5 to approximate a vapor pressure for the mixture. (This value serves as the reference pressure.) For ethane and ethene a reference point of -30 F at saturated conditions has been selected. The following properties are valid for ethane and ethene at these conditions:

Component	Vapor Pressure (Pounds per Square Inch Absolute)	Density	
		Gram per Milliliter	Pounds per Cubic Foot
Ethane	135	0.4741	29.60
Ethene (ethylene)	240	0.4510	28.16

Examples B and C in the comments on this procedure deal with mixtures containing light hydrocarbons when reference densities for the mixtures are not available.

Step 3: In Figure 6A2.22, locate the values of C_1 at the reduced conditions of the reference point and C_2 at the reduced conditions of the desired density.

Step 4: Compute the unknown density, ρ_2 , from equation (6A2.22-1).

COMMENTS ON PROCEDURE 6A3.3

Purpose

The procedure is given for estimating the liquid densities of defined hydrocarbon mixtures. For pure compounds, see Figure 6A2.22.

Limitations

Pseudocritical pressures and temperatures of a mixture are used in the correlation. However, near the critical point this may lead to large errors; it is desirable to use the actual critical values in this area, if available. Also, for methane systems, the pseudocritical values differ greatly from the actual critical values, and rather high errors may result for these systems.

The recommended volumetric average technique for computing the reference density does not take into account the excess volume of mixing. This procedure, if used instead of an experimental reference density, can result in larger errors in the computed density.

Reliability

Using a volumetric average density for a reference condition, an average error of slightly more than 2 percent can be expected. As the reduced temperature approaches 0.95, errors approaching 15 percent may occur.

Literature Source

Figure 6A2.22 is adapted from Lu, *Chem. Eng.* **66** [9] 137 (1959).

Examples

A. Estimate the liquid density of a mixture containing 60.52 mole percent ethylene and 39.48 mole percent *n*-heptane at 900 pounds per square inch absolute and 162.7 F. For this mixture, the density at 49 F and 400 pounds per square inch absolute is known to be 37.55 pounds per cubic foot.

From Chapter 1,

$$T_c(\text{ethylene}) = 48.58$$

$$p_c(\text{ethylene}) = 729.8$$

$$T_c(n\text{-heptane}) = 512.70$$

$$p_c(n\text{-heptane}) = 396.8$$

Where:

T_c = critical temperature, in degrees Fahrenheit.

p_c = critical pressure, in pounds per square inch absolute.

The pseudocritical properties are calculated as follows:

$$T_{pc} = (0.6052)(48.58) + (0.3948)(512.70) = 231.81 \text{ F}$$

$$p_{pc} = (0.6052)(729.8) + (0.3948)(396.8) = 598.33 \text{ pounds per square inch absolute}$$

Where:

T_{pc}, p_{pc} = pseudocritical properties of the mixture, defined as the sum of the products of each individual T_c or p_c and the corresponding mole fraction.

Then

$$T_{r_1} = \frac{49 + 459.7}{231.81 + 459.7} = 0.736 \quad T_{r_2} = \frac{162.7 + 459.7}{231.81 + 459.7} = 0.900$$

$$p_{r_1} = \frac{400}{598.33} = 0.668 \quad p_{r_2} = \frac{900}{598.33} = 1.50$$

Where:

T_r = reduced temperature, T/T_c .

T = temperature, in degrees Rankine.

p_r = reduced pressure, p/p_c .

p = pressure, in pounds per square inch absolute.

PROCEDURE 6A3.4

COMPUTER METHOD FOR THE LIQUID DENSITIES OF
COMPRESSED HYDROCARBON MIXTURES OF DEFINED COMPOSITION

Discussion

The Tait-COSTALD equation, (6A2.23-1), may be used to calculate liquid densities of compressed hydrocarbon mixtures. A set of mixing rules is used to define the mixture properties.

$$\frac{1}{\rho_m} = \left(\frac{1}{\rho_{bp}} \right) \left(1 - C \ln \frac{B + p}{B + p_{bp}} \right) \quad (6A3.4-1)$$

$$\frac{B}{p_{mc}} = -1 + \bar{a}(1 - T_r)^{1/3} + \bar{b}(1 - T_r)^{2/3} + \bar{d}(1 - T_r) + \bar{e}(1 - T_r)^{4/3} \quad (6A3.4-2)$$

$$\bar{e} = \exp(\bar{f} + \bar{g}\omega_{SRK_m} + \bar{h}\omega_{SRK_m}^2) \quad (6A3.4-3)$$

$$C = \bar{j} + \bar{k}\omega_{SRK_m} \quad (6A3.4-4)$$

$$T_r = \frac{T}{T_{mc}} \quad (6A3.4-5)$$

$$T_{mc} = \left[\sum_{i=1}^n \sum_{j=1}^n x_i x_j V_{ij}^* T_{cij} \right] / V_m^* \quad (6A3.4-6)$$

$$V_{ij}^* T_{cij} = (V_i^* T_{ci} V_j^* T_{cj})^{1/2} \quad (6A3.4-7)$$

$$V_m^* = (1/4) \left[\sum_{i=1}^n x_i V_i^* + 3 \left(\sum_{i=1}^n x_i V_i^{*2/3} \right) \left(\sum_{i=1}^n x_i V_i^{*1/3} \right) \right] \quad (6A3.4-8)$$

$$\omega_{SRK_m} = \sum_{i=1}^n x_i \omega_{SRK_i} \quad (6A3.4-9)$$

$$p_{mc} = (z_{mc} R T_{mc}) / V_m^* \quad (6A3.4-10)$$

$$z_{mc} = 0.291 - 0.080 \omega_{SRK_m} \quad (6A3.4-11)$$

$$\log(p_{bp}/p_{mc}) = p_{R_m}^{(0)} + \omega_{SRK_m} p_{R_m}^{(1)} \quad (6A3.4-12)$$

$$p_{R_m}^{(0)} = 5.8031817 \log T_r + 0.07608141 \alpha \quad (6A3.4-13)$$

$$p_{R_m}^{(1)} = 4.86601 \beta \quad (6A3.4-14)$$

$$\alpha = 35.0 - (36.0/T_r) - 96.736 \log T_r + T_r^6 \quad (6A3.4-15)$$

$$\beta = \log T_r + 0.03721754\alpha \quad (6A3.4-16)$$

Where:

ρ_m = density of liquid mixture at temperature T and pressure p , in pound-moles per cubic foot.

ρ_{bp} = bubble point density of liquid mixture at temperature T , in pound-moles per cubic foot.

p = pressure, in pounds per square inch.

p_{bp} = bubble point pressure of mixture at temperature T , in pounds per square inch.

T = temperature, in degrees Rankine.

x_i = mole fraction of component i .

V_i^* = characteristic volume of component i , in cubic feet per pound-mole (see Table 6A2.14).

T_{ci} = critical temperature of component i , in degrees Rankine.

ω_{SRK_i} = acentric factor for component i optimized for vapor pressure data in the Soave-Redlich-Kwong equation of state (see Table 6A2.14).

R = gas constant, 10.731 (pounds per square inch absolute) (cubic feet) per (pound-mole)(degree Rankine).

$$\bar{a} = -9.070217 \quad \bar{d} = -135.1102 \quad \bar{g} = 0.250047 \quad \bar{j} = 0.0861488$$

$$\bar{b} = 62.45326 \quad \bar{f} = 4.79594 \quad \bar{h} = 1.14188 \quad \bar{k} = 0.0344483$$

6A3.4

Procedure

Step 1: Obtain the critical temperature from Chapter 1 and V_i^* and ω_{SRK_i} for each component from Table 6A2.14. If any compound is not listed in Table 6A2.14, use its critical volume from Chapter 1 for V_i^* and the acentric factor from Chapter 2 for ω_{SRK_i} .

Step 2: Calculate the mixture properties using equations (6A3.4-6) through (6A3.4-9). The saturation vapor pressure is obtained using equations (6A3.4-10) through (6A3.4-16).

Step 3: Calculate the bubble point density of the mixture using either Procedure 6A3.1 or 6A3.2.

Step 4: Substitute the values calculated in Steps 1, 2, and 3 in equations (6A3.4-1) through (6A3.4-4) to obtain the liquid density of the mixture at the desired temperature and pressure.

COMMENTS ON PROCEDURE 6A3.4

Purpose

The procedure is an alternate computer method to estimate compressed liquid densities of defined hydrocarbon mixtures.

Limitations

This equation is applicable in the reduced temperature range below 0.95. The method has been found to give erroneous corrections when used with organic (polar) mixtures. In these cases, it is recommended that the saturated density be used rather than correcting it with equation (6A3.4-1).

Reliability

The average error in estimating the density of defined hydrocarbon mixtures is reported at 1 percent. Unsatisfactory results were obtained for nonhydrocarbon (polar) mixtures (32a).

Literature Source

The equation was developed by Thomson, Brobst, and Hankinson, *AIChE Journal* **28** 671 (1982).

Example

Estimate the liquid density of a mixture containing 20 mole percent ethane and 80 mole percent *n*-decane at 160 F and 3000 pounds per square inch absolute.

Chapter 1 gives the following data for the components:

Property	Ethane	<i>n</i> -Decane
Molecular weight	30.07	142.286
Critical temperature, F	89.92	652.00
Critical pressure, psia	706.80	305.20

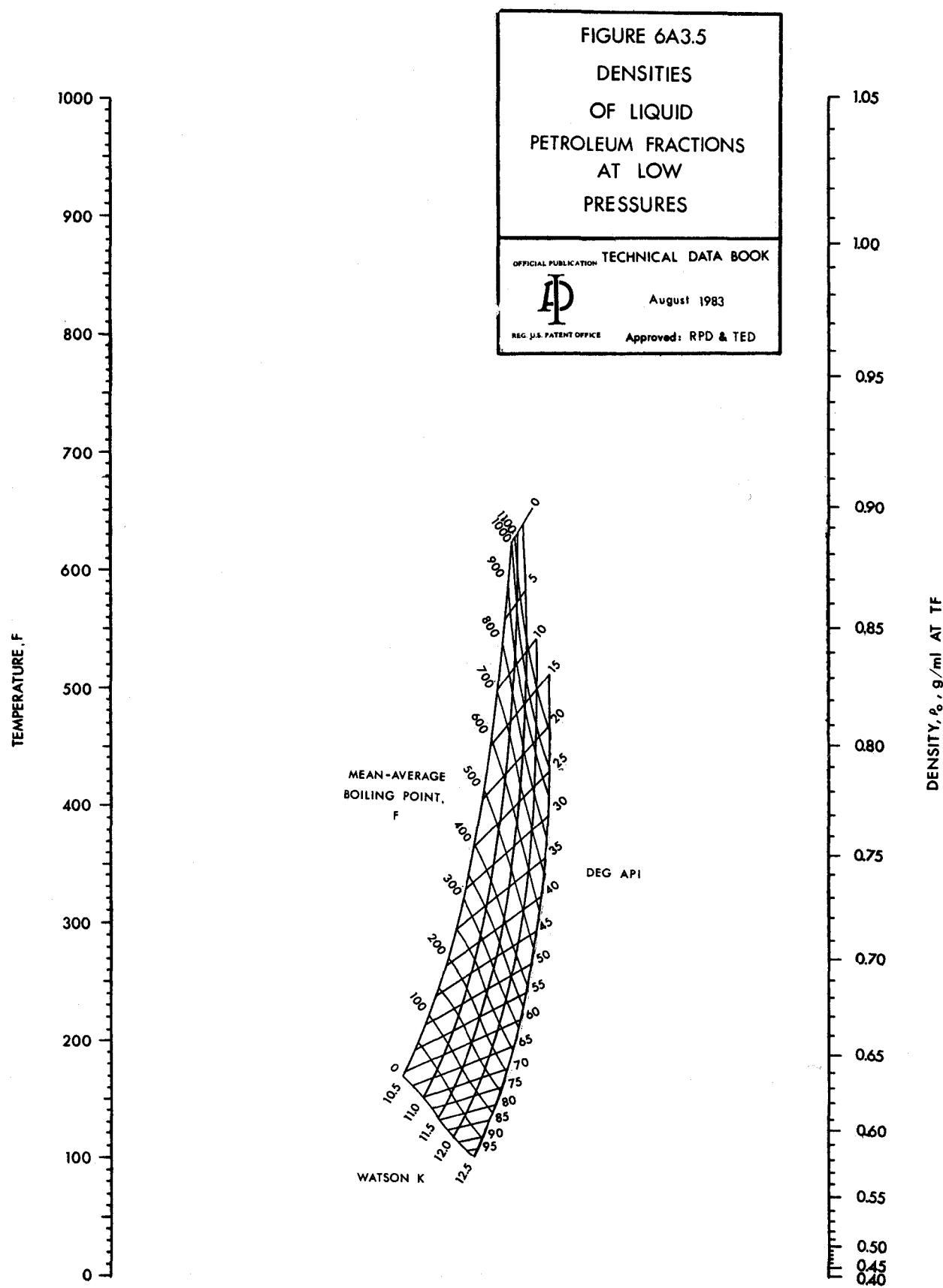
From Table 6A2.14, ω_{SRK_i} is 0.0983 for ethane and 0.4916 for *n*-decane, and V_i^* , in cubic feet per pound-mole, is 2.335 for ethane and 9.919 for *n*-decane.

$$T_{c1} = 89.92 + 459.7 = 549.62 \text{ R}$$

$$T_{c2} = 652.00 + 459.7 = 1,111.7 \text{ R}$$

Calculate the mixture properties using equations (6A3.4-6) through (6A3.4-9). From equation (6A3.4-8),

$$\begin{aligned} V_m^* &= (1/4) \{ (0.2)(2.335) + (0.8)(9.919) + 3[(0.2)(2.335)^{2/3} + (0.8)(9.919)^{2/3}] \\ &\quad \times [(0.2)(2.335)^{1/3} + (0.8)(9.919)^{1/3}] \} \\ &= (1/4) \{ 8.402 + 3[0.3520 + 3.6932] [0.2653 + 1.7189] \} \\ &= 8.1204 \text{ cubic feet per pound-mole} \end{aligned}$$



6A3.5

COMMENTS ON FIGURE 6A3.5

Purpose

This figure provides a graphical method of obtaining the density of liquid petroleum fractions at their saturation pressures or at pressures not far above 1 atmosphere. For high pressures, a pressure correction should be applied as given in Procedures 6A3.7 and 6A3.10.

Limitations

Two of three characterizing parameters (the API gravity at 60 F, the mean average boiling point, and the Watson K factor) must be known or calculated from known data to use this figure. The mean average boiling point and K can be obtained from procedures in Chapter 2 if the API gravity and average molecular weight of the fraction are known.

The characterization factor is also given by the following equation:

$$K = \frac{(\text{MeABP})^{(0.333)}}{\text{sp gr, } 60 \text{ F}/60 \text{ F}} \quad (6A3.5-1)$$

Where:

MeABP = mean average boiling point, in degrees Rankine.

sp gr = specific gravity.

Reliability

Errors in the calculated densities are about 0.3 percent at 1 atmosphere. This amounts to about 0.0024 grams per milliliter.

Special Comment

The following can be used instead of Figure 6A3.5:

T = Temperature, in degrees Rankine.

MeABP = Mean Average Boiling Point, in degrees Rankine.

SG = Specific Gravity

Denl = Liquid Density (lb_m/ft^3)

$$\text{Denl} = A \left[SG^2 - \frac{(B \times SG - C + D \times \text{MeABP})(T - E)}{\text{MeABP}} \right]^{1/2}$$

A = 62.3636

B = 1.2655

C = 0.5098

D = 8.011×10^{-5}

E = 519.67

Literature Source

Adapted from Ritter, Lenoir, Schweppe, *Petrol. Refiner* 37 [11] 225 (1958).

Example

Estimate the liquid density, at 160 F and atmospheric pressure, of a petroleum blend with a mean average boiling point of 538 F and API gravity of 30.6.

Using the mean average boiling point and the API gravity, the pivot point is located, and then a line is constructed through this point and the 160 F point on the left hand scale. The resulting density value is 0.835 gram per milliliter.

The experimental value (20a) is 0.8343 gram per milliliter.

PROCEDURE 6A3.6

ANALYTICAL METHOD FOR THE DENSITIES OF LIQUID PETROLEUM FRACTIONS AT LOW PRESSURES

Discussion

The modified Rackett equation may be used to calculate the density of petroleum fractions at their saturation pressures or at pressures not far above 1 atmosphere if an API gravity or a specific gravity at some temperature is known.

$$\frac{1}{\rho} = \left(\frac{R T_{pc}}{p_{pc}} \right) Z_{RA}^{[1 + (1 - T_r)^{2/7}]} \quad (6A3.6-1)$$

Where:

ρ = density of liquid petroleum fraction, in pound-moles per cubic foot.

R = gas constant, 10.731 (pounds per square inch absolute) (cubic feet) per (pound-mole) (degree Rankine).

T_r = reduced temperature, T/T_{pc} .

T = temperature, in degrees Rankine.

T_{pc} = pseudocritical temperature, in degrees Rankine.

p_{pc} = pseudocritical pressure, in pounds per square inch absolute.

Z_{RA} = an empirically derived constant.

Procedure

Step 1: From the available characterizing parameters, obtain the mean average boiling point (MeABP) and specific gravity at 60 F using procedures given in Chapter 2.

Step 2: Use procedures in Chapters 2 and 4 to calculate the pseudocritical temperature, pseudocritical pressure, and molecular weight.

Step 3: Calculate Z_{RA} from equation (6A3.6-1), using the specific gravity or density at a known temperature.

Step 4: Equation (6A3.6-1) may now be used to predict the density of the petroleum traction at different temperatures.

COMMENTS ON PROCEDURE 6A3.6

Purpose

The procedure is an analytical method to predict the density of petroleum fractions at their saturation pressures or at pressures not far above 1 atmosphere. At least two characterizing parameters for the petroleum fraction should be known for this method to be applied. For high pressures, a pressure correction should be applied as given in Procedures 6A3.7 and 6A3.10.

Reliability

The method had an average error of 0.75 percent when tested against a data set consisting of high-molecular-weight hydrocarbons and petroleum fractions.

Literature Source

Private communication, Spencer, C. F., M. W. Kellogg Co., Houston, Texas (1983).

Example

Estimate the liquid density, at 160 F and atmospheric pressure, of a petroleum blend with a mean average boiling point of 538 F and API gravity of 30.6.

$$\text{MeABP} = 538 + 459.7 = 997.7 \text{ R}$$

$$\text{sp gr, } 60 \text{ F}/60 \text{ F} = 141.5/(30.6 + 131.5) = 0.87292$$

$$\rho, 60 \text{ F} = 0.87292 \times 0.99904 = 0.87208 \text{ gram per milliliter}$$

The molecular weight is determined using the procedure given in Chapter 2.

$$\begin{aligned} M &= 2.0438 \times 10^2 \exp [(0.00218)(997.7)] \exp [-(3.07)(0.87292)] \\ &\quad \times (997.7)^{0.118} \times (0.87292)^{1.88} \\ &= 215.8 \end{aligned}$$

The pseudocritical temperature, T_{pc} , and the pseudocritical pressure, p_{pc} , are calculated.

$$\begin{aligned} T_{pc} &= 24.2787 (997.7)^{0.58848} (0.87292)^{0.3596} \\ &= 1345.4 \text{ R} \end{aligned}$$

$$\begin{aligned} p_{pc} &= 3.12281 \times 10^9 (997.7)^{-2.3125} (0.87292)^{2.3201} \\ &= 264.5 \text{ pounds per square inch absolute} \end{aligned}$$

Using the known density at 60 F and the other quantities computed above, Z_{RA} is calculated from equation (6A3.6-1).

$$T_r = \frac{60 + 459.7}{1345.4} = 0.3863$$

$$\begin{aligned} Z_{RA} &= \left[\left(\frac{1}{0.87208} \right) \left(\frac{264.5}{14.7} \right) \left(\frac{1.8}{1345.4} \right) \left(\frac{215.8}{82.053} \right) \right] \exp \left[\frac{1}{1 + (1 - 0.3863)^{2/7}} \right] \\ &= 0.24593 \end{aligned}$$

At 160 F,

$$T_r = \frac{160 + 459.7}{1345.4} = 0.4606$$

$$\begin{aligned} V &= (82.053) \left(\frac{1345.4}{1.8} \right) \left(\frac{14.7}{264.5} \right) 0.24593 \exp [1 + (1 - 0.4606)^{2/7}] \\ &= 258.6 \text{ cubic centimeters per gram-mole} \end{aligned}$$

$$\rho = \frac{215.8}{258.6} = 0.8344 \text{ gram per milliliter}$$

The experimental value (20a) is 0.8343 gram per milliliter.

PROCEDURE 6A3.7**DENSITIES OF LIQUID PETROLEUM FRACTIONS AT HIGH PRESSURES****Discussion**

Figures 6A3.8 and 6A3.9 correlate densities of petroleum fractions at high pressures. When the density at ambient pressures is found from Figure 6A3.5 or Procedure 6A3.6, the following equation may be used in conjunction with Figures 6A3.8 and 6A3.9 to determine the density at any pressure:

$$\frac{\rho_0}{\rho} = 1.0 - \frac{P}{B_T} \quad (6A3.7-1)$$

Where:

ρ_0 = density of sample at temperature of interest and ambient pressures.

ρ = density of sample at temperature and pressure of interest.

P = pressure, in pounds per square inch gage.

B_T = isothermal secant bulk modulus = $-(1/\rho_0)(\Delta P/\Delta V)_T$

B_{20} = isothermal secant bulk modulus at 20,000 pounds per square inch gage, the temperature of interest, and density ρ_0 .

Procedure

Step 1: Use Figure 6A3.5 or Procedure 6A3.6 to obtain the density of the fraction at the specified temperature and ambient pressures.

Step 2: Obtain the isothermal secant bulk modulus at 20,000 pounds per square inch gage, B_{20} , from Figure 6A3.8 using the density computed in Step 1.

Step 3: Obtain the isothermal secant bulk modulus, B_T , at the desired pressure from Figure 6A3.9. Enter the chart with the modulus B_{20} found in Step 2 and draw a horizontal line to its intersection with the line representing 20,000 pounds per square inch gage. A vertical line drawn through the intersection gives the modulus at any other pressure at the specified temperature.

Step 4: Calculate the density at the selected temperature and pressure from equation (6A3.7-1).

COMMENTS ON PROCEDURE 6A3.7

Purpose

The procedure is given for estimating pressure corrections for the liquid densities of petroleum fractions at high pressures. Figures 6A3.8 and 6A3.9 are parts of this procedure.

Limitations

The liquid density at or near atmospheric pressure must be known or estimated from Figure 6A3.5 or Procedure 6A3.6 for this procedure to be used.

Reliability

At high pressures, the error is about 1.5 percent.

Literature Source

Figures 6A3.8 and 6A3.9 were adapted from Wright, *ASLE Trans.* 10 349 (1967).

Example

Estimate the liquid density, at 68 F and 5400 pounds per square inch gage, of a petroleum fraction with a Watson characterization factor of 12.28 and API gravity of 31.4.

From Figure 6A3.9, the density at 68 F and atmospheric pressure is found to be 0.865 grams per milliliter.

Using Figure 6A3.8, B_{20} at the specified temperature is 339,000 pounds per square inch gage.

From Figure 6A3.9, B_T at 5400 pounds per square inch gage and 68 F is 272,000 pounds per square inch gage.

The density is determined from equation (6A3.7-1).

$$\frac{\rho_0}{\rho} = 1.0 - \frac{p}{B_T} = 1.0 - \frac{5400}{272,000} = 0.9801$$

$$\rho = \frac{0.865}{0.9801} = 0.8826 \text{ grams per milliliter}$$

The experimental value (5a) is 0.8838 grams per milliliter.

PROCEDURE 6A3.10

ANALYTICAL METHOD FOR THE DENSITIES OF LIQUID PETROLEUM FRACTIONS AT HIGH PRESSURES

Discussion

For the generation of a large amount of data, an analytical version of Procedure 6A3.7 provides a more convenient method. From a reference density (value at ambient pressures), the densities at higher pressures can easily be calculated using the analytical forms of Figures 6A3.8 and 6A3.9 given below. The reference density for each specified temperature must be obtained from Figure 6A3.5 or calculated from equation 6A3.6-1.

Figure 6A3.8 is represented by the following equation:

$$\log B_{20} = -6.1(10^{-4})T + 4.9547 + 0.7133\rho \quad (6A3.10-1)$$

Where:

B_{20} = secant bulk modulus at 20,000 pounds per square inch gage and given temperature.

T = temperature, in degrees Fahrenheit.

ρ = density at ambient pressures and given T , in grams per milliliter.

The constant pressure lines in Figure 6A3.9 are correlated by the following equation:

$$B_T = mX + B_I \quad (6A3.10-2)$$

Where:

B_T = secant bulk modulus at the specified pressure.

m = slope of the line.

B_I = secant bulk modulus at the Y -intercept.

X , the unmarked abscissa of Figure 6A3.9, is calculated from the following equation:

$$X = \frac{B_{20} - B_{I,20}}{m_{20}} = \frac{B_{20} - 100,000}{23,170} \quad (6A3.10-3)$$

Where:

$B_{I,20}$ = secant bulk modulus at the intercept of the line representing 20,000 pounds per square inch gage in Figure 6A3.9 (100,000 pounds per square gage).

m_{20} = slope of the line representing 20,000 pounds per square inch gage (23,170).

The intercept, B_I , and the slope, m , at the desired pressure are given by the following equations:

$$B_I = 1.52(10^4) + 4.704p - 2.5807(10^{-5})p^2 + 1.0611(10^{-10})p^3 \quad (6A3.10-4)$$

$$m = 21,646 + 0.0734p + 1.4463(10^{-7})p^2 \quad (6A3.10-5)$$

Where:

p = pressure, in pounds per square inch gage.

Procedure

Step 1: Calculate the density of the fraction at the specified temperature and ambient pressures from Figure 6A3.5 or Procedure 6A3.6.

Step 2: Determine the isothermal secant bulk modulus at 20,000 pounds per square inch gage and the specified temperature from equation (6A3.10-1).

Step 3: Using equation (6A3.10-3) and the value obtained in Step 2, calculate X .

Step 4: Calculate the modulus intercept and slope at the desired pressure from equations (6A3.10-4) and (6A3.10-5).

Step 5: Using the values obtained in Steps 3 and 4, calculate the isothermal secant bulk modulus at the desired pressure from equation (6A3.10-2).

Step 6: Obtain the desired density from equation (6A3.7-1).

COMMENTS ON PROCEDURE 6A3.10**Purpose**

The procedure is given as an alternate analytical method for estimating the pressure correction for the liquid density of a petroleum fraction at any temperature.

Limitations

The liquid density at or near atmospheric pressure must be known or estimated from Figure 6A3.5 or Procedure 6A3.6 for this procedure to be used.

Reliability

The average error for calculated densities is approximately 1.7 percent. As the critical point is approached, the error may be as high as 5 percent.

Literature Source

Private communication, Spencer, C. F., M. W. Kellogg Co., Houston, Texas (June 1982).

Example

Estimate the liquid density, at 68 F and 5400 pounds per square inch gage, of a petroleum fraction with a Watson *K* of 12.28 and an API gravity of 31.4.

From Figure 6A3.5, the density at 68 F and ambient pressures is found to be 0.865.

The isothermal secant bulk modulus at 20,000 pounds per square inch gage is determined from equation (6A3.10-1).

$$\log B_{20} = (-6.1)(10^{-4})(68) + 4.9547 + (0.7133)(0.865) = 5.53$$

$$B_{20} = 339,000 \text{ pounds per square inch gage}$$

The *X* reference is now calculated from equation (6A3.10-3).

$$X = \frac{(339,000 - 100,000)}{23,170} = 10.31$$

The intercept and slope at the desired pressure are now calculated.

$$B_I = 1.52(10^{-4}) + 4.704(5400) - 2.5807(10^{-5})(5400)^2 + 1.0611(10^{-10})(5400)^3$$

$$= 39,860 \text{ pounds per square inch gage}$$

$$m = 21,646 + 0.0734(5400) + 1.4463(10^{-7})(5400)^2$$

$$= 22,046$$

The isothermal secant bulk modulus at desired pressure is:

$$B_T = mX + B_I = (22,046)(10.31) + 39,862$$

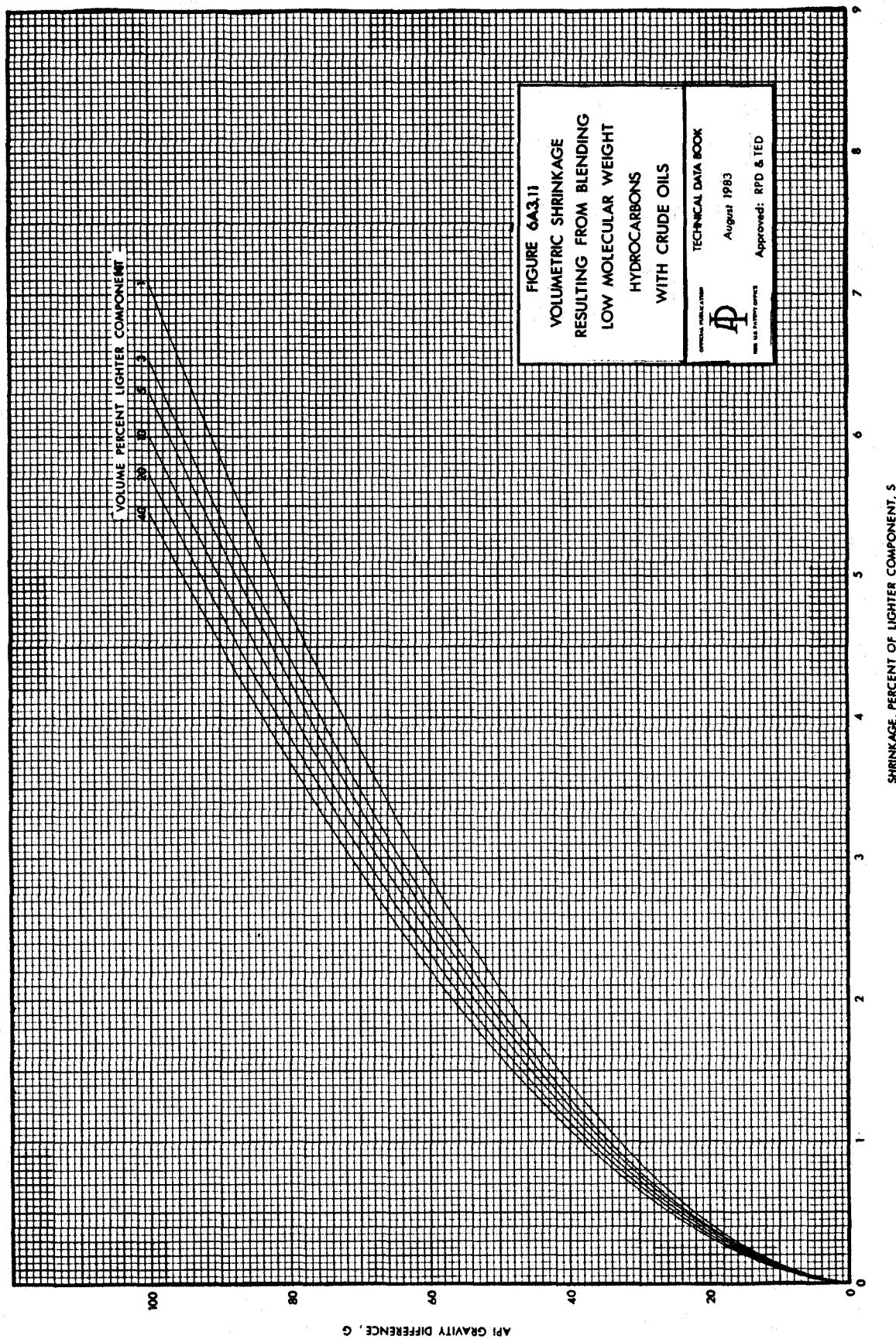
$$= 267,160 \text{ pounds per square inch gage}$$

The density is now determined from equation (6A3.7-1).

$$\frac{\rho_0}{\rho} = 1.0 - \frac{P}{B_T} = 1.0 - \frac{5400}{267,160} = 0.9798$$

$$\rho = \frac{0.865}{0.9798} = 0.8828 \text{ gram per milliliter}$$

The experimental value (5a) is 0.8838 gram per milliliter.



COMMENTS ON FIGURE 6A3.11**Purpose**

The volumetric shrinkage resulting from blending low-molecular-weight hydrocarbons with crude oils is estimated from this figure. This shrinkage occurs when light products such as propane, butane, natural gasoline, and high-gravity produced distillates are mixed with crude oil streams.

The curves shown in Figure 6A3.11 for various concentrations of lighter components were calculated with the aid of the following formula:

$$S = 2.14(10^{-5}) C^{-0.0704} G^{1.76} \quad (6A3.11-1)$$

Where:

S = shrinkage factor, as percent of lighter component volume.

C = concentration, in liquid volume percent, of lighter component in mixture.

G = gravity difference, in degrees API.

Reliability

This equation was not evaluated in the present work. The literature source has determined that it can be used with a high degree of confidence to calculate shrinkage at concentrations up to 21 percent of the lighter component. The equation is not valid at concentrations above 50 percent of the lighter component.

Literature Source

Adapted from API Bull. 2509C, *Volumetric Shrinkage Resulting from Blending Volatile Hydrocarbons with Crude Oils*, 2nd ed., Am. Petrol. Inst., Washington, D.C. (1967).

Example

Determine the volume of a mixture of 95,000 barrels of crude oil having a gravity of 30.7°API at 60 F and 5000 barrels of natural gasoline having a gravity of 86.5°API at 60 F. The gravity difference is

$$86.5 - 30.7 = 55.8^{\circ}\text{API}$$

In Figure 6A3.11, at the intersection of the gravity difference and 5 percent of the lighter component, *S* = 2.3 percent.

The volume of the mixture is calculated as follows:

$$\frac{2.3}{100} (5000) = 115 \text{ barrels shrinkage}$$

$$5000 - 115 = 4885 \text{ barrels natural gasoline}$$

$$4885 + 95,000 = 99,885 \text{ barrels mixture}$$

PROCEDURE 6B1.1

DENSITY OF PURE HYDROCARBON AND NONPOLAR GASES

Discussion

The following equation is to be used to predict the compressibility factor of pure hydrocarbon gases:

$$z = z^{(0)} + \omega z^{(1)} \quad (6B1.1-1)$$

Where:

z = compressibility factor, dimensionless.

$z^{(0)}$ = compressibility factor for the simple fluid, which is tabulated as a function of T_r and p_r in Table 6B1.2 and plotted in Figures 6B1.4 and 6B1.5.

$z^{(1)}$ = correction term for molecular acentricity, which is tabulated as a function of T_r and p_r in Table 6B1.3 and plotted in Figures 6B1.6 and 6B1.7.

T_r = reduced temperature, T/T_c .

T = temperature, in degrees Rankine.

T_c = critical temperature, in degrees Rankine.

p_r = reduced pressure, p/p_c .

p = pressure, in pounds per square inch absolute.

p_c = critical pressure, in pounds per square inch absolute.

ω = acentric factor.

If the vapor is saturated (in equilibrium with the liquid phase), the $z^{(0)}$ and $z^{(1)}$ terms should be interpolated in p_r from the following tabulation rather than Tables 6B1.2 and 6B1.3.

p_r	$z^{(0)}$	$z^{(1)}$	p_r	$z^{(0)}$	$z^{(1)}$
1.00	0.291	-0.080	0.65	0.615	-0.069
0.99	0.35	-0.083	0.60	0.64	-0.063
0.98	0.38	-0.085	0.55	0.665	-0.056
0.97	0.40	-0.087	0.50	0.688	-0.049
0.96	0.41	-0.088	0.45	0.711	-0.041
0.95	0.42	-0.089	0.40	0.734	-0.033
0.94	0.43	-0.089	0.35	0.758	-0.025
0.92	0.45	-0.090	0.30	0.783	-0.018
0.90	0.47	-0.091	0.25	0.809	-0.012
0.85	0.50	-0.090	0.20	0.835	-0.008
0.80	0.53	-0.087	0.15	0.864	-0.005
0.75	0.56	-0.081	0.10	0.896	-0.002
0.70	0.59	-0.075	0.05	0.935	0.000

The compressibility factor obtained from equation (6B1.1-1) determines the vapor volume (or density) in the following equation of state:

$$V = \frac{1}{\rho} = \frac{zRT}{p} \quad (6B1.1-2)$$

Where:

V = molar volume, in cubic feet per pound-mole.

ρ = molar density, in pound-moles per cubic foot.

R = gas constant, 10.731 (pounds per square inch absolute)(cubic feet) per (pound-mole) (degree Rankine).

Procedure

Step 1: Obtain the critical temperature and pressure of the hydrocarbon from Chapter 1 and the acentric factor from Chapter 2.

Step 2: Calculate the reduced temperature and pressure at which a gas density is required.

Step 3: Obtain the correlation terms $z^{(0)}$ and $z^{(1)}$. If the most accurate values are desired, use Tables 6B1.2 and 6B1.3 with linear double interpolation p_r and T_r . When near saturation, the interpolation procedure may not be satisfactory (see Special Comments). If slightly less accurate values are acceptable, they may be obtained rapidly from Figures 6B1.4 through

6B1.7. When the vapor is saturated, use the tabulation presented above with a vapor pressure from Chapter 5 if only temperature is known.

Step 4: Calculate the compressibility factor using equation (6B1.1-1), and the volume or density using equation (6B1.1-2).

This procedure should be followed when T and p are known and V is unknown. A suitable modification (trial-and-error) should be used when V is known and T or p is desired.

COMMENTS ON PROCEDURE 6B1.1

Purpose

This procedure is to be used to predict gas densities of pure hydrocarbons and nonpolar gases. Tables 6B1.2 and 6B1.3 or Figures 6B1.4 through 6B1.7 are required in this procedure. The method is best suited to desk calculations, and Procedure 6B1.8 should be used with digital computers. Methods for hydrocarbon mixtures are given in 6B2.

Limitations

In general, this procedure is not accurate for polar substances.

Reliability

Errors between calculated and experimental compressibility factors are usually less than 1 percent except in the critical region, where errors of 30 percent can occur. This region of maximum uncertainty is indicated in Figure 6B1.4.

The reliability decreases with uncertainties in the critical properties of the compounds.

Notation

The notation used in Tables 6B1.2 and 6B1.3 and Figures 6B1.4 through 6B1.7 was defined for equations (6B1.1-1) and (6B1.1-2).

Special Comments

The broken line in Table 6B1.2 indicates the discontinuity between compressibility factors for liquid (to the right and above) and vapor (to the left and below). Interpolations must not be made across this line. Always use table values that apply to the desired phase only. Near the broken line, any necessary extrapolations should be made with respect to reduced pressure at constant reduced temperature.

For hydrogen, do not use the critical constants listed in Chapter 1 to calculate the reduced properties; use the following values (1b, 6b):

$$T_c = 75 \text{ R}$$

$$p_c = 305 \text{ pounds per square inch absolute}$$

In regions of very rapid change of the simple fluid and correction terms with reduced pressure and/or temperature, a linear interpolation from the tables may not be satisfactory even though the table values are spaced more closely. Here, the figures should be used either directly or as a guide for correcting interpolations made using values from the tables.

The figures may be extrapolated to lower reduced pressures by noting that $z^{(0)}$ approaches unity and $z^{(1)}$ approaches zero as the pressure approaches zero. In many engineering applications, these limiting values may be used for all reduced pressures between 0 and 0.2. If even more precise results are desired than the extrapolated values (rarely), use the following equation:

$$z = 1 + \frac{p_r}{T_r} [(0.1445 + 0.073\omega) - (0.330 - 0.46\omega)T_r^{-1} - (0.1385 + 0.50\omega)T_r^{-2} - (0.0121 + 0.097\omega)T_r^{-3} - 0.0073\omega T_r^{-8}] \quad (6B1.1-3)$$

Literature Sources

Tables 6B1.2 and 6B1.3 were generated from the generalized correlation of Lee and Kesler, *AICHE Journal* 21 510 (1975). Equation (6B1.1-3) and the table for saturated vapor compressibility factors were taken from Pitzer et al., *J. Am. Chem. Soc.* 77 3433 (1955).

PROCEDURE 6B1.8

ALTERNATE (COMPUTER) METHOD FOR THE DENSITY OF PURE HYDROCARBON AND NONPOLAR GASES

Discussion

The following method, which was used to generate the tables in Procedure 6B1.1, is recommended for estimating the density of pure hydrocarbon and nonpolar gases by a digital computer.

$$z = z^{(0)} + \frac{\omega}{\omega^{(h)}} (z^{(h)} - z^{(0)}) \quad (6B1.8-1)$$

Where:

z = compressibility factor, dimensionless.

$z^{(0)}$ = compressibility factor for the simple fluid, which is obtained from equation (6B1.8-2).

$z^{(h)}$ = compressibility factor for the heavy reference fluid (*n*-octane), which is obtained from equation (6B1.8-2).

ω = acentric factor of the compound for which the density is sought.

$\omega^{(h)}$ = acentric factor for the heavy reference fluid (*n*-octane) = 0.3978.

The compressibility factors for the simple fluid $z^{(0)}$ and the heavy reference fluid $z^{(h)}$ are obtained from the following equation.

$$z^{(i)} = \frac{p_r V_r}{T_r} = 1 + \frac{B}{V_r^2} + \frac{C}{V_r^5} + \frac{D}{T_r^3 V_r^2} \left(\beta + \frac{\gamma}{V_r^2} \right) \exp \left(\frac{-\gamma}{V_r^2} \right) \quad (6B1.8-2)$$

Where:

$z^{(i)} = z^{(0)}$ when the constants are those listed below for the simple fluid.

$z^{(i)} = z^{(h)}$ when the constants are those listed below for the heavy reference fluid.

p_r = reduced pressure, p/p_c .

p = pressure, in pounds per square inch absolute.

p_c = critical pressure of the compound whose density is sought, in pounds per square inch absolute.

$V_r = p_c V / R T_c$.

V = molar volume of the simple fluid or of the heavy reference fluid, as the case may be, in cubic feet per pound-mole.

R = gas constant, 10.731 (pounds per square inch absolute)(cubic feet) per (pound-mole) (degree Rankine).

T_c = critical temperature of the compound whose density is sought, in degrees Rankine.

T_r = reduced temperature, T/T_c .

T = temperature, in degrees Rankine.

$B = b_1 - b_2/T_r - b_3/T_r^2 - b_4/T_r^3$

$C = c_1 - c_2/T_r + c_3/T_r^3$

$D = d_1 + d_2/T_r$

Two sets of constants are given below, one set for the simple fluid and the other set for the heavy reference fluid.

Constant	Simple Fluid	Heavy Reference Fluid
b_1	0.1181193	0.2026579
b_2	0.265728	0.331511
b_3	0.154790	0.027655
b_4	0.030323	0.203488
c_1	0.0236744	0.0313385
c_2	0.0186984	0.0503618
c_3	0.0	0.016901
c_4	0.042724	0.041577
$d_1 \times 10^4$	0.155488	0.48736
$d_2 \times 10^4$	0.623689	0.0740336
β	0.65392	1.226
γ	0.060167	0.03754

Procedure

Step 1: Obtain the critical temperature and pressure from Chapter 1 and the acentric factor from Chapter 2.

Step 2: Calculate the reduced temperature and reduced pressure at which the density is desired.

Step 3: Solve equation 6B1.8-2 for V_r , using the constants for the simple fluid. Since the equation is not explicit in V_r , an iterative procedure will be required. Having obtained V_r for the simple fluid, use the reduced conditions obtained in Step 2 to calculate $z^{(0)} = p_r V_r / T_r$.

Step 4: Repeat Step 3 for the heavy reference fluid using the same reduced temperature and pressure. Hence, obtain $z^{(n)}$.

Step 5: Use equation 6B1.8-1 to obtain the compressibility factor z for the gas under consideration.

Step 6: Evaluate the volume from the relation $V = zRT/p$.

COMMENTS ON PROCEDURE 6B1.8

Purpose

This procedure is presented for calculating gas densities of pure hydrocarbons and non-polar gases using a digital computer. Methods for mixtures are given in 6B2.

Limitations

In this work, the procedure has not been tested with data for nonhydrocarbons. The literature source, however, indicates general agreement for nonpolar or slightly polar non-hydrocarbons so that reasonable results may be expected.

Reliability

Errors between calculated and experimental compressibility factors are usually less than 1 percent except in the immediate vicinity of the critical region, where errors as high as 30 percent can occur. The original literature source gives the range of applicability of the equation as a reduced temperature of 0.3 to 4.0 and a reduced pressure of 0 to 10.0. Based on a limited amount of testing, it was determined that the equation may be used up to reduced pressures of 20 with little additional error. The reliability decreases with uncertainties in the critical properties of the compounds.

Special Comments

The following special considerations must be taken into account when solving the equations.

The equation has several volume roots, and the solution can converge on the wrong value. These incorrect values are easily identified because they differ substantially from the expected value. Suitable checks must be built into the solution to guard against possible convergence to the wrong root.

For saturated vapors, both temperature and pressure must be used as input parameters (with vapor pressure predictions from Chapter 5 when necessary) and the calculations performed as if the point were in the homogeneous region.

For hydrogen, do not use the critical constants listed in Chapter 1 to calculate the reduced properties; use the following values (1b, 6b):

$$T_c = 75 \text{ R}$$

$$p_c = 305 \text{ pounds per square inch absolute}$$

Literature Source

The equations in this procedure were developed by Lee and Kesler, *AIChE Journal* 21 510 (1975).

PROCEDURE 6B2.1

DENSITY OF HYDROCARBON AND NONPOLAR GAS MIXTURES

Discussion

The tables and figures of Procedure 6B1.1 are to be applied to hydrocarbon mixtures by using the pseudocritical temperature and pressure instead of the true critical temperature and pressure to calculate reduced conditions. The pseudocritical properties, which are defined as the molar averages of the component true critical properties, are given in Chapter 4 for mixtures of defined and undefined composition and blends of the two. The mixture acentric factor, which is defined as the molar average of the component acentric factors, may be estimated for undefined mixtures from Chapter 2. The following are summaries of these definitions:

$$T_{pc} = \sum_{i=1}^n x_i T_{ci} \quad (6B2.1-1)$$

Where:

T_{pc} = pseudocritical temperature, in degrees Rankine.

T_{ci} = critical temperature of component i , in degrees Rankine.

n = number of components in the mixture.

x_i = mole fraction of component i .

$$p_{pc} = \sum_{i=1}^n x_i p_{ci} \quad (6B2.1-2)$$

Where:

p_{pc} = pseudocritical pressure, in pounds per square inch absolute.

p_{ci} = critical pressure of component i , in pounds per square inch absolute.

$$\omega = \sum_{i=1}^n x_i \omega_i \quad (6B2.1-3)$$

Where:

ω = mixture acentric factor.

ω_i = acentric factor of component i .

Procedure

Step 1: For mixtures of known composition, obtain the critical pressures and temperatures for all of the components from Chapter 1 and the acentric factors from Chapter 2.

Step 2: Calculate the pseudocritical temperature and pressure using equations (6B2.1-1) and (6B2.1-2) and the mixture acentric factor using equation (6B2.1-3). (For petroleum fractions and blends of petroleum fractions with mixtures of known composition, obtain the pseudocritical conditions from Chapter 4 and the mixture acentric factor from Chapter 2.) Calculate the reduced temperature and pressure.

Step 3: Calculate the gas density using Steps 3 and 4 of Procedure 6B1.1 with the reduced conditions calculated previously.

COMMENTS ON PROCEDURE 6B2.1

Purpose

This procedure is to be used with Procedure 6B1.1 to estimate the gas densities of mixtures of hydrocarbons with other hydrocarbons and/or with nonpolar nonhydrocarbon substances.

Limitations

In general, the method is not applicable to mixtures containing polar components.

Reliability

Errors in calculated compressibility factors rarely exceed 2 percent except in the critical region, where 15-percent errors should be expected and errors of 50 percent can occur. This region of maximum uncertainty is the same as that indicated in Figure 6B1.4.

When compared with approximately 6500 data points for a wide variety of hydrocarbon mixtures of known composition, the overall average error was 4 percent, with well over 90 percent of the errors less than 2 percent.

The reliability of the modification for mixtures of undefined composition was not evaluated.

Special Comments

For hydrocarbon-hydrocarbon mixtures that do not contain methane, slightly better results are obtained in the immediate critical region using true rather than pseudocritical temperatures and pressures. This region is defined approximately by the following pseudoreduced condition boundaries: $1.0 < T_r < 1.2$, and $1.0 < p_r < 3.0$. True critical conditions are correlated in Chapter 4. Notice that the liquid phase can exist in this region even though the pseudoreduced temperature is greater than unity (see Introduction to Chapter 4).

For supercritical temperatures ($T_r > 1$) and high pressures ($p_r > 5$), the error can be reduced to approximately 1 percent by using the following mixture correspondence pressure instead of the pseudocritical pressure which is defined by equation (6B2.1-2):

$$p_{mc} = \frac{RT_{pc} \sum_{i=1}^n x_i z_{ci}}{\sum_{i=1}^n x_i V_{ci} M_i} \quad (6B2.1-4)$$

Where:

p_{mc} = mixture correspondence pressure, in pounds per square inch absolute.

R = gas constant, 10.731 (pounds per square inch absolute)(cubic feet) per (pound-mole) (degree Rankine).

z_{ci} = critical compressibility factor of component i (from Chapter 2).

V_{ci} = critical volume of component i (from Chapter 1), in cubic feet per pound.

M_i = molecular weight of component i (from Chapter 1).

More reliable gas densities can be obtained under most temperature-pressure conditions using the mixture correspondence rules of Lee and Kesler (4b), Joffe (2b), Stewart et al. (9b), or Leland and Mueller (5b). However, the small advantage in accuracy does not justify the added labor involved in using these methods.

For mixtures containing hydrogen, do not use the hydrogen critical constants listed in Chapter 1 to calculate the pseudocritical properties. For hydrogen, use the following values (1b, 6b): $T_c = 75$ R and $p_c = 305$ pounds per square inch absolute.

Literature Sources

Equations (6B2.1-1) and (6B2.1-2) were given by Kay, *Ind. Eng. Chem.*, **28** 1014 (1936). Equation (6B2.1-4) was developed by Prausnitz and Gunn, *AICHE Journal*, **4** 430 (1958).

Examples

A. Estimate the molar volume of a gaseous mixture of 90 mole percent propane and 10 mole percent benzene at 460 F and 4000 pounds per square inch absolute.

CHAPTER 7

THERMAL PROPERTIES

7.0 INTRODUCTION

Heat effects accompany changes in temperature, pressure, phase, and chemical nature. Enthalpies, heat capacities, heat capacity ratios, and entropies of the substances involved are required to predict the magnitude of these heat effects. These properties (particularly heat capacity) are also used frequently in correlations of other physical properties and design parameters such as the thermal conductivity and the Prandtl number. Methods for predicting these important thermal properties are presented in this chapter for pure hydrocarbons and their mixtures, both for defined and undefined composition.

This chapter was prepared for use primarily with nonreacting systems. The enthalpy basis does not include heat of formation data, so the enthalpies of products and reactants cannot be subtracted to give the heat of reaction. Further, the figures and procedures are all designed to give thermal properties on a perpound basis, whereas a molar basis would be more convenient for reacting systems. The approach taken here is the most convenient for the thermal property calculations that are common in the petroleum industry.

The effect of temperature on the enthalpy, heat capacity, and entropy of pure hydrocarbons and their defined mixtures is partly determined from data for the pure substances in the ideal gas state. Extensive tabulations for hydrocarbons and nonhydrocarbons have been prepared by the Thermodynamics Research Center (75). Coverage of 180 of the most common compounds of interest to the petroleum industry are given in this chapter both in tabular and equation form.

Throughout this chapter, procedures for both desk and computer calculations are presented in a parallel structure. The complete desk method is presented first, followed by the corresponding computer method. No computer program listings are presented; only the pertinent equations are given. Subroutines to implement each computer method are listed separately in Chapter 16.

Both the desk and computer methods are based on the theorem of corresponding states. The methods are internally consistent for density and all the thermodynamic properties. In most cases, values for tables and graphs used in the desk methods were generated from the corresponding computer method. Unfortunately, neither is consistent with the vapor-liquid equilibrium predictions of Chapter 8. Both are comparable in accuracy when compared with existing data.

Corresponding States Methods

Most of the desk method correlations follow the general form:

$$G = G^{(0)} + \omega G^{(1)}$$

Where:

G = property being predicted at T and p .

$G^{(0)}$ = property of the simple fluid, which is tabulated as a function of T_r and p_r .

$G^{(1)}$ = correction term for molecular acentricity, which is tabulated as a function of T_r and p_r .

T = temperature, in degrees Rankine.

T_r = reduced temperature, T/T_c .

T_c = critical temperature, in degrees Rankine.

p = pressure, in pounds per square inch absolute.

p_r = reduced pressure, p/p_c .

p_c = critical pressure, in pounds per square inch absolute.

ω = acentric factor (Chapter 1).

In most cases, values for the tables and graphs used in the desk methods were generated from the corresponding computer method, using a general equation of the form:

$$G = G^{(0)} + \frac{\omega}{\omega^{(h)}} [G^{(h)} - G^{(0)}]$$

Where:

$G^{(h)}$ = property of heavy reference fluid at T_r, p_r .

$\omega^{(h)}$ = acentric factor of heavy reference fluid.

The computer methods in this chapter use *n*-octane ($\omega = 0.3978$) as the heavy reference fluid.

The Benedict-Webb-Rubin (12-14) equation of state, as modified by Lee and Kesler (42) and used to calculate densities in Chapter 6, is the basis for the calculation of thermal properties in the Data Book. It is the most accurate generalized correlation available, being most accurate in the subcooled and superheated regions. However, the accuracy is slightly reduced at saturated conditions and near the critical and retrograde regions when applied to widely boiling mixtures.

1. Mixtures of Defined Composition: Both the desk and computer methods that are used throughout this chapter to calculate the effect of pressure on thermal properties are based on the extended theorem of corresponding states. In other words, it is postulated that two compounds which possess like values of auxiliary parameters and are in identical

conditions of reduced temperature and pressure will behave identically.

Application of these methods to pure compounds is straightforward; the critical temperatures and pressures are used directly to calculate reduced conditions. For mixtures, an imaginary critical point is postulated to exist such that the mixture corresponds in behavior to a pure substance having an identical critical point (and auxiliary parameters). However, in a small region near the critical point, a better approximation to mixture behavior can be obtained by using the true critical conditions.

A number of equations have been proposed to calculate the mixture correspondence conditions of temperature and pressure from the true critical constants of the components. The earliest and best known equations were given by Kay (37), who approximated the mixture correspondence conditions by the molar average pure component conditions. In his book the term "pseudocritical conditions" is reserved for conditions calculated by this relationship of Kay. The results of all other methods are referred to as mixture correspondence conditions.

Although the various equations for calculating the mixture correspondence conditions are all more complex than Kay's rule, for close-boiling mixtures of chemically similar compounds, all reduce to approximately the same result as Kay's rule. For more complex mixtures, several of the methods (35, 42, 44, 71) produce slightly better results than Kay's pseudocritical equations under most temperature-pressure conditions. However, the small increase in accuracy does not justify the use of these complex equations for desk calculations. Accordingly, the recommended desk methods for calculating the effect of pressure on the thermodynamic properties of mixtures are extensions of the pure compound method using the pseudocritical point as defined by Kay rather than the true critical point. For computer applications, the complexity of the equations is unimportant, so the somewhat more accurate mixing rules of Lee and Kesler (42) are recommended.

The general method for predicting the total gas or liquid enthalpy, gas heat capacity, or gas entropy of hydrocarbon mixtures of known composition is, therefore, to calculate the weight average of the ideal gas properties and correct the entire mixture for pressure using a pseudocritical approach. This differs from the method commonly used in the petroleum industry, which is weight averaging the properties of pure components at the operating temperature and pressure. The weight-averaging method is equivalent to the recommended approach only when the components of the mixture are close boiling members of a single family of hydrocarbons (i.e., paraffins, olefins, naphthenes, or aromatics) and when the operating pressure on a gas mixture is less than the vapor pressures of any one of the pure components or when the operating temperature for a liquid mixture is

less than the critical temperatures of any one of the pure components. The common method of using the saturated vapor enthalpy for the component enthalpy when the operating pressure is greater than the vapor pressure of that component is unsatisfactory and becomes increasingly poor as pressure increases. Similarly, the common practice of extrapolating the saturated liquid enthalpies into the supercritical region for a component of a liquid mixture involves many uncertainties. Further, the commonly used weight-averaging technique neglects nonidealities of mixing entirely, whereas an allowance (although not precise) is provided with the pseudocritical approach.

In a small region near the critical point, the true mixture critical conditions produce better results than the pseudocritical or the various mixture correspondence points for nonmethane systems. This region is defined approximately by the pseudoreduced limits: $1.0 < T_r < 1.2$ and $1.0 < p_r < 3.0$. The predictions in this difficult region are not good in either case but not much worse than corresponding results for pure hydrocarbons.

Data are not available to determine the reliability of the pseudocritical or mixture correspondence approaches for mixtures exhibiting unusual (non-Type I) critical loci, but the accuracy of both computer and desk methods is probably worse than quoted. Fortunately, most systems of interest are Type I, but unusual behavior can occur even for hydrocarbon systems. The various critical loci are described in the Introduction to Chapter 4.

The pseudocritical temperature is usually lower than the true critical temperature for Type I systems, so both liquid and vapor phases can exist at pseudoreduced temperatures greater than unity. Under all conditions, but particularly in this region, it is necessary to know the existing phase conditions before selecting the appropriate property correlation from this chapter. If doubt exists, obtain the vapor-liquid equilibrium conditions for the operating temperature and pressure from Chapter 8 to determine whether the desired mixture is in the vapor, liquid, or vapor-liquid equilibrium state. In the last case, the two phases must be treated separately, and the phase compositions and amounts must first be calculated from Chapter 8.

2. Mixtures of Undefined Composition: For petroleum fractions, the composition is generally not known, so the mixture correspondence equations cannot be used. The pseudocritical conditions from Chapter 4 are used instead, but they are subject to the restrictions outlined in the previous section. In order to apply any mixing rules to petroleum fractions, it is necessary to characterize the proportion and nature of the mixture constituents by the various average boiling points and a characterization factor. These approximations limit the usefulness of the existing correlations for the effect of pressure on the thermal properties of petroleum fractions.

In working with petroleum fractions, the effect of temperature on thermal properties is also difficult to estimate reliably. Pure hydrocarbon and defined mixture data are available, but they must be correlated for use with petroleum fractions in terms of a characterization factor and the API gravity. This invariably increases the uncertainty in the results, particularly for fractions containing appreciable amounts of aromatic and unsaturated constituents, neither of which correlate well with these parameters.

In spite of all the uncertainties in predicting the temperature and pressure effects on the thermal properties of petroleum fractions, the existing correlations reproduce experimental data for straight-run petroleum fractions rather well. The correlations are not reliable at conditions near the critical point, however.

Reliability of the Correlations

All the correlations in this chapter are least accurate in the immediate critical region. Generally, separate errors are quoted for both the critical and distant regions, but the transition from one set of errors to the other is obviously not sharp. Judgment must be exercised in estimating the reliability of a given predicted value. As an aid, the regions of maximum uncertainty are indicated on the figures when possible. These are characterized by behavior such that a small change in (reduced) temperature or pressure causes an appreciable change in the thermal property.

Calculation of Enthalpy

Since enthalpy is a relative quantity, its value is set equal to zero at zero absolute temperature in the ideal gas state. This is in line with API Project 44, TRC Tables, and many other related reference books.

Ideal gas enthalpies for 180 hydrocarbons can be obtained from Procedure 7A1.1. Equations are given with the appropriate coefficients for calculating these enthalpies on the basis used in this book. Procedure 7H1.1 illustrates use of the enthalpies to estimate the heat effects in reacting systems.

Enthalpy-temperature diagrams for 17 pure hydrocarbons are presented in Section 7B1, and enthalpy-entropy (Mollier) diagrams for 7 of the same hydrocarbons are given in Section 7B2. Either set may be used to determine the enthalpy of a pure hydrocarbon in the liquid or real gas state, although the Mollier diagrams are useful primarily for compression or expansion calculations. It is not recommended that the enthalpies of defined hydrocarbon mixtures be estimated by the weight average of the pure-component enthalpies from these enthalpy charts. As described, this approach entirely neglects heats of mixing, which can be large for mixtures of wide-boiling hydrocarbons or members of different homologous series.

For pure hydrocarbons other than the 17 for which enthalpy-temperature diagrams are presented, the liquid and real gas enthalpies are to be calculated using Procedure 7B3.1 for desk calculation or Procedure 7B3.7 for computer calculation. This procedure involves adding a pressure effect estimated by using the theorem of corresponding states to the ideal gas enthalpies from Procedure 7A1.1. For defined mixtures, the approach is modified using a mixture correspondence point as described in Procedure 7B4.1.

For petroleum fractions, the equations of Lee and Kesler (43) provide accurate desk and computer methods. Procedure 7B4.2 is represented by a set of figures for low pressure, vapor and liquid enthalpies and an equation for pressure correction. To apply the pressure correction equation to a petroleum fraction, the necessary pseudocritical properties and characterization parameters must be obtained from Chapters 4 and 2, respectively. Procedure 7B4.7 is the corresponding computer method.

Calculation of Heat of Vaporization

A correlating equation and coefficients for calculating heat of vaporization at various temperatures for all compounds in Table 7A1.2 for which experimental heat of vaporization data are available are given in Procedure 7C1.1 and Table 7C1.2.

The heats of vaporization of a number of pure hydrocarbons are plotted directly in Figures 7C1.3 through 7C1.14. When experimental data for any desired pure hydrocarbon are not given, the general method of prediction, using Figure 7C1.15 is to be used. Figure 7C1.15, which is based on the Lee-Kesler enthalpy departure equations, is quite accurate. As presented in the procedure, extrapolations to low temperatures are best made using the Watson Equation (81). The Lee-Kesler enthalpy departure equations are also recommended for computer calculation of heat of vaporization in Procedure 7C1.16.

For mixtures, heat of vaporization predictions are considerably more complex. The vaporization may take place at constant composition with temperature or pressure varying (isobaric integral and isothermal integral, respectively), or at constant temperature and pressure with composition varying (differential heat of vaporization). All three cases require a knowledge of the vapor-liquid equilibrium involved. For isobaric integral heats of vaporization, dew- and bubble-point temperatures must be known; for isothermal integral, dew- and bubble-point pressures; and for differential, the composition of the liquid and vapor phases. These conditions must be estimated from Chapter 8 before calculating the enthalpy change, as outlined in Procedure 7C2.1.

A simplified approach is taken for petroleum fractions. For these, the enthalpy charts (Figures 7B4.3 through

PROCEDURE 7A1.1**THERMAL PROPERTIES OF PURE IDEAL GASES****Discussion**

The following thermodynamically consistent equations are recommended for the prediction of thermal properties of pure ideal gases:

For the enthalpy,

$$H = A + BT + CT^2 + DT^3 + ET^4 + FT^5 \quad (7A1.1-1)$$

Where:

H = ideal gas enthalpy at T , in Btu per lb.

T = temperature, in degrees Rankine.

A, B, C, D, E, F = derived coefficients.

For the heat capacity,

$$C_p = B + 2CT + 3DT^2 + 4ET^3 + 5FT^4 \quad (7A1.1-2)$$

Where:

C_p = ideal gas heat capacity at constant pressure at T , in Btu per (lb) (deg R).

For the entropy,

$$S = B \ln(T) + 2CT + \frac{3}{2}DT^2 + \frac{4}{3}ET^3 + \frac{5}{4}FT^4 + G \quad (7A1.1-3)$$

Where:

S = ideal gas entropy at T and 14.7 psia, in Btu per (lb) (deg R).

G = derived coefficient.

Table 7A1.2 gives the coefficients for the above equations.

Since $H = 0$ at 0 R for the ideal gas (refer to Introduction), the coefficient A should be ideally zero, but the coefficient was allowed to take a value to improve the fit at higher temperatures. By the same token, the coefficients B and C for equation 7A1.1-3 must be zero for $S = 0$ at 0 R and 14.7 psia. But, recognizing that $\ln(T) = \infty$ at $T = 0$ and entropy difference between 0 and 1 R is very small, S is set to zero, for convenience, at 1 R instead of 0 R.

For convenience, tabulated values for pure ideal gas enthalpy, heat capacity and entropy at various temperatures are given in Tables 7A1.3 through 7A1.5 for 180 compounds on the data book bases. The values for these compounds were calculated from the above equations and the coefficients in Table 7A1.2.

Procedure

For the desired compound, use the coefficients from Table 7A1.2 in equations (7A1.1-1), (7A1.1-2), and (7A1.1-3).

COMMENTS ON PROCEDURE 7A1.1

Purpose

This procedure, which includes Tables 7A1.2 through 7A1.5, is to be used to calculate the thermal properties of ideal gases as a function of temperature.

Limitations

This method should be used only within the specified temperature region. Due to the polynomial nature of the equations, extrapolations beyond the specified temperature range may lead to large errors.

Reliability

The enthalpies and entropies are estimated to be reliable to within 1%, and heat capacities to within 5% within the temperature range of the correlations. Large errors may be encountered if the equations are used outside the specified temperature limits.

Special Comments

Different enthalpy bases may be used for different compounds in calculations involving only physical changes because the effect of the different bases will cancel.

The heat capacities from this procedure are for isobaric (constant pressure) conditions. The isochoric (constant volume) heat capacity may be calculated from the isobaric heat capacity by the following equation.

$$C_v = C_p - R/M \quad (7A1.1-4)$$

Where:

C_p = ideal gas heat capacity at constant pressure, in Btu per (lb) (deg R).

C_v = ideal gas heat capacity at constant volume, in Btu per (lb) (deg R).

R = ideal gas constant, 1.986 Btu per (lb-mole) (deg R).

M = molecular weight, lb per lb-mole.

Literature Sources

The data were obtained from TRC Thermodynamic Tables—Hydrocarbons and Nonhydrocarbons, Thermodynamic Research Center, The Texas A&M University System, College Station, Texas (extant 1988). For hydrogen sulfide, sulfur dioxide, and ammonia, the data were taken from McBride, et al., SP-3001, National Aeronautical and Space Administration, Washington, D.C. (1963).

Equations (7A1.1-1) through (7A1.1-3) were originally correlated by Passut and Danner, *Ind. Eng. Chem. Process Des. & Develop.* **11** 543 (1972).

PROCEDURE 7A1.8

METHOD FOR CALCULATING THE IDEAL GAS ENTHALPY AND ENTROPY AT ANY TEMPERATURE

Discussion

The ideal gas enthalpy of formation at any desired temperature T can be determined from the ideal gas enthalpy of formation at 77 deg F by using the following equation.

$$\Delta H_{f_T}^0 = \Delta H_{f_{77}}^0 + \int_{536.7}^T \Delta C_p^0 dT \quad (7A1.8-1)$$

Where:

$\Delta H_{f_T}^0$ = ideal gas enthalpy of formation of the compound at temperature T , Btu per lb-mole.

$\Delta H_{f_{77}}^0$ = ideal gas enthalpy of formation of the compound at 77 F, Btu per lb-mole.

ΔC_p^0 = difference in heat capacity of the compound (C_nH_m) and the heat capacity of the elements which constitute the compound,

$(nC + \frac{m}{2}H_2)$, in Btu per (lb-mole) (deg R).

T = temperature, degrees Rankine.

Similarly, the ideal gas entropy at any desired temperature T can be determined from the ideal gas entropy at 77 F by:

$$S_T^0 = S_{77}^0 + \int_{536.7}^T \frac{C_p^0}{T} dT \quad (7A1.8-2)$$

Where:

S_T^0 = ideal gas entropy of the compound at temperature T and 14.7 psia, Btu per (lb) (deg R).

S_{77}^0 = ideal gas entropy of the compound at 77 F and 14.7 psia relative to that at absolute zero temperature in a perfectly ordered solid state, Btu per (lb) (deg R).

C_p^0 = ideal gas heat capacity, Btu per (lb) (deg R).

T = temperature, degrees Rankine.

This procedure does not directly yield the ideal gas enthalpy of the compound. This quantity may be obtained using Equation (7A1.8-3).

$$H_T^0 = \int_0^T C_p^0 dT \quad (7A1.8-3)$$

Where:

H_T^0 = ideal gas enthalpy at temperature T , referred to the base enthalpy of 0 Btu/lb for the ideal gas at 0 R, Btu per lb.

T = temperature, degrees Rankine.

Procedure

(a) For the ideal gas enthalpy of formation

Step 1: For the desired compound obtain $\Delta H_{f_{77}}^0$ from Chapter 1.

Step 2: Use the specific ideal gas heat capacity equation for hydrocarbons available in Procedure 7A1.1 for C_p^0 . Calculate ΔC_p^0 .

Step 3: Use Equation 7A1.8-1 to calculate $\Delta H_{f_T}^0$.

7A1.8

(b) For ideal gas entropy

Step 1: For the desired compound obtain $S_{f,77}^0$ from Procedure 7A1.1-1, and Table 7A1.2.

Step 2: Use the specific ideal gas heat capacity equation for hydrocarbons available in Procedure 7A1.1 for C_p^0 .

Step 3: Use equation 7A1.8-2 to calculate S_T^0 .

(c) For the ideal gas enthalpy

Step 1: Use the specific ideal gas heat capacity equation for hydrocarbons available in Procedure 7A1.1.

Step 2: Use equation 7A1.8-3 to calculate H_T^0 .

COMMENTS ON PROCEDURE 7A1.8

Purpose

This procedure is to be used to obtain the ideal gas enthalpy of formation, entropy, and enthalpy at any temperature.

Special Comments

The isobaric ideal gas heat capacity of the compounds, C_p^0 , varies over the temperature range for the integrations in Equations (7A1.8-1), (7A1.8-2), and (7A1.8-3). The simplest procedure is to approximate C_p^0 as a constant. In many cases this is an oversimplification which can lead to severe inaccuracies in the calculated ideal gas entropy and enthalpy. A better approach is to use specific equations for C_p^0 and perform an analytical integration. Specific ideal gas heat capacity equations for hydrocarbons are available in Procedure 7A1.1 and Table 7A1.2 as well as other sources.

If a specific equation for C_p^0 versus temperature cannot be obtained for the compound under consideration, an alternative is to use Procedure 7A1.8 (Benson's method) to generate ideal gas heat capacities at various temperatures in the desired temperature range. These heat capacities then can be fitted to a polynomial in temperature using any standard regression technique. Once the regression parameters have been obtained, it is a simple matter to integrate the polynomial expression. As an example, when the following regression equation is used for C_p^0 :

$$C_p^0 = a_0 + a_1 T + a_2 T^2 + a_3 T^3$$

Where:

a_0, a_1, a_2, a_3 = equation coefficients.

Equations (7A1.8-2) and (7A1.8-3) then become:

$$S_T^0 = S_{77}^0 + a_0 \ln \frac{T}{536.7} + a_1(T - 536.7) + \frac{a_2}{2}(T^2 - 536.7^2) + \frac{a_3}{3}(T^3 - 536.7^3)$$

$$H_T^0 = \Delta H_{f77}^0 + a_0(T - 536.7) + \frac{a_1(T^2 - 536.7^2)}{2} + \frac{a_2(T^3 - 536.7^3)}{3} + \frac{a_3(T^4 - 536.7^4)}{4}$$

Where:

T = temperature, degrees Rankine.

Alternatively, the calculated C_p^0 values at various temperatures could be integrated numerically using Simpson's rule or any other numerical integration procedure.

Example

Calculate the ideal gas enthalpy of formation of *n*-butane at 200 F.

From Chapter 1, $\Delta H_{f77}^0 = -929.42$ for butane.

Butane has a chemical formula C_4H_{10} .

ΔC_p^0 will be the difference in the ideal gas heat capacity of C_4H_{10} and the ideal gas heat capacity of its elements (4 C + 10/2 H₂).

We will use equation 7A1.1-2 as the expression for heat capacity

$$C_p = B + 2CT + 3DT^2 + 4ET^3 + 5FT^4 \quad (7A1.1-2)$$

The coefficients for this equation are given in Table 7A1.2.

7A1.8

$$\begin{aligned}
 \Delta H_{f_T}^0 &= \Delta H_{f_77}^0 + \int_{536.7}^{659.7} [(B_{C_4H_{10}} - 4B_C - 5B_{H_2}) + 2(C_{C_4H_{10}} - 4C_C - 5C_{H_2})T^0 \\
 &\quad + 3(D_{C_4H_{10}} - 4D_C - 5D_{H_2})T^2 + 4(E_{C_4H_{10}} - 4E_C - 5E_{H_2})T^3 \\
 &\quad + 5(F_{C_4H_{10}} - 4F_C - 5F_{H_2})T^4] dT \\
 \Delta H_{f_T}^0 &= -929.42 - 2143.89 \\
 &= -3073.31 \text{ Btu per lb.}
 \end{aligned}$$

PROCEDURE 7B3.1**ENTHALPY OF PURE HYDROCARBON LIQUIDS AND REAL GASES****Discussion**

The following equation is to be used to predict the effect of pressure on the enthalpy of pure hydrocarbons:

$$\left(\frac{\tilde{H}^0 - \tilde{H}}{RT_c} \right) = \left(\frac{\tilde{H}^0 - \tilde{H}}{RT_c} \right)^{(0)} + \omega \left(\frac{\tilde{H}^0 - \tilde{H}}{RT_c} \right)^{(1)} \quad (7B3.1-1)$$

Where:

$\left(\frac{\tilde{H}^0 - \tilde{H}}{RT_c} \right)$ = the dimensionless effect of pressure on enthalpy.

$\left(\frac{\tilde{H}^0 - \tilde{H}}{RT_c} \right)^{(0)}$ = effect of pressure on enthalpy for the simple fluid, which is tabulated as a function of T_r and p_r in Table 7B3.2 and plotted in Figure 7B3.4.

$\left(\frac{\tilde{H}^0 - \tilde{H}}{RT_c} \right)^{(1)}$ = correction term for molecular acentricity, which is tabulated as a function of T_r and p_r in Table 7B3.3 and plotted in Figure 7B3.5 and 7B3.6.

T_r = reduced temperature, T/T_c .

T = temperature, in degrees Rankine.

T_c = critical temperature, in degrees Rankine.

p_r = reduced pressure, p/p_c .

p = pressure, in psia.

p_c = critical pressure, in psia.

ω = acentric factor.

The dimensionless pressure effect term is used in the following equation to determine the total enthalpy of the hydrocarbon:

$$H = H^0 - \frac{RT_c}{M} \left(\frac{\tilde{H}^0 - \tilde{H}}{RT_c} \right) \quad (7B3.1-2)$$

Where:

H = total enthalpy referred to the basis enthalpy of 0 Btu per lb for the ideal gas at 0 R, in British thermal units per pound. \tilde{H} is the analogous molar quantity.

H^0 = ideal gas enthalpy, in British thermal units per pound. \tilde{H}^0 is the analogous molar quantity.

R = gas constant = 1.986 Btu per (lb-mole) (deg R).

M = molecular weight, in lb per lb-mole.

Procedure

Step 1: Obtain the molecular weight, critical temperature, critical pressure and the acentric factor from Chapter 1.

Step 2: Calculate the reduced temperature and pressure at which an enthalpy is desired.

Step 3: Obtain the correlation terms $\left(\frac{\tilde{H}^0 - \tilde{H}}{RT_c} \right)^{(0)}$ and $\left(\frac{\tilde{H}^0 - \tilde{H}}{RT_c} \right)^{(1)}$. If the most accurate values are desired, use Tables 7B3.2 and 7B3.3 with linear double interpolation in p_r and T_r . When near saturation, the interpolation procedure may not be satisfactory (see Special Comments). If slightly less accurate values are acceptable, they may be obtained rapidly from Figures 7B3.4 through 7B3.6.

Step 4: Calculate the dimensionless pressure effect term using equation (7B3.1-1).

Step 5: Obtain the ideal gas enthalpy from Procedure 7A1.1.

Step 6: Calculate the total enthalpy using equation (7B3.1-2).

COMMENTS ON PROCEDURE 7B3.1

Purpose

This procedure is to be used to predict enthalpies of pure hydrocarbons in the liquid and real gas states when the desired values are not immediately available from Figures 7B1.1 through 7B1.19. Tables 7B3.2 and 7B3.3 or Figures 7B3.4 through 7B3.6 are required in this procedure. The method is best suited to desk calculations, and Procedure 7B3.7 should be used with electronic computers. Ideal gas enthalpies from Procedure 7A1.1 are required in either case. Mixtures are treated in Section 7B4.

Limitations

In general, this procedure is not accurate for polar substances.

Reliability

Differences between calculated and experimental pressure effects on enthalpy are generally less than 3 Btu per pound. In the critical region, errors as high as 15 Btu per pound can occur. The reliability of the method decreases with increasing uncertainty in the critical properties.

Notation

The notation used in Tables 7B3.2 and 7B3.3 and Figures 7B3.4 through 7B3.6 was defined for equations (7B3.1-1) and (7B3.1-2).

Special Comments

The broken lines in Tables 7B3.2 and 7B3.3 indicate the discontinuity between liquid (to the right and above) and vapor (to the left and below) enthalpies. Interpolations must not be made across this line; always use table values which apply to the desired phase only. Near the broken line, the extrapolations which are necessary should be made with respect to reduced pressure at constant reduced temperature.

For saturated vapors or liquids (i.e., at their vapor pressures), do not use the two-phase border outlined on Figure 7B3.4. This border applies only when the acentric factor is zero, and, as acentricity increases, the reduced vapor pressure decreases at constant reduced temperature. The best procedure is to obtain the vapor pressure from Chapter 5 and proceed as if the phase were homogeneous.

In regions of very rapid change of the simple fluid and correction terms with reduced pressure and/or temperature, a linear interpolation from the tables may not be satisfactory even though the table values are spaced more closely. Here, the figures should be used either directly or as a guide for interpolation corrections to the results from the tables.

The figures may be extrapolated to lower reduced pressures by noting that $\left(\frac{\tilde{H}^0 - \tilde{H}}{RT_c}\right)^{(0)}$ and

$\left(\frac{\tilde{H}^0 - \tilde{H}}{RT_c}\right)^{(1)}$ approach zero as the pressure approaches zero. In many engineering applications, these limiting values may be used for all reduced pressures between 0 and 0.2. If even more precise results than the extrapolated values are desired (rarely), use the following equation:

$$\begin{aligned} \left(\frac{\tilde{H}^0 - \tilde{H}}{RT_c}\right) = & -p_r [(0.1445 + 0.073 \omega) - (0.660 - 0.92 \omega)T_r^{-1} - (0.4155 + 1.50 \omega)T_r^{-2} \\ & - (0.0484 + 0.388 \omega)T_r^{-3} - 0.0657 \omega T_r^{-8}] \end{aligned} \quad (7B3.1-3)$$

where symbols were defined for equation (7B3.1-1).

Literature Sources

Tables 7B3.2 and 7B3.3 were generated using the generalized correlation of Lee and Kesler, *AIChE Journal* 21 510 (1975). Figures 7B3.4 through 7B3.6 are direct plots of the tables. Equation (7B3.1-3) was developed by Pitzer and Curl, *J. Am. Chem. Soc.* 79 2369 (1957).

PROCEDURE 7B3.7

ALTERNATE (COMPUTER) METHOD FOR THE ENTHALPY OF PURE HYDROCARBON LIQUIDS AND REAL GASES

Discussion

The following generalized correlation, which was used to generate Tables 7B3.2 and 7B3.3, is recommended for calculating the pressure effect on the enthalpy of pure hydrocarbon liquids and gases by a digital computer.

The equation to be used is:

$$\left(\frac{\tilde{H}^0 - \tilde{H}}{RT_c} \right) = \left(\frac{\tilde{H}^0 - \tilde{H}}{RT_{c,0}} \right)^{(0)} + \frac{\omega}{\omega^{(h)}} \left[\left(\frac{\tilde{H}^0 - \tilde{H}}{RT_{c,h}} \right)^{(h)} - \left(\frac{\tilde{H}^0 - \tilde{H}}{RT_{c,0}} \right)^{(0)} \right] \quad (7B3.7-1)$$

Where:

$\left(\frac{\tilde{H}^0 - \tilde{H}}{RT_c} \right)$ = the dimensionless effect of pressure on enthalpy of the fluid of interest.

$\left(\frac{\tilde{H}^0 - \tilde{H}}{RT_{c,0}} \right)^{(0)}$ = effect of pressure on enthalpy for the simple fluid, to be calculated from equation (7B3.7-2).

$\left(\frac{\tilde{H}^0 - \tilde{H}}{RT_{c,h}} \right)^{(h)}$ = effect of pressure on enthalpy for the heavy reference fluid (*n*-octane), to be calculated from equation (7B3.7-2).

T_c = critical temperature of the fluid for which the enthalpy is desired, in degrees Rankine.

ω = acentric factor of the fluid for which the pressure effect on enthalpy is being sought.

$\omega^{(h)}$ = acentric factor of the heavy reference fluid = 0.3978.

The dimensionless effects of pressure on the enthalpies of the simple fluid and the heavy reference fluid are to be calculated from the following equation:

$$\left(\frac{\tilde{H}^0 - \tilde{H}}{RT_{c,i}} \right)^{(i)} = -T_r \left\{ z^{(i)} - 1 - \frac{b_2 + 2b_3/T_r + 3b_4/T_r^2}{T_r V_r} - \frac{c_2 - 3c_3/T_r^2}{2T_r V_r^2} + \frac{d_2}{5T_r V_r^5} + 3E \right\} \quad (7B3.7-2)$$

Where:

$$E = \frac{c_4}{2T_r^3 \gamma} \left\{ \beta + 1 - \left(\beta + 1 + \frac{\gamma}{V_r^2} \right) \exp \left(-\frac{\gamma}{V_r^2} \right) \right\}$$

$\left(\frac{\tilde{H}^0 - \tilde{H}}{RT_{c,i}} \right)^{(i)} = \left(\frac{\tilde{H}^0 - \tilde{H}}{RT_{c,0}} \right)^{(0)}$ when the equation is applied to the simple fluid.

$\left(\frac{\tilde{H}^0 - \tilde{H}}{RT_{c,i}} \right)^{(i)} = \left(\frac{\tilde{H}^0 - \tilde{H}}{RT_{c,h}} \right)^{(h)}$ when the equation is applied to the heavy reference fluid.

T_r = reduced temperature, T/T_c .

T_c = critical temperature in degrees Rankine.

T = temperature, in degrees Rankine.

$V_r = p_c V / RT_c$, is obtained from Procedure 6B1.8.

$z^{(i)} = z^{(0)}$ or $z^{(h)}$, depending on whether the equation is applied to the simple fluid or the heavy reference fluid.

$z^{(0)}$ = compressibility factor of the simple fluid, obtained from Procedure 6B1.8.

$z^{(h)}$ = compressibility factor of the heavy reference fluid, obtained from Procedure 6B1.8.

$b_2, b_3, b_4, c_2, c_3, c_4, d_2, \gamma$ and β are two sets of constants, one set for the simple fluid and another for the heavy reference fluid. The values of the constants are given in Procedure 6B1.8.

7B3.7

With the term for dimensionless pressure effect on enthalpy from equation (7B3.7-1), the total enthalpy for the fluid of interest may be found from the following equation:

$$H = H^0 - \frac{RT_c}{M} \left(\frac{\tilde{H}^0 - \tilde{H}}{RT_c} \right)^{(0)} \quad (7B3.7-3)$$

Where:

H = total enthalpy in British thermal units per pound, referred to the basis enthalpy of 0 Btu per lb for the ideal gas at 0 R. \tilde{H} is the analogous molar quantity.

H^0 = ideal gas enthalpy, in British thermal units per pound. \tilde{H}^0 is the analogous molar quantity.

R = gas constant, 1.986 Btu per (lb-mole) (deg R).

M = molecular weight, in lb per lb-mole.

Procedure

Step 1: Obtain the critical temperature, critical pressure, the molecular weight, and the acentric factor from Chapter 1.

Step 2: Calculate the reduced temperature and pressure at which the enthalpy is desired.

Step 3: Use Procedure 6B1.8 to determine the compressibility factor of the simple fluid at the reduced temperature and pressure calculated in Step 2. Retain T_r , V_r , and the constants b_2 , b_3 , b_4 , c_2 , c_3 , c_4 , d_2 , γ and β for the simple fluid.

Step 4: Use equation (7B3.7-2) to obtain $\left(\frac{\tilde{H}^0 - \tilde{H}}{RT_c} \right)^{(0)}$.

Step 5: Repeat Step 3 for the heavy reference fluid.

Step 6: Use equation (7B3.7-2) to obtain $\left(\frac{\tilde{H}^0 - \tilde{H}}{RT_c} \right)^{(h)}$.

Step 7: Use equation (7B3.7-1) to obtain $\left(\frac{\tilde{H}^0 - \tilde{H}}{RT_c} \right)$.

Step 8: Obtain the ideal gas enthalpy from Procedure 7A1.1 and use equation (7B3.7-3) to obtain the enthalpy of the real fluid.

COMMENTS ON PROCEDURE 7B3.7

Purpose

This procedure is presented to be used with a digital computer to calculate enthalpies of pure hydrocarbon liquids and gases. The results from Procedures 6B1.8 and 7A1.1 are required directly in this procedure. For mixtures, use the method described in Comments on Procedure 7B4.1.

Limitations

This procedure has not been extensively tested with data for nonhydrocarbons. However, reasonable results should be expected for nonpolar and slightly polar nonhydrocarbons.

Reliability

Differences between calculated and experimental pressure effects on enthalpy are generally less than 3 Btu per pound. In the critical region, errors as high as 15 Btu per pound can occur.

The equations may be used between reduced temperatures of 0.3 and 4.0 and between reduced pressures of 0 and 10.0. However, it is believed that the equation can be used for reduced pressures as high as 20 or above, with very little additional error. The reliability of the method decreases with increasing uncertainties in the critical properties.

Special Comments

For saturated vapors, use both temperature and pressure as input (with the vapor pressure predictions from Chapter 5, when necessary) and perform the calculations as if the point were in the homogeneous region.

Literature Source

The equations in this procedure were developed by Lee and Kesler, *AICHE Journal* 21 510 (1975).

PROCEDURE 7B4.1**LIQUID AND REAL GAS ENTHALPY OF HYDROCARBON MIXTURES****Discussion**

The tables and figures of Procedure 7B3.1 are to be applied to hydrocarbon mixtures by using the pseudocritical temperature and pressure to calculate reduced conditions instead of the true critical temperature and pressure. The pseudocritical properties, which are approximated as the molar averages of the component true critical properties, are given in Chapter 4 for mixtures of defined and undefined composition and blends of the two. The mixture acentric factor, which is defined as the molar average of the component acentric factors, may be estimated for undefined mixtures from Chapter 2. These approximations are summarized below:

$$T_{pc} = \sum_{i=1}^n x_i T_{ci} \quad (7B4.1-1)$$

Where:

T_{pc} = pseudocritical temperature, in degrees Rankine.

T_{ci} = critical temperature of component i , in degrees Rankine.

n = number of components in the mixture.

x_i = mole fraction of component i .

$$p_{pc} = \sum_{i=1}^n x_i p_{ci} \quad (7B4.1-2)$$

Where:

p_{pc} = pseudocritical pressure, in pounds per square inch absolute.

p_{ci} = critical pressure of component i , in pounds per square inch absolute.

$$\omega = \sum_{i=1}^n x_i \omega_i \quad (7B4.1-3)$$

Where:

ω = mixture acentric factor.

ω_i = acentric factor of component i .

The results from these equations are used to calculate the reduced conditions so that Procedure 7B3.1 may be used to calculate the effect of pressure on the mixture enthalpy. This pressure correction is then subtracted from the ideal gas enthalpy of the mixture, which is defined as:

$$H^0 = \sum_{i=1}^n x_{\omega i} H_i^0 \quad (7B4.1-4)$$

Where:

H^0 = ideal gas enthalpy, in British thermal units per pound. The subscript i refers to component i in the n component mixture.

$x_{\omega i}$ = weight fraction of component i .

Procedure

Step 1: For mixtures of known composition, obtain from Chapter 1 the molecular weights and the critical pressures and temperatures and the acentric factors for all of the components. (For hydrogen, use $T_c = 75$ R, $p_c = 305$ psia, and $\omega = 0$.)

Step 2: Calculate the pseudocritical temperature and pressure using equations (7B4.1-1) and (7B4.1-2) and the mixture acentric factor using equation (7B4.1-3). [For blends of petroleum fractions with mixtures of known composition, obtain the pseudocritical conditions from Chapter 4 and the acentric factor for the petroleum fraction portion from Chapter 2. Complete the acentric factor calculation using equation (7B4.1-3)].

Calculate the reduced temperature and pressure.

Step 3: Calculate the ideal gas enthalpy of the mixture using equation (7B4.1-4). Input enthalpies for pure hydrocarbons are to be taken from Procedure 7A1.1. (For blends of hydrocarbons with petroleum fractions, obtain the ideal gas enthalpy for the petroleum fraction portion from Procedure 7B4.2. Do not make a pressure correction.) Calculate the molecular weight of the mixture (with input for the petroleum fraction portion, if present, from Chapter 2).

Step 4: Calculate the effect of pressure on mixture enthalpy using Steps 3 and 4 of Procedure 7B3.1 and the total mixture enthalpy using Step 6 of the same procedure.

COMMENTS ON PROCEDURE 7B4.1

Purpose

This procedure is to be used with Procedure 7B3.1 to estimate the enthalpies of mixtures of hydrocarbons which may contain nonpolar nonhydrocarbon substances. Mixtures of known composition and blends of known compounds with petroleum fractions are treated. For petroleum fractions alone, use Procedure 7B4.2.

Limitations

In general, the method is not applicable to mixtures containing polar components.

Reliability

Differences between calculated and experimental pressure effects on enthalpy are generally less than 3 Btu per pound. In the critical region, errors as high as 20 Btu per pound may occur for mixtures containing molecules of widely dissimilar size and shape. In these cases the use of a simple molar average of the critical properties, as calculated by equations (7B4.1-1) and (7B4.1-2), often leads to high errors.

When compared with approximately 4,000 data points for hydrocarbon mixtures of known composition over a wide range of temperature and pressure, the overall average error was about 4 Btu per pound, with a majority of the errors less than 3 Btu per pound.

The reliability of the modification for blends of hydrocarbons with mixtures of undefined composition was not tested.

Special Comments

For hydrocarbon-hydrocarbon mixtures which do not contain methane, slightly better results are obtained in the immediate critical region if true rather than pseudocritical temperatures and pressures are used. This region is defined approximately by the following pseudoreduced condition boundaries. $1.0 < T_r < 1.2$ and $1.0 < p_r < 3.0$. True critical conditions are correlated in Chapter 4. Notice that the liquid phase can exist in this region even though the pseudoreduced temperature is greater than unity (see Introduction).

For supercritical temperatures ($T_r > 1$) and high pressures ($p_r > 5$), the error can be reduced slightly by using the following mixture correspondence pressure instead of the pseudocritical pressure defined by equation (7B4.1-2):

$$p_{mc} = \frac{RT_{pc} \sum_{i=1}^n x_i z_{ci}}{\sum_{i=1}^n x_i V_{ci} M_i} \quad (7B4.1-5)$$

Where:

p_{mc} = mixture correspondence pressure, in psia.

R = gas constant = 10.731 (psia) (cu ft) per (lb-mole) (deg R).

z_{ci} = critical compressibility factor of component i (from Chapter 1).

V_{ci} = critical volume of component i (from Chapter 1), in cubic feet per pound.

M_i = molecular weight of component i (from Chapter 1), in lb per lb-mole.

More reliable enthalpies can be obtained under most temperature-pressure conditions by using the mixture correspondence rules of Lee and Kesler (42), Joffe (35), Stewart et al. (71), or Leland and Mueller (44). However, the small advantage in accuracy does not justify the added labor involved in using these methods.

For computer enthalpy calculations, Procedure 7B3.7 may be adapted to mixtures using the mixture correspondence point as described in Procedure 6B2.2 for gas densities. Mixtures of known composition, petroleum fractions, and blends of the two may be treated. The reliability for mixtures of known composition is approximately the same as quoted previously. For petroleum fractions, obtain the necessary ideal gas enthalpies from Procedure 7B4.2 without using a pressure correction.

Literature Sources

Equations (7B4.1-1) and (7B4.1-2) were given by Kay, *Ind. Eng. Chem.* **28** 1014 (1936). Equation (7B4.1-5) was developed by Prausnitz and Gunn, *AICHE* **4** 430 (1958).

PROCEDURE 7B4.2

ENTHALPY OF PETROLEUM FRACTIONS

Discussion

This procedure, which includes Figures 7B4.3 through 7B4.6, is to be used to determine the enthalpy of petroleum fractions. Figures 7B4.3 through 7B4.6 are direct plots of liquid and vapor enthalpies of petroleum fractions at 0 atm to 1 atm. Each figure is applicable to a different value of the Watson characterization factor (defined in Chapter 2).

Corrections for pressure effects are made by using Procedure 7B3.1. Calculate the pseudocritical properties by using the methods of Chapter 4 and the molecular weight and acentric factor from Chapter 2. Pressure corrections are not necessary for the liquid phase if the reduced temperature is less than 0.8 and the reduced pressure is less than 1.0.

Heats of vaporization at 0 atm to 1 atm are simply the difference between vapor and liquid enthalpies read from the solid lines. Superatmospheric latent heats should be taken from the difference between the vapor and liquid enthalpies after corrections for pressure effects are made for each phase.

Procedure

Step 1: Using the available inspection data for the fraction, determine the Watson characterization factor, K , with the methods of Chapter 2.

Step 2: Calculate the pseudocritical temperature and pressure using the methods of Chapter 4.

Step 3: Calculate the reduced temperature and pressure.

Step 4: Use the two figures from Figures 7B4.3 through 7B4.6 which bracket the Watson K factor to read the 0 atm to 1 atm enthalpy directly from the solid lines (designated VAP for vapor and LQ for liquid) of API gravity. If the fraction is a liquid with $T_r < 0.8$ and $p_r < 1.0$, the desired enthalpy may be obtained directly by linear interpolation in Watson K . If not, proceed to Step 5.

Step 5: Use the methods of Chapter 2 to determine the molecular weight and acentric factor for the fraction.

Step 6: For the vapor phase, pressure corrections for each figure may be calculated by using Procedure 7B3.1 directly. For liquids, the difference between the pressure correction terms

$\left(\frac{\tilde{H}^0 - \tilde{H}}{RT_c}\right)$ at the temperature and pressure in question and the same temperature and the critical pressure is the required pressure correction. Expressed mathematically:

$$\left(\frac{\tilde{H}^0 - \tilde{H}}{RT_c}\right)_{\text{liq.}} = \left(\frac{\tilde{H}^0 - \tilde{H}}{RT_c}\right)_{\text{liq. at } T, p} - \left(\frac{\tilde{H}^0 - \tilde{H}}{RT_c}\right)_{\text{liq. at } T, p_r = 1.0}$$

No correction for pressure effects are needed for the liquid phase below a reduced temperature of 0.8 and a reduced pressure of 1.0.

Step 7: After correcting for pressure effects for each figure, the desired enthalpy may be obtained by linear interpolation in Watson K .

Note that heats of vaporization may be calculated by taking the difference between the vapor and liquid enthalpies at any given temperature and pressure.

COMMENTS ON PROCEDURE 7B4.2

Purpose

This procedure, which includes Figures 7B4.3 through 7B4.6 is to be used to determine the enthalpy and total heat of vaporization of petroleum fractions. For the enthalpy of petroleum fractions mixed with identifiable hydrocarbons, use Procedure 7B4.1.

Limitations

This method is not reliable in the immediate critical region.

Reliability

Outside the critical region, this procedure is estimated to be reliable to within 3 Btu per pound for liquids and about 5 Btu per pound for vapors. In the critical region, errors around 10 Btu per pound for liquids and 15 Btu per pound for vapors, with occasional errors as high as 40 Btu per pound may be expected. The accuracy of this method relies heavily on the accuracy of the pseudocritical properties, the molecular weight, and acentric factor.

Special Comments

If the ASTM distillation data and molecular type analysis for the fraction are available, the pseudocompound method of Huang and Daubert, *Ind. Eng. Chem. Proc. Des. and Develop.* **13** 359 (1974), is recommended over Procedure 7B4.2. The accuracy of the pseudocompound method is about 3 Btu per pound for liquids and vapors in both the critical and noncritical regions.

Literature Sources

Private communication, B. I. Lee and M. G. Kesler, Mobil Oil Corp., Princeton, N.J. (January 1975).

Example

Calculate the vapor enthalpy at 600 F and 50 psia of a petroleum fraction with an average boiling point of 407.2 F and an API gravity of 43.5 (specific gravity of 0.8086).

From the definition of the characterization factor,

$$K = \frac{(407.2 + 459.7)^{1/3}}{0.8086} = 11.8$$

From the methods in Chapter 4, $T_{pc} = 751$ F and $p_{pc} = 314$ psia. Then,

$$T_r = \frac{T}{T_{pc}} = \frac{(600 + 459.7)}{(751 + 459.7)} = 0.875$$

$$p_r = \frac{p}{p_{pc}} = \frac{50}{314} = 0.159$$

From Figure 7B4.5, at 600 F, interpolation between API gravities of 40 and 50 give an ideal gas (zero pressure) enthalpy of 519 Btu per pound.

Using the methods in Chapter 2, the fraction was found to have a molecular weight of 168 and an acentric factor of 0.422. From the Procedure 7B3.1,

$$\left(\frac{\tilde{H}^0 - \tilde{H}}{RT_c} \right) = 0.325$$

Thus, the total enthalpy under the desired conditions is:

$$H = 519 - \frac{(1.986)(751 + 459.7)(0.325)}{164}$$

$$= 514 \text{ Btu per pound.}$$

An experimental value was found to be 516 Btu per pound.

PROCEDURE 7B4.7**ALTERNATE (COMPUTER) METHOD FOR ENTHALPY OF PETROLEUM FRACTIONS****Discussion**

The following equations, which were used to generate Figures 7B4.3 through 7B4.6, are recommended for estimating the enthalpy of petroleum fractions using a digital computer.

Region I. Liquid phase where $T_r \leq 0.8$ and $P_r \leq 1.0$, the equation is:

$$H_L = A_1 [T - 259.7] + A_2 [T^2 - (259.7)^2] + A_3 [T^3 - (259.7)^3] \quad (7B4.7-1)$$

Where:

H_L = enthalpy of liquid petroleum fraction with $T_r \leq 0.8$ and $P_r \leq 1.0$, in British thermal units per pound.

$$A_1 = 10^{-3} \left[-1171.26 + (23.722 + 24.907 \text{ sp gr}) K + \frac{(1149.82 - 46.535 K)}{\text{sp gr}} \right].$$

$$A_2 = 10^{-6} \left[(1.0 + 0.82463 K) \left(56.086 - \frac{13.817}{\text{sp gr}} \right) \right].$$

$$A_3 = -10^{-9} \left[(1.0 + 0.82463 K) \left(9.6757 - \frac{2.3653}{\text{sp gr}} \right) \right].$$

p_r = reduced pressure = p/p_{pc} .

p = pressure, psia.

p_{pc} = pseudocritical pressure, psia.

T_r = reduced temperature = T/T_{pc} .

T = temperature, degrees Rankine.

T_{pc} = pseudocritical temperature, degrees Rankine.

K = Watson characterization factor.

sp gr = specific gravity, 60 F/60 F.

No correction for pressure effects is needed for the liquid phase below a reduced temperature of 0.8 and reduced pressure of 1.0.

Region II. Vapor phase or liquid phase with $T_r > 0.8$ or $p_r > 1.0$, the equation is:

$$H = H_L^\dagger + B_1 [T - 0.8T_{pc}] + B_2 [T^2 - 0.64(T_{pc})^2] + B_3 [T^3 - 0.512(T_{pc})^3] \\ + \frac{RT_{pc}}{M} \left[4.507 + 5.266\omega - \left(\frac{\tilde{H}^0 - \tilde{H}}{RT_{pc}} \right) \right] \quad (7B4.7-2)$$

Where:

H = enthalpy of petroleum fraction in Region II, Btu per lb.

H_L^\dagger = liquid enthalpy at a reduced temperature of 0.8 calculated by equation (7B4.7-1) in British thermal units per pound.

$$B_1 = 10^{-3} \left[-356.44 + 29.72K + B_4 \left(295.02 - \frac{248.46}{\text{sp gr}} \right) \right].$$

$$B_2 = 10^{-6} \left[-146.24 + (77.62 - 2.772K) K - B_4 \left(301.42 - \frac{253.87}{\text{sp gr}} \right) \right].$$

$$B_3 = 10^{-9} [-56.487 - 2.95B_4].$$

$$B_4 = \left[\left(\frac{12.8}{K} - 1.0 \right) \left(1.0 - \frac{10.0}{K} \right) (\text{sp gr} - 0.885) (\text{sp gr} - 0.70) (10^4) \right]^2$$

for $10.0 < K < 12.8$ with $0.70 < \text{sp gr} < 0.885$.

$B_4 = 0$ for all other cases.

M = molecular weight, in lb per lb-mole.

R = gas constant, 1.986 Btu per (lb-mole) (deg R).

$\left(\frac{\tilde{H}^0 - \tilde{H}}{RT_{pc}} \right)$ = dimensionless pressure effect on enthalpy, obtained from Procedure 7B3.2.

ω = acentric factor.

Procedure

Step 1: Using the available inspection data for the fraction, determine the Watson characterization factor and the molecular weight, using the methods of Chapter 2.

Step 2: Calculate the pseudocritical temperature and pseudocritical pressure of the fraction, using the methods of Chapter 4.

Step 3: Calculate an acentric factor (ω) for the fraction, using the methods given in Chapter 2.

Step 4: Calculate the reduced temperature and pressure. If the fraction is in the vapor phase, or in the liquid phase with either $T_r > 0.8$ or $P_r > 1.0$, proceed directly to Step 6.

Step 5: Calculate the liquid enthalpy from equation (7B4.7-1). This is the desired enthalpy for the petroleum fraction.

Step 6: Calculate $H_L \dagger$ using equation (7B4.7-1) with $T = 0.8 T_{pc}$

Step 7: Using Procedure 7B3.1, calculate the enthalpy pressure correction term, $\left(\frac{\tilde{H}^0 - \tilde{H}}{RT_c} \right)$. This step may be disregarded if $p_r < 0.01$.

Step 8: Use equation (7B4.7-2) to calculate the desired enthalpy for the petroleum fraction.

Note that heats of vaporization may be calculated by taking the difference between the vapor and liquid enthalpies at any given temperature and pressure.

COMMENTS ON PROCEDURE 7B4.7

Purpose

This procedure is presented as an alternate to Procedure 7B4.2, to be used for calculating the enthalpy of petroleum fractions with a digital computer.

Limitations

This method is not reliable in the immediate critical region.

Reliability

Outside the critical region, this procedure is estimated to be reliable to within 3 Btu per pound for liquids and about 5 Btu per pound for vapors. In the critical region, errors around 10 Btu per pound for liquids and 15 Btu per pound for vapors, with occasional errors as high as 40 Btu per pound may be expected. The accuracy of this method relies heavily on the accuracy of the pseudocritical properties, the molecular weight, and acentric factor.

Special Comments

If the ASTM distillation data and molecular type analysis for the fraction are available, the pseudocompound method of Huang and Daubert, *Ind. Eng. Chem. Proc. Des. and Develop.* **13** 359 (1974), is recommended over Procedure 7B4.2. The accuracy of the pseudocompound method is about 3 Btu per pound for liquids and vapors in both the critical and noncritical regions.

Literature Sources

Private communication, B. I. Lee and M. G. Kesler, Mobil Oil Corp. Princeton, N.J. (January 1975).

PROCEDURE 7C1.1**HEAT OF VAPORIZATION OF PURE HYDROCARBONS****Discussion**

The following thermodynamically consistent equation is recommended for calculating the heat of vaporization of pure hydrocarbon fluids at saturation pressure for temperatures between the normal boiling point and $T_r = 0.9$:

$$H_{vap} = A(1-T_r)^B + CT_r \quad (7C1.1-1)$$

Where:

H_{vap} = Heat of vaporization at T_r in Btu per lb.

T_r = reduced temperature.

A, B, C = derived coefficients.

Table 7C1.2 gives the coefficients for the above equation.

Procedure

For the desired compounds, use the coefficients from Table 7C1.2 in equation (7C1.1-1).

COMMENTS ON PROCEDURE 7C1.1**Purpose**

This procedure, which includes Table 7C1.2, is to be used to calculate the heat of vaporization of pure hydrocarbons at saturation pressure as a function of temperature.

Limitations

This method should be used only within the specified temperature region.

Reliability

The heat of vaporization is estimated to be reliable to within 3 percent. Large errors may be encountered if the equation is used outside the specified temperature range.

Literature Sources

The data were obtained from the DIPPR-Compilation data bank as reported by Daubert and Danner (extant 1988) and from TRC Thermodynamic Tables-Hydrocarbons and Nonhydrocarbons, Thermodynamic Research Center, The Texas A & M University System, College Station, Texas (extant 1988). Additional data were obtained from Chapter 1. API monograph series were used to obtain data for tetralin (API publication 705, October 1978), phenanthrene (API publication 708, January 1979), *cis* and *trans* decalin (API publication 706, October 1978), naphthalene (API publication 707, October 1978), indan (API publication 714, April 1980) and acenaphthalene (API publication 715, January 1981).

PROCEDURE 7C1.16**ALTERNATE (COMPUTER) METHOD FOR THE
HEAT OF VAPORIZATION OF PURE HYDROCARBONS****Discussion**

For a pure compound, the heat of vaporization is the difference between the saturated vapor and saturated liquid enthalpies, both phases being in equilibrium at a given temperature. This difference can be represented by the following:

$$\lambda = \left[H^0 - \frac{RT_c}{M} \left(\frac{\tilde{H}^0 - \tilde{H}}{RT_c} \right) \right]_{\text{sat vapor at } T, p_v} - \left[H^0 - \frac{RT_c}{M} \left(\frac{\tilde{H}^0 - \tilde{H}}{RT_c} \right) \right]_{\text{sat liquid at } T, p_v} \quad (7C1.16-1)$$

Where:

λ = heat of vaporization for pure hydrocarbon, in Btu per lb.

H^0 = ideal gas enthalpy of pure hydrocarbon at T , in Btu per lb.

$\left(\frac{\tilde{H}^0 - \tilde{H}}{RT_c} \right)$ = dimensionless effect of pressure on enthalpy.

T = temperature, in degrees Rankine.

T_c = critical temperature, in degrees Rankine.

p_v = vapor pressure of pure compound at T , in psia.

R = gas constant, 1.986 Btu per (lb-mole) (deg R).

M = molecular weight, in lb per lb-mole.

Equation 7C1.16-1 can be simplified to:

$$\lambda = \frac{RT_c}{M} \left[\left(\frac{\tilde{H}^0 - \tilde{H}}{RT_c} \right)_{\text{sat liquid at } T, p_v} - \left(\frac{\tilde{H}^0 - \tilde{H}}{RT_c} \right)_{\text{sat vapor at } T, p_v} \right] \quad (7C1.16-2)$$

Procedure

Step 1: Obtain values of T_c , p_c , ω and molecular weight of the pure hydrocarbon from Chapter 1.

Step 2: Use the methods of Chapter 5 to calculate the vapor pressure exerted by the pure hydrocarbon at the desired temperature.

Step 3: Calculate the reduced temperature and, using the vapor pressure found in Step 2, calculate the reduced pressure.

Step 4: Follow steps 3 and 7 of Procedure 7B3.7 to obtain the enthalpy pressure effect terms for the saturated liquid and saturated vapor phases.

Step 5: Use equation (7C1.16-2) to calculate the desired heat of vaporization.

COMMENTS ON PROCEDURE 7C1.16

Purpose

This procedure is to be used to predict the heat of vaporization for pure hydrocarbons that are not covered in the direct plots, Figures 7C1.3 through 7C1.12. For mixtures, use the method in Section 7C2. This procedure can be used for both desk and digital computer calculations.

Limitations

This procedure has not been tested with data for nonhydrocarbons.

Reliability

Heats of vaporization calculated by this method are estimated to be reliable to within 2 percent. Errors as high as 10 percent may occur in the immediate critical region.

Literature Source

The method is derived from Lee and Kesler, *AIChE Journal* **21** 510 (1975).

PROCEDURE 7C2.1**HEAT OF VAPORIZATION OF MIXED HYDROCARBONS****Discussion**

In the vaporization of mixtures, three different latent heat effects can be of interest, namely isobaric integral, isothermal integral, and differential heats of vaporization. The two integral heat changes apply to the complete vaporization of the liquid to a vapor of identical composition with either temperature or pressure constant. For calculational purposes, only one phase exists for integral heats of vaporization, which is initially liquid and finally vapor. The differential heat of vaporization is the enthalpy change occurring when a portion of the charge has been vaporized at constant temperature and pressure, forming a vapor phase of one composition and a liquid of another (overall composition of both phases is the same as the charge). The term differential implies the existence of two equilibrium phases at all times.

The following procedure is to be used to calculate these heats of vaporization. Vapor-liquid equilibrium data are required regardless of the latent heat change.

Procedure

Step 1: The feed composition ($x_{f_1}, x_{f_2}, \dots, x_{f_i}$, mole fraction) must be known for all three heats of vaporization. For integral heats of vaporization, go to Step 2, and for differential, go to Step 5.

Step 2: For integral isobaric conditions, the pressure, p , must be known, and for integral isothermal, the temperature, T . In either case, all the mole fractions of each component i are equal in both phases, $x_i = y_i = x_{f_i}$.

Step 3: For isobaric conditions, the dew- and bubble-point temperatures, T_{DP} and T_{BP} , must be known, and for isothermal conditions the pressures, p_{DP} and p_{BP} . If these are not known experimentally, they should be obtained by a trial-and-error procedure from Chapter 8. The dew-point temperature or pressure is that value for which the predicted equilibrium K -values are such that

$$\sum_{i=1}^n \frac{y_i}{K_i} = 1, \text{ and the bubble-point conditions are reached when } \sum_{i=1}^n K_i x_i = 1.$$

Step 4: Knowing the bubble-point and dew-point temperatures and pressures and the system composition, obtain the liquid and vapor enthalpies from Procedure 7B4.1. (Notice that Procedure 7B4.1 is written for weight fractions and gives enthalpy per pound of mixture.) The integral heat of vaporization is simply the difference between these values. If the feed stream is not at the bubble- or dew-point conditions, an additional temperature or pressure effect on enthalpy must be calculated using Procedure 7B4.1.

Step 5: To calculate differential heats of vaporization, the temperature and pressure must be known, as well as the feed composition. If the compositions of the equilibrium liquid and vapor phases (both different from the feed) are not known from another source, calculate them using the methods of Chapter 8. After obtaining equilibrium K -values at T and p , solve the following equations simultaneously for all the liquid mole fractions, x_i , the vapor mole fractions, y_i , the moles liquid per mole of feed, L , and the moles vapor per mole of feed, V :

$$\begin{aligned}\sum x_i &= 1 \\ \sum y_i &= 1 \\ y_i &= K_i x_i \\ x_{f_i} &= x_i L + y_i V\end{aligned}$$

Step 6: Knowing the temperature and pressure and all the phase compositions, obtain the liquid, vapor, and feed enthalpies from Procedure 7B4.1. (Notice that Procedure 7B4.1 is written for weight fractions and gives enthalpy per pound of mixture.) The differential heat of vaporization is then:

$$\lambda_{diff} = \frac{M_f}{M_v V} \left(\frac{M_L H_L L + M_V H_V V}{M_f} - H_f \right) \quad (7C2.1-1)$$

Where:

λ_{diff} = differential heat of vaporization, in Btu per lb vaporized.

M = average molecular weight of mixture, in lb per lb-mole.

H = mixture enthalpy from Procedure 7B4.1, in Btu per lb.

Subscripts f , V , and L = the feed stream, equilibrium vapor stream, and equilibrium liquid stream, respectively.

The heat necessary per pound of feed (rather than per pound vaporized) is $\frac{M_V V}{M_f} \lambda_{diff}$. The quantity λ_{diff} is the differential heat of vaporization only if the feed is saturated (i.e., at its dew- or bubble-point pressure according to whether it is a vapor or liquid). If the feed is not saturated, λ_{diff} is the sum of the differential heat of vaporization and the sensible heat to reach saturation.

COMMENTS ON PROCEDURE 7C2.1

Purpose

This procedure is to be used to estimate the heats of vaporization of hydrocarbon mixtures of defined composition under the various possible restraints in pressure, temperature, and composition. Use Procedure 7B4.2 for the heats of vaporization of petroleum fractions (undefined composition).

Limitations

This procedure depends upon a prior knowledge of the phase equilibria relationships, and it is difficult to predict these relationships reliably. The accuracy and usefulness of this method will decrease with increasing uncertainty in the equilibrium relationships.

Reliability

The overall reliability of this procedure must be estimated for the system at hand from the errors arising in the individual steps.

Special Comment

The results determined from this method are not necessarily thermodynamically consistent with the fugacities corresponding to the equilibrium K -values from Chapter 8.

Examples

A. Estimate the isobaric integral heat of vaporization of a 40 mole percent propene-60 mole percent 2-methylpropane mixture at 200 psia where the dew- and bubble-point temperatures are 150.8 F and 136.0 F, respectively.

Inasmuch as the process is a total (integral) vaporization, $x_1 = y_1 = x_{f_1}$ and $x_2 = y_2 = x_{f_2}$. The following tabulation of critical properties, molecular weights and the acentric factors was obtained from Chapter 1. The ideal gas enthalpies were obtained from Procedure 7A1.1:

	Mole Fraction	Temperature		Crit. Pres- sure, psia	Acentric Factor, ω	Mole- cular Wt., M	Wt. Fraction x_w	Ideal Gas Enthalpy H^0 Btu per lb	
		Deg F	Deg R					136.0 F	150.8 F
Propene	0.400	196.9	656.6	669.0	0.1424	42.08	0.326	160.99	166.92
2-Methylpropane	0.600	275.0	734.7	529.1	0.1770	58.12	0.674	157.74	164.27
Molar average	—	—	703.5	585.1	0.1632	51.70	—	—	—
Weight average	—	—	—	—	—	—	1.00	158.80	165.13

For both phases, the reduced pressure is $\frac{200.0}{585.1} = 0.342$. The vapor and liquid enthalpies are calculated according to Procedure 7B4.1:

Temp. Deg F	Reduced Temp.	$\left(\frac{\tilde{H}^0 - \tilde{H}}{RT_c}\right)^{(0)}$	$\left(\frac{\tilde{H}^0 - \tilde{H}}{RT_c}\right)^{(1)}$	$\left(\frac{\tilde{H}^0 - \tilde{H}}{RT_c}\right)$	$H^0 - H$	H^0	H
Liquid 136.0	0.847	4.320	4.906	5.102	137.93	158.80	20.87
Vapor 150.8	0.868	0.508	0.392	0.659	17.86	165.13	147.27

The integral heat of vaporization is $14.27 - 20.87 = 126.4$

B. Estimate the differential heat of vaporization of a 50 mole percent propene-50 mole percent 2-methylpropane mixture initially at its bubble point of 128.2 F and 200 psia. The product vapor and liquid phases are withdrawn at 137.0 F and 200 psia, with the equilibrium vapor containing 60.0 mole percent propene and the liquid containing 38.8 mole percent propene.

Steps 5 and 6 of the procedure should be used. A material balance determines values for L and V .

$$\begin{aligned} \text{For propene, } 0.50 &= 0.388 L + 0.600 V \\ \text{For 2-methylpropane, } 0.50 &= 0.612 L + 0.400 V \\ \text{Solving simultaneously, } L &= 0.472 \text{ and } V = 0.528 \end{aligned}$$

PROCEDURE 7D1.9

ALTERNATE (COMPUTER) METHOD FOR LIQUID HEAT CAPACITIES OF PURE HYDROCARBONS BELOW THE NORMAL BOILING POINT

Discussion

The following equations are to be used for calculating the isobaric heat capacities of pure hydrocarbon liquids by means of a digital computer. These equations are to be applied only below the normal boiling point. For higher temperatures, use Procedure 7D1.10.

For normal alkanes with five or more carbon atoms, and for the homologous series of isoalkanes, 1-alkenes and the *n*-alkylcyclohexanes, use:

$$C_p = a + bT_{rb} + cT_{rb}^2 + dT_{rb}^3 + n[\Delta a + \Delta bT_{rb} + \Delta cT_{rb}^2 + \Delta dT_{rb}^3] \quad (7D1.9-1)$$

Where:

C_p = isobaric heat capacity, in Btu per (lb) (deg R).

T_{rb} = T/T_b .

T = temperature at which the heat capacity is desired, in degrees Rankine.

T_b = normal boiling point, in degrees Rankine.

$a, b, c, d, \Delta a, \Delta b, \Delta c$ and Δd are constants, different for each homologous series, as tabulated below.

n = number of carbon atoms in the hydrocarbon for which C_p is to be calculated.

Constants for use with equation (7D1.9-1):

Constants	<i>n</i> -Alkanes	Isoalkanes	1-Alkenes	<i>n</i> -Alkyl cyclohexanes
a	0.84167	-0.03083	0.14510	0.26796
b	-1.47040	1.77589	1.26233	0.04311
c	1.67165	-2.50661	-2.03775	-0.06164
d	-0.59198	1.20202	1.06953	0.0
Δa	-0.003826	0.079670	0.067176	0.004331
Δb	-0.000747	-0.335664	-0.304272	-0.003439
Δc	0.041126	0.499756	0.478026	0.039338
Δd	-0.013950	-0.221740	-0.221610	0.0

For the homologous series *n*-alkylbenzenes and for the light alkanes methane through butane use:

$$C_p = (a_1 + b_1 T_{rb} + c_1 T_{rb}^2 + d_1 T_{rb}^3)^{\left(\frac{n_2 - n}{n_2 - n_1}\right)} \cdot (a_2 + b_2 T_{rb} + c_2 T_{rb}^2 + d_2 T_{rb}^3)^{\left(\frac{n - n_1}{n_2 - n_1}\right)} \quad (7D1.9-2)$$

Where:

C_p = isobaric heat capacity, in Btu per (lb) (deg R) for all aromatics; in Btu per (lb-mole) (deg R) for the light alkanes.

T_{rb} = T/T_b , same as in equation (7D1.9-1).

$a_1, b_1, c_1, d_1, a_2, c_2, d_2, n_1$ and n_2 are constants as tabulated below.

n = number of carbon atoms in the hydrocarbon for which C_p is to be calculated.

Constants for use with equation (7D1.9-2):

Constant	Light Alkanes	<i>n</i> -Alkyl-benzenes
a_1	14.7486	0.55158
b_1	-9.8198	-1.12912
c_1	12.9505	2.00806
d_1	-4.8349	-0.91821
a_2	13.1830	0.53865
b_2	54.3924	-1.11510
c_2	-72.8410	2.12851
d_2	37.1562	-1.01959
n_1	1	9
n_2	4	10

For the *n*-alkylcyclopentanes use:

$$C_p = (a_1 + b_1 T_{rb} + c_1 T_{rb}^2 + d_1 T_{rb}^3) \left(\frac{\ln n/8}{\ln 5/8} \right) + (a_2 + b_2 T_{rb} + c_2 T_{rb}^2 + d_2 T_{rb}^3) \left(\frac{\ln 5/n}{\ln 5/8} \right) \quad (7D1.9-3)$$

Where:

C_p = isobaric heat capacity, in Btu per (lb) (deg R).

T_{rb} = T/T_b , same as in equation (7D1.9-1).

n = number of carbon atoms in the hydrocarbon for which C_p is to be calculated.

$a_1, b_1, c_1, d_1, a_2, b_2, c_2, d_2$ are constants as tabulated below.

Constants for use with equation (7D1.9-3):

Constant	<i>n</i> -Alkyl cyclopentanes
a_1	0.32010
b_1	-0.01800
c_1	0.03292
d_1	0.12834
a_2	0.44974
b_2	-0.53041
c_2	0.96861
d_2	-0.31487

For the individual hydrocarbons ethene, propene, 1-butene and isobutane use:

$$C_p = a + bT_{rb} + cT_{rb}^2 + dT_{rb}^3 \quad (7D1.9-4)$$

Where:

C_p = isobaric heat capacity, in Btu per (lb) (deg R).

T_{rb} = T/T_b , same as in equation (7D1.9-1)

a, b, c , and d are constants, tabulated below.

Constants for use with equation (7D1.9-4):

Hydrocarbon	Ethene	Propene	1-Butene	Isobutane
a	0.71418	0.64766	0.63192	0.32575
b	-0.29525	-0.43638	-0.46311	0.22823
c	0.15407	0.31228	0.33869	-0.14714
d	—	—	—	0.12786

For all isomeric paraffins, use equation (7D1.9-1) with the isoalkane constants (except isobutane, where equation (7D1.9-4) is to be used).

For all olefins (except ethene, propene, and 1-butene), use equation (7D1.9-1) with the 1-alkene constants.

For all naphthenes (except cyclopentane), and all alkylcyclohexanes, use equation (7D1.9-1) with the *n*-alkylcyclohexane constants.

For all aromatics, use equation (7D1.9-2) with the *n*-alkylbenzene constants.

For cyclopentane and all alkylcyclopentanes, use equation (7D1.9-3) with the *n*-alkylcyclopentane constants.

Procedure

Step 1: Obtain the normal boiling point for the desired hydrocarbon from Chapter 1. Also evaluate the number of carbon atoms where applicable.

Step 2: Decide upon the suitable equation and the suitable set of constants, consistent with the classifications given in the procedure.

Step 3: Calculate the reduced normal boiling point and evaluate the isobaric heat capacity with the appropriate equation from among equations (7D1.9-1) through (7D1.9-4).

COMMENTS ON PROCEDURE 7D1.9

Purpose

This procedure is to be used for computer calculations of isobaric heat capacities of pure hydrocarbon liquids at temperatures less than the normal boiling point. For computer calculations at high temperatures, use Procedure 7D1.6.

Limitations

The procedure gives isobaric heat capacities. However, inasmuch as it applies only to temperatures below the normal boiling point, the predicted values are identical to saturated liquid heat capacities within the limits required for engineering design.

Reliability

Differences between experimental and predicted values of heat capacities average 2 percent. Maximum errors of 20 percent can occur.

Special Comments

Procedure 7D1.6 may be used as an alternate to Procedure 7D1.9 for reduced temperatures 0.45 and above. However, Procedure 7D1.6 requires both the temperature and pressure as input quantities. The vapor pressure may be calculated by the methods of Chapter 5.

Literature Source

Equations (7D1.9-1) through (7D1.9-4), along with the tables of constants, were developed by Hadden, *J. Chem. Eng. Data* **15** 92 (1970).

PROCEDURE 7D1.10

ALTERNATE (COMPUTER) METHOD FOR LIQUID HEAT CAPACITIES OF PURE HYDROCARBONS ABOVE THE NORMAL BOILING POINT

Discussion

For computer calculations of the isobaric heat capacities of pure liquid hydrocarbons at or above the normal boiling point, equations (7D3.10-1) through (7D3.10-5) should be used. For temperatures below the normal boiling point, better accuracy can be obtained with Procedure 7D1.9.

Procedure

Follow Steps 1 through 8 of Procedure 7D3.6. In Step 3, obtain the root for the liquid volume from Procedure 6B1.8.

COMMENTS ON PROCEDURE 7D1.10

Purpose

This procedure is to be used for computer calculations of the isobaric heat capacity of pure hydrocarbon liquids at temperatures at or above the normal boiling point. For temperatures below the normal boiling point, Procedure 7D1.9 is recommended.

Limitations

The procedure applies to the isobaric heat capacity of the liquid. At the temperatures of applicability, the isobaric and saturated heat capacities may differ appreciably. (See Special Comments.)

Reliability

Above a reduced temperature of 0.45 the average error by this method is less than 3 percent. Errors seldom exceed 5 percent though errors up to 15 percent may occur. Reliability decreases rapidly as the critical temperature is approached. The error also increases with increasing inaccuracies in the input critical properties and acentric factor.

This procedure may be used below a reduced temperature of 0.45. Errors in these cases, however, are considerably larger and Procedure 7D1.9 is recommended.

Special Comments

The procedure requires both the temperature and the pressure as input quantities. However, if only the temperature is available, and the saturated liquid heat capacity is desired, obtain the vapor pressure from Chapter 5 and proceed as if both temperature and pressure were available.

This procedure may be used instead of Procedure 7D1.9 for temperatures below the normal boiling point. However, large errors may occur at reduced temperatures less than 0.45.

Literature Source

The equations to be used in this procedure were developed by Lee and Kesler, *AICHE Journal* 21 510 (1975).

PROCEDURE 7D2.1**LIQUID HEAT CAPACITY OF DEFINED HYDROCARBON MIXTURES****Discussion**

The following equation is to be used to estimate the heat capacity of liquid hydrocarbon mixtures when the composition is known:

$$C = \sum_{i=1}^n x_{wi} C_i \quad (7D2.1-1)$$

Where:

C = isobaric or saturated (consistent throughout the equation) liquid heat capacity at the operating conditions, in Btu per (lb) (deg R). Subscript i indicates a pure component in the n component mixture.

x_{wi} = weight fraction of component i .

Procedure

Step 1: Obtain liquid heat capacities of all the components at the desired conditions from Figure 7D1.3 or Procedure 7D1.4, depending on the temperature.

Step 2: Combine the heat capacities with equation (7D2.1-1).

COMMENTS ON PROCEDURE 7D2.1

Purpose

This procedure is to be used to estimate the heat capacities of liquid hydrocarbon mixtures when the composition is known. For petroleum fractions (undefined composition), use Figure 7D2.2. The input heat capacities for the pure substances may be obtained from Figure 7D1.3 or Procedure 7D1.4.

Limitations

In this procedure, the heat of mixing is assumed to be zero, which is valid only for mixtures of neighboring members of a homologous series. Although acceptable within the limits required for engineering design for most hydrocarbon mixtures, it should be used cautiously for blends having appreciable amounts of two or more different hydrocarbon families.

Equation (7D2.1-1) is strictly applicable only to isobaric heat capacities where all the component quantities are for identical pressure and temperature conditions. The equation may also be used for saturated heat capacities, provided the (vapor) pressures of the components do not differ appreciably (i.e., at low temperatures or, if the temperature is high, for substances which are approximately equivalent in volatility).

The procedure is not to be used at reduced temperatures greater than 0.95, where no existing method is reliable for the liquid phase.

Reliability

The reliability of this procedure depends entirely on the system and composition under consideration. The predicted heat capacities are usually too large by an approximate average of 5 percent. The deviations are largest at the midpoints of composition where, for example, the procedure is in error by 17 percent for the system benzene-diphenylmethane. The procedure works well (approximately 3-percent error) for the benzene-cyclohexane and cyclopentane-2,2-dimethylbutane systems.

Special Comment

Avoid using heat capacities in calculations for which enthalpies can be used instead, except when the enthalpy differences are very small.

Example

Estimate the heat capacity of a mixture of 55.2 mole percent benzene and 44.8 mole percent cyclohexane at 72.1 F and atmospheric pressure.

From Figure 7D1.3, for benzene, $C_p1 = 0.396$ Btu per (lb) (deg R), and, for cyclohexane $C_p2 = 0.432$ Btu per (lb) (deg R).

From Chapter 1, the molecular weights are, for benzene, $M_1 = 78.11$, and, for cyclohexane $M_2 = 84.16$. The weight fraction of benzene is:

$$x_{w1} = \frac{(78.11)(0.552)}{(78.11)(0.552) + (84.16)(0.448)} = 0.534$$

thus,

$$x_{w2} = 0.466$$

The mixture heat capacity is calculated using equation (7D2.1-1):

$$C_p = (0.534)(0.396) + (0.466)(0.432) = 0.412 \text{ Btu per (lb) (deg R)}$$

An experimental value is 0.422 Btu per (lb) (deg R).

PROCEDURE 7D2.2

7D2.2

ISOBARIC HEAT CAPACITY OF PETROLEUM FRACTION LIQUIDS

Discussion

The isobaric heat capacity of a liquid petroleum fraction may be estimated using this procedure.

for $T_r \leq 0.85$,

$$C_p = A_1 + A_2 T + A_3 T^2 \quad (7D2.2-1)$$

Where:

C_p = isobaric heat capacity for liquid petroleum fraction in Btu per (lb) (deg R)

$$A_1 = -1.17126 + (0.023722 + 0.024907 \text{ sp gr})K + \frac{(1.14982 - 0.046535 K)}{\text{sp gr}}$$

$$A_2 = (10^{-4})(1.0 + 0.82463 K) \left(1.12172 - \frac{0.27634}{\text{sp gr}} \right).$$

$$A_3 = (-10^{-8})(1.0 + 0.82463 K) \left(2.9027 - \frac{0.70958}{\text{sp gr}} \right).$$

T_r = reduced temperature, T/T_{pc} .

T = temperature in degrees Rankine.

T_{pc} = pseudocritical temperature in degrees Rankine.

K = Watson characterization factor.

sp gr = specific gravity 60 F/60 F.

Procedure

Step 1: Using the available inspection data for the fraction, determine the characterization factor with the methods of Chapter 2.

Step 2: Calculate the pseudocritical temperature using the methods in Chapter 4.

Step 3: Calculate the reduced temperature.

Step 4: Use equation (7D2.2-1) to calculate the heat capacity.

COMMENTS ON PROCEDURE 7D2.2**Purpose**

This procedure is to be used to estimate the isobaric heat capacities of petroleum fraction liquids. For mixtures of defined composition, use Procedure 7D2.1, and for pure hydrocarbons, Figure 7D1.3 or Procedure 7D1.4.

Limitations

This method is not reliable above a reduced temperature of 0.85.

Reliability

This procedure was tested for 135 points of data with reduced temperatures less than 0.85 with an average absolute deviation and average absolute deviation of 0.01 Btu per (lb) (deg R) and 1.7% respectively. The procedure is most accurate when the reduced temperature is less than 0.6 with the error increasing as temperature increases. The procedure is thermodynamically consistent with the (accurate) primary methods for calculating enthalpies for petroleum fractions.

Special Comments

If a molecular type analysis is available for the fraction, the pseudocritical method of Huang and Daubert, *Ind. Eng. Chem. Proc. Des. and Develop.* 13 359 (1974), is recommended over Procedure 7D2.2.

This method is consistent with Procedures 7B4.2 and 7B4.7.

Literature Source

Private communication, B. I. Lee and M. G. Kesler, Mobil Oil Corp., Princeton, NJ (January, 1975).

Example

Estimate the heat capacity at atmospheric pressure and 325 F of a straight run petroleum fraction having an API gravity of 44.4 and the following ASTM D86 distillation properties:

Distillation, percent by volume	10	30	50	70	90
Temperature, deg F	304	313	321	329	341

The volumetric average boiling point is 321.6 F. From Chapter 6, the specific gravity is 0.8044 which gives a characterization parameter of 11.45.

From Chapter 2, the mean average boiling point is 319 F, and from Chapter 4, the pseudocritical temperature is 670 deg F. The reduced temperature is 0.694. Since $T_r < 0.85$, equation (7D2.2-1) is applicable.

$$A_1 = -1.17126 + (0.023722 + 0.024907 (0.8044)) (11.45) + \frac{(1.14982 - 0.046535 (11.45))}{0.8044} = 0.09678 .$$

$$A_2 = (10^{-4}) (1.0 + 0.82463 (11.45)) \left(1.12172 - \frac{0.27634}{0.8044} \right) = 8.1258 \times 10^{-4} .$$

$$A_3 = (-10^{-8}) (1.0 + 0.82463 (11.45)) \left(2.9027 - \frac{0.70958}{0.8044} \right) = -2.1099 \times 10^{-7} .$$

$$C_p = (0.09678) + (8.1258 \times 10^{-4}) (325. + 459.7) + (-2.1099 \times 10^{-7}) (325. + 459.7)^2 .$$

$$C_p = 0.6045 \text{ Btu per (lb)(deg R)} .$$

PROCEDURE 7D3.1**ISOBARIC HEAT CAPACITY OF PURE HYDROCARBON REAL GASES AND LIQUIDS****Discussion**

The following equation is to be used to predict the effect of pressure on the isobaric heat capacity of pure hydrocarbons:

$$\left(\frac{\tilde{C}_p^0 - \tilde{C}_p}{R}\right) = \left(\frac{\tilde{C}_p^0 - \tilde{C}_p}{R}\right)^{(0)} + \omega \left(\frac{\tilde{C}_p^0 - \tilde{C}_p}{R}\right)^{(1)} \quad (7D3.1-1)$$

Where:

$\left(\frac{\tilde{C}_p^0 - \tilde{C}_p}{R}\right)$ = the dimensionless effect of pressure on isobaric heat capacity.

$\left(\frac{\tilde{C}_p^0 - \tilde{C}_p}{R}\right)^{(0)}$ = effect of pressure on isobaric heat capacity for the simple fluid, which is tabulated as a function of T_r and p_r in Table 7D3.2 and is plotted in Figure 7D3.4.

$\left(\frac{\tilde{C}_p^0 - \tilde{C}_p}{R}\right)^{(1)}$ = correction term for molecular acentricity, which is tabulated as a function of T_r and p_r in Table 7D3.3 and is plotted in Figure 7D3.5.

T_r = reduced temperature, T/T_c .

T = temperature, in degrees Rankine.

T_c = critical temperature, in degrees Rankine.

p_r = reduced pressure, p/p_c .

p = pressure, in psia.

p_c = critical pressure, in psia.

ω = acentric factor.

The dimensionless pressure effect term is used in the following equation to determine the actual heat capacity of the real gas:

$$C_p = C_p^0 - \frac{R}{M} \left(\frac{\tilde{C}_p^0 - \tilde{C}_p}{R}\right) \quad (7D3.1-2)$$

Where:

C_p = isobaric heat capacity of the real gas, in Btu per (lb) (deg R). \tilde{C}_p is the analogous molar quantity.

C_p^0 = isobaric heat capacity of the ideal gas, in Btu per (lb) (deg R). \tilde{C}_p^0 is the analogous molar quantity.

R = gas constant = 1.986 Btu per (lb-mole) (deg R).

M = molecular weight, lb per lb-mole.

Procedure

Step 1: Obtain the molecular weight, critical temperature, critical pressure, and the acentric factor from Chapter 1.

Step 2: Calculate the reduced temperature and pressure at which a heat capacity is desired.

Step 3: Obtain the correlation terms $\left(\frac{\tilde{C}_p^0 - \tilde{C}_p}{R}\right)^{(0)}$ and $\left(\frac{\tilde{C}_p^0 - \tilde{C}_p}{R}\right)^{(1)}$. If the most accurate values are desired, use Table 7D3.2 and 7D3.3 with linear double interpolation in p_r and T_r . When near saturation, the interpolation procedure may not be satisfactory (see Special Comments). If slightly less accurate values are acceptable, they may be obtained rapidly from Figures 7D3.4 and 7D3.5.

Step 4: Calculate the dimensionless pressure effect term using equation (7D3.1-1).

Step 5: Obtain the ideal gas heat capacity from Procedure 7A1.1.

Step 6: Calculate the heat capacity of the real gas using equation (7D3.1-2).

COMMENTS ON PROCEDURE 7D3.1

Purpose

This procedure is to be used to predict isobaric heat capacities of pure hydrocarbons in the real gas state. Tables 7D3.2 and 7D3.3 or Figures 7D3.4 and 7D3.5 are required in this procedure. The procedure is best suited to desk calculations. Procedure 7D3.6 should be used for computer calculations. Ideal gas heat capacities from Procedure 7A1.1 are required in either case. Mixtures are treated in Section 7D4.

Equations (7D3.1-1) and (7D3.1-2) are also used in Procedure 7D1.4 to predict heat capacities of liquids at high temperatures.

Limitations

In general, this procedure is not accurate for polar substances.

Reliability

Differences between calculated and experimental pressure effects on heat capacity rarely exceed 0.05 Btu per (lb) (deg F) except in the critical region, where 0.3 Btu per (lb) (deg F) or even more can occur. The error of the method increases with increasing uncertainty in the pure-component critical properties.

Notation

The notation used in Tables 7D3.2 and 7D3.3 and Figures 7D3.4 and 7D3.5 was defined for equations (7D3.1-1) and (7D3.1-2).

Special Comments

The broken lines in Tables 7D3.2 and 7D3.3 indicate the discontinuity between liquid (to the right and above) and vapor (to the left and below) heat capacities. Interpolations cannot be made across this line; always use table values which apply to the vapor phase only. Near the broken lines the extrapolations that are necessary should be made with respect to reduced pressure at constant reduced temperature.

For saturated vapors (i.e., at their vapor pressures), do not use the two-phase border outlined in Figure 7D3.4. This border applies only when the acentric factor is zero, and, as acentricity increases, the reduced vapor pressure decreases at constant reduced temperature. The best procedure is to obtain the vapor pressure from Chapter 5 and proceed as if the phase were homogeneous.

In regions of very rapid change of the simple fluid and correction terms with reduced pressure and/or temperature, a linear interpolation from the tables may not be satisfactory even though the table values are spaced more closely. Here, the figures should be used either directly or as a guide for interpolation corrections to the results from the tables.

The figures may be extrapolated to lower reduced pressures by noting that $\left(\frac{\tilde{C}_p^0 - \tilde{C}_p}{R}\right)^{(0)}$ and

$\left(\frac{\tilde{C}_p^0 - \tilde{C}_p}{R}\right)^{(1)}$ approach zero as the pressure approaches zero. In many engineering applications, these limiting values may be used for all reduced pressures between 0 and 0.2. If even more precise results than the extrapolated values are desired (rarely), use the following equation:

$$\left(\frac{\tilde{C}_p^0 - \tilde{C}_p}{R}\right) = -p_r [(0.660 - 0.92\omega)T_r^{-2} + (0.831 + 3.0\omega)T_r^{-3} + (0.145 + 1.16\omega)T_r^{-4} + 0.526\omega T_r^{-9}] \quad (7D3.1-3)$$

Literature Sources

Tables 7D3.2 and 7D3.3 were generated using the generalized correlation developed by Lee and Kesler, *AIChE Journal* **21** 510 (1975). Figures 7D3.4 and 7D3.5 are direct plots of these tables. Equation (7D3.1-3) was developed by Pitzer and Curl, *J. Am. Chem. Soc.* **79** 2369 (1957).

T_r = reduced temperature, T/T_c .

T = temperature, in degrees Rankine.

T_c = critical temperature of the fluid whose heat capacity is desired, in deg R.

$V_r = p_c V / RT_c$, is obtained from Procedure 6B1.8.

$$B = b_1 - b_2/T_r - b_3/T_r^2 - b_4/T_r^3.$$

$$C = c_1 - c_2/T_r + c_3/T_r^3.$$

$$D = d_1 + d_2/T_r.$$

$b_1, b_2, b_3, b_4, c_1, c_2, c_3, d_1, d_2, c_4, \gamma$ and β are two sets of constants, one for the simple fluid and another for the heavy reference fluid. The values of the constants are given in Procedure 6B1.8.

With the dimensionless effect of pressure on the isobaric heat capacity from equation (7D3.6-1), the total heat capacity may be found from the following equation:

$$C_p = C_p^0 - \frac{R}{M} \left(\frac{\tilde{C}_p^0 - \tilde{C}_p}{R} \right) \quad (7D3.6-5)$$

Where:

C_p = isobaric heat capacity of the real gas, in Btu per (lb) (deg R). \tilde{C}_p is the analogous molar quantity.

C_p^0 = isobaric heat capacity of the ideal gas, in Btu per (lb) (deg R). \tilde{C}_p^0 is the analogous molar quantity.

R = gas constant = 1.986 Btu per (lb-mole) (deg R).

M = molecular weight, in lb per lb-mole.

Procedure

Step 1: Obtain the critical temperature, critical pressure, the molecular weight and the acentric factor from Chapter 1.

Step 2: Calculate the reduced temperature and reduced pressure at which the heat capacity is desired.

Step 3: Use Procedure 6B1.8 to obtain the value of $V_r = p_c V / RT_c$ for the simple fluid. Retain T_r, V_r and all the constants for the simple fluid.

Step 4: Use equations (7D3.6-3) and (7D3.6-4) to evaluate $(\partial p_r / \partial T_r)V_r$ and $(\partial p_r / \partial V_r)_{T_r}$ for the simple fluid.

Step 5: Use Procedure 7E1.6 to obtain $\left(\frac{\Delta \tilde{C}_v}{R} \right)^{(0)}$, the isochoric heat capacity departure for the simple fluid.

Step 6: Use equation (7D3.6-2) to evaluate $\left(\frac{\tilde{C}_p^0 - \tilde{C}_p}{R} \right)^{(0)}$, the dimensionless effect of pressure on the isobaric heat capacity of the simple fluid.

Step 7: Repeat Steps 3 through 6 for the heavy reference fluid, to obtain $\left(\frac{\tilde{C}_p^0 - \tilde{C}_p}{R} \right)^{(h)}$.

Step 8: Combine $\left(\frac{\tilde{C}_p^0 - \tilde{C}_p}{R} \right)^{(0)}$ and $\left(\frac{\tilde{C}_p^0 - \tilde{C}_p}{R} \right)^{(h)}$ according to equation (7D3.6-1) to obtain the dimensionless effect of pressure on the isobaric heat capacity of the gas under consideration.

Step 9: Obtain C_p^0 , the ideal gas heat capacity from Procedure 7A1.1, and combined with equation (7D3.6-5) to get the isobaric heat capacity.

COMMENTS ON PROCEDURE 7D3.6**Purpose**

The procedure is presented for computer calculations of the isobaric heat capacities of pure hydrocarbon gases. The results from Procedures 6B1.8 and 7E1.6 are directly needed in this procedure. The results from Procedure 7A1.1 are also indirectly used. The isobaric heat capacities of mixed gases are treated in Section 7D4.

Limitations

This procedure is mainly intended for use with hydrocarbons. Large errors might occur when used with polar gases.

Reliability

Differences between the calculated and experimental pressure effect on heat capacity rarely exceed 0.03 Btu per (lb) (deg F) except in the critical region where 0.2 Btu per (lb) (deg F) errors could be expected and errors of 2 Btu per (lb) (deg F) or more can occur. The reliability of the method decreases with increasing uncertainties in the critical properties. The equations are recommended for reduced pressures up to 10. However, they may be used up to reduced pressures of 20 or more with only a slight increase in error.

Special Comments

For saturated vapors, use both temperature and pressure as input (with the vapor pressure predictions from Chapter 5 when necessary) and perform all calculations as if the point were in the homogeneous region.

Literature Source

The equations in this procedure were developed by Lee and Kesler, *AICHE Journal* 21 510 (1975).

PROCEDURE 7D4.1**ISOBARIC HEAT CAPACITY OF HYDROCARBON GAS MIXTURES****Discussion**

The tables and figures of Procedure 7D3.1 are to be applied to hydrocarbon mixtures by using the pseudocritical temperature and pressure to calculate reduced conditions instead of the true critical temperature and pressure. The pseudocritical properties, which are approximated as the molar averages of the component true critical properties, are given in Chapter 4 for mixtures of defined and undefined composition and blends of the two. The mixture acentric factor, which is defined as the molar average of the component acentric factors, may be estimated for undefined mixtures from Chapter 2. These approximations are summarized below:

$$T_{pc} = \sum_{i=1}^n x_i T_{ci} \quad (7D4.1-1)$$

Where:

T_{pc} = pseudocritical temperature, in degrees Rankine.

T_{ci} = critical temperature of component i , in degrees Rankine.

n = number of components in the mixture.

x_i = mole fraction of component i .

$$p_{pc} = \sum_{i=1}^n x_i p_{ci} \quad (7D4.1-2)$$

Where:

p_{pc} = pseudocritical pressure, in psia.

p_{ci} = critical pressure of component i , in psia.

$$\omega = \sum_{i=1}^n x_i \omega_i \quad (7D4.1-3)$$

Where:

ω = mixture acentric factor.

ω_i = acentric factor of component i .

The results from these equations are used to calculate the reduced conditions so that Procedure 7D3.1 may be used to calculate the effect of pressure on the mixture heat capacity. This pressure correction is then subtracted from the ideal gas heat capacity of the mixture, which is defined as:

$$C_p^0 = \sum_{i=1}^n x_{wi} C_{pi}^0 \quad (7D4.1-4)$$

Where:

C_p^0 = ideal gas heat capacity, in Btu per (lb) (deg R). The subscript i refers to component i in the n component mixture.

x_{wi} = weight fraction of component i .

Procedure

Step 1: For mixtures of known composition, obtain the molecular weights, the critical pressures and temperatures, and the acentric factors for all of the components from Chapter 1.

(For hydrogen, use $T_c = 75$ R, $p_c = 305$ psia, and $\omega = 0$.)

Step 2: Calculate the pseudocritical temperature and pressure using equations (7D4.1-1) and (7D4.1-2), and the mixture acentric factor using equation (7D4.1-3). (For blends of petroleum fractions with mixtures of known composition, obtain the pseudocritical conditions from Chapter 4 and the acentric factor for the petroleum fraction portion from Chapter 2. Complete the acentric factor calculation using equation (7D4.1-3)).

Calculate the reduced temperature and pressure.

Step 3: Calculate the ideal gas isobaric heat capacity of the mixture using equation (7D4.1-4). Input heat capacities for pure hydrocarbons are to be taken from Procedure 7A1.1. (For blends of hydrocarbons with petroleum fractions, obtain the ideal gas heat capacity of the petroleum fraction portion from Figure 7D4.2). Calculate the molecular weight of the mixture (with input for the petroleum fraction portion, if present, from Chapter 2).

Step 4: Calculate the effect of pressure on heat capacity using Steps 3 and 4 of Procedure 7D3.1, and the total mixture heat capacity using Step 6 of the same procedure.

COMMENTS ON PROCEDURE 7D4.1

Purpose

This procedure is to be used with Procedure 7D3.1 to estimate the heat capacities of mixtures of hydrocarbons which may contain nonpolar nonhydrocarbon substances. Mixtures of known composition and blends of known compounds with petroleum fractions are treated. For petroleum fractions alone, use Figure 7D4.2.

Limitations

In general, the method is not applicable to mixtures containing polar components.

Reliability

Differences between calculated and experimental pressure effects on heat capacity are estimated to average 0.05 Btu per (lb) (deg F) except in the critical region, where 0.3 Btu per (lb) (deg F) errors should be expected and errors of 5 Btu per (lb) (deg F) or more can occur. The region of maximum uncertainty is the same as that indicated in Figure 7D3.4.

The reliability of the modification for mixtures of undefined composition is unknown.

Special Comments

For hydrocarbon-hydrocarbon mixtures which do not contain methane, slightly better results are obtained in the immediate critical region using true rather than pseudocritical temperatures and pressures. This region is defined approximately by the following pseudoreduced condition boundaries: $1.0 < T_r < 1.2$ and $1.0 < p_r < 3.0$. True critical conditions are correlated in Chapter 4. Notice that the liquid phase can exist in this region even though the pseudoreduced temperature is greater than unity (see Introduction).

For supercritical temperatures ($T_r > 1$) and high pressures ($p_r > 5$), the error can be reduced using the following mixture correspondence pressure instead of the pseudocritical pressure defined by equation (7E4.1-2):

$$p_{mc} = \frac{RT_{pc} \sum_{i=1}^n x_i z_{ci}}{\sum_{i=1}^n x_i V_{ci} M_i} \quad (7D4.1-5)$$

Where:

p_{mc} = mixture correspondence pressure, in psia.

R = gas constant = 10.731 (psia) (cu ft) per (lb-mole) (deg R).

z_{ci} = critical compressibility factor of component i (from Chapter 2).

V_{ci} = critical volume of component i (from Chapter 1) in cubic feet per pound.

M_i = molecular weight of component i (from Chapter 1), in lb per lb-mole.

More reliable pressure effects on heat capacity can be obtained under most temperature-pressure conditions using the mixture correspondence rules of Joffe (35), Stewart, et al. (71), Lee and Kesler (42), or Leland and Mueller (44). However, the small advantage in accuracy does not justify the added labor involved in using these methods.

For computer heat capacity calculations, Procedure 7D3.6 may be adapted to mixtures using the mixture correspondence point as described (for gas densities) in Procedure 6B2.2. Mixtures of known composition, petroleum fractions, and blends of the two may be treated. The reliability for mixtures of known composition is approximately the same as quoted previously. For petroleum fractions, obtain the necessary ideal gas heat capacities from Figure 7D4.2.

Literature Sources

Equations (7D4.1-1) and (7D4.1-2) were given by Kay, *Ind. Eng. Chem.* **28** 1014 (1936).

Equation (7D4.1-5) was developed by Prausnitz and Gunn, *AIChE Journal* **4** 430 (1958).

PROCEDURE 7D4.2**ISOBARIC HEAT CAPACITY OF PETROLEUM FRACTION VAPORS****Discussion**

The isobaric heat capacity of a vapor phase petroleum fraction may be estimated using this procedure. This method is suitable for both desk and digital computer calculations. The equation is:

$$C_p = A_1 + A_2 T + A_3 T^2 - \frac{R}{M} \left(\frac{\tilde{C}_p^0 - \tilde{C}_p}{R} \right) \quad (7D4.2-1)$$

Where:

C_p = isobaric heat capacity for vapor phase petroleum fraction in Btu per (lb) (deg R).

$$A_1 = -0.35644 + 0.02972 K + A_4 (0.29502 - 0.24846 / sp gr).$$

$$A_2 = -(10^{-4}) \left[2.9247 - (1.5524 - 0.05543 K) K + A_4 \left(6.0283 - \frac{5.0694}{sp gr} \right) \right]$$

$$A_3 = -(10^{-7}) (1.6946 + 0.0844 A_4).$$

$$A_4 = \left[\left(\frac{12.8}{K} - 1.0 \right) \left(1.0 - \frac{10.0}{K} \right) (sp gr - 0.885) (sp gr - 0.70) (10^4) \right]^2 \text{ for}$$

$$10.0 < K < 12.8 \text{ with } 0.70 < sp gr < 0.885.$$

$$A_4 = 0.0 \text{ for all other cases.}$$

T = temperature in degrees Rankine.

K = Watson characterization factor.

R = gas constant = 1.986 Btu per (lb-mole) (deg R).

M = molecular weight, in lb per lb-mole.

$\left(\frac{\tilde{C}_p^0 - \tilde{C}_p}{R} \right)$ = dimensionless effect of pressure on isobaric heat capacity, obtained from Procedure 7D3.1.

Procedure

Step 1: Using the available inspection data for the fraction, determine the Watson characterization factor, K , with the methods of Chapter 2.

Step 2: Calculate the pseudocritical temperature and pressure for the fraction using the methods of Chapter 4.

Step 3: Use the methods of Chapter 2 to determine the molecular weight and acentric factor for the fraction.

Step 4: Calculate the reduced temperature and pressure.

Step 5: Use Procedure 7D3.1 to calculate the heat capacity pressure effect term, $\left(\frac{\tilde{C}_p^0 - \tilde{C}_p}{R} \right)$.

Step 6: Calculate the desired heat capacity using equation (7D4.2-1).

COMMENTS ON PROCEDURE 7D4.2

Purpose

This procedure is to be used to estimate the isobaric heat capacities of petroleum fraction vapors. This method is suitable for desk and digital computer calculations. For mixtures of defined composition, use Procedure 7D4.1.

Limitations

This method is not reliable in the immediate critical region.

Reliability

This procedure has not been tested with experimental data, but is thermodynamically consistent with the (accurate) primary methods for calculating enthalpies for petroleum fractions.

Special Comments

If a molecular type analysis is available for the fraction, the pseudocompound method of Huang and Daubert *Ind. Eng. Chem. Proc. Des. and Develop.* 13 359 (1974), is recommended over Procedure 7D4.2.

This method is consistent with Procedures 7B4.2 and 7B4.7.

Literature Source

Private communication, B. I. Lee and M. G. Kesler, Mobil Oil Corp., Princeton, N.J. (January 1975).

Example

Estimate the heat capacity at 885 F and 205 psia of a straight run petroleum fraction having an API gravity of 44.4 and the following ASTM D 86 distillation properties:

Distillation, percent by volume	10	30	50	70	90
Temperature, deg F	304	313	321	329	391

The volumetric average boiling point is 321.6 F. From Chapter 6, the specific gravity is 0.8044, which gives a characterization factor of 11.45.

From Chapter 2, the mean average boiling point is 319 F.

This boiling point is used with the methods of Chapter 4 to give a pseudocritical temperature of 670 F and a pseudocritical pressure of 395 psia.

Using the methods of Chapter 2, the molecular weight is 131 and the acentric factor is 0.3532.

The reduced properties are:

$$T_r = \frac{885 + 459.7}{670 + 459.7} = 1.19 \quad p_r = \frac{205}{395} = 0.52.$$

From Procedure 7D3.1, the pressure correction term is:

$$\left(\frac{\tilde{C}_p^0 - \tilde{C}_p}{R} \right) = -1.107$$

Use of equation (7D4.2-1) will give the desired heat capacity:

$$A_4 = \left[\left(\frac{12.8}{11.45} - 1.0 \right) \left(1.0 - \frac{10.0}{11.45} \right) (0.8044 - 0.885) (0.8044 - 0.70) (10^4) \right]^2.$$

$$A_4 = 1.5785.$$

$$A_1 = -0.35644 + (0.02972) (11.45) + (1.5785) \left(0.29502 - \frac{0.24846}{0.8044} \right).$$

$$A_1 = -0.03802.$$

$$A_2 = -(10^{-4}) \left[2.9247 - [1.5524 - 0.05543 (11.45)] (11.45) + 1.5785 \left(6.0283 - \frac{5.0694}{0.8044} \right) \right].$$

$$A_2 = 8.01544 \times 10^{-4}.$$

$$A_3 = -(10^{-7}) [1.6946 + 0.0884 (1.5785)].$$

$$A_3 = -1.83413 \times 10^{-7}.$$

$$C_p = -0.03802 + (8.01544 \times 10^{-4}) (885 + 459.7) - (1.83413 \times 10^{-7}) (885 + 459.7)^2 \\ - \frac{1.986}{131} (-1.107)$$

$$C_p = 0.7249 \text{ Btu per (lb) (deg R).}$$

PROCEDURE 7E1.1

HEAT CAPACITY RATIO OF PURE HYDROCARBON REAL GASES AND LIQUIDS

Discussion

The following equation is to be used to predict the effect of pressure on the isochoric heat capacity of pure hydrocarbons:

$$\left(\frac{\tilde{C}_v^0 - \tilde{C}_v}{R} \right) = \left(\frac{\tilde{C}_v^0 - \tilde{C}_v}{R} \right)^{(0)} + \omega \left(\frac{\tilde{C}_v^0 - \tilde{C}_v}{R} \right)^{(1)} \quad (7E1.1-1)$$

$\left(\frac{\tilde{C}_v^0 - \tilde{C}_v}{R} \right)$ = the dimensionless effect of pressure on isochoric heat capacity.

$\left(\frac{\tilde{C}_v^0 - \tilde{C}_v}{R} \right)^{(0)}$ = effect of pressure on isochoric heat capacity for the simple fluid, which is tabulated as a function of T_r and p_r in Table 7E1.2 and plotted in Figure 7E1.4.

$\left(\frac{\tilde{C}_v^0 - \tilde{C}_v}{R} \right)^{(1)}$ = correction term for molecular acentricity, which is tabulated as a function of T_r and p_r in Table 7E1.3 and plotted in Figure 7E1.5.

T_r = reduced temperature, T/T_c .

T = temperature, in degrees Rankine.

T_c = critical temperature, in degrees Rankine.

p_r = reduced pressure, p/p_c .

p = pressure, in psia.

p_c = critical pressure, in psia.

ω = acentric factor.

The dimensionless pressure effect term is used in the following equation to determine the actual isochoric heat capacity of the real gas:

$$C_v = C_p^0 - \frac{R}{M} \left[1 + \left(\frac{\tilde{C}_v^0 - \tilde{C}_v}{R} \right) \right] \quad (7E1.1-2)$$

Where:

C_v = isochoric heat capacity of the real gas, in Btu per (lb) (deg R). C_v is the analogous molar quantity.

C_p^0 = isobaric heat capacity of the ideal gas, in Btu per (lb) (deg R). After subtracting the R/M term, this quantity becomes C_v^0 , the isochoric heat capacity of the ideal gas.

R = gas constant = 1.986 Btu per (lb-mole) (deg R).

M = molecular weight, in lb per lb-mole.

The heat capacity ratio, κ , is calculated by dividing the C_p value from Procedure 7D3.1 by the C_v from equation (7E1.1-2).

Procedure

Step 1: Obtain the molecular weight, critical temperature, critical pressure and the acentric factor from Chapter 1.

Step 2: Calculate the reduced temperature and pressure at which a heat capacity is desired.

Step 3: Obtain the correlation terms $\left(\frac{\tilde{C}_v^0 - \tilde{C}_v}{R} \right)^{(0)}$ and $\left(\frac{\tilde{C}_v^0 - \tilde{C}_v}{R} \right)^{(1)}$. If the most accurate values are desired, use Tables 7E1.2 and 7E1.3 with linear double interpolation in p_r and T_r . When near saturation, the interpolation procedure may not be satisfactory (see Special Comments). If slightly less accurate values are acceptable, they may be obtained rapidly from Figures 7E1.4 and 7E1.5.

Step 4: Calculate the dimensionless pressure effect term using equation (7E1.1-1).

Step 5: Obtain the ideal gas heat capacity from Procedure 7A1.1.

Step 6: Calculate the isochoric heat capacity, C_v , of the real gas using equation (7E1.1-2).

Step 7: Obtain the isobaric heat capacity, C_p , of the real gas using Procedure 7D3.1.

Step 8: Calculate the heat capacity ratio $\kappa = C_p/C_v$, from the results of Steps 6 and 7.

COMMENTS ON PROCEDURE 7E1.1

Purpose

This procedure is to be used to predict heat capacity ratios of pure hydrocarbons in the real gas state. Tables 7E1.2 and 7E1.3 or Figures 7E1.4 and 7E1.5 are required in this procedure. The method is best suited to desk calculations, and Procedure 7E1.6 should be used with digital computers. Ideal gas heat capacities from Procedure 7A1.1 are required in either case. Mixtures are treated in Section 7E2.

Equation (7E1.1-2) defines the isochoric (constant volume) heat capacity of the real gas, which may also be obtained using this procedure.

Limitations

In general, this procedure is not accurate for polar substances.

Reliability

Differences between calculated and experimental heat capacity ratios rarely exceed 2 percent except in the critical region, where 10 percent errors should be expected and errors as high as 100 percent can occur. The reliability of the method decreases with increasing uncertainties in the critical properties.

Notation

The notation used in Tables 7E1.2 and 7E1.3 and Figures 7E1.4 and 7E1.5 was defined for equations (7E1.1-1) and (7E1.1-2).

Special Comments

The broken lines in Tables 7E1.2 and 7E1.3 indicate the discontinuity between liquid (to the right and above) and vapor (to the left and below) isochoric heat capacities. Interpolations cannot be made across this line; always use table values which apply to the vapor phase only. Near the broken lines, the extrapolations which are necessary should be made with respect to reduced pressure at constant reduced temperature.

For saturated vapors or liquids (i.e., at their vapor pressure), do not use the two-phase border outlined in Figure 7E1.4. This border applies only when the acentric factor is zero, and as acentricity increases, the reduced vapor pressure decreases at constant reduced temperature. The best procedure is to obtain the vapor pressure from Chapter 5 and proceed as if the phase were homogeneous.

In regions of very rapid change of the simple fluid and correction terms with reduced pressure and/or temperature, a linear interpolation from the tables may not be satisfactory even though the table values are spaced more closely. Here, the figures should be used either directly or as a guide for interpolation corrections to the results from the tables.

For reduced pressures between 0 and 0.2, which are below the correlation range, the heat capacity ratio should be calculated using the ideal gas heat capacity only:

$$\kappa = \frac{C_p}{C_v} \cong \frac{C_p^0}{C_p^0 - \frac{R}{M}} \quad (7E1.1-3)$$

This equation is a simple modification in which it is assumed that nonideality corrections in numerator and denominator cancel.

Literature Sources

Tables 7E1.2 and 7E1.3 were generated using the generalized correlation of Lee and Kesler, *AIChE Journal* 21 510 (1975). Figures 7E1.4 and 7E1.5 are direct plots of these tables.

PROCEDURE 7E1.6**ALTERNATE (COMPUTER) METHOD FOR THE HEAT CAPACITY RATIO OF PURE REAL GASES AND LIQUIDS****Discussion**

The following generalized method, which was used to generate Tables 7E1.2 and 7E1.3, is recommended for calculating the isochoric heat capacity of pure hydrocarbon gases by a digital computer.

The equation to be used is:

$$\left(\frac{\tilde{C}_v^0 - \tilde{C}_v}{R} \right) = \left(\frac{\tilde{C}_v^0 - \tilde{C}_v}{R} \right)^{(0)} + \frac{\omega}{\omega^{(h)}} \left[\left(\frac{\tilde{C}_v^0 - \tilde{C}_v}{R} \right)^{(h)} - \left(\frac{\tilde{C}_v^0 - \tilde{C}_v}{R} \right)^{(0)} \right] \quad (7E1.6-1)$$

Where:

$\left(\frac{\tilde{C}_v^0 - \tilde{C}_v}{R} \right)$ = the dimensionless effect of pressure on isochoric heat capacity.

$\left(\frac{\tilde{C}_v^0 - \tilde{C}_v}{R} \right)^{(0)}$ = effect of pressure on the isochoric heat capacity for the simple fluid to be calculated from equation (7E1.6-2).

$\left(\frac{\tilde{C}_v^0 - \tilde{C}_v}{R} \right)^{(h)}$ = effect of pressure on the isochoric heat capacity for the heavy reference fluid (*n*-octane) to be calculated from equation (7E1.6-2).

ω = acentric factor of the gas for which the pressure effect on isochoric heat capacity is sought.

$\omega^{(h)}$ = acentric factor of the heavy reference fluid = 0.3978

The dimensionless effect of pressure on the isochoric heat capacity of the simple fluid and of the heavy reference fluid are to be calculated from the following equation:

$$\left(\frac{\tilde{C}_v^0 - \tilde{C}_v}{R} \right)^{(i)} = - \frac{2(b_3 + 3b_4/T_r)}{T_r^2 V_r} + \frac{3c_3}{T_r^3 V_r^2} + 6E \quad (7E1.6-2)$$

Where:

$$E = \frac{c_4}{2T_r^3 \gamma} \left\{ \beta + 1 - \left(\beta + 1 + \frac{\gamma}{V_r^2} \right) \exp \left(-\frac{\gamma}{V_r^2} \right) \right\} \quad (7E1.6-3)$$

$\left(\frac{\tilde{C}_v^0 - \tilde{C}_v}{R} \right)^{(i)} = \left(\frac{\tilde{C}_v^0 - \tilde{C}_v}{R} \right)^{(0)}$ when the equation is applied to the simple fluid.

$\left(\frac{\tilde{C}_v^0 - \tilde{C}_v}{R} \right)^{(i)} = \left(\frac{\tilde{C}_v^0 - \tilde{C}_v}{R} \right)^{(h)}$ when the equation is applied to the heavy reference fluid.

T_r = reduced temperature, T/T_c .

T_c = critical temperature of the fluid for which the isochoric heat capacity is desired, in degrees Rankine.

T = temperature, in degrees Rankine.

$V_r = p_c V / RT_c$, is obtained from Procedure 6B1.8.

$b_2, b_3, b_4, c_3, c_4, \gamma$, and β are two sets of constants, one set for the simple fluid and another for the heavy reference fluid. The values of the constants are given in Procedure 6B1.8.

The total isochoric heat capacity may be calculated from the following equation:

$$C_v = C_p^0 - \frac{R}{M} \left[1 + \left(\frac{\tilde{C}_v^0 - \tilde{C}_v}{R} \right) \right] \quad (7E1.6-4)$$

Where:

C_v = isochoric heat capacity of the real gas, in Btu per (lb) (deg R). \tilde{C}_v is the analogous molar quantity.

C_p^0 = isobaric heat capacity of the ideal gas, in Btu per (lb) (deg R). After subtracting the R/M term, this quantity becomes C_v^0 , the isochoric heat capacity of the ideal gas.

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R = gas constant = 1.986 Btu per (lb-mole) (deg R).
 M = molecular weight, in lb per lb-mole.

The heat capacity ratio is calculated by combining the isobaric heat capacity from Procedure 7D3.6 and the isochoric heat capacity from equation (7E1.6-4) as follows:

$$\kappa = C_p/C_v \quad (7E1.6-5)$$

Where:

κ = heat capacity ratio.
 C_p = isobaric heat capacity, in Btu per (lb) (deg R).
 C_v = isochoric heat capacity, in Btu per (lb) (deg R).

Procedure

Step 1: Obtain the critical temperature, critical pressure, and the molecular weight from Chapter 1 and the acentric factor from Chapter 2.

Step 2: Calculate the reduced temperature and reduced pressure at which the heat capacity ratio is desired.

Step 3: Use Procedure 6B1.8 to obtain the value of $V_r = p_c V / RT_c$, for the simple fluid. Retain T_r , V_r and the constants b_2 , b_3 , b_4 , c_3 , c_4 , γ , and β for the simple fluid.

Step 4: Use equation (7E1.6-2) to calculate $\left(\frac{\tilde{C}_v^0 - \tilde{C}_v}{R}\right)^{(0)}$, the dimensionless effect of pressure on the isochoric heat capacity of the simple fluid.

Step 5: Repeat Steps 3 and 4 for the heavy reference fluid and, hence, obtain $\left(\frac{\tilde{C}_v^0 - \tilde{C}_v}{R}\right)^{(h)}$, the dimensionless effect of pressure on the isochoric heat capacity of the heavy reference fluid.

Step 6: Use equation (7E1.6-1) to obtain $[\tilde{C}_v^0 - C_v]/R$.

Step 7: Use equation (7E1.6-4) to calculate the isochoric heat capacity.

Step 8: Use Procedure 7D3.6 to calculate C_p , the isobaric heat capacity. Hence, find the heat capacity ratio κ , according to equation (7E1.6-5).

COMMENTS ON PROCEDURE 7E1.6

Purpose

This procedure is presented to be used with a digital computer to calculate the heat capacity ratios of pure hydrocarbon gases. The results from Procedures 6B1.8 and 7D3.6 are also required in this procedure, which also involves the indirect use of Procedure 7A1.1. Equation 7E1.6-4 of this procedure can be used to calculate the isochoric heat capacity, rather than the heat capacity ratio, if this quantity alone is required.

Limitations

This procedure is mainly intended for use with hydrocarbons. Large errors might occur when used with polar gases. Reasonable results can be expected for nonpolar nonhydrocarbons.

Reliability

Errors between calculated and experimental heat capacity ratios rarely exceed 2 percent except in the critical region, where 10 percent errors should be expected and 50 percent errors can occur. The error of the method increases with increasing uncertainty in the pure component critical properties. The equations are recommended for reduced pressures up to 10. However, they may be used up to reduced pressures of 20 or more with only slight increase in error.

Special Comments

For saturated vapors, use both temperature and pressure as input (with the vapor pressure predictions from Chapter 5, when necessary), and perform the calculations as if the point were in the homogeneous region.

Literature Source

Equations (7E1.6-1) through (7E1.6-4) were developed by Lee and Kesler, *AIChE Journal* 21 510 (1975).

PROCEDURE 7E2.1**HEAT CAPACITY RATIO OF HYDROCARBON GAS MIXTURES****Discussion**

The tables and figures of Procedure 7E1.1 are to be applied to hydrocarbon mixtures by using the pseudocritical temperature and pressure to calculate reduced conditions instead of the true critical temperature and pressure. The pseudocritical properties, which are approximated as the molar averages of the component true critical properties, are given in Chapter 4 for mixtures of defined and undefined composition and blends of the two. The mixture acentric factor, which is defined as the molar average of the component acentric factors, may be estimated for undefined mixtures from Chapter 2. These approximations are summarized below:

$$T_{pc} = \sum_{i=1}^n x_i T_{ci} \quad (7E2.1-1)$$

Where:

T_{pc} = pseudocritical temperature, in degrees Rankine.

T_{ci} = critical temperature of component i , in degrees Rankine.

n = number of components in the mixture.

x_i = mole fraction of component i .

$$p_{pc} = \sum_{i=1}^n x_i p_{ci} \quad (7E2.1-2)$$

Where:

p_{pc} = pseudocritical pressure, in psia.

p_{ci} = critical pressure of component i , in psia.

$$\omega = \sum_{i=1}^n x_i \omega_i \quad (7E2.1-3)$$

Where:

ω = mixture acentric factor.

ω_i = acentric factor of component i .

The results from these equations are used to calculate the reduced conditions so that Procedures 7D3.1 and 7E1.1 may be used to calculate the effect of pressure on the mixture isobaric and isochoric heat capacities. To get the total isobaric and isochoric heat capacities, these pressure corrections are then combined with the ideal gas isobaric heat capacity of the mixture, which is defined as:

$$C_p^0 = \sum_{i=1}^n x_{wi} C_{pi}^0 \quad (7E2.1-4)$$

Where:

C_{pi}^0 = ideal gas heat capacity, in Btu per (lb) (deg F). The subscript i refers to component i in the n component mixture.

x_{wi} = weight fraction of component i .

Procedure

Step 1: For mixtures of known composition, obtain the molecular weights, the critical pressures and temperatures, and the acentric factors for all of the components from Chapter 1. (For hydrogen, use $T_c = 75$ R, $p_c = 305$ psia, and $\omega = 0$.)

Step 2: Calculate the pseudocritical temperature and pressure using equations (7E2.1-1) and (7E2.1-2) and the mixture acentric factor using equation (7E2.1-3). [For blends of petroleum fractions with mixtures of known composition, obtain the pseudocritical conditions from Chapter 4 and the acentric factor for the petroleum fraction portion from Chapter 2. Complete the acentric factor calculation using equation (7E2.1-3).]

Calculate the reduced temperature and pressure.

Step 3: Calculate the isobaric ideal gas heat capacity of the mixture using equation (7E2.1-4). Input heat capacities for pure hydrocarbons are to be taken from Procedure 7A1.1. (For blends of hydrocarbons with petroleum fractions, obtain the ideal gas heat capacity of the petroleum fraction portion from Figure 7D4.2.) Calculate the molecular weight of the mixture (with input for the petroleum fraction portion, if present, from Chapter 2).

Step 4: Calculate the effect of pressure on isobaric heat capacity using Steps 3 and 4 of Procedure 7D3.1 and the total mixture isobaric heat capacity using Step 6 of the same procedure.

Step 5: Calculate the effect of pressure on isochoric heat capacity using Steps 3 and 4 of Procedure 7E1.1 and the total mixture isochoric heat capacity using Step 6 of the same procedure.

Step 6: Calculate the heat capacity ratio, $\kappa = C_p/C_v$, from the results of Steps 4 and 5.

COMMENTS ON PROCEDURE 7E2.1

Purpose

This procedure is to be used with Procedure 7E1.1 to estimate the heat capacity ratios of mixtures of hydrocarbons which may contain nonpolar nonhydrocarbon substances. Mixtures of known composition and blends of known compounds with petroleum fractions are treated.

Limitations

In general, the method is not applicable to mixtures containing polar components.

Reliability

Errors between calculated and experimental heat capacity ratios are estimated to average 2 percent except in the critical region, where 15-percent errors should be expected and errors of 100 percent can occur. The region of maximum uncertainty is the same as that indicated in Figure 7E1.4.

The reliability of the modification for mixtures of undefined composition is unknown.

Special Comments

For hydrocarbon-hydrocarbon mixtures which do not contain methane, slightly better results are obtained in the immediate critical region using true rather than pseudocritical temperatures and pressures. This region is defined approximately by the following pseudoreduced condition boundaries: $1.0 < T_r < 1.2$ and $1.0 < p_r < 3.0$. True critical conditions are correlated in Chapter 4. Notice that the liquid phase can exist in this region even though the pseudoreduced temperature is greater than unity (see Introduction).

For supercritical temperatures ($T_r > 1$) and high pressures ($p_r > 5$), the error can be reduced using the following mixture correspondence pressure instead of the pseudocritical pressure defined by equation (7E2.1-2):

$$p_{mc} = \frac{RT_{pc} \sum_{i=1}^n x_i z_{ci}}{\sum_{i=1}^n x_i V_{ci} M_i} \quad (7E2.1-5)$$

Where:

p_{mc} = mixture correspondence pressure, in pounds per square inch absolute.

R = gas constant = 10.731 (psia) (cu ft) per (lb-mole) (deg R).

z_{ci} = critical compressibility factor of component i (from Chapter 1).

V_{ci} = critical volume of component i (from Chapter 1) in cubic feet per pound.

M_i = molecular weight of component i (from Chapter 1), in lb per lb-mole.

More reliable heat capacity ratios can be obtained under most temperature-pressure conditions using the mixture correspondence rules of Joffe (35), Stewart et al. (71), Leland and Mueller (44) or Lee and Kesler (42). However, the small advantage in accuracy does not justify the added labor involved in using these methods.

For computer heat capacity calculations, Procedure 7E1.6 may be adapted to mixtures using the mixture correspondence point as described in Procedure 6B2.2 for gas densities. Mixtures of known composition, petroleum fractions, and blends of the two may be treated. The reliability for mixtures of known composition is approximately the same as quoted previously. For a petroleum fraction, obtain the necessary isobaric ideal gas heat capacity from Procedure 7D4.2.

Literature Sources

Equations (7E2.1-1) and (7E2.1-2) were given by Kay, *Ind. Eng. Chem.* **28** 1014 (1936). Equation (7E2.1-4) was developed by Prausnitz and Gunn, *AIChE Journal* **4** 430 (1958).

PROCEDURE 7F1.1**ENTROPY OF PURE HYDROCARBON REAL GASES****Discussion**

The following equation is to be used to predict the effect of pressure on the entropy of pure hydrocarbons:

$$\left(\frac{\tilde{S}^0 - \tilde{S}}{R}\right) = \left(\frac{\tilde{S}^0 - \tilde{S}}{R}\right)^{(0)} + \omega \left(\frac{\tilde{S}^0 - \tilde{S}}{R}\right)^{(1)} + \ln p \quad (7F1.1-1)$$

Where:

$\left(\frac{\tilde{S}^0 - \tilde{S}}{R}\right)$ = the dimensionless effect of pressure on entropy.

$\left(\frac{\tilde{S}^0 - \tilde{S}}{R}\right)^{(0)}$ = effect of pressure on entropy for the simple fluid, which is tabulated as a function of T_r and p_r in Table 7F1.2 and plotted in Figures 7F1.4 and 7F1.5.

$\left(\frac{\tilde{S}^0 - \tilde{S}}{R}\right)^{(1)}$ = correction term for molecular acentricity, which is tabulated as a function of T_r and p_r in Table 7F1.3 and plotted in Figures 7F1.6 and 7F1.7.

T_r = reduced temperature, T/T_c .

T = temperature, in degrees Rankine.

T_c = critical temperature, in degrees Rankine.

p_r = reduced pressure, p/p_c .

p = pressure, in psia.

p_c = critical pressure, in psia.

ω = acentric factor.

\ln = the natural logarithm.

The dimensionless pressure effect term is used in the following equation to determine the total entropy of the hydrocarbon:

$$S = S^0 - \frac{R}{M} \left(\frac{\tilde{S}^0 - \tilde{S}}{R} \right) \quad (7F1.1-2)$$

Where:

S = total entropy, referred to the basis entropy of 1 Btu per (lb) (deg R) for the ideal gas at 0 R and 1 atm, in Btu per (lb) (deg R). \tilde{S} is the analogous molar quantity.

S^0 = ideal gas entropy, in Btu per (lb) (deg R). \tilde{S}^0 is the analogous molar quantity.

R = gas constant = 1.986 Btu per (lb-mole) (deg R).

M = molecular weight, in lb per lb-mole.

Procedure

Step 1: Obtain the molecular weight, critical temperature, critical pressure, and the acentric factor from Chapter 1.

Step 2: Calculate the reduced temperature and pressure at which an entropy is desired.

Step 3: Obtain the correlation terms $\left(\frac{\tilde{S}^0 - \tilde{S}}{R}\right)^{(0)}$ and $\left(\frac{\tilde{S}^0 - \tilde{S}}{R}\right)^{(1)}$. If the most accurate values are desired, use Tables 7F1.2 and 7F1.3 with linear double interpolation in p_r and T_r . When near saturation, the interpolation procedure may not be satisfactory (see Special Comments). If slightly less accurate values are acceptable, they may be obtained rapidly from Figures 7F1.4 through 7F1.7.

Step 4: Calculate the dimensionless pressure effect term using equation (7F1.1-1).

Step 5: Obtain the ideal gas entropy from Procedure 7A1.1.

Step 6: Calculate the total entropy using equation (7F1.1-2).

COMMENTS ON PROCEDURE 7F1.1**Purpose**

This procedure is to be used to predict entropies of pure hydrocarbons in the liquid and real gas states. Tables 7F1.2 and 7F1.3 or Figures 7F1.4 through 7F1.5 are required in this procedure. The method is best suited to desk calculations, and Procedure 7F1.6 should be used with digital computers. Ideal gas entropies from Procedure 7A1.1 are required in either case. Mixture entropies are treated in Section 7F2.

Limitations

In general, this procedure is not accurate for polar substances.

Reliability

This procedure was not compared with experimental data, but is thermodynamically consistent with the (accurate) primary methods for compressibility factor, enthalpy, and fugacity. Accordingly, it should be quite reliable except in the critical region. This region of maximum uncertainty is indicated in Figures 7F1.4 through 7F1.6. The reliability of the method decreases with increasing uncertainties in the critical properties.

Notation

The notation used in Tables 7F1.2 and 7F1.3 and Figures 7F1.4 through 7F1.7 was defined for equations (7F1.1-1) and (7F1.1-2).

Special Comments

The broken line in Table 7F1.2 indicates the discontinuity between liquid (to the right and above) and vapor (to the left and below) entropies. Interpolations must not be made across this line; always use table values which apply to the desired phase only. The extrapolations which are necessary should be made with respect to reduced pressure at constant reduced temperature.

For saturated vapors or liquid (i.e., at their vapor pressures), do not use the two-phase border outlined in Figure 7F1.4. This border applies only when the acentric factor is zero, and as acentricity increases, the reduced vapor pressure decreases at constant reduced temperature. The best procedure is to obtain the vapor pressure from Chapter 5 and proceed as if the phase were homogeneous.

In regions of very rapid change of the simple fluid and correction terms with reduced pressure and/or temperature, a linear interpolation from the tables may not be satisfactory even though the table values are spaced more closely. Here, the figures should be used either directly or as a guide for interpolation corrections to the results from the tables.

The figures may be extrapolated to lower reduced pressures by noting $\left(\frac{\tilde{S}^0 - \tilde{S}}{R}\right)^{(0)}$ and $\left(\frac{\tilde{S}^0 - \tilde{S}}{R}\right)^{(1)}$ approach zero as the pressure approaches 1 psia. In many engineering applications, these limiting values may be used in equation (7F1.1-1) for all reduced pressures between 0 and 0.2, but the $\ln p$ term in equation (7F1.1-1) must be retained. If even more precise results than the extrapolated values are desired (rarely), use the following equation:

$$\begin{aligned} \left(\frac{\tilde{S}^0 - \tilde{S}}{R}\right) = & \ln p - p_r [- (0.330 - 0.46\omega) T_r^{-2} - (0.2770 + 1.00\omega) T_r^{-3} - (0.0363 + 0.29\omega) T_r^{-4} \\ & - 0.00584\omega T_r^{-9}] \end{aligned} \quad (7F1.1-3)$$

Literature Sources

Tables 7F1.2 and 7F1.3 were generated using the generalized correlation of Lee and Kesler, *AIChE Journal* **21** 510 (1975). Figures 7F1.4 through 7F1.7 are direct plots of Tables 7F1.2 and 7F1.3. Equation (7F1.1-3) was developed by Pitzer and Curl, *J. Am. Chem. Soc.* **79** 2369 (1957).

PROCEDURE 7F1.7

ALTERNATE (COMPUTER) METHOD FOR THE ENTROPY OF PURE HYDROCARBON LIQUIDS AND REAL GASES

Discussion

The following generalized correlation, which was used to generate Tables 7F1.2 and 7F1.3, is recommended for calculating the entropy of pure hydrocarbon liquids and gases by a digital computer.

Three other procedures, those for density, fugacity, and enthalpy, are required to use this method. The results are combined using the following equation:

$$\left(\frac{\tilde{S}^0 - \tilde{S}}{R} \right) = \left(\frac{\tilde{H}^0 - \tilde{H}}{RT} \right) + \ln \left(\frac{f}{p} \right) + \ln p \quad (7F1.7-1)$$

Where:

$\left(\frac{\tilde{S}^0 - \tilde{S}}{R} \right)$ = the dimensionless effect of pressure on entropy.

$\left(\frac{\tilde{H}^0 - \tilde{H}}{RT} \right)$ = the dimensionless effect of pressure on enthalpy from Procedure 7B3.7.

$\ln(f/p)$ = the dimensionless fugacity term from Procedure 7G1.8.

p = pressure in psia.

The total entropy is found using the dimensionless pressure effect on entropy with the following equation:

$$S = S^0 - \frac{R}{M} \left(\frac{\tilde{S}^0 - \tilde{S}}{R} \right) \quad (7F1.7-2)$$

Where:

S = total entropy referred to the basis entropy of 1 Btu per (lb) (deg R) for the ideal gas at 0 R and 1 atm, in Btu per (lb) (deg R). \tilde{S} is the analogous molar quantity.

S^0 = ideal gas entropy, in Btu per (lb) (deg R). \tilde{S}^0 is the analogous molar quantity.

R = gas constant = 1.986 Btu per (lb-mole) (deg R).

M = molecular weight, in lb per lb-mole.

Procedure

Step 1: Use Procedure 6B1.8 to determine the compressibility factor of the simple fluid and the reference fluid at the desired reduced pressure and temperature conditions. Retain T , T_r , p and p_r from this procedure; obtain M from Chapter 1.

Step 2: Obtain the term for dimensionless effect of pressure on enthalpy from Procedure 7B3.7.

Multiply this quantity by (T_r/T) to obtain $\left(\frac{\tilde{H}^0 - \tilde{H}}{RT} \right)$.

Step 3: Obtain the dimensionless fugacity term from equation (7G1.7-1).

Step 4: Combine these terms according to equation (7F1.7-1).

Step 5: Determine the ideal gas entropy with Procedure 7A1.1 using the equation rather than the tabular form of the procedure.

Step 6: Calculate the total entropy using equation (7F1.7-2).

COMMENTS ON PROCEDURE 7F1.7

Purpose

This procedure is presented to be used with a digital computer to calculate entropies of pure hydrocarbon gases and liquids. The results from Procedures 6B1.8, 7B3.7, and 7G1.7 are required directly in this procedure, which also involves the indirect use of Procedure 7A1.1.

Limitations

In general, this procedure is not accurate for polar substances.

Reliability

This procedure was not compared with experimental data, but is thermodynamically consistent with the accurate computer methods for compressibility factor, enthalpy, and fugacity. Accordingly, it should be quite reliable except in the critical region.

Special Comments

For saturated vapors, use both temperature and pressure as input (with the vapor pressure predictions from Chapter 5, when necessary) and perform the calculations as if the point were in the homogeneous region.

PROCEDURE 7F2.1**ENTROPY OF DEFINED HYDROCARBON GAS MIXTURES****Discussion**

The tables and figures of Procedure 7H1.1 are to be applied to hydrocarbon mixtures by using the pseudocritical temperature and pressure to calculate reduced conditions instead of the true critical temperature and pressure. The pseudocritical properties, which are approximated as the molar averages of the component true critical properties, are given in Chapter 4. The mixture acentric factor is defined as the molar average of the component acentric factors. These approximations are summarized below:

$$T_{pc} = \sum_{i=1}^n x_i T_{ci} \quad (7F2.1-1)$$

Where:

T_{pc} = pseudocritical temperature, in degrees Rankine.

T_{ci} = critical temperature of component i , in degrees Rankine.

n = number of components in the mixture.

x_i = mole fraction of component i .

$$p_{pc} = \sum_{i=1}^n x_i p_{ci} \quad (7F2.1-2)$$

Where:

p_{pc} = pseudocritical pressure, in psia.

p_{ci} = critical pressure of component i , in psia.

$$\omega = \sum_{i=1}^n x_i \omega_i \quad (7F2.1-3)$$

Where:

ω = mixture acentric factor.

ω_i = acentric factor of component i .

The results from these equations are used to calculate the reduced conditions so that Procedure 7F1.1 may be used to calculate the effect of pressure on the mixture entropy. This pressure correction is then subtracted from the ideal gas entropy of the mixture, which is defined as:

$$S^0 = \sum_{i=1}^n \left[x_{wi} S_i^0 - \frac{R}{M} (x_i \ln x_i) \right] \quad (7F2.1-4)$$

Where:

S^0 = ideal gas entropy, in Btu per (lb) (deg R). The subscript i refers to component i in the n component mixture.

x_{wi} = weight fraction of component i .

R = gas constant = 1.986 Btu per (lb-mole) (deg R).

M = molar average molecular weight of the mixture, in lb per lb-mole.

$$= \sum_i x_i M_i$$

x_i = mole fraction of component i .

M_i = molecular weight of component i , in lb per lb-mole.

Unlike enthalpy and heat capacity, the ideal gas entropy of the mixture includes a correction for mixing (the logarithmic term).

Procedure

Step 1: For mixtures of known composition, obtain the molecular weights, the critical pressures and temperatures, and the acentric factors for all of the components from Chapter 1 (For hydrogen, use $T_c = 75$ R, $p_c = 305$ psia, and $\omega = 0$.)

7F2.1

Step 2: Calculate the pseudocritical temperature and pressure using equations (7F2.1-1) and (7F2.1-2) and the mixture acentric factor using equation (7F2.1-3).

Calculate the reduced temperature and pressure.

Step 3: Calculate the ideal gas entropy of the mixture using equation (7F2.1-4). Input entropies for pure hydrocarbons are to be taken from Procedure 7A1.1. Calculate the average molecular weight of the mixture.

Step 4: Calculate the effect of pressure on entropy using Steps 3 and 4 of Procedure 7F1.1 and the total mixture entropy using Step 6 of the same procedure.

COMMENTS ON PROCEDURE 7F2.1

Purpose

This procedure is to be used with Procedure 7F1.1 to estimate the entropy of mixtures of hydrocarbons which may contain nonpolar nonhydrocarbon substances. Only mixtures of known composition can be treated.

Limitations

In general, the method is not applicable to mixtures containing polar components.

Reliability

This procedure was not evaluated against experimental data, but is thermodynamically consistent with the methods for compressibility factor, enthalpy, and heat capacity. Accordingly, it should be quite reliable except in the critical region. This region of maximum uncertainty is indicated in Figures 7F1.4 through 7F1.6.

Special Comments

For hydrocarbon-hydrocarbon mixtures which do not contain methane, slightly better results are obtained in the immediate critical region using true rather than pseudocritical temperatures and pressures. This region is defined approximately by the following pseudoreduced condition boundaries: $1.0 < T_r < 1.2$ and $1.0 < p_r < 3.0$. True critical conditions are correlated in Chapter 4. Notice that the liquid phase can exist in this region even though the pseudoreduced temperature is greater than unity (see Introduction).

For supercritical temperatures ($T_r > 1$) and high pressures ($p_r > 5$), the error can be reduced using the following mixture correspondence pressure instead of the pseudocritical pressure defined by equation (7F2.1-2):

$$P_{mc} = \frac{RT_{pc} \sum_{i=1}^n x_i z_{ci}}{\sum_{i=1}^n x_i V_{ci} M_i} \quad (7F2.1-5)$$

Where:

P_{mc} = mixture correspondence pressure, in psia.

R = gas constant = 10.731 (psia) (cu ft) per (lb-mole) (deg R).

z_{ci} = critical compressibility factor of component i (from Chapter 1).

V_{ci} = critical volume of component i (from Chapter 1), in cubic feet per pound.

M_i = molecular weight of component i (from Chapter 1).

More reliable entropies can be obtained under most temperature-pressure conditions using the mixture correspondence rules of Lee and Kesler (42), Joffe (35), Stewart, et al. (71), or Leland and Mueller (44). However, the small advantage in accuracy does not justify the added labor involved in using these methods.

For computer entropy calculations, Procedure 7F1.7 may be adapted to mixtures using the mixture correspondence point as described in Procedure 6B2.2 for gas densities.

Petroleum fractions cannot be treated using this procedure, because all compositions must be known to calculate the ideal entropy of mixing.

Literature Sources

Equations (7F2.1-1) and (7F2.1-2) were given by Kay, *Ind. Eng. Chem.* **28** 1014 (1936). Equation (7F2.1-5) was developed by Prausnitz and Gunn, *AICHE Journal* **4** 430 (1958).

Example

Estimate the entropy of a 47.25 mole percent methane-52.75 mole percent propane mixture at 310 F and 1,500 psia.

The following tabulation of critical properties, molecular weights, and acentric factors was obtained from Chapter 1. Ideal gas entropies at 1 psia were taken from Procedure 7A1.1.

	Mole Fraction	Critical Temperature, T_c			$\frac{p_c}{\text{per Square Inch Absolute}}$	Acentric Factor, ω	Molecular Weight, M	Weight Fraction, x_w	Ideal Gas Entropy, S^0 [Btu Per (Lb) (Deg R)]
		Degrees Fahrenheit	Degrees Rankine	Critical					
				T_c					
Methane	0.4725	-116.6	343.1	667.8	0.0108	16.04	0.2457	2.986	
Propane	0.5275	206.0	665.7	616.3	0.1517	44.09	0.7543	1.631	
Molar Average	—	—	513.3	640.6	0.0851	30.84	—	—	
Weight Average	—	—	—	—	—	—	1.0000	1.964	

The reduced temperature is $\frac{310 + 459.7}{513.3} = 1.50$, and the reduced pressure is $\frac{1,500}{640.6} = 2.34$

The ideal gas entropy of the mixture from equation (7F2.1-4) is:

$$S^0 = 1.964 - \frac{1.986}{30.84} (0.4725) (\ln 0.4725) - \frac{1.986}{30.84} (0.5275) (\ln 0.5275) = 2.008$$

$$\left(\frac{\tilde{S}^0 - \tilde{S}}{R} \right)^{(0)} = 0.611 \quad \left(\frac{\tilde{S}^0 - \tilde{S}}{R} \right)^{(1)} = 0.176$$

$$\left(\frac{\tilde{S}^0 - \tilde{S}}{R} \right) = 0.611 + (0.0851) (0.176) + \ln 1,500 = 7.939$$

$$S = 2.008 - \frac{1.986}{30.84} (7.939) = 1.497 \text{ Btu per (lb) (deg R)}$$

PROCEDURE 7G1.1

FUGACITY OF PURE HYDROCARBONS

Discussion

The following equation is to be used to predict the fugacity of pure hydrocarbons as a function of temperature and pressure:

$$\log \frac{f}{p} = \left(\log \frac{f}{p} \right)^{(0)} + \omega \left(\log \frac{f}{p} \right)^{(1)} \quad (7G1.1-1)$$

Where:

f = fugacity at T and p , in psia.

T = temperature, in degrees Rankine.

T_r = reduced temperature, T/T_c .

T_c = critical temperature, in degrees Rankine.

p = pressure in psia.

p_r = reduced pressure, p/p_c .

p_c = critical pressure, in psia.

$\left(\log \frac{f}{p} \right)^{(0)}$ = fugacity of the simple fluid, which is tabulated as a function of T_r and p_r in Table 7G1.2 and plotted in Figures 7G1.4 and 7G1.5.

$\left(\log \frac{f}{p} \right)^{(1)}$ = correction term for molecular acentricity, which is tabulated as a function of T_r and p_r in Table 7G1.3 and plotted in Figures 7G1.6 and 7G1.7.

ω = acentric factor.

Procedure

Step 1: Obtain the critical temperature, critical pressure, and the acentric factor from Chapter 1.

Step 2: Calculate the reduced temperature and pressure at which the fugacity is desired.

Step 3: Obtain the correlation terms $\left(\log \frac{f}{p} \right)^{(0)}$ and $\left(\log \frac{f}{p} \right)^{(1)}$. If the most accurate values are desired, use Tables 7G1.2 and 7G1.3 with linear double interpolation in p_r and T_r . When near saturation, the interpolation procedure may not be satisfactory (see Special Comments). If slightly less accurate values are acceptable, they may be obtained rapidly from Figures 7G1.4 through 7G1.7.

Step 4: Calculate the log of the fugacity coefficient using equation (7G1.1-1). After the antilogarithm has been taken, this value is to be multiplied by the pressure to obtain the desired fugacity.

COMMENTS ON PROCEDURE 7G1.1

Purpose

This procedure is to be used to predict fugacities of pure hydrocarbons in the liquid and real gas states. Tables 7G1.2 and 7G1.3 or Figures 7G1.4 through 7G1.7 are required in this procedure. The method is best suited to desk calculations. Procedure 7G1.8 should be used with digital computers.

Limitations

In general, this procedure is not accurate for polar substances.

Reliability

This procedure was not compared with experimental data, but is thermodynamically consistent with the (accurate) primary methods for compressibility factor, enthalpy, and heat capacity. Accordingly, it should be quite reliable except in the critical region. The reliability of the method decreases with increasing uncertainty in the pure component critical properties.

7G1.1

Notation

The notation used in Tables 7G1.2 and 7G1.3 and Figures 7G1.4 through 7G1.7 were defined for equation (7G1.1-1).

Special Comments

The broken lines in Tables 7G1.2 and 7G1.3 indicate the discontinuity (in slope) between liquid (to the right and above) and vapor (to the left and below) fugacities. Interpolations must not be made across these lines; always use table values which apply to the desired phase only. The extrapolations which are necessary should be made with respect to reduced pressure at constant reduced temperature.

In regions of very rapid change of the simple fluid and correction terms with reduced pressure and/or temperature, a linear interpolation from the tables may not be satisfactory even though the table values are spaced more closely. Here, the figures should be used either directly or as a guide for interpolation corrections to the results from the tables.

The figures may be extrapolated to lower reduced pressures by noting that $(\log f/p)^{(0)}$ and $(\log f/p)^{(1)}$ approach zero as the pressure approaches zero. In many engineering applications, these limiting values may be used for all reduced pressures between 0 and 0.2.

Literature Sources

Tables 7G1.2 and 7G1.3 were prepared by Lee and Kesler, *AICHE Journal*, 21 510 (1975). Figures 7G1.4 through 7G1.7 are direct plots of Tables 7G1.2 and 7G1.3.

Example

Calculate the fugacity of 2-methylpropane at 370 F and 4,000 psia.

From Chapter 1, $T_c = 275.0$ F, $p_c = 529.1$ psia, and $\omega = 0.1756$. The reduced temperature is $\frac{370 + 459.7}{275 + 459.7} = 1.13$ and the reduced pressure is $\frac{4,000}{529.1} = 7.56$.

To determine $\left(\log \frac{f}{p} \right)^{(0)}$ from Table 7G1.2, interpolate first in reduced pressure. Figure 7G1.4 shows that neither interpolation can be safely performed linearly; therefore, the values must be taken from Figure 7G1.4.

$$\text{At } T_r = 1.10, \quad \left(\log \frac{f}{p} \right)^{(0)} = -0.493$$

$$\text{At } T_r = 1.15, \quad \left(\log \frac{f}{p} \right)^{(0)} = -0.435$$

Combining these,

$$\left(\log \frac{f}{p} \right)^{(0)} = -0.493 + (-0.435 + 0.493) \left(\frac{1.13 - 1.10}{1.15 - 1.10} \right)$$

$$\left(\log \frac{f}{p} \right)^{(0)} = -0.458.$$

$$\text{Similarly, } \left(\log \frac{f}{p} \right)^{(1)} = 0.033$$

The dimensionless fugacity coefficient term is next calculated using equation (7G1.1-1):

$$\log \frac{f}{p} = -0.458 + (0.1756)(0.033) = -0.452$$

The fugacity coefficient is antilog $(0.548 - 1.0) = 0.353$, and the fugacity is $(0.353)(4000) = 1412$ psia.

An experimental fugacity is 1425 psia.

PROCEDURE 7G1.8**COMPUTER METHOD FOR FUGACITY OF PURE HYDROCARBONS****Discussion**

The following generalized correlation, which was used to generate Tables 7G1.2 and 7G1.3 is recommended for calculating the fugacity of pure hydrocarbons with a digital computer. The equation is:

$$\left(\ln \frac{f}{p} \right) = \left(\ln \frac{f}{p} \right)^{(0)} + \frac{\omega}{\omega^{(h)}} \left[\left(\ln \frac{f}{p} \right)^{(h)} - \left(\ln \frac{f}{p} \right)^{(0)} \right] \quad (7G1.8-1)$$

Where:

f = fugacity of pure hydrocarbon, psia.

p = pressure, psia.

$\left(\ln \frac{f}{p} \right)^{(0)}$ = simple fluid fugacity coefficient function, to be calculated from equation (7G1.8-2).

$\left(\ln \frac{f}{p} \right)^{(h)}$ = heavy reference fluid (*n*-octane) fugacity coefficient function, to be calculated from equation (7G1.8-2).

ω = acentric factor of compound for which fugacity is desired.

$\omega^{(h)}$ = acentric factor of heavy reference fluid = 0.3978.

The fugacity coefficient functions, $\left(\ln \frac{f}{p} \right)^{(0)}$ and $\left(\ln \frac{f}{p} \right)^{(h)}$ may be calculated from the following equation:

$$\left(\ln \frac{f}{p} \right)^{(i)} = z^{(i)} - 1 - \ln [z^{(i)}] + \frac{B}{V_r} + \frac{C}{2V_r^2} + \frac{D}{5V_r^5} + E \quad (7G1.8-2)$$

Where:

$B = b_1 - b_2/T_r - b_3/T_r^2 - b_4/T_r^3$.

$C = c_1 - c_2/T_r + c_3/T_r^3$.

$D = d_1 + d_2/T_r$.

$$E = \frac{c_4}{2T_r^3\gamma} \left\{ \beta + 1 - \left(\beta + 1 + \frac{\gamma}{V_r^2} \right) \exp \left(-\frac{\gamma}{V_r^2} \right) \right\} .$$

$\left(\ln \frac{f}{p} \right)^{(i)} = \left(\ln \frac{f}{p} \right)^{(0)}$ when applied to the simple fluid.

$\left(\ln \frac{f}{p} \right)^{(i)} = \left(\ln \frac{f}{p} \right)^{(h)}$ when applied to the heavy reference fluid.

$z^{(i)}$ = compressibility factor of either simple fluid ($z^{(0)}$) or heavy reference fluid ($z^{(h)}$), depending on which fugacity function is being calculated. Both are obtained from Procedure 6B1.8.

T_r = reduced temperature, T/T_c .

T = temperature in degrees Rankine.

T_c = critical temperature in degrees Rankine.

$$V_r = \text{reduced volume} = \frac{p_c V}{R T_c}, \text{ obtained from Procedure 6B1.8.}$$

$b_1, b_2, b_3, b_4, c_1, c_2, c_3, c_4, d_1, d_2, \gamma$ and β are two sets of constants, one for the simple fluid and the other for the heavy reference fluid, given in Procedure 6B1.8.

Procedure

Step 1: Obtain critical temperature, critical pressure, and acentric factor for the desired compound from Chapter 1.

Step 2: Calculate the reduced temperature and pressure.

Step 3: Use Procedure 6B1.8 to calculate compressibility factors $z^{(0)}$ and $z^{(h)}$ and the reduced volume of the simple and heavy fluids.

Step 4: Calculate $\left(\ln \frac{f}{p} \right)^{(0)}$ from equation (7G1.8-2).

Step 5: Repeat Step 4 for heavy reference fluid to calculate $\left(\ln \frac{f}{p} \right)^{(h)}$.

Step 6: Use equation (7G1.8-1) to calculate $\left(\ln \frac{f}{p} \right)$.

Step 7: Calculate the fugacity by multiplying the antilogarithm of $\left(\ln \frac{f}{p} \right)$ by the pressure.

COMMENTS ON PROCEDURE 7G1.8

Purpose

This procedure is presented as an alternate to Procedure 7G1.1 for use with a digital computer to calculate fugacities of pure hydrocarbon liquids and real gases. The results from Procedure 6B1.8 are required directly in this procedure.

Limitations

This procedure was not compared with experimental data, but is thermodynamically consistent with the (accurate) computer methods for compressibility factor, enthalpy and heat capacity. Accordingly, it should be quite reliable except in the critical region. The reliability of the method decreases with increasing uncertainty in the critical properties.

Literature Sources

The fugacity coefficient functions and the constants for both simple fluid and heavy reference fluid terms were taken from Lee and Kesler, *AIChE Journal*, **21** 510 (1975).

PROCEDURE 7H1.1

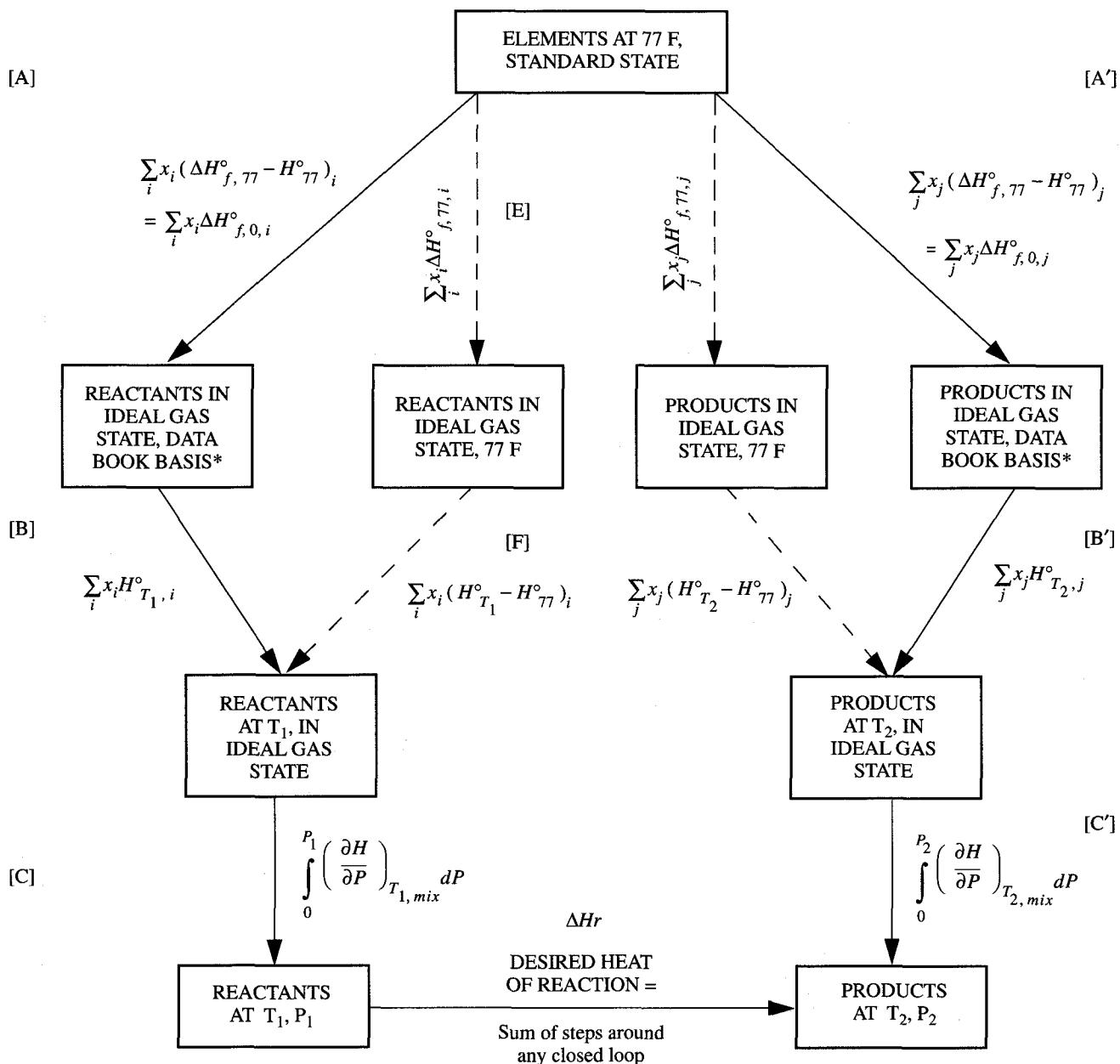
7H1.1

HEAT EFFECTS IN REACTING SYSTEMS

Discussion

The enthalpy basis used in this book does not include heat of formation allowances, so an additional step must be added when estimating enthalpies for systems which undergo chemical reaction. This procedure illustrates the calculations which are required to estimate the enthalpy changes associated with the conversion of one homogeneous vapor or liquid mixture to another when the reactant and product mixtures are not necessarily at the same pressure and temperature conditions.

The figure below shows the various steps in the calculation. The enthalpy change involved in taking the elements from the standard state at 77 F to the reactants at T_1 and P_1 , will be the sum of Steps A, B, and C. This is shown on the left side of the figure. Similarly, the right side shows the steps for taking the elements from their standard states at 77 F, to the products at T_2 and P_2 . This will be a sum of Steps A', B', and C'.



*Data Book basis is $H = 0$ for the ideal gas at 0 R.

The heat effects in reacting systems are calculated by algebraically summing the enthalpy changes associated with each of the steps indicated by a solid line in the figure.

Steps B and B' involve application of Procedure 7A1.1 to obtain the temperature effect for the ideal gas enthalpy. Steps C and C' use Procedure 7B4.1 to obtain the pressure effect. In order to complete the loop, one has to evaluate the sum of Steps A and A', which gives the heat of reaction of the ideal gas mixture based on 1 pound of reacting mixture. This is evaluated by the following equation:

$$\Delta H_r^\circ = \sum_j x_{w_j} \Delta H_{f,0,j} - \sum_i x_{w_i} \Delta H_{f,0,i} \quad (7H1.1-1)$$

ΔH_r° = heat of reaction of the ideal gas mixture based on 1 lb of reacting mixture, in Btu per pound.

j = component in the product stream.

x_{w_i} = weight fraction of the component.

$\Delta H_{f,0}$ = heat of formation of the component in the Data Book basis state from the elements in their standard states at 77 F, in Btu per pound.

i = component in the reactant stream.

Procedure

Step 1: Calculate the total enthalpy of the product and reactant streams using Procedures 7A1.1 and 7B4.1. For the reactants, this is the sum of Steps B and C, and for the products, Steps B' and C'.

Step 2: Obtain the basis state heat of formation of each substance from Table 7H1.2 and calculate the heat of reaction of the ideal gas, using equation (7H1.1-1).

Step 3: Calculate the total enthalpy change of reaction, ΔH_r , which is the algebraic sum of the heat effects around the solid path in the above figure, i.e.,

$$\Delta H_r = -\Delta H_{BC} + \Delta H_r^\circ + \Delta H_{B'C'}.$$

A negative enthalpy change, ΔH_r , indicates that an exothermic chemical reaction has taken place.

COMMENTS ON PROCEDURE 7H1.1

Purpose

This procedure, which includes Table 7H1.2, is to be used to estimate the heat effects accompanying a chemical reaction. Procedures 7A1.1 and 7B4.1 are involved.

Limitations

As written, the procedure is limited to homogeneous phases of both reactant and product streams and to mixtures of defined composition.

Reliability

The overall reliability of the method depends on the errors introduced through the use of Procedure 7B4.1 and on the nature of the reaction. If the reaction is such that small differences between large heats of formation are obtained from equation (7H1.1-1), the results will be less precise. The overall reliability should be estimated from the constituent steps at the conditions of interest. The individual heats of formation are accurate to within approximately 1 percent.

Special Comments

The heat effects for reacting systems, as shown in the preceding figure, are calculated by algebraically summing the enthalpy changes around any closed loop, shown by the solid lines. The dotted lines represent an alternate route in which the intermediate stage involves the ideal gas at 77 F rather than at the Data Book basis. The two routes give identical results provided the appropriate equations (as shown in the figure) are used for calculating the enthalpy changes. The standard heat of formation is defined as the enthalpy of a compound at 77 F relative to its elements at 77 F. Values of the standard heat of formation for components not listed in Table 7H1.2 are available from the tables of API Research Project 44 or other standard reference compilations. The Data Book basis heat of formation is defined as the enthalpy of a compound at 0 R and the ideal gas relative to the elements at 77 F. Thus, if a standard heat of formation is available, a Data Book base heat of formation may be calculated by the following equation:

$$\Delta H_{f,0} = \Delta H_{f,77}^\circ - \Delta H_{77}^\circ$$

Where:

$\Delta H_{f,0}$ = heat of formation in the basis state.

$\Delta H^{\circ}_{f,77}$ = standard heat of formation (77 F).

ΔH°_{77} = ideal gas enthalpy at 77 F relative to the ideal gas enthalpy of $H = 0$ at 0 R as given by Procedure 7A1.1.

This procedure can be used for both the hydrocarbons and nonhydrocarbons listed in Section 7A1 (or mixtures of the two groups) despite the two different enthalpy bases. The Data Book basis state cancels in the combined Steps A + B.

As written, the procedure is not sufficiently general to cover all reactive situations. However, suitable modifications should be apparent from the illustration.

Example

Estimate the total enthalpy change (per pound of reactants) which accompanies the reaction described in the following tabulation. Compositions are given in mole percent.

	Reactants	Products
Ethene	2.25
Benzene	0.47
Methylbenzene	3.56
Ethylbenzene	9.70	9.09
1,2-Dimethylbenzene	42.60	31.21
1,3-Dimethylbenzene	46.70	44.52
1,4-Dimethylbenzene	1.00	8.90
Temperature, deg F	900	920
Pressure, psia	200	190

In the following tabulation, critical constants, molecular weights, and acentric factors were obtained from Chapter 1, ideal gas enthalpies from Procedure 7A1.1, and heats of formation from Table 7H1.2:

	Mole Fraction	Critical			Acentric Factor, ω	Molecular Weight, M	Enthalpy, H^0 (Btu per lb)	Basis State Heat of Formation, $\Delta H_{f,0}$ (Btu per lb)
		Temperature		Critical Pressure, p_c (psia)				
		Deg F	Deg R	(psia)				
Reactants								
Ethylbenzene	0.097	651.2	1,110.9	524	0.3011	106.17	0.097	479.57
1,2-Dimethylbenzene	0.426	675.0	1,134.7	541	0.3136	106.17	0.426	489.55
1,3-Dimethylbenzene	0.467	651.0	1,110.7	514	0.3311	106.17	0.467	470.32
1,4-Dimethylbenzene	0.010	649.6	1,109.3	509	0.3243	106.17	0.010	472.35
Molar average	1,120.9	526	0.3182	106.17
Weight average	1.000	479.43
Products								
Ethene	0.025	48.6	508.3	730	0.0852	28.05	0.007	621.77
Benzene	0.005	552.2	1,011.9	710	0.2108	78.11	0.004	445.17
Methylbenzene	0.036	605.6	1,065.3	596	0.2641	92.14	0.032	468.93
Ethylbenzene	0.091	651.2	1,110.9	524	0.3036	106.17	0.093	491.96
1,2-Dimethylbenzene	0.312	675.0	1,134.7	541	0.3127	106.17	0.319	492.74
1,3-Dimethylbenzene	0.445	651.0	1,110.7	514	0.3260	106.17	0.455	482.46
1,4-Dimethylbenzene	0.089	649.6	1,109.3	509	0.3259	106.17	0.091	484.56
Molar average	1,104.2	534	0.3110	103.90
Weight average	1.000	487.17
								-2.63

7H1.1

The enthalpies of the products and reactants are calculated using Procedure 7B4.1:

	Reduced Temperature	Reduced Pressure	$\left(\frac{\tilde{H}^0 - \tilde{H}}{RT_c}\right)^{(0)}$	$\left(\frac{\tilde{H}^0 - \tilde{H}}{RT_c}\right)^{(1)}$	$\left(\frac{\tilde{H}^0 - \tilde{H}}{RT_c}\right)$	$H^0 - H$	* H^0	H
Reactants	1.21	0.380	0.285	0.14	0.328	6.875*	479.43	472.56‡
Products	1.25	0.356	0.249	0.11	0.283	5.965†	487.17	481.21§

As indicated in the preceding tabulation, $\Delta H_{BC} = 468.69$, and $\Delta H_{B'C'} = 481.98$. Using equation (7H1.1-1),

$$\Delta H_r^\circ = -2.63 - (-13.85) = 11.22 \text{ Btu per pound.}$$

The total enthalpy change is:

$$\Delta H_r = -472.56 + 11.22 + 481.21 = 19.87 \text{ Btu per pound.}$$

* ΔH_C .

† $\Delta H_{C'}$.

‡ ΔH_{BC} .

§ $\Delta H_{B'C'}$.

CHAPTER 8

VAPOR-LIQUID EQUILIBRIUM K-VALUES

8-0 INTRODUCTION

Vapor-liquid equilibrium relationships are conveniently defined in terms of the distribution coefficient, $K_i = y_i/x_i$. If the components form an ideal solution in the liquid phase and if the saturated vapors of the individual components are perfect gases, the system may be considered an ideal system. Under these conditions, Raoult's and Dalton's laws apply and:

$$K_i = \frac{y_i}{x_i} = \frac{p_i^*}{P} \quad (8-0.1)$$

Where:

- K_i = vapor-liquid equilibrium constant for component i at the given temperature and pressure.
- y_i = mole fraction of component i in the vapor.
- x_i = mole fraction of component i in the liquid.
- p_i^* = vapor pressure of component i .
- P = total pressure of the system.

This relationship is valid only for ideal systems, but it may be used as a reasonably good approximation for systems of close-boiling homologs at low pressures (less than approximately 30 psia) where the vapors of the individual components do not deviate appreciably from perfect gas behavior.

The relationship given as equation (8-0.1) does not hold at elevated pressures or for mixtures that do not obey Raoult's law. Further, it cannot be used if the temperature is above the critical point of any of the components. The concept of fugacity was introduced as a more convenient and more generally useful function for equilibrium calculations. The *ideal* K -value was defined as:

$$K_{ideal} = \frac{f_i^L}{f_i^V} \quad (8-0.2)$$

Where:

- f_i^L = fugacity of component i in the pure liquid state at stated system temperature and pressure.
- f_i^V = fugacity of component i in the pure vapor state at stated system temperature and pressure.

The fugacities are obtainable from one of a number of generalized fugacity charts or equations such as given in Chapter 7. The ideal K -values for each component are a function of temperature and pressure only.

Although the ideal K -value is a good approximation for many real physical situations, it is unsatisfactory for high pressures, low temperatures, and where the mixtures are increasingly complex. Particularly important is the effect of mixture composition on the K -value at higher pressures. Two approaches have been used to incorporate the effect of composition into the calculation of equilibrium data: further development of the fugacity relationships and the introduction of a third parameter, the convergence pressure. The correlations given in this chapter are based on both approaches.

Analytical Fugacity Methods

When vapor and liquid phases are in equilibrium, the fugacity of each component in the liquid phase is equal to its fugacity in the vapor phase, $\bar{f}_i^L = \bar{f}_i^V$.

The gas phase fugacity is defined by:

$$\bar{f}_i^V = \phi_i^V y_i p \quad (8-0.3)$$

Where:

ϕ_i^V = gas phase fugacity coefficient.

The liquid phase fugacity may be written in two equivalent forms:

$$\bar{f}_i^L = \gamma_i^L x_i v_i p = \phi_i^L x_i p \quad (8-0.4)$$

Where:

γ_i^L = activity coefficient of component i in the liquid mixture.

$v_i = \frac{f_i^L}{p}$ = fugacity coefficient of component i as a pure liquid.

ϕ_i^L = fugacity coefficient of component i in the liquid mixture.

The K -value relationships are:

$$K_i = \frac{\gamma_i^L v_i}{\phi_i^V} = \frac{\phi_i^L}{\phi_i^V} \quad (8-0.5)$$

When a liquid phase model such as the Chao Seader (2) regular solution equation is used, the liquid fugacity is calculated from the expression containing the activity coefficient.

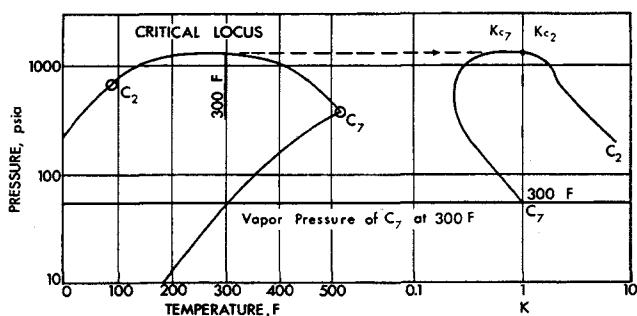


Figure 8-0.1—Convergence Pressure in the Binary System Ethane-n-Heptane (14)

If an equation of state is being used such as the Soave equation, the liquid phase fugacity is calculated from the liquid phase fugacity coefficient. In both cases, an equation of state is used to compute the gas phase fugacity coefficient.

The latter type of correlation is recommended in this chapter for hydrocarbon and certain nonhydrocarbon computer calculations. (The activity coefficient approach is used for correcting *K*-values for solvent effects.) The fugacity coefficient of a component in any phase, α , is given rigorously by the expression:

$$\ln \phi_i^\alpha = \frac{1}{RT} \int_V^\infty \left[\left(\frac{\partial p}{\partial n_i} \right)_{T, V, n_j \neq i} - \frac{RT}{V} \right] dV - \ln Z$$

To find an equilibrium point by this procedure requires a trial-and-error procedure since the volume is a function of composition. Hence, the composition must be known to start the calculational sequence. The Soave method (29), Procedure 8D1.1 in this chapter, gives a more than adequate representation of phase equilibrium of hydrocarbon and nonhydrocarbon containing mixtures over a wide range of conditions. The procedure is simple computationally and is, therefore, very fast.

The phase behavior of undefined mixtures can be predicted by a similar procedure. Procedures 8D1.5 and 8D1.6 of this chapter provide a means to determine the equilibrium behavior of undefined mixtures and mixtures of both defined and undefined components, respectively.

Close-Boiling Systems: Vapor-liquid equilibria for systems of close-boiling compounds (i.e., ethane-ethylene, propane-propylene, etc.) can be determined in the same fashion as any other hydrocarbon mixture. In general, an interaction parameter is required to more accurately model the phase behavior (relative volatility) of these binary pairs. Several systems of this type were examined using Procedure 8D1.1 and adequate predictions were obtained.

Oxygenated Compounds: Oxygenated compounds (alcohols, ethers, etc.) can be modelled using Procedure

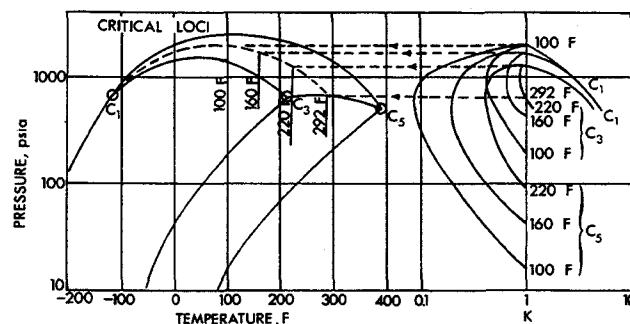


Figure 8-0.2—Convergence Pressure in the Ternary System Methane-Propane-n-Pentane (14)

8D1.1 although errors are excessive for systems that have more than 20 percent by weight of the oxygen containing compound in the liquid phase. Binary interaction parameters obtained from experimental data must be used to obtain satisfactory predictions. Interaction parameters for some binary systems are listed in Table 8D1.4.

Graphical Methods

An alternate composition correlating parameter is convergence pressure, and a number of *K*-value correlations are based on this. Among these are the NGPA (8), Winn (37), Cajander et al. (1), and Hadden and Grayson (14) methods.

Convergence Pressure: The convergence pressure of a hydrocarbon system is the pressure at which the vapor-liquid *K*-values of all the components of a system appear to converge at *K* = 1 at the system temperature. This occurs at the critical conditions since at this point the liquid and vapor phases become identical. The concept is illustrated for a binary system in Figure 8-0.1, where the left portion is the conventional pressure-temperature phase diagram similar to that discussed in Chapter 4 and the right-hand diagram, the pressure-*K*-value relationships for the two components at a given temperature meet at the *K* = 1 line (i.e., the convergence pressure). The line for the higher boiling component also crosses the *K* = 1 line at its vapor pressure.

Provided the system lies between the critical temperature of the binary components, the convergence pressure depends on the temperature only and can be determined from the experimental critical locus data for the system. For multi-component systems, however, the liquid-phase composition as well as the temperature must be considered. Convergence pressures for these systems can be obtained by treating the mixtures as a fictitious binary (8, 14, 17, 22). In the ternary

system of methane-propane-*n*-pentane, for example, the propane-*n*-pentane pair may be assumed to be the higher boiling component of a fictitious binary with methane the other component. For the ternary system in which the ratio of propane to *n*-pentane remains constant (1.5 moles per mole), the *K*-values are shown in Figure 8-0.2. Also shown are the critical locus data for each binary of the system. The transfer of convergence pressure from the pressure-*K*-value graph to the pressure-temperature graph defines a new critical locus shown as a dashed line in the figure. It is important to note from phase rule considerations, as confirmed in Figure 8-0.2, that the convergence pressure is a function of the temperature and of the liquid-phase composition exclusive of the lightest component concentration.

Kesler et al. (17) developed the method of estimating convergence pressures of more complex multicomponent mixtures which is outlined in detail in the procedures of this chapter.

Hydrocarbon System Equilibrium Data: Vapor-liquid *K*-values of hydrocarbon mixtures may be estimated from the nomographs of Procedure 8A1.1. The convergence pressure parameter necessary in the calculation may be estimated by the methods and from the graphs provided as part of the procedure.

In the fractionation of narrow-boiling mixtures, the accuracy of the *K*-values becomes increasingly important, and values obtained by the generalized correlation given as Procedure 8A1.1 are usually not suitable. This is particularly true for fractionations of essentially binary systems such as ethane-ethene, propane-propene, *n*-butane-isobutane, ethane-

propane, propane-butane, etc. Experimental data specific to the system should be used in preference, and the reader is referred to the extensive bibliographies of the literature (3, 4, 5, 9, 16, 23, 25, 26, 27, 33, 34). The procedure is also not suitable for mixtures which may form azeotropes.

Hydrocarbon-Hydrogen Equilibrium Data: The *K*-values for systems of hydrocarbons and hydrogen can be obtained from Procedure 8B1.1. The hydrogen *K*-values are obtained from a chart on which the system temperature and pressure and the MABP of the hydrogen-free liquid are parameters. The hydrocarbon *K*-values are obtained from the charts of Procedure 8A1.1 and corrected for the presence of hydrogen. The method is applicable to pressures up to 4500 psia and temperatures from -260 F to 800 F.

Hydrocarbon-Nonhydrocarbon Gas Equilibrium Data: For systems containing a hydrocarbon and a non-hydrocarbon gas other than hydrogen, Procedure 8C1.1 should be used. The method is limited to certain specific non-hydrocarbons and in some instances to the experimental data from which it was developed. In no case should it be used for system pressures above 1000 psia.

When experimental data are available, they should be used in preference to the generalized correlations when the highest degree of accuracy is required. Comprehensive bibliographies of the literature are available (9, 33, 34). Also, the *Gas Processors Association Research Report* (5), RR 64C, contains a large data set of tested experimental data. Finally, the documentation report for this chapter referred to in the preface contains a complete listing of all references used in evaluating the analytical procedures in this chapter.

COMMENTS ON PROCEDURE 8A1.1

Purpose

This procedure is to be used to estimate hydrocarbon vapor-liquid equilibrium K -values. For hydrogen, Procedure 8B1.1 is to be used, and for other nonhydrocarbon gases, Procedure 8C1.1 is given.

Because of the large number of calculational routes used to estimate K -values, the remainder of this procedure is subdivided into four separate supplementary procedures (8A1.1A through 8A1.1C), each of which applies to a different mode of calculation. Figures 8A1.2 through 8A1.18 also are included in this procedure.

Limitations

The correlation is limited to hydrocarbon mixtures of known composition and to petroleum fractions at temperatures from -260 F to 800 F and at pressures up to 5000 psia. Do not use this procedure for binary mixtures of close-boiling hydrocarbons or for mixtures which may form azeotropes.

Reliability

The K -values determined by this procedure exhibit an average error of seven percent for light non-methane containing mixtures of paraffins, olefins, and naphthenes based on Figures 8A1.16 and 8A1.17. For mixtures containing methane, the average error is 15 percent. For aromatic systems, Figures 8A1.16 and 8A1.17 can be expected to yield K -values with an average error of 14 percent. For heavy hydrocarbon mixtures, Figure 8A1.18 predicts K -values for all components within 15 percent.

Notation

The notation used is defined in the nomenclature of the procedure diagram for K -value calculations.

Figure 8A1.3 gives an overview of critical loci of hydrocarbon systems. Dashed lines on Figures 8A1.4 and 8A1.5 indicate limited or estimated data as reported by the researcher. Dashed lines on Figures 8A1.6 through 8A1.13 are estimated data using Chapter 4 methods.

The paraffin hydrocarbons shown in Figures 8A1.3 through 8A1.13 are designated as C_1 to C_{16} where the subscripts indicate the number of carbon atoms. 2-methyl paraffins are designated by $i - C_n$. Other branch compounds are denoted by name. Olefins are designated as $C_2^=$ for ethene, $C_3^=$ for propene, and $1 - C_4^=$ for 1-butene.

Special Comment

Enlarged copies of Figures 8A1.16, 8A1.17, and 8A1.18 are provided in the back of the binder.

Critical loci of methane hydrocarbon systems where the hydrocarbon contains six or more carbons are not Type I (see Chapter 4). These systems tend to form multiple liquid and solid phases at temperatures in the proximity of the methane critical temperatures and are classified as Type II and III. Such abnormal behavior can be expected when the freezing point of the heavy component is close to the critical temperature of the light component.

Description of Areas in Figure 8A1.14

The K -nomographs (Figures 8A1.16 through 8A1.18) are based on a convergence pressure of 5000 psia; at other convergence pressures, they require, in general, a correction due to effects of composition. Figure 8A1.14 is an *approximate* guide to the use of Procedures 8A1.1A, B, and C in applying the correction at corresponding regions of operating and convergence pressures.

Briefly, conditions denoted by Area A require no further correction to the K -values. The region is characterized by high convergence pressures and relatively low operating pressures; at higher operating pressures, the convergence pressures are near 5000 psia. An example of such conditions is methane-n-decane at 100 F and 500 psia.

Area C pertains to operating pressures exceeding two-tenths of the convergence pressure. The K -values are most sensitive to convergence pressure in this region, particularly as the P_{op}/P_{cv} ratio increases. A special procedure is recommended for accurate calculation of P_{cv} in this region.

Examples of Area B mixtures would be (1) a mixture of C_4 and C_5 hydrocarbons at 100 F and (2) a naturally occurring gas mixture of C through C_6 hydrocarbons at pressures up to about 500 psi.

Literature Sources

The procedure is from Hadden and Grayson, *Hydrocarbon Process. Petrol. Refiner* 40[9] 207 (1961). It is supplemented by material from the *Engineering Data Book*, Mobil Corporation, New York.

8A1.1

Figure 8A1.18 was developed by Kesler (18).
Procedure 8A1.1C was adapted from Kesler et al. (17).

Examples

A. Estimate the convergence pressure at an operating temperature of 100 F of a mixture having a boiling range equivalent to that for methane (C_1) to decane (C_{10}):

Light component: C_1 (methane)

$$\text{Average heavy component: } \frac{C_2 + C_{10}}{2} = C_6$$

From Figure 8A1.4 the convergence pressure is 2900 psi.

B. Determine which convergence pressure graph should be used for a mixture having a boiling range equivalent to that from propane (C_3) to nonane (C_9):

Light component: C_3 (propane)

$$\text{Average heavy component: } \frac{C_4 + C_9}{2} = C_{6.5} \text{ (use } C_7\text{)}$$

Figure 8A1.7 would be used for the convergence pressure.

C. Determine which convergence pressure graph should be used for each of the following mixtures, A and B:

Component		Mole Fraction*		
Number of Carbon Atoms	Name	Mixture A Reflux Drum Liquid	Mixture B Reboiler Bottoms	
-	Hydrogen	0.0009	Negligible	0.17×10^{-14}
1	Methane	0.018	Light component	0.67×10^{-14}
2	Ethane	0.051		0.43×10^{-5}
3	Propane	0.080		0.61×10^{-4}
4	Butane	0.274	Average heavy component	0.009
5	Pentane	0.363		0.049
6	Hexane	0.168		0.130
7	Heptane	0.045		0.186
8†	“225”‡	0.21×10^{-4}		0.188
9†	“275”‡	0.16×10^{-6}	Negligible	0.103
10†	“325”‡	0.32×10^{-22}		0.083
11†	“375”‡	0.17×10^{-83}		0.252
Total		1.000 +		1.000 +
		Average heavy component		Average heavy component
		$= \frac{C_2 + C_7}{2} = C_{4.5}$ (use C_5)		$= \frac{C_5 + C_{11}}{2} = C_8$

Figure 8A1.4 would apply.

Figure 8A1.8 would apply.

* From typical computer tray-to-tray results.

† Approximate.

‡ Mid-boiling point of a fraction having a 50 F boiling range.

PROCEDURE 8A1.1A**VAPOR-LIQUID EQUILIBRIUM K-VALUES FOR HYDROCARBON SYSTEMS IN AREA A****Discussion**

Procedure 8A1.1 is to be used for all preliminary calculations toward estimating K -values for hydrocarbons. If the estimated convergence pressure and operating pressure conditions are such that the point with these coordinates falls in Area A of Figure 8A1.14, the following steps are to be followed to complete the estimation of the K -values.

Procedure

Step 1: For identifiable hydrocarbons having normal boiling points below 210 F, locate the point on the temperature-pressure grid of Figure 8A1.16 or 8A1.17 corresponding to the operating temperature and pressure. For identifiable hydrocarbons having normal boiling points above 210 F and for petroleum fractions characterized by a true boiling point (TBP) curve, locate the point on the temperature-pressure grid of Figure 8A1.18.

Step 2: Lay the hairline of a nomograph reader through this point and through the component point (or through the boiling point of the component, if the component is not shown on the scale).

Step 3: Read the desired K -value at the point of intersection of the hairline with the K -scale. When using the low-temperature nomograph (Figure 8A1.16) for methane in light hydrocarbons, multiply the methane nomograph K -value by the correction indicated on the inserted chart.

COMMENTS ON PROCEDURE 8A1.1A

Purpose

This procedure is to be used to complete the estimation of vapor-liquid equilibrium K -values for hydrocarbons when the operating conditions are such that the point falls in Area A of Figure 8A1.14. The preliminary calculations are performed using Procedure 8A1.1, which is the master procedure for estimating hydrocarbon K -values under any conditions.

Special Comment

For Limitations, Reliability, Notation, and Literature Sources, see Comments on Procedure 8A1.1.

Examples

A. What is the K -value for methane in an unstabilized gasoline at 100 F and 200 psia?

From curve D, Figure 8A1.2, for stabilizer the convergence pressure is approximately 3000 psia. In Figure 8A1.14, the combination of operating and convergence pressure falls in Area A. Hence, read K directly in Figure 8A1.17 for the operating temperature and pressure. The resulting K -value is 14.7 using the C_7 to C_{12} component point for methane (see example figure).

B. What is the K -value at 100 F and 200 psia for a component of the gasoline in Example A having a boiling point of 190 F?

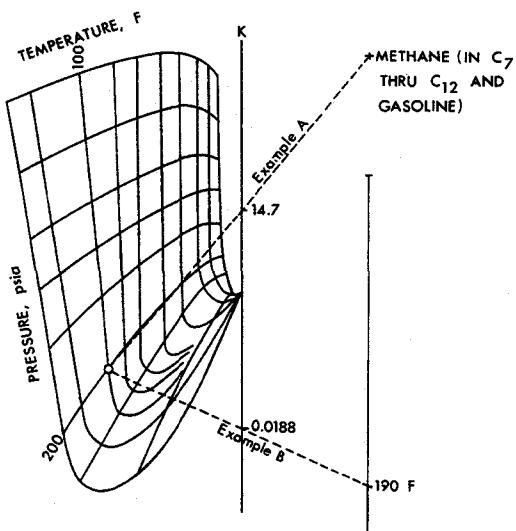
As determined in Example A, the operating conditions are in Area A so the K -value can be read directly in Figure 8A1.17. The result is 0.0188 (see example figure).

C. What is the K -value at 500 F and 100 psia for *n*-decane in a Mid-Continent crude oil containing the naturally occurring methane and all other heavier components?

From curve M, Figure 8A1.2, the convergence pressure is approximately 7000 psia at 500 F, so the point for the operating and convergence pressure falls in Area A in Figure 8A1.14. From Chapter 1, the boiling point of *n*-decane is 345.5 F. Since the boiling point of *n*-decane is higher than 210 F, the K -value for *n*-decane is read from Figure 8A1.18, $K = 0.80$.

D. What is the K -value for the 700 F mid-boiling-point fraction with the other circumstances the same as in Example C?

From Figure 8A1.18, for a component of 700 F boiling point, $K = 0.009$.



PROCEDURE 8A1.1B

VAPOR-LIQUID EQUILIBRIUM K -VALUES FOR HYDROCARBON SYSTEMS IN AREA B

Discussion

Procedure 8A1.1 is to be used for all preliminary calculations toward estimating K -values for hydrocarbons. If the estimated convergence pressure and the operating pressure conditions are such that the point with these coordinates falls in Area B of Figure 8A1.14, or if the operating temperature is less than or equal to the critical temperature of the light component, the following steps are to be followed to complete the estimation of K -values.

Procedure

Step 1: Determine the grid pressure from Figure 8A1.15 for the estimated convergence pressure and operating pressure.

Step 2: Locate the point on the temperature-pressure grid (Figures 8A1.16 to 8A1.18) corresponding to the temperature and pressure of operation.

Step 3: Connect the temperature and pressure point to the $K = 1.0$ point.

Step 4: Spot the point on this line where it is crossed by the pressure equal to the grid pressure.

Step 5: Lay the hairline of a nomograph reader through this grid point and the component point.

Step 6: Read the K -value at the point of intersection of the hairline with the K -scale.

COMMENTS ON PROCEDURE 8A1.1B

Purpose

This procedure is to be used to complete the estimation of vapor-liquid equilibrium K -values for hydrocarbons when the operating conditions are such that the point falls in Area B of Figure 8A1.14 and under certain other conditions outlined under Discussion. The preliminary calculations are performed using Procedure 8A1.1, which is the master procedure for estimating hydrocarbon K -values under any conditions.

Special Comment

For Limitations, Reliability, Notation, and Literature Sources, see Comments on Procedure 8A1.1.

Examples

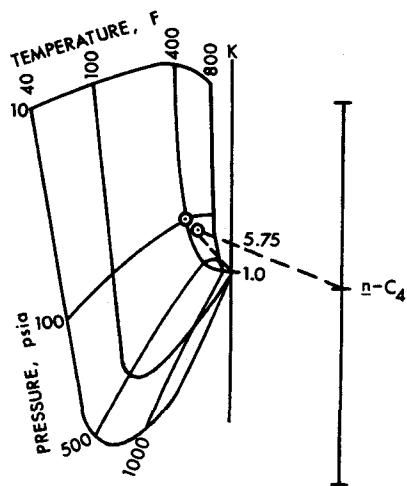
A. What is the K -value at 400 F and 100 psia for *n*-butane in a depropanized 400 F end-point gasoline system?

The estimated convergence pressure is 680 psia from Figure 8A1.2, curve A. The combination of operating and convergence pressure falls in Area B in Figure 8A1.14. Hence, the grid pressure correction is required before reading the K -value. In Figure 8A1.15, a grid pressure of 117 psia is read as the ordinate for the given operating and convergence pressures.

Locate the operating pressure and temperature in Figure 8A1.17, and connect this point to the $K = 1.00$ point. Spot the point on this line corresponding to the grid pressure. Connect this grid pressure point with the point on the nomograph component scale, and read the K -value for *n*-butane as 5.75 (see example figure).

B. Compute the reboiler temperature of a gasoline stabilizer operating at 165 psia. The composition of the liquid in the reboiler is shown in the following tabulation. Assume that the gasoline has properties similar to those used in making Figure 8A1.2.

For the first trial, assume the reboiler temperature is 350 F. The estimated convergence pressure is 940 psia (from the propane-gasoline critical locus of Figure 8A1.2, curve B). This system falls into Area B of Figure 8A1.14. Therefore, a grid correction is required. From Figure 8A1.15, the grid pressure is 190 psia. Follow Steps 2 through 4 of the procedure to determine the grid point in Figures 8A1.17 and 8A1.18.



8A1.1B

Using these figures, the K -values obtained are listed in the following tabulation:

	Liquid Composition (Mole Fraction)	K -Value (Figures 8A1.17 and 8A1.18)	$y = Kx$
C_3	0.0013	5.32	0.0069
$n-C_4$	0.0759	3.00	0.2277
$n-C_5$	0.1802	1.70	0.3063
$n-C_6$	0.2570	1.01	0.2596
$n-C_7$	0.1460	0.600	0.0876
235*	0.1043	0.420	0.0438
285*	0.0918	0.245	0.0225
335*	0.0901	0.138	0.0124
385*	0.0534	0.074	0.0042
Total	1.0000		0.9709

*Mid-boiling point of a petroleum fraction with a 50 F boiling range.

In this computation, inasmuch as the summation of the vapor mole fraction, y , is less than unity, a higher temperature should be used in the next trial to vaporize more liquid. Because the trial-and-error procedure is straightforward, the additional trials are not shown here.

C. What are the K -values for methane and ethane at -100 F and 100 psia in a methane-ethane system?

The convergence pressure from Figure 8A1.4 is 750 psia. The combination of operating and convergence pressure falls in Area B in Figure 8A1.14. Hence, the grid pressure correction is required before reading the K -value. In Figure 8A1.15 a grid pressure of 115 psia is read. Following the procedure previously outlined in Example A and using Figure 8A1.16:

$$\text{Methane } K = 6.20 (1.047) = 6.49$$

Where 1.047 is the correction factor for methane.

$$\text{Ethane } K = 0.337$$

PROCEDURE 8A1.1C

VAPOR-LIQUID EQUILIBRIUM K-VALUES FOR HYDROCARBON SYSTEMS IN AREA C

Discussion

Procedure 8A1.1 is to be used for all preliminary calculations toward estimating K -values of hydrocarbons. If the conditions are such that the desired point falls in Area C of Figure 8A1.14, the following steps are to be followed to calculate the convergence pressure and complete the estimation of K -values. This procedure is an interpolation scheme for estimating convergence pressure.

Procedure

Separate the multicomponent mixture into two sets of components: those with critical temperatures less than the operating temperature ($T_c < T_{op}$), and those with critical temperatures greater than T_{op} . Obtain the critical temperatures, critical volumes, critical pressures and acentric factors of all the components from Chapters 1, 2, and 4.

When the mixture contains only three components, the lightest component is the pseudolight, and the pseudoheavy is computed as described in Part B.

When methane is the lightest component in the mixture and the heaviest component has a critical temperature greater than *n*-hexane, use 275 R and 600 psia for the critical constants of methane.

A. Pseudolight Component

Use the set of components with $T_c < T_{op}$. Starting with the two lightest components in the mixture (1 and 2):

Step 1: Calculate the normalized mole fractions.

$$X_1 = \frac{x_1}{(x_1 + x_2)} \quad (8A1.1C-1)$$

$$X_2 = 1 - X_1 \quad (8A1.1C-2)$$

Step 2: Compute the true critical temperature of the binary mixture by Procedure 4B1.1.

Step 3: Compute the true critical pressure of the mixture from the following equation:

$$p_c = p_{pc} \left[1 + \frac{(5.808 + 4.93\omega) (T_c - T_{pc}) W}{T_{pc}} \right] \quad (8A1.1C-3)$$

Where:

$p_{pc} = \sum X_i p_{ci}$ (pseudocritical pressure in pounds per square inch absolute).

$T_{pc} = \sum X_i T_{ci}$ (pseudocritical temperature in degrees Rankine).

$\omega = \sum X_i \omega_i$.

$W = 2.23 - 8.65\omega + 12.42\omega^2$.

Compute the pseudocritical volume of the mixture from:

$$V_c = \sum X_i V_{ci}$$

Treat this binary as the lightest pure component in the mixture having a composition of $x = (x_1 + x_2)$ and T_c , p_c , V_c , ω as calculated. If there are no other components remaining in the set, this is the pseudolight component. If another component exists in the set, assign the binary the role of the lightest component and repeat steps 1 to 3. Continue until all components with $T_c < T_{op}$ have been treated.

B. Pseudoheavy Component

Follow the procedure in Part A except start with the set of components having $T_c > T_{op}$. Starting with the two heaviest components in this set (1 and 2):

Step 1: Calculate the normalized mole fractions from equations (8A1.1C-1) and (8A1.1C-2).

Step 2: Compute the true critical temperature of the mixture by Procedure 4B1.1.

Step 3: Compute the true critical pressure as in Part A, equation (8A1.1C-3).

Treat this binary as the heaviest pure component in the mixture having a composition of $x = (x_1 + x_2)$ and T_c , p_c , V_c , ω as calculated. If there are no other components in the set, this is the pseudoheavy component. If another component exists in the set, assign the binary the role of the heaviest component and repeat steps 1 to 3. Continue until all components with $T_c > T_{op}$ have been treated.

8A1.1C

C. Once the pseudolight and pseudoheavy components are formed, calculate the convergence pressure from equation (8A1.1C-3) where:

$$X_1 = \frac{V_{ch} (T_{op} - T_{ch})}{[V_{cl} (T_{cl} - T_{op}) + V_{ch} (T_{op} - T_{ch})]} \quad (8A1.1C-4)$$

$$X_h = 1.0 - X_1 \quad (8A1.1C-5)$$

Where:

V_{cl} = critical volume of pseudolight component.

V_{ch} = critical volume of pseudoheavy component.

T_{cl} = critical temperature of pseudolight component.

T_{ch} = critical temperature of pseudoheavy component.

COMMENTS ON PROCEDURE 8A1.1C

Purpose

This procedure is to be used to complete the estimation of vapor-liquid equilibrium K -values for hydrocarbons when the operating conditions are such that the point falls in Area C of Figure 8A1.14 or under certain other circumstances as noted under Discussion. The preliminary calculations are performed using Procedure 8A1.1, which is the master procedure for estimating hydrocarbon K -values under any conditions.

Special Comment

For Limitations, Reliability, Notation, and Literature Sources, see Comments on Procedure 8A1.1.

Example

Calculate the dew-point temperature and equilibrium liquid composition at 1500 psia for a mixture containing 68.9, 10.8, and 20.3 mole percent of methane, propane, and pentane, respectively, in the vapor phase.

This example illustrates the iterative procedure required when the liquid composition is not known. It is necessary to assume the temperature and convergence pressure and calculate an approximate liquid-phase composition to check the assumed conditions, repeating until no further change occurs.

For Trial 1, assume 250 F for the temperature and read the convergence pressure from the C_1 through C_5 critical locus in Figure 8A1.4. The estimate is $p_{cv} = 1880$ psia. In Figure 8A1.15, the grid pressure is $p_g = 2940$ psia. From Figure 8A1.17 read the K -values as:

Trial 1

	Molecular Weight	API Gravity	$K@$ 250 F	y_i	$x_i = y_i/K_i$
C_1	—	—	1.86†	0.689	0.3704
C_3	44.1	147.2	0.86	0.108	0.1256
$n-C_5$	72.2	92.8	0.44	0.203	0.4614
				1.000	0.9574

† K -value for C_1 in a 90 API solvent.

Since $\sum x < 1$, assume 225 F for the second trial. Calculate the convergence pressure from the estimated liquid composition.

Trial 2

Component	Critical Temperature (degrees Rankine)	Critical Pressure (pounds per square inch absolute)	ω	Critical Volume (cubic feet per pound mole)
C_1	343.4	667.8	0.0108	1.585
C_3	666.0	616.3	0.1517	3.243
$n-C_5$	845.7	529.1	0.2486	4.874

According to the procedure, since this is a ternary system the pseudolight component is methane and the pseudoheavy component is a mixture of C_3 and $n-C_5$. The pseudolight component therefore has the properties of methane.

PROCEDURE 8B1.1

VAPOR-LIQUID EQUILIBRIUM *K*-VALUES FOR SYSTEMS CONTAINING HYDROCARBONS AND HYDROGEN

Discussion

The following procedure is useful for calculating the vapor-liquid equilibrium *K*-values for multi-component hydrogen-hydrocarbon-nonhydrocarbon systems.

Procedure

Step 1: Determine *K*-values for the hydrocarbons, including methane, from the *K*-nomographs (Figures 8A1.16, 8A1.17, and 8A1.18 using a convergence pressure of 5000 psia) at the system temperature and the system pressure.

Step 2: Determine *K*-values of nonhydrocarbons from Figure 8C1.2 or 8C1.3.

Step 3: Determine or estimate the vapor and liquid compositions and calculate a molal average boiling point (MABP) of the hydrogen-free liquid and of the total vapor.

Step 4: From Figure 8B1.2 determine the *K*-value of hydrogen.

Step 5: From Figure 8B1.3 determine the correction factors for the nonmethane hydrocarbon *K*-values for the presence of hydrogen. From the insert of Figure 8B1.3 determine the multiplying correction for the presence of methane.

Step 6: Calculate the corrected *K*-values for hydrocarbons (except methane, which requires no correction in multicomponent hydrogen systems) by multiplying together the three factors from Steps 1 and 5. Nonhydrocarbons require no correction.

Step 7: For naphthenic and aromatic hydrocarbons obtain the correction factor for the hydrogen *K*-value from Procedure 8B1.5. Multiply the hydrogen *K*-value by this correction.

Step 8: Repeat Steps 2 through 7 until the assumed and calculated compositions check within an acceptable tolerance.

For mixtures without methane, the procedure is the same except that no correction factor for the presence of methane is required. For binary mixtures of hydrogen and methane, use Figure 8B1.4 for the *K*-value of methane.

COMMENTS ON PROCEDURE 8B1.1

Purpose

This procedure is to be used to determine the K -values for systems containing nonhydrocarbons and hydrocarbons. Although developed primarily for hydrogen-paraffin-olefin systems, the K -values for hydrogen can be suitably corrected for the presence of aromatics.

Limitations

The correlation is not applicable for pressures above 10,000 psia, for temperatures lower than -300 F or higher than 900 F (but not above a pseudocritical temperature of 0.9 for the hydrocarbons in the liquid phase), or to hydrocarbon mixtures having an MABP of the liquid ($MABP_L$) above 700 F.

Reliability

The correlations of K -values for hydrogen-hydrocarbon systems have been tested against experimental data. The results are given in the following tabulation:

Figure	Pressure (pounds per square inch absolute)	Temperature (degrees Fahrenheit)	Number of Experimental Points	Average Deviation (percent)
8B1.2	10 to 10,000	-300 to 900	395	12
8B1.3	10 to 4,500	-260 to 800	380	23
8B1.4	10 to 5,000	-300 to -150	27	8.3

Special Comments

At low hydrogen concentrations (below 5 mole percent in the vapor) and pressures below 1500 psia, the original hydrocarbon nomographs, Figures 8A1.16, 8A1.17, and 8A1.18 can be used without the correction of Figure 8B1.3 for the presence of hydrogen.

The original correlation was developed and has been tested with data for hydrogen in paraffins, olefins, naphthenes, and aromatics. Based on limited data a correction for hydrogen-naphthalene systems and hydrogen-aromatic mixtures was developed and is provided.

Literature Source

The procedure was developed by Shen, *Proc. API* 44[III] 23 (1964). The naphthalene and aromatic correction was adapted by Graboski and Daubert (11) from Kouzel (20) and Kesler (19).

Examples

A. Calculate the K -values of the components at -100 F and 1000 psia of a hydrogen-ethene-ethane system, the feed composition of which is:

Mole Percent	
Hydrogen	32.25
Ethene	41.68
Ethane	26.07
Total	<u>100.00</u>

For pure hydrocarbon mixtures, from Figure 8A1.16:

$$\begin{aligned} K_{C_2H_4(nomo)} &= 0.180 \\ K_{C_2H_6(nomo)} &= 0.102 \end{aligned}$$

Assuming $MABP_L$ of -130 F (between those of ethene and ethane) as a first approximation, from Figure 8B1.2:

$$K_{H_2} = 22.7$$

Assuming $MABP_V = -300$ F (between those of hydrogen and ethene), from Figure 8B1.3:

$$K\text{-value correction} = 0.85$$

Then,

$$\begin{aligned} K_{C_2H_4} &= (0.85)(0.180) = 0.153 \\ K_{C_2H_6} &= (0.85)(0.102) = 0.0867 \end{aligned}$$

PROCEDURE 8B1.5

HYDROGEN K-VALUE CORRECTION FOR THE PRESENCE OF NAPHTHENES AND AROMATICS

Discussion

This procedure is used to correct hydrogen *K*-values for the presence of naphthenic and aromatic hydrocarbons.

Procedure

Step 1: Determine the MABP and specific gravity of the hydrogen-free liquid phase. For hydrocarbons, use the data in Chapters 1 and 6. For C₁ through C₄ hydrocarbons and nonhydrocarbons establish the apparent specific gravity from Table 8B1.7.

Step 2: Using the normal boiling points and specific gravities of normal paraffins from Chapter 1, determine a specific gravity, called the equivalent normal paraffin specific gravity, at the MABP.

Step 3: From Figure 8B1.6, locate the pseudosolubility parameters for the actual and equivalent paraffin liquid phases. For binary mixtures, Table 8B1.7 may be used in place of Figure 8B1.6.

Step 4: Calculate the correction factor for the hydrogen *K*-value from equation (8B1.5-1).

$$\ln \gamma = \left[\frac{V_{H_2}}{RT} \left\{ (\delta_{H_2} - \bar{\delta})^2 - (\delta_{H_2} - \bar{\delta}^*)^2 \right\} \right] \quad (8B1.5-1)$$

Where:

γ = correction factor.

V_{H_2} = 31.0 cm³ per g-mole.

δ_{H_2} = 3.25 (cal/cm³)^{1/2}.

R = 1.987 (cal) per (g-mole) (deg K).

T = absolute temperature, in degrees Kelvin.

$\bar{\delta}$ = pseudosolubility parameter of the actual hydrogen free liquid in (cal per cm³)^{1/2}.

$\bar{\delta}^*$ = pseudosolubility parameter of the equivalent normal paraffin in (cal per cm³)^{1/2}.

Step 5: Multiply the hydrogen *K*-value from Procedure 8B1.1 by the correction factor in Step 4.

COMMENTS ON PROCEDURE 8B1.5

Purpose

This procedure is used to correct hydrogen *K*-values in systems containing naphthenic and aromatic hydrocarbons.

Limitations

The procedure has the same restrictions as those on Procedure 8B1.1.

Reliability

The procedure has been tested with limited data. It has been found to yield errors in hydrogen *K*-values of 10 to 15 percent when compared with experimental data.

Literature Source

The procedure was developed by Graboski and Daubert (11) based on the work of Kouzel (20) and Kesler (19).

Example

As a step in a calculation from Procedure 8B1.1, calculate the *K*-value of hydrogen in a mixture of hydrogen-hydrogen sulfide and a light natural fraction at 100 F and 500 psia. The liquid composition is as follows:

Component	Liquid Mole Percent
Hydrogen	1.70
Hydrogen Sulfide	15.65
Fraction	82.65

The fraction has a specific gravity of 0.797 and an MABP of 301 F. The boiling point of H₂S is -76.6 F and its apparent specific gravity is 0.789 from Table 8B1.7. The molecular weights are 127 and 34 for the fraction and H₂S, respectively.

The MABP of the hydrogen-free liquid phase is determined from the composition data.

$$X_{i, \text{H}_2\text{-free}} = \frac{x_i}{1 - x_{\text{H}_2}}$$

$$X_{\text{H}_2\text{S}, \text{H}_2\text{-free}} = \frac{0.1565}{1 - 0.017} = 0.1592$$

$$\text{MABP}_{\text{H}_2\text{-free}} = \sum (X_{i, \text{H}_2\text{-free}}) (T_{b_i})$$

Where:

T_{b_i} = normal boiling point in degrees Fahrenheit.

$$\text{MABP}_{\text{H}_2\text{-free}} = (0.1592)(-76.6) + (0.8408)(301) = 240.9 \text{ F.}$$

$$\text{sp gr } 60/60 = 1/\sum [(MW_{i, \text{H}_2\text{-free}})/(\text{sp gr } 60/60)_i].$$

$$MW_{i, \text{H}_2\text{-free}} = \frac{X_i MW_i}{\sum X_j MW_j}.$$

$$MW_{\text{H}_2\text{S}, \text{H}_2\text{-free}} = \frac{0.1592(34.0)}{0.1592(34.0) + (0.8408)(127.0)} = 0.048.$$

$$\text{sp gr } 60/60 = 1/\left(\frac{0.0482}{0.789} + \frac{0.9518}{0.797}\right) = 0.7966.$$

From Chapter 1, the equivalent normal paraffin lies between *n*-heptane ($T_b = 209.17$, sp gr = 0.6882) and *n*-octane ($T_b = 258.2$, sp gr = 0.7068). The average specific gravity by interpolating with boiling point is:

$$\text{sp gr} = 0.6882 + \frac{(240.9 - 209.17)}{(258.2 - 209.17)} (0.7068 - 0.6882) = 0.7002$$

From Figure 8B1.6, read

$$\bar{\delta} = 8.06 (\text{cal}/\text{cm}^3)^{1/2}$$

$$\bar{\delta}^* = 7.51 (\text{cal}/\text{cm}^3)^{1/2}$$

From equation (8B1.5-1)

$$\ln \gamma = \frac{31.0}{(1.987)(311)} \left[(3.25 - 8.06)^2 - (3.25 - 7.51)^2 \right]$$

$$\ln \gamma = 0.2502$$

or

$$\gamma = 1.284$$

From Procedure 8B1.1 the hydrogen *K*-value is 41.0. The corrected hydrogen *K*-value is therefore:

$$K_{\text{H}_2} = (41.0)(1.284) = 52.66$$

An experimental *K*-value is 50.9.

This corrected *K*-value is used in the flash calculation in Procedure 8B1.1 to obtain the liquid composition for the next trial.

PROCEDURE 8C1.1

VAPOR-LIQUID EQUILIBRIUM *K*-VALUES FOR SYSTEMS CONTAINING HYDROCARBONS AND NONHYDROCARBON GASES

Discussion

This procedure is used to determine the vapor-liquid equilibrium *K*-values for mixtures of non-hydrocarbon gases other than hydrogen with hydrocarbons. Hydrocarbon *K*-values are determined by Procedure 8A1.1.

Procedure

Step 1: Locate the component points in Figure 8C1.2 or 8C1.3.

Step 2: Locate the point on the temperature-pressure grid of Figure 8C1.2 or 8C1.3 corresponding to the operating temperature and pressure.

Step 3: Lay the hairline of a nomograph reader through each component point and the temperature-pressure point.

Step 4: Read the *K*-values at the point of intersection of the hairline with the *K*-scale.

Step 5: For systems where the *K*-value of a reference system was determined, calculate the *K*-value correction using equation (8C1.1-1).

$$\ln \gamma = \frac{1}{RT} \left[V_1 (\delta_1 - \bar{\delta})^2 - V_2 (\delta_2 - \delta^*)^2 \right] \quad (8C1.1-1)$$

Where:

V_1 = molar volume from Table 8B1.7 for the nonhydrocarbon in question.

V_2 = molar volume of the nonhydrocarbon in the reference mixture (preferably the same as in the real mixture) from Table 8B1.7.

R = 1.987 (cal) per (g-mole) (deg K).

T = temperature, in degrees Kelvin.

δ_1 = solubility parameter of the nonhydrocarbon in the real mixture (from Table 8B1.7) in (cal per cm³)^{1/2}.

δ_2 = solubility parameter of the nonhydrocarbon in the reference mixture (from Table 8B1.7) in (cal per cm³)^{1/2}.

$\bar{\delta}$ = pseudosolubility parameter of the nonhydrocarbon free reference mixture in (cal per cm³)^{1/2}.

δ^* = solubility parameter of the hydrocarbon in the reference mixture in (cal per cm³)^{1/2}.

$\bar{\delta}$ may be obtained from Table 8B1.7 for binary mixtures or calculated using the method given in Procedure 8B1.5 for hydrogen *K*-value correction.

Step 6: Compute the *K*-value by multiplying the reference mixture *K*-value by the correction factor from Step 5.

COMMENTS ON PROCEDURE 8C1.1

Purpose

This procedure is to be used to determine the *K*-values for systems containing hydrocarbons and the nonhydrocarbon gases except hydrogen. Figures 8C1.2 and 8C1.3 are used in the procedure.

Limitations

The procedure was developed based on a limited amount of data. When estimating *K*-values using the reference mixture procedure the best results will be obtained when the reference mixture and the real mixture contain the same nonhydrocarbon. The procedure using the reference compound applies only to highly supercritical nonhydrocarbon fluids (N₂, CO, O₂). Other fluids noted on the figures cannot be used as reference systems.

Reliability

- a. *Supercritical:* For supercritical fluids, the error in predicted *K*-value is 15 percent, based on data for nitrogen and carbon monoxide. Extrapolation to other solutes could yield larger errors.

b. *Subcritical*: For hydrogen sulfide, the average error is 11 percent. For carbon dioxide, the average error is 14 percent. For other systems, errors of 18 percent can be expected.

Special Comments

Data on the solubility of hydrocarbon gases in water, the water content of natural gases in contact with liquid water, and vapor-solid equilibrium ratios of hydrocarbons in hydrate systems are given in Chapter 9.

Enlarged copies of Figures 8C1.2 and 8C1.3 are given in the back of the binder.

Additional points can be added to the nomographs as data become available.

Literature Sources

Figures 8C1.2 and 8C1.3 were prepared by modification of the vapor-liquid equilibria charts of Hadden and Grayson, *Hydrocarbon Process. Petrol. Refiner* 40 [9] 207 (1961). The correction procedure was adapted by Graboski and Daubert (11) from Kouzel (20). The correlation for H_2S was developed by Kesler (19).

Examples

A. Find the K -value of carbon monoxide in *n*-octane at 392 F and 500 psia.

From Figure 8C1.3, the K -value of CO in propane at 392 F, 500 psia (hypothetical) is 8.1.

Since the system is a binary, the pseudosolubility parameter of the CO-free actual mixture may be obtained directly from Table 8B1.7 as 7.55 (cal/cm^3) $^{1/2}$. The data for CO from Table 8B1.7 are as follows: $V = 35.2$ ($\text{cm}^3/\text{g-mole}$); $\delta = 3.13$ (cal/cm^3) $^{1/2}$. For propane Table 8B1.7 gives $\delta = 6.40$ (cal/cm^3) $^{1/2}$.

The activity correction is therefore:

$$\ln \gamma = \frac{(35.2)}{(1.987)(473)} \left[(3.13 - 7.55)^2 - (3.13 - 6.40)^2 \right]$$

$$\ln \gamma = 0.3315$$

$$\gamma = 1.393$$

or $K_{\text{CO}} = (1.393)(8.1) = 11.28$

An experimental K -value is 11.49.

B. Find the K -value of H_2S in *n*-nonane at 400 F and 186.6 psia.

From Figure 8C1.3, the reference point for H_2S is read on the curved scale at the value of 186.6 psia. The K -value is then read as 8.0. An experimental value is 8.53.

C. Estimate the K -value of oxygen in a light petroleum fraction with a specific gravity of 0.80 and a mole average boiling point of 350 F at 100 F and 250 psia.

From Figure 8C1.3, there are no data available for oxygen systems. Choose nitrogen in *n*-butane as the reference and read the K -value of nitrogen as 22.

Apply equation (8C1.1) using component (1) as oxygen and component (2) as nitrogen. The solubility parameter of the fraction from Figure 8B1.6 is 8.0 (cal/cm^3) $^{1/2}$. From Table 8B1.7 and Figure 8B1.6, the following properties are available:

Compound	Molar Volume (cm^3 per g-mole)	Solubility Parameter (cal/cm^3) $^{1/2}$
Oxygen	28.4	4.00
Nitrogen	53	4.44
<i>n</i> -butane	—	6.77
Light fraction	—	8.00

Compute the K -value correction as:

$$\ln \gamma = \frac{28.4}{(1.987)(311)} (4.00 - 8.00)^2 - \frac{(53.0)}{(1.987)(311)} (4.44 - 6.77)^2$$

$$\ln \gamma = 0.2697$$

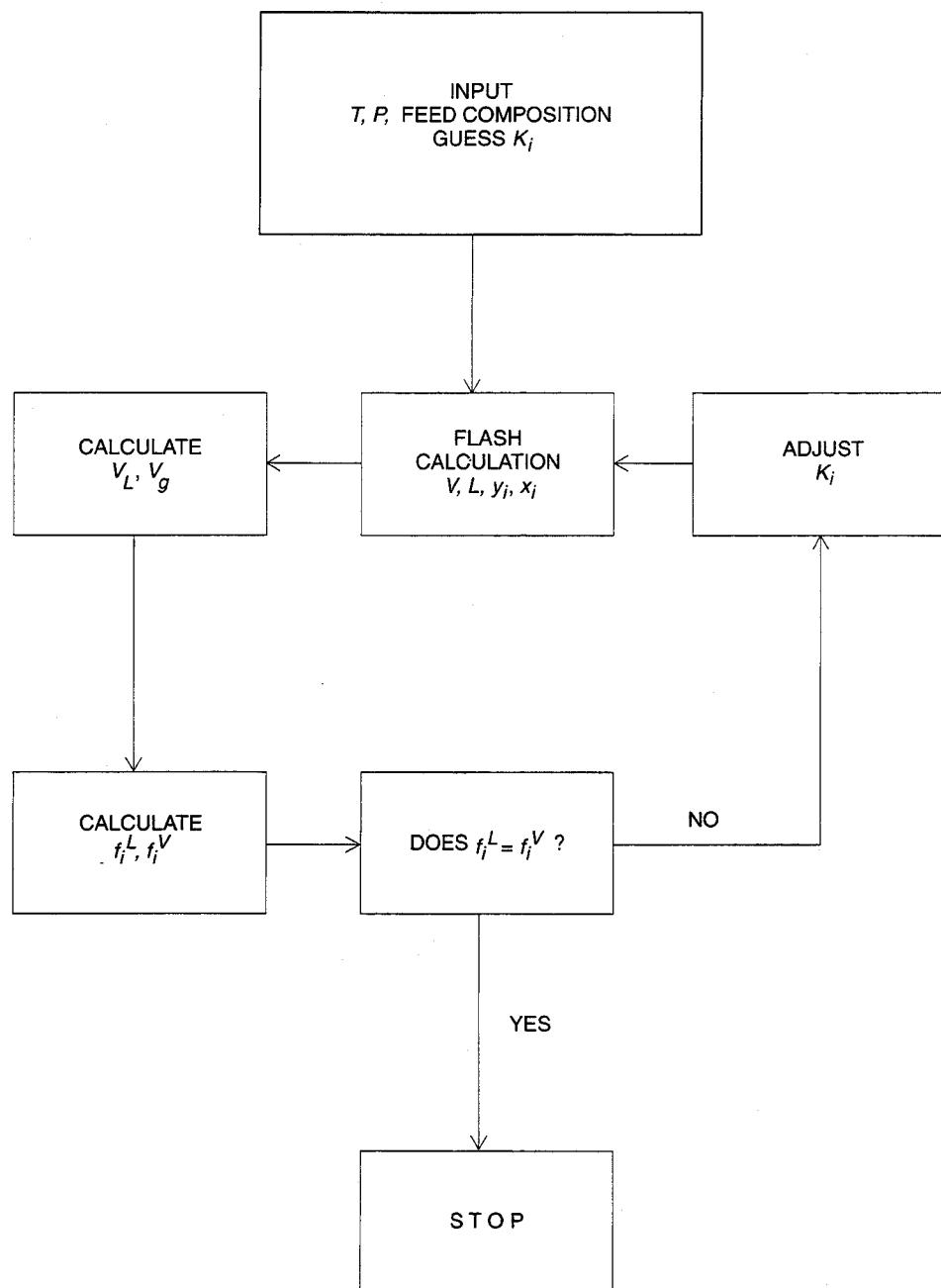
or $\gamma = 1.3096$

Therefore, the oxygen K -value is:

$$K = (1.3096)(22.0) = 28.81$$

No experimental value is available.

PROCEDURE 8D1.1 (Continued)
PROCEDURE DIAGRAM FOR K-VALUE CALCULATIONS



COMMENTS ON PROCEDURE 8D1.1**Purpose**

This procedure may be used to estimate hydrocarbon and nonhydrocarbon vapor-liquid equilibrium K -values. For completely defined mixtures, Procedure 8D1.1 is followed directly. For mixtures of undefined components, Procedure 8D1.5 must be followed in addition to Procedure 8D1.1. For mixtures containing both defined and undefined components, Procedure 8D1.6 should be used. If the nonhydrocarbons N_2 , H_2S , CO_2 , CO , H_2 , methanol, ethanol, diisopropyl ether, or MTBE are present, obtain the recommended binary interaction parameters from Table 8D1.4. If the generalized equations for interaction parameters are used, the required solubility parameters may be obtained from Table 8B1.7 or calculated by equation (8B1.7-1).

Limitations

This procedure is limited to hydrocarbons and the nonhydrocarbons, hydrogen, hydrogen sulfide, carbon dioxide, carbon monoxide, and nitrogen. Other nonhydrocarbons, such as oxygenated compounds, may be added using interaction parameters determined from experimental data. Predictions for these nonhydrocarbons, however, may not be as accurate as the compounds listed above.

The correlation has been tested against a wide variety of mixtures and has been found to be applicable at all temperatures of interest. The procedure is generally most accurate when the liquid phase reduced temperature is greater than 0.50 based on Kay's rule for the critical temperature of the mixture. It is most accurate for pressures below 3000 psia. Caution should also be exercised, however, when using this method close to the mixture critical point.

Accuracy

K -value predictions of binary and multicomponent hydrocarbon mixtures excluding methane are typically less than 10 percent. Generally, K -value predictions for the light component(s) are better than those for heavier component(s).

For methane systems, overall errors in the K -value are about nine percent when using optimized interaction parameters.

For mixtures containing nonhydrocarbons, expected errors in K -value predictions when using optimal interaction parameters are 10 to 15 percent for the nonhydrocarbon and less than 10 percent for the hydrocarbon.

For mixtures containing methanol or ethanol, errors are typically 30 percent for the alcohol K -value and 10 percent for the hydrocarbon K -value. This method should not be used for situations where the alcohol is more than 20 percent by weight in the liquid phase. Mixtures of MTBE or diisopropyl ether with hydrocarbons typically yield errors of approximately 10 percent for all K -values. Caution should be used when the ether is more than 20 percent by weight in the liquid phase.

For multicomponent systems involving hydrocarbons and nonhydrocarbons, K -value errors will be similar to those for binary systems if the hydrocarbon portion represents the majority of the mixture. For systems with a relatively small hydrocarbon content, larger errors may be expected.

Literature Sources

The procedure is from Soave, *Chem. Eng. Sci.*, 27, 1197 (1972). It is adapted and supplemented by Graboski and Daubert (10, 11) and Moysan et al. (22). Energy constant enhancements and new interaction parameters are based on previously unpublished work by Thorwart and Daubert (31, 32).

$$\alpha_i = 0.0147 + 0.933\alpha_i^o - 0.010 \quad (TMFP) \quad (8D1.5-18)$$

Equation (8D1.5-18) improved the accuracy of the Soave result for whole crude data. In equation (8D1.5-18), α_i^o is the original Soave α , as calculated from equation (8D1.5-7) and TMFP is given by:

$TMF_P = 10.0 - \text{the calculated flash volume when}$
 $\text{the 20 percent TBP temperature is}$
 $\text{used as the flash temperature (at a}$
 $\text{pressure of 14.7 pounds per square}$
 inch absolute).

To use the α modification, the 20 percent TBP temperature is used as a flash temperature, and TMFP is evaluated from equation (8D1.5-19). If TMFP is positive, no α modification is required. If TMFP is negative, the value of TMFP is substituted into equation (8D1.5-18) and the modified values of α are used along with the remainder of the Soave procedure to determine the flash volume.

Procedure

Step 1: Given a TBP curve and specific gravity data for a petroleum fraction, divide the mixture into fractions, each with a boiling range of approximately 50 F. For narrow boiling fractions, the boiling range of each component should be 10 to 25 F, depending on the volume distilled for a given temperature range.

Step 2: Estimate the critical properties for each pseudocomponent using Procedures 4D3.3 and 4D4.3. The molecular weights may be evaluated from Procedure 2B2.1. The critical properties of any pure components can be obtained from Chapter 1 or estimated if necessary as described in Chapter 4.

Step 3: Calculate the acentric factors, ω_i for each pseudocomponent using the Lee Kesler equation [AIChE J., 21(3), 510 (1975)].

Step 4: Obtain a set of initial K -values, using a method outlined in this chapter, or some other suitable source.

Step 5: Perform a flash calculation, using equation (8D1.5-9) and (8D1.5-10) to find x_i , y_i , and V .

Step 6: Refer to Table 3C1.1 and choose the appropriate set of coefficients for equation (8D1.5-8).

Step 7: Solve for a_i , b_i , b , α_i , SL_i , α_{ij} , a_{ij} , $\alpha\bar{a}$, A , B , and Z using equations (8D1.5-2) through (8D1.5-8) and (8D1.5-12) through (8D1.5-14). Since $\alpha\bar{a}$, b , A , B , and Z depend on the phase of the system, they must be solved separately for the liquid and vapor phases.

Step 8: Using equations (8D1.5-11) and (8D1.5-15), the fugacities of each component are evaluated in both the liquid and vapor phases.

Step 9: If the fugacities are equal for each component in both phases, then the equilibrium K -values are correct and the flash volume can then be determined from equations (8D1.5-16) and (8D1.5-17). Otherwise, the K -values must be readjusted and the entire procedure from Step 4 repeated.

Optional

Step 10: For whole crude data, it is recommended that the 20 percent TBP temperature be used as a flash temperature at a pressure of one atmosphere and the flash volume calculated using Steps 1 through 9 above. If the resultant flash volume is below 10 percent, no modification of the above procedure is necessary. Otherwise, an α modification may be used as given by equations (8D1.5-18) and (8D1.5-19).

$$\alpha_i = 0.0147 + 0.933\alpha_i^{\circ} - 0.010 \text{ (TMFP)} \quad (8D1.5-18)$$

Equation (8D1.5-18) improved the accuracy of the Soave result for whole crude data. In equation (8D1.5-18), α_i° is the original Soave α , as calculated from equation (8D1.5-7) and TMFP is given by:

$$\text{TMFP} = 10.0 - \text{the calculated flash volume when the 20 percent TBP temperature is used as the flash temperature (at a pressure of 14.7 pounds per square inch absolute).} \quad (8D1.5-19)$$

To use the α modification, the 20 percent TBP temperature is used as a flash temperature, and TMFP is evaluated from equation (8D1.5-19). If TMFP is positive, no α modification is required. If TMFP is negative, the value of TMFP is substituted into equation (8D1.5-18) and the modified values of α are used along with the remainder of the Soave procedure to determine the flash volume.

Procedure

Step 1: Given a TBP curve and specific gravity data for a petroleum fraction, divide the mixture into fractions, each with a boiling range of approximately 50 F. For narrow boiling fractions, the boiling range of each component should be 10 to 25 F, depending on the volume distilled for a given temperature range.

Step 2: Estimate the critical properties for each pseudocomponent using Procedures 4D3.3 and 4D4.3. The molecular weights may be evaluated from Procedure 2B2.1. The critical properties of any pure components can be obtained from Chapter 1 or estimated if necessary as described in Chapter 4.

Step 3: Calculate the acentric factors, ω_i , for each pseudocomponent using the Lee Kesler equation [AIChE J., 21(3), 510 (1975)].

Step 4: Obtain a set of initial K -values, using a method outlined in this chapter, or some other suitable source.

Step 5: Perform a flash calculation, using equation (8D1.5-9) and (8D1.5-10) to find x_i , y_i , and V .

Step 6: Refer to Table 3C1.1 and choose the appropriate set of coefficients for equation (8D1.5-8).

Step 7: Solve for a_i , b_i , \bar{b} , α_i , SL_i , α_{ij} , a_{ij} , $\alpha\bar{a}$, A , B , and Z using equations (8D1.5-2) through (8D1.5-8) and (8D1.5-12) through (8D1.5-14). Since $\alpha\bar{a}$, b , A , B , and Z depend on the phase of the system, they must be solved separately for the liquid and vapor phases.

Step 8: Using equations (8D1.5-11) and (8D1.5-15), the fugacities of each component are evaluated in both the liquid and vapor phases.

Step 9: If the fugacities are equal for each component in both phases, then the equilibrium K -values are correct and the flash volume can then be determined from equations (8D1.5-16) and (8D1.5-17). Otherwise, the K -values must be readjusted and the entire procedure from Step 4 repeated.

Optional

Step 10: For whole crude data, it is recommended that the 20 percent TBP temperature be used as a flash temperature at a pressure of one atmosphere and the flash volume calculated using Steps 1 through 9 above. If the resultant flash volume is below 10 percent, no modification of the above procedure is necessary. Otherwise, an α modification may be used as given by equations (8D1.5-18) and (8D1.5-19).

COMMENTS ON PROCEDURE 8D1.5

Purpose

This procedure is to be used to estimate the vapor-liquid equilibrium K -values as well as the flash volume of petroleum fractions.

Limitations

The procedure is most accurate for predicting flash volumes in the range of 20 to 90 percent.

The procedure has been tested on a variety of petroleum fractions and has been determined to be applicable at all temperatures of interest, but it only has been evaluated for pressures from atmospheric to 500 pounds per square inch absolute.

Reliability

For flash volumes above 25 percent, the average error in the Soave predicted flash volume is approximately five percent of the value regardless of the nature of the petroleum fraction. For flash volumes below 25 percent, the average error is approximately 25 percent for whole crudes and heavy residua, and it may be considerably higher for narrow boiling fractions although insufficient data were available for estimating the error of narrow boiling fractions in this flash volume range.

Where:

a_i = energy constant of component i .

b_i = volume constant of component i .

T_{c_i} = critical temperature of component i in degrees Rankine.

p_{c_i} = critical pressure of component i in pounds per square inch absolute.

R = gas constant = 10.731 (psia) (cu ft) per (lb-mole) (deg R).

For all defined components α_i is given by equation (8D1.6-5).

$$\alpha_i = \left[1 + S_{1i} \left(1 - \frac{1}{\sqrt{T_{r_i}}} \right) + S_{2i} \frac{\left(1 - \frac{1}{\sqrt{T_{r_i}}} \right)^2}{\sqrt{T_{r_i}}} \right]^{-1} \quad (8D1.6-5)$$

Where:

$$T_{r_i} = \text{reduced temperature of component } i = \frac{T}{T_{c_i}}$$

S_{1i}, S_{2i} = pure component parameters for species i (Tables 8D1.2-3).

For components where S_1 and S_2 are not available, S_2 can be set equal to zero; and S_1 may be estimated by

$$S_{1i} = 0.48508 + 1.55171\omega_i - 0.15613\omega_i^2 \quad (8D1.6-6)$$

Where:

ω_i = acentric factor of component i .

D. Equation Constants for Undefined Components

The undefined components in a mixture must first be characterized as one or more pseudocomponents using the procedures of Chapters 2 through 4 of the Technical Data Book. It is assumed that some information is available for the undefined mixture (Watson K factor, average boiling point, distillation data, etc.). For each pseudocomponent, a pseudocritical temperature and pressure must be determined using Procedures 4D3.1 and 4D4.1 of the Technical Data Book. Also, an acentric factor must be obtained using Procedure 2B3.1 of the Technical Data Book. The procedure for determining equation constants for defined components can then be used to determine a_i and b_i . To determine the α_i parameter for each pseudocomponent, use equation (8D1.6-5) by setting S_2 equal to zero and determining S_1 from the acentric factor. In this way, the undefined components in the mixture are approximated as one (or more) single components.

E. Equations for Composition Averaged Parameters

The composition averaged parameters αa and b are calculated from equations (8D1.6-7) and (8D1.6-8).

$$\alpha a = \sum \sum x_i x_j \alpha_{ij} a_{ij} \quad (8D1.6-7)$$

$$b = \sum x_i b_i \quad (8D1.6-8)$$

The cross mixture parameter $\alpha_{ij} a_{ij}$ is given by equation (8D1.6-8).

$$\alpha_{ij} a_{ij} = (1 - k_{ij}) \sqrt{\alpha_i \alpha_j a_i a_j} \quad (8D1.6-9)$$

Where:

k_{ij} = interaction coefficient.

In these equations, the pseudocomponents are treated as single components in the mixture.

F. Interaction Coefficients

Binary interaction coefficients for pairs of defined components can be obtained from Table 8D1.4 or estimated with equations (8D1.4-1) through (8D1.4-5) if possible. Interaction coefficients for pseudocomponent pairs and defined hydrocarbon/pseudocomponent pairs should be set equal to zero. For pseudocomponent interactions with inorganic gases, use equations (8D1.4-1) through (8D1.4-5). If solubility parameters are required to estimate the interaction coefficient, they may be calculated from the equation given in Table 8B1.7, where the heat of vaporization of petroleum fractions can be calculated from the methods of Chapter 7 and molecular weight can be approximated from Chapter 2.

Procedure

The equilibrium K -values are determined in exactly the same fashion as Procedure 8D1.1.

Step 1: For the defined components, obtain the critical temperature, critical pressure, and acentric factor for each component from Chapter 1.

Step 2: For the undefined pseudocomponents, use procedures in Chapters 2 through 4 to obtain the pseudocritical temperature and pressure and the acentric factor.

Step 3: Obtain α_i , a_i , and b_i from equations (8D1.1-3) to (8D1.1-6) for all components and pseudocomponents.

Step 4: Obtain a set of initial K -values for the mixture based on ideal K -values, the graphical procedures in this chapter, or some other suitable source.

Step 5: Based on the desired objective (equilibrium flash, dew, or bubble point) perform a flash calculation to obtain T , P , y_i , and x_i based on the assumed K -values.

Step 6: Using T and x_i apply equations (8D1.6-7) through (8D1.6-9) with the appropriate k_{ij} to obtain the mixture parameters αa and b in the liquid phase.

Step 7: Repeat Step 6 for the vapor phase using T and y_i .

Step 8: Find the liquid and vapor phase volumes from equation (8D1.6-1) using the appropriate αa and b parameters.

Step 9: Compute the fugacity coefficients of all components in both phases from equation (8D1.6-2).

Step 10: Check fugacities to see if they match in both phases for each component.

Step 11: If they do not match, adjust the estimated K -values and proceed to Step 5. If they do match, stop the calculation.

COMMENTS ON PROCEDURE 8D1.6

Purpose

This procedure is to be used to estimate vapor-liquid equilibrium for mixtures of petroleum fractions and defined compounds. The undefined portion of the mixture is treated as one or more "pure" pseudocomponents which are characterized with pseudocritical temperatures and pressures and an acentric factor. Once this characterization is complete, the method is almost identical to Procedure 8D1.1.

Limitations

This procedure is limited to defined components and narrow boiling undefined mixtures. Typically, the boiling range of the undefined mixture should not exceed 300 F. Some characterization of the undefined mixture is required so that other procedures throughout this book can be used to determine critical properties and the acentric factor.

Accuracy

Treating an undefined mixture as a single component is a very course approximation. However, narrow boiling mixtures can be modelled in this way with a fair degree of accuracy. If distillation data are available, it is recommended that wider boiling mixtures be approximated as several pseudofractions to better model the mixture. Typical K -value errors for the undefined portion of the mixture are in the range of one to 20 percent. Errors for the defined components are of the same order as Procedure 8D1.1.

Example

Perform an equilibrium flash calculation for a mixture of hydrogen, hydrogen sulfide, and a narrow boiling hydrocracker fraction at 400 F and 1000 psia. Characterization data for the fraction are listed below.

Characterization of Hydrocracker Fraction

Boiling Range	150 F to 400 F
Volume Average Boiling Point (VABP)	333.6 F
Slope of ASTM Distillation Curve (10 to 90%)	2.0
Molecular Weight	127.4
Specific Gravity	0.797

8D1.6

The information listed above can be used to determine the necessary parameters of the fraction for this procedure. Figure 7C1.15 is used to obtain a heat of vaporization of 62.6 cal/gm. This is used with Procedure 8B1.7 to obtain a solubility parameter of $6.79 \text{ (cal/cm}^3\text{)}^{1/2}$. Using Procedure 2B1.1, the mean average boiling point is 322.1 F. The pseudocritical temperature and pressure are determined using Procedures 4D3.1 and 4D4.1, respectively. The calculated critical properties are: $T_c = 669.61 \text{ F}$ and $P_c = 383.64 \text{ psia}$. Finally, Procedure 2B3.1 is used to calculate an acentric factor of 0.3617. The critical properties and acentric factors for hydrogen sulfide are obtained from Chapter 1, and those for hydrogen are listed in Procedure 8D1.1. To summarize, the necessary parameters are:

	$T_c (\text{°R})$	$P_c (\text{psia})$	ω
Hydrogen (1)	59.77	188.10	-0.2200
Hydrogen Sulfide (2)	672.12	1300.00	0.0827
Fraction (3)	1129.28	383.64	0.3617

The equation of state parameters a_i , b_i , and α_i can now be calculated using equations (8D1.6-3) through (8D1.6-6). The constant S_1 which is used in equation (8D1.6-5) is determined using equation (8D1.6-6) because values for this parameter are not available in Table 8D1.2 for any of the mixture constituents. Values for the constant S_2 for hydrogen and hydrogen sulfide can be obtained from Table 8D1.3; it is set equal to zero for the fraction.

Two interaction parameters are considered non-zero. The hydrogen-fraction interaction coefficient can be determined by equation (8D1.4-5) ($k_{13} = 0.6857$), and the hydrogen sulfide-fraction interaction coefficient is calculated using equation (8D1.4-1) ($k_{23} = 0.0629$). All other interaction coefficients are set to equal zero. These coefficients are used to calculate the mixture parameters from equations (8D1.6-7) through (8D1.6-9).

At this point at iterative flash calculation which is detailed in Procedure 8D1.1 is used to determine the equilibrium K -values of all components in the mixture. The results are

	K-Value	
	Predicted	Experimental
Hydrogen	10.68	11.99
Hydrogen Sulfide	2.12	2.13
Fraction	0.0755	0.0745

CHAPTER 9

PHASE EQUILIBRIA IN SYSTEMS CONTAINING WATER

9-0 INTRODUCTION

Water Solubilities

Water-containing systems of interest to the petroleum and natural gas industries involve all three states: vapor, liquid, and solid. These systems are characterized by partial miscibility in the liquid phase under certain conditions. Sources of phase equilibria data for water-hydrocarbon systems are listed in Table 9-0.2. Data marked as rejected in Table 9-0.2 were found to be inconsistent and were not used in the development of this chapter. Data marked as not evaluated were added to Table 9-0.2 after the completion of the chapter. Additional water-hydrocarbon solubility references can be found in the IUPAC Solubility Data Series (199a). A partial listing of sources of data for solubilities of nonhydrocarbon gases in water is given in Table 9-0.3.

Water-Hydrocarbon Mutual Solubilities

In all binary water-hydrocarbon systems, the complete phase relations are described by a three-dimensional pressure-temperature-composition diagram. As an example of the solubility relationships, pressure-composition slices at three different constant temperatures are shown in Figure 9-0.1. In each, the solubilities (liquid-phase composition) are given by the heavy lines. As indicated, these solubilities occur at low pressures in a vapor-liquid equilibrium system and at high pressures in a liquid-liquid equilibrium system. At an intermediate (three-phase) pressure, vapor-liquid-liquid equilibrium occurs. With the three phases present in the binary system, only one degree of freedom (rather than two) exists, and a unique three-phase solubility and a unique pressure result for each temperature. This three-phase pressure may be closely approximated in binary water-hydrocarbon systems by adding the vapor pressures of the two pure components at

the existing temperature. The three-phase solubilities for water in a number of hydrocarbons are given in Procedure 9A1.1 and for hydrocarbons in water in Procedure 9A2.1. The solubilities of some solid, polynuclear aromatics in water are given in Procedure 9A2.3, and the solubilities of water in liquid hydrocarbon mixtures are given in Procedure 9A1.3. Procedure 9A1.5 is used to calculate the solubility of water in pure hydrocarbons and hydrocarbon mixtures whenever Procedures 9A1.1 and 9A1.3 cannot be used. The solubility of hydrocarbons in water under vapor-liquid-liquid equilibrium conditions at 77 F is given in Procedure 9A2.6.

As shown in Figure 9-0.1, pressure has an appreciable influence on solubility in the vapor-liquid region and a very small influence in the liquid-liquid region. Thus, although Procedure 9A1.1 and Procedure 9A2.1 are directly applicable only to vapor-liquid-liquid equilibrium, the procedures are good approximations of the solubility at pressures above the sum of the vapor pressures of the components where only two liquid phases exist. Procedure 9A2.3 is equivalent to Procedure 9A2.1--the only difference is that the hydrocarbon-rich phase is solid in this case. The influence of pressure on the solubilities is even smaller here. The equilibrium phases are hydrocarbon-rich solid in equilibrium with water-rich liquid with or without a vapor phase.

Small amounts of impurities or minor components can seriously alter the solubility characteristics of a mixture. For example, if a small amount of an aromatic hydrocarbon (which has a relatively strong affinity for water) is present as an impurity in a predominantly paraffin system, the mutual solubility with water will be increased far more than would be predicted from a molar average solubility for the hydrocarbons. More regular behavior is expected for mixtures of hydrocarbons from a single homologous series.

Solubilities of Hydrocarbons and Nonhydrocarbons Gases in Water

The water content of natural gases in contact with liquid water at 60 F and 14.7 psia is

given in Procedure 9A3.1 along with a salinity correction factor. The salinity correction factor is to be used when salt is in the liquid-water phase. The solubility of hydrocarbons in aqueous salt solutions is given in Procedure 9A5.1. Procedure 9A6.1 is a computer method for phase equilibrium calculations for water-hydrocarbon systems using the modified Soave-Redlich-Kwong equation of state.

Henry's constants for selected gases in water are given in Procedure 9A7.1. This procedure is only valid for low and intermediate pressures. Equilibrium concentrations of binary and ternary sour gas systems in water are given in Procedure 9A7.3, and the pH of ammonia and hydrogen sulfide in water is given in Procedure 9A8.1.

Salt Effects on Solubilities of Hydrocarbons and Nonhydrocarbon Gases in Water

Salt effects on the solubilities of nonelectrolytes in water are very complex and difficult to model. Most salts have a salting-out effect on nonpolar solutes (i.e., the solubility of the solute decreases as the salt concentration increases), but some salts have the reverse effect. For a polar solute, the effect of each salt is different. Solubilities in water as a function of salt concentration can generally be correlated by an empirical relationship known as the Setschenow equation (128a, 197a).

Table 9A5.2 gives the literature sources and Setschenow constants for solubilities of hydrocarbons in different aqueous salt solutions. Table 9-0.4 gives a partial listing of literature sources for the salt effects on solubilities of nonhydrocarbon gases in water.

Gas Hydrates

In the most common water-light-hydrocarbon phase equilibria, which involve a solid phase, the solid phase is a gas hydrate. The hydrate has a network of hydrogen-bonded water molecules with small cavities distributed throughout the solid structure in a well-defined pattern.

The structure is stabilized only when some or all of the cavities contain small "solute" molecules which interact feebly with the water through forces similar to those between molecules in a liquid.

The gas hydrate is not a chemical compound; it is a clathrate inclusion compound.

Two different structures exist (Types I and II) each having two different-size cavities.

The smallest size solute molecules (top group of Table 9-0.5) fit into all the cavities in Structure I, slightly larger molecules (middle group of Table 9-0.5) fit into only the large cavities in Structure I, and larger molecules (bottom group of Table 9-0.5) fit into the large cavities of Structure II. A Structure II hydrate will not form with all the cavities filled by a single solute. However, when a small molecule with strong hydrate-forming tendencies (such as hydrogen sulfide) is present, it can fit into the small and some of the large cavities to stabilize a Structure II hydrate containing large molecules (Table 9-0.6) which would not otherwise form a hydrate. Molecules larger than those in Table 9-0.6 will not form hydrates because the water molecules encaging the solute would be too distant to form the hydrogen bonds that stabilize the structure.

As indicated in Table 9-0.5, there exists for each group in the table a theoretical composition that corresponds to the definite ratio of filled cavities to water molecules in the structure. Experimentally determined compositions generally indicate the presence of slightly more water per mole of solute than predicted from the structure. This implies that more cavities than predicted are empty and that these clathrates are potentially nonstoichiometric compounds. The composition is relatively insensitive to pressure-temperature conditions, but a small effect has been reported.

Since hydrate composition is fairly constant, the phase relations can be described by two-dimensional pressure-temperature diagrams (see Figure 9-0.7) which are constant-composition slices from the complete three-dimensional cube. In these three diagrams, the hydrate region is in

the low-temperature, high-pressure area to the left of the heavy lines. If the overall composition is that of the hydrate (F_2), hydrate alone will exist in this region, whereas if either excess water (e.g., overall composition F_1) or excess solute (e.g., F_3) is present, the excess will appear with the hydrate. The excess component will exhibit phase relations almost as if it were pure, so that a water melting-point line extends into the hydrate region for overall composition F_1 , and the vapor pressure curve for the solute extends into the hydrate region for F_3 . Similarly, outside the hydrate forming region, the interactions between solute and water are so small that only very small melting-point depressions and boiling-point elevations are exhibited, and the phase relations are essentially those of the pure components.

The upper quadruple point, where hydrate coexists with vapor solute, liquid solute, and liquid water, is called the critical decomposition point. The implications of this title are misleading because hydrates actually can be made to coexist with liquid water and liquid solute above this critical decomposition temperature (T_{cd}) by using very high pressures.

The phase diagrams shown in Figure 9-0.7 are general for all systems except those containing compounds that have critical temperatures below room temperature. In this case, the solute cannot be liquefied to give an upper quadruple point, so no critical decomposition point occurs.

Hydrate systems typically exhibit strong metastable tendencies, so that it is difficult to initiate hydrate formation in the absence of the common nucleating influences such as excess pressure, supercooling, agitation, and seeding. Similarly, the hydrate phase will occasionally persist in regions where decomposition is favored. Nucleation occurs most readily when the water phase is liquid, but hydrates will also form in systems containing solid or vapor water. The latter case can occur in natural gas transmission pipelines. As the water concentration of the

system becomes progressively smaller (F_3 , F_4 , F_5 , F_6), the dew-point pressure is increased (see last diagram in Figure 9-0.7) until the dewpoint line extends into the hydrate region. Below this line in the hydrate region, the hydrate can be formed directly from vapor solute and vapor water.

Hydrate formation conditions for a number of binary systems containing water and hydrocarbons or related compounds are presented in Figures 9B1.1 and 9B1.2. Additional data for ternary systems containing two solutes are available in the literature (see Table 9-0.8). Procedure 9B1.3 calculates the formation conditions for natural gases of various specific gravities relative to air. Since specific gravity does not satisfactorily characterize the composition of a natural gas, this procedure is accurate only to about 10 percent, and errors of 40 percent in predicting formation pressures are possible.

Hydrate formation conditions may also be predicted accurately by the computer method given in Procedure 9B2.1. This procedure is complex and should be used only if many predictions will be made. (A version of this method is available on the Time-Share System as the proprietary Peng-Robinson hydrate program. It is equivalent in accuracy to Procedure 9B2.1 for multicomponent systems.)

Hydrates are known primarily as nuisances that block natural gas pipelines. In a pipeline, hydrate formation conditions can be reached when the gas is cooled as a result of expansion through a valve or some other constriction. Graphic correlations for determining the permissible expansions of natural gases of various specific gravities have been developed by Katz (67b) from Mollier diagrams and K charts. These charts (Figures 9B1.13 through 9B1.16) permit a very rapid determination of the amount of expansion ($\Delta H = 0$) that can occur in natural gases before hydrate formation conditions are reached.

Further information on gas hydrates is available in a number of reviews (9b, 10b, 14b, 16b,

20b, 26b-28b, 31b, 60b, 63b, 66b, 93b, 103b, 111b, 1115b, 116b, 139b, 144b). The following are particularly comprehensive: Schroeder (111b), Deaton and Frost (31b), Parent (93b), Katz et al. (68b), Van der Waals and Platteeuw (144b), Kase (66b), and Byk and Fomina (16b).

Hydrate formation in gas pipelines may be avoided by addition of a suitable inhibitor such as methanol, ethylene glycol, or diethylene glycol. Figures 9-0.9 and 9-0.10 are presented as typical examples of the higher pressures which may be used without danger of hydrate formation when inhibitors are present.

Use of Procedure 9B2.1 requires knowledge of gas phase compositions on a water-free basis. However, recent research shows that water content of gases is an important factor in determining whether or not hydrates will form. Information and data for water content of methane and natural gases are found in References 1c and 35c.

More information on dehydration can be located in References 1c-36c. This list is not complete, and additional information sources on dehydration are given in References 31b, 10c, and 28c.

A comprehensive evaluation by T. E. Daubert of the GPA/SIM, Equiphase, GPA/AQUASIM, and API/HYDRATE programs with an extensive data base was published by the Gas Processor's Association (150b) and should be consulted for both recent data and evaluations.

Recent work and a prediction method CSMHYD on hydrates are given in a monograph by E. D. Sloan, Jr. (151b).

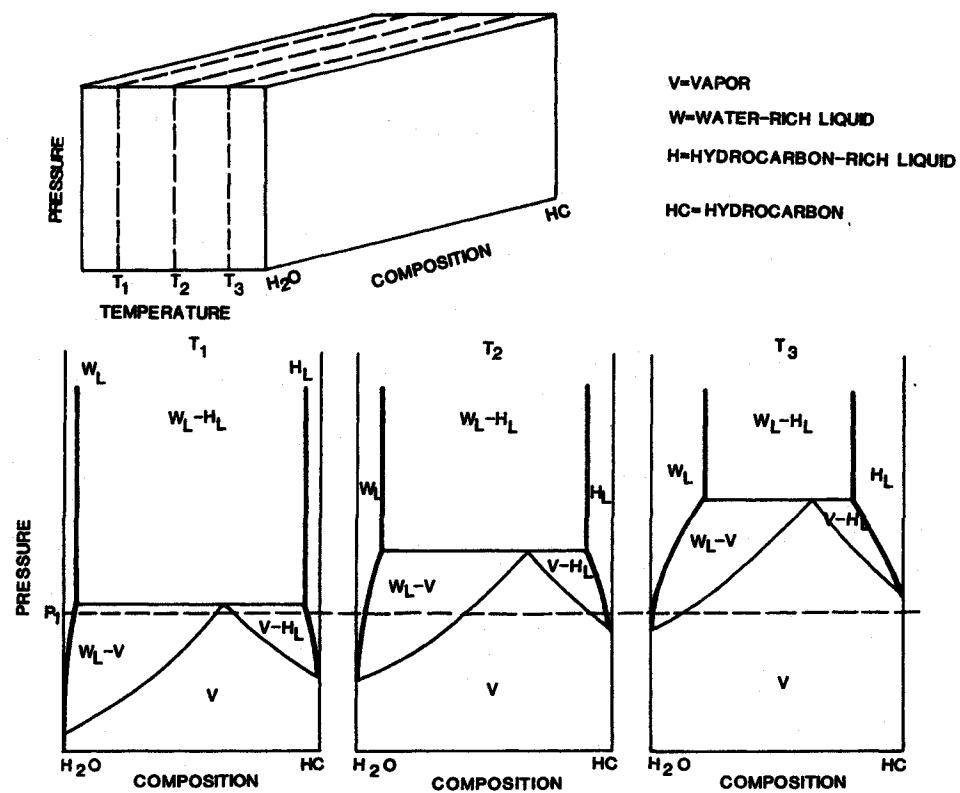


Figure 9-0.1—Water-Hydrocarbon Solubility Phase Relations

9A1 SOLUBILITY OF WATER IN HYDROCARBONS

PROCEDURE 9A1.1

SOLUBILITY OF WATER IN PURE LIQUID HYDROCARBONS UNDER VAPOR LIQUID LIQUID EQUILIBRIUM CONDITIONS

Discussion

The following equation is to be used to calculate the solubility of water in various pure liquid hydrocarbons under vapor-liquid-liquid equilibrium conditions over the temperature range that is given in Table 9A1.2 for each compound. Table 9A1.2 also lists the three-phase critical temperature and the critical solubility when they are known.

$$\log X_w = a_1 - \frac{a_2}{T} + a_3 T \quad (9A1.1-1)$$

Where:

- X_w = Solubility of water, mole fraction.
- a_1, a_2, a_3 = Component specific constants (see Table 9A1.2)
- T = Absolute temperature, degrees Rankine.

Procedure

Step 1: Read the constants a_1 , a_2 , and a_3 for the given hydrocarbon from Table 9A1.2.

Step 2: Calculate the solubility with Equation (9A1.1-1).

Purpose

The solubilities of water in various pure hydrocarbons can be calculated over the temperature ranges given in Table 9A1.2.

Limitations

The valid temperature range for each hydrocarbon is given in Table 9A1.2. Extrapolation outside these ranges is not recommended. The effectiveness of the equation decreases as the temperature approaches the three-phase critical temperature.

The equation applies only when three phases (vapor, liquid hydrocarbon, liquid water) are in equilibrium. Because of small mutual solubilities, the three-phase pressure of water-hydrocarbon systems is approximately the sum of the vapor pressures of the water and the liquid hydrocarbon. The solubilities for pressures greater than the sum of the vapor pressures (i.e., two liquid phases only) may be approximated by the three-phase solubilities calculated by the procedure, except when the desired temperature is near the critical solution temperature. Liquid-phase solubilities at pressures appreciably less than the sum of the vapor pressures (i.e., vapor and only one liquid phase) are less than those calculated by the procedure. For this situation, the original data sources listed in Table 9-0.2 should be consulted.

Reliability

The reliability of the solubilities is estimated at \pm 6.5 percent.

Literature Sources

The constants for the equation were regressed from the data found in the references noted in Table 9A1.2.

Example

Calculate the solubility of water in benzene at 104 F under vapor-liquid-liquid equilibrium.

From Table 9A1.2, the appropriate constants are $a_1 = -595$, $a_2 = -1591$, and $a_3 = 0.1980 \times 10^{-2}$. The temperature is $459.67 + 104 = 563.67$ R. Using equation (9A1.1-1), the value is found to be 4.99×10^{-3} .

An experimental value for the solubility of water in benzene at 104 F is 4.95×10^{-3} (76a).

PROCEDURE 9A1.3**SOLUBILITY OF WATER IN UNDEFINED
LIQUID HYDROCARBON MIXTURES****Discussion**

The following equation is to be used to calculate the mole fraction of water in undefined liquid hydrocarbon mixtures.

$$\log (X_w) = A_1 + \frac{A_2}{T} \quad (9A1.3-1)$$

Where:

- A_1, A_2 = Component specific constants (See Table 9A1.4)
- X_w = Solubility of water in the undefined liquid hydrocarbon mixture.
- T = Absolute temperature, degrees Rankine.

Procedure

- Step 1:* Read the constants A_1 and A_2 for the given mixture from Table (9A1.4).
- Step 2:* Calculate the solubility with Equation (9A1.3-1).

COMMENTS ON PROCEDURE 9A1.3

9A1.3

Purpose

The procedure calculates the solubility of water in undefined liquid hydrocarbon mixtures.

Limitations

The procedure covers the conditions when a relatively small amount of water phase is in contact with the hydrocarbon mixture. It may not represent the conditions when the hydrocarbon mixture is in the presence of a very large amount of water wherein the hydrocarbon composition is changed due to the selective solubility in water of the individual hydrocarbons or hydrocarbon classes.

The procedure can be used at all pressures above those that would cause appreciable vaporization of the hydrocarbon solvent. The procedure is not reliable for pressures low enough to cause the more volatile components of the hydrocarbon mixtures to vaporize.

Reliability

The procedure is estimated to be reliable within ± 5 percent.

Special Comment and Literature Sources

The physical properties and literature sources for the undefined mixtures are tabulated below:

	Gravity (°API)	Molecular Weight	Watson Characteri- zation Factor ^a	Reference
Naphtha	54.3	147	12.2	75a
Kerosine	42.0	173	11.8	75a
Kerosine	47.2	170	12.0	76a
Lubricating oil	29.3	425	12.4	75a
Paraffin oil	28.8	350	12.1	76a
Gasoline	68.6	95	12.2	37a
JP-3 fuel	54.7	112	11.7	114a
JP-4 fuel	51.5	125	11.8	40a

^aDefined in Chapter 2.

Example

Calculate the solubility of water in naphtha at 397 F.

From Table 9A1.4, the appropriate constants are $A_1 = 2.94$ and $A_2 = -3314.3$. The temperature is $459.67 + 397 = 856.67$ R. Using Equation (9A1.3-1), the value is found to be 0.1179.

An experimental value for the solubility of water in naphtha at 397 F is 0.1191 (75a).

9A2 SOLUBILITY OF HYDROCARBONS IN WATER**PROCEDURE 9A2.1****SOLUBILITY OF HYDROCARBONS IN WATER UNDER
VAPOR LIQUID LIQUID EQUILIBRIUM CONDITIONS****Discussion**

The following equation is to be used to calculate the solubility of various pure hydrocarbons in water under vapor-liquid-liquid equilibrium conditions.

$$\log (X_{hc}) = a_1 + \frac{a_2}{T} + \frac{a_3}{T^2} \quad (9A2.1-1)$$

Where:

X_{hc}	=	Solubility of hydrocarbon in the water-rich phase, mole fraction.
a_1, a_2, a_3	=	Constants that are specific to each hydrocarbon.
T	=	Absolute temperature, degrees Rankine.

Procedure

Step 1: Read the constants a_1 , a_2 and a_3 for the given hydrocarbon from Table (9A2.2)

Step 2: Calculate the solubility with Equation (9A2.1-1).

COMMENTS ON PROCEDURE 9A2.1

9A2.1

Purpose

The solubilities of various hydrocarbons can be calculated across the temperature ranges given in Table 9A2.2

Limitations

The valid temperature range for each hydrocarbon is given in Table 9A2.2. Extrapolation outside these ranges is not recommended. The equation applies only when three phases (vapor, liquid hydrocarbon, liquid water) are in equilibrium. Because of the small mutual solubilities, the three-phase pressure for water-hydrocarbon systems is approximately the sum of the vapor pressures of water and the hydrocarbon. The solubilities for pressures greater than the sum of the vapor pressures (i.e., two liquid phases only) may be approximated by the three-phase solubilities calculated from the equation, except where the desired temperature is near the critical solution temperature. Liquid-phase solubilities at pressures appreciably less than the sum of the vapor pressures (i.e., vapor and one liquid phase only) are less than those calculated by the equation. In this case, the original data sources listed in Table 9-0.2 should be consulted.

Reliability

Errors from this equation average less than 9%.

Special Comment

Small amounts of impurities may seriously alter solubility characteristics. In particular, small amounts of aromatics, olefins, or diolefins will increase the solubility of a paraffin mixture more than would be predicted from the molar average solubility.

The temperature range listed in Table 9A2.2 for ethylcyclohexane does not include its three phase critical which is 550.9 F, and 60.3 mole % of ethylcyclohexane.

Literature Sources

The constants for the equation were regressed from the data found in the references noted in Table 9A2.2.

Example

Calculate the solubility of propane in water at 100 F under vapor-liquid-liquid equilibrium.

Using the appropriate constants, $a_1 = 6.07$, $a_2 = -11404$, and $a_3 = 3323964$, and a temperature of $459.67 + 100 = 559.67$ R, the above equation predicts a value of 0.000202 mole fraction.

The experimental value is 0.000203 mole fraction (9a).

TABLE 9A2.2
PARAMETERS FOR EQUATION (9A2.1-1)
SOLUBILITY OF HYDROCARBONS IN WATER

Compound:	a ₁	a ₂	a ₃	Temp. Range (F)	Reference Numbers
Propane	6.07	-11404	3323964	60-206	(109a)
n-Butane	2.00	-6280	1526314	100-280	(121a,177a)
n-Pentane	8.07	-14815	4185818	40-301	(136a,171a)
n-Hexane	10.63	-18127	5031401	59-434	(136a,171a,216a)
- 1-Butene	1.60	-5423	1371020	77-291	(27a,124a,136a)
1-Hexene	7.81	-14178	3937141	77-430	(22a,199a)
2-Methylpentane	7.83	-14993	4196810	77-301	(136a,171a)
2,3-Dimethylbutane	7.66	-14717	4146971	77-301	(171a)
n-Heptane	19.76	-30125	8649917	59-369	(136a,171a)
3,3-Dimethylpentane	7.86	-15132	4146501	77-303	(170a)
n-Octane	11.65	-20299	5510785	59-535	(22a,171a,228a)
n-Nonane	17.02	-27743	7822312	59-278	(171a)
1-Octene	8.74	-15761	4107697	100-530	(22a)
-Cyclopentane	14.99	-22960	6763217	77-389	(136a,171a)
Cyclohexane	3.49	-8152	2006973	41-493	(116a,199a,216a)
Methylcyclohexane	17.48	-26539	7632308	77-419	(136a,171a,199a)
Ethylcyclohexane	11.77	-20034	5659580	101-535	(22a,228a)
n-Butylcyclohexane	12.31	-21565	5953221	200-530	(22a)
Benzene	4.31	-8053	2103571	40-563	(3a,19a,61a,80a,136a,179a,199a,216a)
Toluene	4.53	-8836	2301672	14-572	(3a,19a,80a,136a)
- Ethylbenzene	14.19	-19795	5231973	33-563	(19a,22a,82a,136a,145a,228a)
- n-Propylbenzene	3.67	-10402	2784662	59-432	(82a)
- Isopropylbenzene	-5.52	2141	-1341135	77-177	(71a)
- Mesitylene	-7.12	2716	-883003	59-113	(189a)
m-Diethylbenzene	9.77	-17042	4799910	100-530	(22a)
- Ethenylbenzene	3.62	-7667	1844017	45-149	(119a)

PROCEDURE 9A2.3

9A2.3

SOLUBILITIES OF SOLID, POLYNUCLEAR AROMATICS IN WATER

Discussion

The following equation is to be used to predict the solubilities of various solid, polynuclear aromatics in liquid water.

$$\log X_{hc} = a_1 + a_2 T \quad (9A2.3-1)$$

Where:

- X_{hc} = Solubility of solid, polynuclear aromatic, mole fraction.
T = Absolute temperature, degrees Rankine.
 a_1, a_2 = Constants that are unique to each solid, polynuclear aromatic.

Procedure

- Step 1:* Read constants a_1 and a_2 from Table 9A2.4 for the appropriate solid polynuclear aromatic.
- Step 2:* Calculate the solubility with Equation (9A2.3-1).

COMMENTS ON PROCEDURE 9A2.3**Purpose**

The solubilities of various solid, polynuclear aromatics in liquid water can be calculated.

Limitations

The equation applies only when there is a solid hydrocarbon-rich phase in equilibrium with a water-rich liquid phase (i.e. approximately below the melting point of the solid, polynuclear aromatic.) The pressure effects on the solubilities are negligible.

Reliability

The equation reproduces experimental data to within ± 5 percent.

Literature Sources

Naphthalene (164a, 194a, 199a, 222a)

Biphenyl (194a, 199a, 222a)

Acenaphthene (164a, 194a, 222a)

Fluorene (164a, 194a, 222a)

Phenanthrene (134a, 194a, 199a, 222a)

1-Methylphenanthrene (134a, 194a)

Pyrene (164a, 194a, 199a, 222a)

Anthracene (134a, 164a, 194a, 222a)

2-Methylnaphthalene (134a, 194a)

Benz(e)pyrene (194a)

Example

Find the solubility of fluorene in water at 77 F.

From Table 9A2.4, the coefficients, a_1 and a_2 , are given as $a_1 = -13.255$ $a_2 = 0.0122$.

Equation (9A2.3-1) then gives

$$\log X_{hc} = -13.255 + 0.0122 (77 + 459.67)$$

$$\log X_{hc} = -6.7076$$

$$X_{hc} = 1.96 \times 10^{-7}$$

An experimental value for the solubility of fluorene in water at 77 F is 2.146×10^{-7} (164a).

PROCEDURE 9A2.6**SOLUBILITY OF HYDROCARBONS IN WATER UNDER VAPOR-LIQUID-LIQUID EQUILIBRIUM CONDITIONS AT 77 F****Discussion**

The following equation is to be used to predict the solubility of pure hydrocarbons in water under vapor-liquid-liquid equilibrium conditions at 77 F:

$$-\log X_{hc} = a_1 + a_2 C + a_3 C^2 \quad (9A2.6-1)$$

Where:

- X_{hc} = Solubility of hydrocarbon, mole fraction.
- a_1, a_2, a_3 = Coefficients that depend on the homologous series of the given hydrocarbon (see Table 9A2.7).
- C = Carbon number of the hydrocarbon

Procedure

Step 1: Determine the homologous series of the hydrocarbon and read the coefficients, a_1 , a_2 , and a_3 for this series from Table 9A2.7.

Step 2: Determine the carbon number of the hydrocarbon. Calculate the solubility using equation (9A2.6-1).

COMMENTS ON PROCEDURE 9A2.6

9A2.6

Purpose and Discussion

Procedure 9A2.6 is to be used for predicting solubilities of pure liquid hydrocarbons in water under vapor-liquid-liquid equilibrium conditions at 77F.

Limitations

Procedure 9A2.6 is applicable only to pure liquid hydrocarbons and should not be extended to hydrocarbon mixtures. Also, the procedure is not applicable to hydrocarbons that cannot be classified as belonging to any one of the 9 homologous series listed in Table 9A2.7.

Reliability

This procedure reproduces the experimental data to within an average error of 10 percent.

Literature Sources

The original Procedure 9A2.6 was developed by V. N. Kabadi and R. P. Danner, *Hydrocarbon Processing* 58 [5] 245 (1979). It was modified by the API Technical Data Book Project Staff (1996).

Example

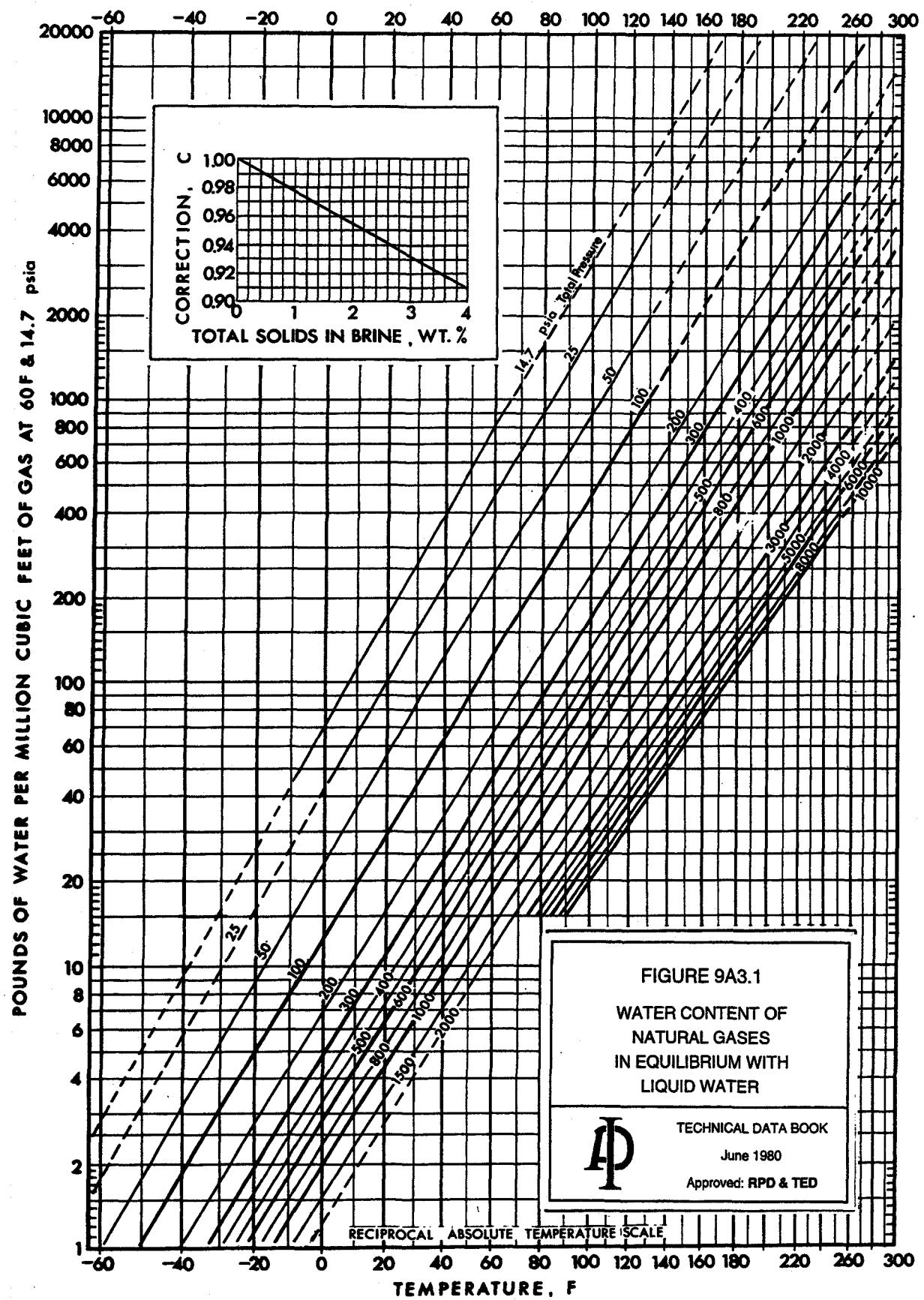
Find the solubility of benzene in water at 77F under vapor-liquid-liquid equilibrium conditions.

From Table 9A2.7 for benzene, $a_1 = -0.4628$, $a_2 = 0.6916$ and $a_3 = -0.8410 \times 10^{-2}$. The carbon number of benzene is 6. Using equation (9A2.6-1) the solubility is calculated to be 4.13×10^{-4} .

The experimental solubility of benzene in water at 77 F is 4.11×10^{-4} (146a).

TABLE 9A2.7
COEFFICIENTS FOR PROCEDURE 9A2.6

Homologous Series	Coefficients for Equation (9A2.6-1)		
	a_1	a_2	$a_3(10^3)$
n-Paraffin	1.6708	0.6386	0.5538
Paraffin with one branch	9.6776	-2.2691	26.3567
Paraffin with two branches	0.0000	1.0157	-2.0577
Naphthene	4.4465	-0.3285	6.3729
Naphthene with one branch	11.8697	-2.5294	23.2027
Alkene	8.4469	-1.6631	17.2448
Cycloalkene	0.4247	0.5682	1.2414
Acetylene	-0.9415	0.9839	-0.7961
Benzene or n-Alkylbenzene	-0.4628	0.6916	-0.8410



Purpose

This figure shows the water content of natural gas in equilibrium with water. A salinity correction chart is provided for use when the liquid-water phase contains salt.

A calculation method has been developed and is presented in the special comments section.

Limitations

Figure 9A3.1 is reliable for natural gases of specific gravity of 0.8 or less (air = 1.0). A molecular weight correction chart is available in the literature (141a). This correction chart is not given here, however, because in a study with a few defined hydrocarbon gas systems, absolute errors as high as 110 percent were found, and there was no significant trend to the errors as a function of specific gravity.

Reliability

For natural gases with a specific gravity of 0.8 or less, the standard deviation of the chart from published data is 4 percent, with a negligibly small bias.

Notation

The broken lines indicate extrapolations beyond the limits of the available literature data.

Special Comments

To use the salinity correction, the water content read from the main chart should be multiplied by the correction factor C, which corresponds to the appropriate salt concentration in the liquid water phase.

At low temperatures and high pressures, hydrate formation can occur (see Section 9B).

The following equations are to be used to calculate the pounds of water per million cubic feet of natural gas at 60 F & 14.7 psia.

$$Y = (-0.0227wt + 1) 10^{\left[-2.3205[\log P]^{0.53} - \frac{3888}{T} + 12.9 \right]} \quad (9A3.1-1)$$

Where:

Y = Pounds of water per million cubic feet of natural gas at 60 F & 14.7 psia.

T = Absolute temperature, degrees Rankine.

P = Pressure, psia.

wt = wt% of total solids in brine.

This equation has an estimated reliability of 9.5% with a -0.9% bias, for natural gases with a specific gravity of 0.8 or lower, and is only reliable for natural gases with a specific gravity of 0.8 or less (air = 1.0).

Literature Source

Figure 9A3.1 was adapted from McKetta and Wehe, *Petrol. Refiner* 37 [8] 153 (1958).

Example

Find the water content of a natural gas at 100 F and 300 pounds per square inch absolute that is in equilibrium with a liquid-water phase containing 0.4 percent salt.

For pure water, the water content is given by the main chart in Figure 9A3.1 at 160 pounds water per million cubic feet of gas. From the salinity correction chart, the correction factor C is 0.99. Therefore, the corrected water content is $(0.99)(160) = 158$ pounds of water per million cubic feet of gas.

The equation presented in the special comments gives a water content of 157.1 pounds of water per million cubic feet of gas.

9A5 SALT EFFECTS ON SOLUBILITY OF HYDROCARBONS IN WATER

9A5.1

PROCEDURE 9A5.1

SOLUBILITY OF HYDROCARBONS IN AQUEOUS SALT SOLUTIONS

Discussion

Knowing the solubility of a hydrocarbon in water, the following equation is to be used to calculate the solubility of the hydrocarbon in an aqueous salt solution:

$$\log \frac{X}{X_0} = -K_s C, \quad (9A5.1-1)$$

Where:

X = Solubility of hydrocarbon in salt solution, mole fraction.

X_0 = Solubility of hydrocarbon in water, mole fraction.

K_s = Setschenow constant, in liters per gram equivalent. (Constants for hydrocarbons in different salt solutions at different temperatures and pressures are listed in Table 9A5.2.)

C , = salt concentration of solution, in gram equivalents per liter.

Procedure

Step 1: Knowing the temperature and pressure, read values of K_s and X_0 for the hydrocarbon-salt-water system from Table 9A5.2. If K_s and X_0 are not given for the system of interest, the procedure cannot be used. If K_s and X_0 are listed at temperatures and pressures close to the temperature and pressure of interest, calculate values of K_s and X_0 by interpolation or extrapolation. If the temperature and pressure of interest are far from those given, the procedure is not applicable.

Step 2: Calculate the solubility of the hydrocarbon in the aqueous salt solution using equation (9A5.1-1).

COMMENTS ON PROCEDURE 9A5.1**Purpose**

Procedure 9A5.1 is presented as a method for calculating the solubility of hydrocarbons in aqueous salt solutions, knowing the solubility in pure liquid water.

Limitations

Procedure 9A5.1 can be used only for the hydrocarbon-salt-water systems listed in Table 9A5.2. Also, it can be used only in the range of temperatures and pressures listed in Table 9A5.1. (Interpolations within, or moderate extrapolations out of, the given temperature-pressure range are permissible.) The procedure should not be used at temperatures and pressures far from the values listed in Table 9A5.2.

Reliability

Equation (9A5.1-1), with K_s and X_0 at different temperatures and pressures listed in Table 9A5.2, reproduces the experimental data to within an average error of ± 10 percent.

Literature Sources

Equation (9A5.1-1) was taken from the original work of J. Setschenow, *Z. Phys. Chem.* 4 117 (1889). A discussion of the relationship is also given by Long and McDevit, *Chem. Rev.* 51 128 (1952).

Example

Find the solubility of methane in a 4N aqueous sodium chloride solution at a temperature of 125 F and 500 atmospheres.

From Table 9A5.2, for the methane-NaCl-water system at 124.7 F and 500 atmospheres, $X_0 = 0.00373$ mole fraction and $K_s = 0.120$. Assume the same values at 125 F and 500 atmospheres.

Then, from equation (9A5.1-1):

$$-\log \frac{X}{X_0} = 0.120(4)$$

$$\log \frac{X}{X_0} = -0.48$$

$$\frac{X}{X_0} = 0.3311$$

$$X = 0.3311 (0.00373)$$

$$X = 0.00124.$$

The experimental value for solubility is 0.0013 (160a).

9A6.1

librium calculation, note that no matter which solution technique for the volume is employed, it must be repeated for all the phases, since a and b depend on the composition of each phase.

B. Fugacity Coefficient

The fugacity of a component in a phase may be calculated once the fugacity coefficient has been evaluated. The relationship between the fugacity and the fugacity coefficient is given by equation (9A6.1-3):

$$f_i^N = \phi_i^N X_i p \quad (9A6.1-3)$$

Where:

f_i^N = fugacity of Component i in Phase N .

ϕ_i^N = fugacity coefficient of Component i in Phase N .

X_i = mole fraction of Component i in Phase N .

p = total pressure.

In terms of the modified Soave equation, the fugacity coefficient in a liquid or a vapor phase for water-hydrocarbon systems may be calculated from equation (9A6.1-4) once the volume of that phase has been determined:

$$\ln \phi_i^N = \frac{b_i}{b} (Z - 1) - \ln (Z - B) - \frac{A}{B} \left[\frac{2 \sum_j X_j a_{ij} + \epsilon}{a} - \frac{b_i}{b} \right] \ln \left(1 + \frac{B}{Z} \right) \quad (9A6.1-4)$$

Where:

b_i = volume parameter of Component i .

a_{ij} = energy parameter for an ij pair.

$$A = \frac{aP}{R^2 T^2}$$

$$B = \frac{bP}{RT}$$

$$\epsilon = \sum_j (2X_w X_j - X_w^2 X_j) a'_{wj}, \text{ if } i \text{ refers to water.}$$

$$\epsilon = X_w^2 a'_{wi} - \sum_j X_w^2 X_j a'_{wj}, \text{ if } i \text{ refers to hydrocarbon.}$$

a'_{wi} = secondary energy parameter for a water-hydrocarbon pair.

C. Equation Constants for Pure Components

The equation constants for all pure components are calculated from the critical temperature, the critical pressure, and the acentric factor.

$$a_i = 0.42747 \left(\frac{R^2 T_{ci}^2}{p_{ci}} \right) \alpha_i \quad (9A6.1-5)$$

$$b_i = 0.08664 \left(\frac{RT_{ci}}{p_{ci}} \right) \quad (9A6.1-6)$$

Where:

a_i = energy parameter for Component i .

b_i = volume parameter for Component i .

T_{ci} = critical temperature of Component i , in degrees Rankine.

p_{ci} = critical pressure of Component i , in pounds per square inch absolute.

R = gas constant

= 10.731 (pounds per square inch) (cubic feet) per (pound-mole) (degrees Rankine).

For hydrocarbons, α_i is given by

$$\alpha_i = \left[1 + S_i (1 - \sqrt{T_{ri}}) \right]^2 \quad (9A6.1-7)$$

Where:

$$T_{ri} = \text{reduced temperature of } i = \frac{T}{T_{ci}}$$

$$S_i = 0.48508 + 1.55171 \omega_i - 0.15613 \omega_i^2$$

ω_i = acentric factor of i .

For water, α_i is given by

$$\alpha_w = \left[1 + 0.662 \left(1 - T_{rw}^{0.8} \right) \right]^2 \quad (9A6.1-8)$$

Where:

$$T_{r_w} = \text{reduced temperature of water} = T/T_c$$

D. Equations for Composition-Averaged Parameters

The composition-averaged parameters a and b are calculated from equations (9A6.1-9) and (9A6.1-10):

$$a = \sum \sum X_i X_j a_{ij} (1 - k_{ij}) + \sum a'_{wi} X_w^2 X_i \quad (9A6.1-9)$$

$$b = \sum X_i b_i \quad (9A6.1-10)$$

Where:

$$a_{ij} = \sqrt{a_i a_j}$$

k_{ij} = binary interaction coefficient.

a'_{wi} = secondary energy parameter for interaction between water and Hydrocarbon i .

E. Binary Interaction Coefficient

The binary interaction coefficients for hydrocarbon-hydrocarbon pairs are zero. The binary interaction coefficients between water and different homologous series of hydrocarbons are given in Table 9A6.2.

F. Secondary Energy Parameter a'_{wi}

The secondary energy parameter for a water-hydrocarbon pair is given by a group contribution method. Different groups constituting hydrocarbons are defined. The secondary energy parameter is given by the sum of the group contributions of different groups forming a hydrocarbon molecule multiplied by a temperature dependence in terms of reduced temperature of water. Equations (9A6.1-11) and (9A6.1-12) give the secondary energy parameter:

$$a'_{wi} = G_i \left[1 - T_{r_w}^{0.8} \right] \quad (9A6.1-11)$$

$$G_i = \sum_j g_j \quad (9A6.1-12)$$

Where:

G_i = sum of the group contributions of different groups forming a hydrocarbon molecule in atm (m^3/gmol)².

$$T_{r_w} = \text{reduced temperature of water} = T/T_c^{\text{H}_2\text{O}}$$

g_j = group contribution of Group j .

Different hydrocarbon groups and their group contributions are given in Table 9A6.3.

Procedure

Step 1: For water and hydrocarbons in the mixture, obtain the critical temperature and pressure from Chapter 1 and the acentric factor from Chapter 2.

Step 2: Obtain a_i and b_i from equations (9A6.1-5) through (9A6.1-8).

Step 3: Obtain a set of initial K values for the mixture based on ideal K values or some other suitable source.

Step 4: Based on the desired objective (equilibrium flash, dew, or bubble point), perform a flash calculation to obtain T , P , and the compositions of the coexisting phases based on the assumed K values.

Step 5: Using T and the phase compositions, apply equations (9A6.1-9) through (9A6.1-11) with the appropriate k_{ij} and G_i to obtain mixture parameters a and b in the different phases.

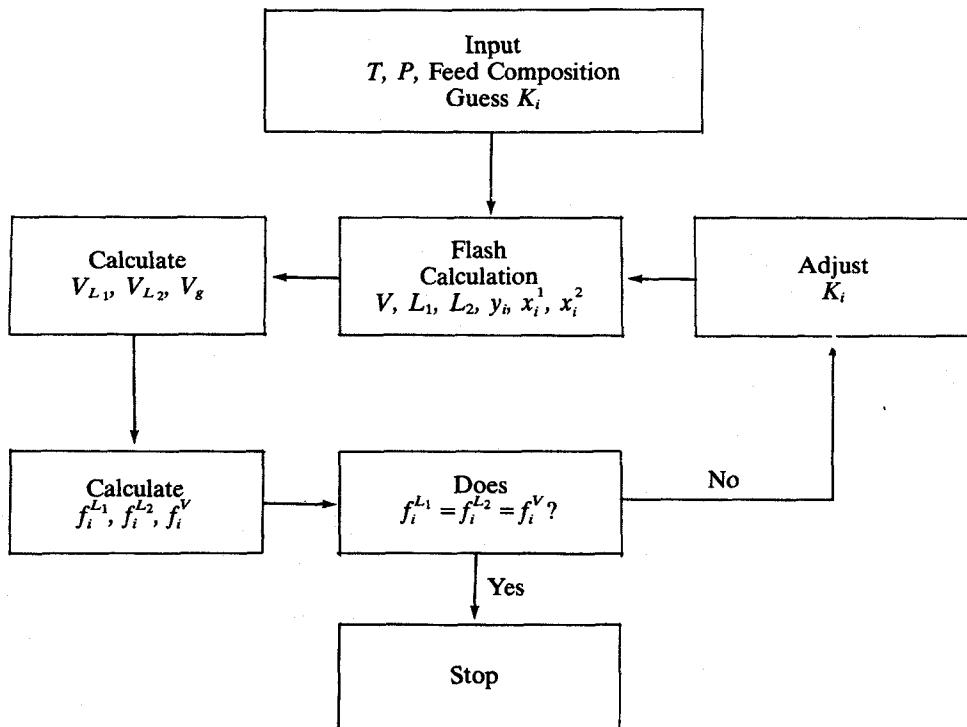
Step 6: Find the liquid- and vapor-phase volumes from equation (9A6.1-2) using the appropriate a and b parameters.

Step 7: Compute the fugacity coefficients of all components in all the phases from equation (9A6.1-4).

Step 8: Check the fugacities to see if they match in all the phases for each component.

Step 9: If they do not match, adjust the estimated K values and proceed to Step 4. If they do match, stop the calculation.

PROCEDURE DIAGRAM FOR PHASE COMPOSITION CALCULATIONS



NOTE: The diagram is for a three-phase calculation. L_1 and L_2 correspond to the two liquid phases and g to the vapor phase. x_i^1 and x_i^2 correspond to compositions in the two liquid phases and y_i to the composition in the vapor phase. The same procedure would be followed for a two-phase calculation.

COMMENTS ON PROCEDURE 9A6.1

Purpose

This procedure is to be used to estimate the compositions of the coexisting phases for hydrocarbon-water systems under vapor-liquid, liquid-liquid, or vapor-liquid-liquid equilibrium.

Limitations

The correlation was developed for hydrocarbons up to C₁₀. Caution should be used in applying it to heavier hydrocarbons, close to the three-phase critical point, or at temperatures greater than 550 F.

The correlation cannot be used if a hydrocarbon cannot be classified as belonging to one of the homologous series listed in Table 9A6.2.

Reliability

For hydrocarbons up to C₁₀ and temperatures below 550 F, an average error of 37 percent may be expected for solubility of water in hydrocarbons and 45 percent for solubility of hydrocarbons in water. The corresponding errors in the K values of water and hydrocarbons may be expected to be about 30 percent.

Literature Sources

The original Soave equation of state is from G. Soave, *Chem. Eng. Sci.* 27 1197 (1972). It was modified for water-hydrocarbon systems by V. N. Kabadi and R. P. Danner (101a).

COMMENTS ON PROCEDURE 9A7.1

9A7.1

Purpose

Procedure 9A7.1 is presented as a method for calculating the Henry's constant of selected gases in water.

Limitations

Procedure 9A7.1 is applicable only in the pressure ranges specified in Table 9A7.2.

Use the method of T. J. Edwards, J. Newman, and J. M. Prausnitz, (54a) to correct the Henry's constant calculated from equation (9A7.1-1) for application at high pressures.

Reliability

For the temperature and pressure ranges given in table 9A7.2, the Henry's constants calculated from equation (9A7.1-1) reproduce experimental data to within ± 10 percent. Individual compound errors are given in Table 9A7.2.

Literature Sources

Equation 9A7.1-1 was developed by T. J. Edwards, J. Newman, and J. M. Prausnitz (54a). Coefficients were determined by the API Technical Data Book project staff (1996).

Example

Calculate the solubility of hydrogen sulfide in water at 77 F and 1 atmosphere partial pressure of the gas.

From Table 9A7.2, for hydrogen sulfide the coefficients B_1 , B_2 , B_3 , and B_4 are:

$$B_1 = -65864.7, B_2 = -215.127, B_3 = 0.185874, B_4 = 1384.15$$

$$T = 77 + 459.67 = 536.67 \text{ R}$$

Equation (9A7.1-1) gives

$$\ln(H) = \frac{-65864.7}{536.67} + -215.127\ln(536.67) + (0.185874(536.67)) + 1384.15$$

$$H = 8266.8 \text{ psia/mole fraction of gas}$$

The solubility of hydrogen sulfide in water is

$$X = \frac{PP_{\text{gas}}}{H} = \frac{14.696}{8266.8}$$

$$X = 0.00178$$

The experimental value is 0.00182 (86d).

TABLE 9A7.2
COEFFICIENTS FOR PROCEDURE 9A7.1

Gas	Temperature Range (F)	Pressure* Range (psia)	B1	B2	B3	B4	Average Percent Error
Oxygen	32-158	3-17	101704.9	385.375	-0.353734	-2408.51	3.5
Hydrogen	32-212	9-17	117.8	15.373	-0.023159	-70.48	4.1
Hydrogen Sulfide	32-140	5-65	-65864.7	-215.127	0.185874	1384.15	2.0
Nitrogen	32-212	3-32	25211.0	118.943	-0.123571	-714.14	5.7
Ammonia	68-600	0.4-568	-11142.1	-7.893	0.001284	72.62	19.0
Carbon Monoxide	32-500	14.7-1998	-8662.7	-5.654	-0.012030	71.85	4.7
Carbon Dioxide	32-392	2-69	46808.7	191.186	-0.175793	-1184.42	17.3
Methyl Mercaptan	100-600	44-2067	-13781.6	-12.347	-0.005968	114.49	33.2
Sulfur Dioxide	50-158	0.01-32	634896.5	2296.520	-2.047604	-14512.89	22.6
Helium	32-527	14.7-145	-17587.5	-42.873	0.020141	306.02	16.2
Argon	32-563	14.4-30.4	-23594.7	-51.464	0.023640	368.02	7.1
Nitrous Oxide	32-77	14.7	234056.3	946.088	-0.932964	-5871.51	1.7
Nitric Oxide	32-176	14.7	-23522.2	-54.228	0.030256	381.48	0.3
Chlorine	50-77	0.85-14.7	-105739.0	0.000	-0.370512	404.68	23.9
Bromine	32-140	14.7	30706.4	156.042	-0.157961	-946.18	0.5
Iodine	32-255	14.7	-6389.7	-12.490	-0.016055	112.34	0.4
Methane	34-340	14.7-450	-35166.6	-92.170	0.059614	626.14	3.6
Ethane	42-340	14.7-400	-14411.4	-11.467	-0.012828	118.83	7.5
Propane	41-310	14.7-400	-70492.0	-181.505	0.114412	1224.04	5.3
n-Butane	38-340	14.7-400	-20552.5	-22.455	-0.010089	198.28	6.2
Isobutane	41-220	14.7-150	-94172.5	-293.567	0.238630	1906.36	5.3

* partial pressure of gases

**PROCEDURE 9A7.3
EQUILIBRIUM CONCENTRATIONS OF SOUR
GAS SYSTEMS IN WATER**

Discussion

The following equations are used to calculate the equilibrium concentration for binary and ternary systems of ammonia and hydrogen sulfide gases in water. Binary system equilibrium concentrations can be calculated using Equation (9A7.3-1). Ternary system equilibrium concentrations can be calculated iteratively using Equation (9A7.3-2). Required input includes operating temperature in degrees Fahrenheit, and the partial pressure of the selected components in millimeters of mercury.

$$\log(PP) = A_1 * PPM^2 + A_2 * PPM + A_3 * T + A_4 \quad (9A7.3-1)$$

$$\log(PP) = C_1 * PPM^2 + C_2 * PPM + C_3 * Z_M + C_4 \quad (9A7.3-2)$$

Where:

PP = Partial Pressure (mmHg)

PPM = Log(parts per million wt.)

T = Temperature (R)

Z_M = Function of molar ratio. (see special comments)

Procedure

BINARY SYSTEMS

Step 1: Read the constants A₁, A₂, A₃, and A₄ for the given component from Table 9A7.4.

Step 2: Calculate the weight concentration in parts per million at the operating temperature and partial pressure of the gas.

TERNARY SYSTEMS

Step 1: Obtain the operating temperature and initial guesses of partial pressure for NH₃ and H₂S.

Step 2: Calculate the molar rate of ammonia to hydrogen sulfide.

Step 3: Select and calculate the Z term based on the temperature and molar ratio.

Step 4: Using the partial pressure, Z term, and appropriate constants from Table 9A7.4 calculate the partial pressure of the selected component from Equation 9A7.3-2.

Step 5: Repeat Steps 2-4 for the other component.

Step 6: Repeat steps 2-6 until the partial pressures converge.

COMMENTS ON PROCEDURE 9A7.3**Purpose**

This procedure is given for estimating the equilibrium concentrations of ammonia and hydrogen sulfide in water from the system temperature and partial pressure of the gas.

Limitations

This procedure is limited to a temperature range of 80-300 F and to concentrations below 10% for the gas. Extrapolation beyond these limits is not recommended.

Reliability

Within the limits of the correlation, the average errors for Equation (9A7.3-1) and Equation (9A7.3-2) are 7.72% and 8.41% respectively. The bias for the two equations are -0.38% and -0.49% respectively.

Special Comments

The procedure will interpolate between the temperatures listed in Table 9A7.4 for the ternary system by using an inverse lever rule.

The Z term in equation 9A7.3-2 is a function of the molar ratio. The actual function is determined from Table 9A7.4. The possible functions are:

1. $\frac{1}{M^2}$
2. $\log(M)$
3. $1 - \frac{M^2}{6} + \frac{M^4}{120}$

where M = molar ratio of ammonia to hydrogen sulfide.

The third Z can also be expressed as $\frac{\sin(M)}{M}$.

Literature Sources

This procedure was correlated from a method developed by S. A. Newman, *Hydrocarbon Processing* 70 [9,10,11] (1991).

Examples**BINARY SYSTEM**

Find the equilibrium concentration of ammonia in water at 248 F and partial pressure of 3.54 psia for ammonia.

From Equation (9A7.3-1) and the constants in Table 9A7.4, the weight concentration for ammonia is 10085.42 ppm at the operating conditions. The experimental concentration is 8770 ppm by wt. (229a).

TERNARY SYSTEM

Find the concentration of ammonia and hydrogen sulfide in water at 248 F when the partial pressure of hydrogen sulfide is 82.5 mmHg and the weight concentration is 7000 ppm.

From Equation (9A7.3-2) and the parameters in Table 9A7.4, the molar ratio of ammonia to hydrogen sulfide in water is calculated to be 5.57. The experimental molar ratio is 4.8 (81d).

9A8 pH OF NONHYDROCARBON GASES IN WATER

PROCEDURE 9A8.1

pH OF AMMONIA AND HYDROGEN SULFIDE GASES IN WATER

Discussion

The following equations are to be used to calculate the pH for binary and ternary systems of ammonia and hydrogen sulfide gases in water. The pH for a binary system can be calculated using Equation (9A8.1-1). Required input for binary systems include the component of choice, the operating temperature, and the weight concentration of the chosen component in parts per million. The pH for a ternary system can be calculated using Equation (9A8.1-2). Required input for ternary systems include the operating temperature and the molar ratio of ammonia to hydrogen sulfide in water.

$$\text{pH} = A_1 * \text{PPM} + A_2 * T + A_3 \quad (9A8.1-1)$$

$$\log(\text{pH}) = C_1 * \log[\log(M)] + C_2 * \log(M) + C_3 * T + C_4 \quad (9A8.1-2)$$

Where:

PPM = Log(Parts per million wt.)

T = Temperature (R)

M = Moles NH₃/moles H₂S in solution

Procedure

- Step 1:* Select the appropriate equation based on the system composition: Equation (9A8.1-1) for binary systems, Equation (9A8.1-2) for ternary systems.
- Step 2:* Obtain the related coefficients from Table 9A8.2.
- Step 3:* From the selected Equation, calculate the pH from the operating temperature and either the weight concentration (in ppm wt) for binary systems or the ammonia/hydrogen sulfide molar ratio for ternary systems.

COMMENTS ON PROCEDURE 9A8.1

Purpose

This procedure is given for estimating the system pH of ammonia and hydrogen sulfide in water from the temperature and the equilibrium concentration of the gases.

Limitations

This procedure is limited to concentrations below 10 wt% for the gases. For binary systems, the temperature range is limited to 80-300 F and 80-200 F for ammonia/water and hydrogen sulfide/water systems, respectively. For ternary systems, the temperature range is 80-150 F. Extrapolation beyond these limits is not recommended.

Reliability

The reliability of the pH values has been found to be within ± 5 percent.

Literature Source

This procedure was correlated from a procedure developed by S. A. Newman, *Hydrocarbon Processing*, 70 [11] 139 (1991).

Example

Find the pH of an ammonia/hydrogen sulfide /water system at an operating temperature of 80 F with an ammonia/hydrogen sulfide molar ratio of 2.0.

From Equation (9A8.1-2), the pH is calculated to be 8.6 at the operating conditions. An experimental value for the pH at these conditions is 9.73 (79d).

Δv_w^a = molar difference in volume between the empty hydrate lattice and ice.

Δh_w^f = heat of fusion.

Δv_w^f = change of volume due to fusion.

dP/dT = slope of pressure-temperature curve for the reference hydrate.

Finally, the experimental chemical potential is calculated by equation (9B2.1-15) or (9B2.1-16).

If ice is present,

$$\Delta \mu_w^a(T, P) = \Delta \mu_w^a(T, P_R) + \Delta v_w^a(P - P_R) \quad (9B2.1-15)$$

If water is present,

$$\Delta \mu_w^L(T, P) = \Delta \mu_w^L(T, P_R) + (\Delta v_w^a + \Delta v_w^f)(P - P_R) \quad (9B2.1-16)$$

C. Composition

The composition of the hydrate phase may be calculated by equation (9B2.1-17).

$$Y_j = \frac{\sum_m v_m \theta_{mj}}{\sum_m v_m \sum_i \theta_{mi}} \quad (9B2.1-17)$$

Where:

Y_j = mole fraction of Component j in the hydrate phase on a water-free basis.

Procedure

A. Procedure for Pressure Prediction

Step 1: For each component, obtain the critical temperature and pressure from Chapter 1, the acentric factor from Chapter 2, the Soave equation-of-state parameters from Chapter 8, and the solubility data from Chapter 9.

Step 2: Enter the temperature and the composition of the gas phase on a water-free basis.

Step 3: Check Table 9B2.3 to determine if T is higher than the upper quadruple point of the hydrate-forming gases. If so, no hydrate will form and the procedure is stopped.

Step 4: Estimate the formation pressure. A good estimate would be the formation pressure of the reference hydrate at the given temperature, from equation (9B2.1-12).

Step 5: Determine which hydrate structure is formed. If a Structure II-forming gas is present, assume Structure II is formed. If not, assume Structure I is formed.

Step 6: Calculate the Langmuir constants using equations (9B2.1-9) through (9B2.1-11) and Table 9B2.4.

Step 7: Calculate the experimental chemical potential difference at the reference pressure using equation (9B2.1-13) or (9B2.1-14).

Step 8: Calculate the fugacity coefficients of the gases and the mole fraction of water in the water-rich liquid phase, if applicable.

Step 9: Calculate a new pressure by solving equation (9B2.1-7) or (9B2.1-8) and equation (9B2.1-15) or (9B2.1-16) simultaneously. If the new pressure is not equal to the old pressure, reestimate pressure and return to Step 8.

Step 10: If only the structure assumed in Step 5 is formed, go to Step 12. If Structure II was assumed, save the answer, assume Structure I will form, and repeat Steps 6 through 9 until the correct pressure is determined.

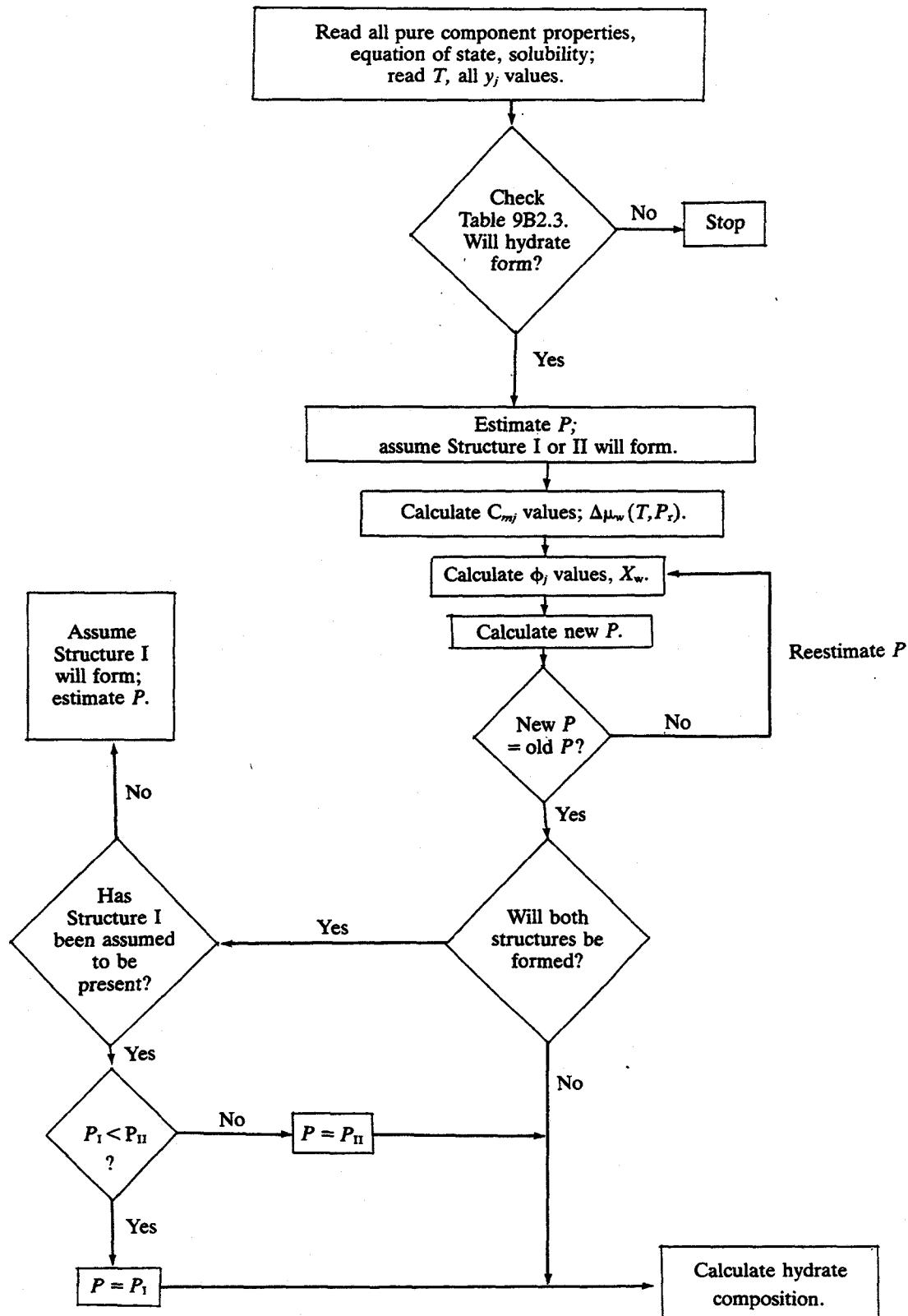
Step 11: Compare the two pressures. If they are equal, both hydrate structures are formed. If they are not equal, the lower pressure is correct, and the structure associated with that pressure will be formed.

Step 12: Calculate the hydrate phase composition if desired, using equation (9B2.1-17).

B. Procedure for Temperature Prediction

Follow the same procedure for pressure prediction, except enter an estimated rather than an experimental temperature. Adjust the temperature each time through the iteration until the calculated pressure equals the given pressure.

FLOW DIAGRAM FOR PREDICTION OF GAS HYDRATE FORMATION PRESSURE



COMMENTS ON PROCEDURE 9B2.1**Purpose**

This procedure is to be used to estimate the formation conditions of hydrates formed from hydrocarbons and related gases. The vapor-phase composition on a water-free basis must be known. The procedure is used to estimate the hydrate formation pressure at a given temperature or the formation temperature at a given pressure. The hydrate-phase composition on a water-free basis may also be computed using this procedure. The required parameters are given in Tables 9B2.2 through 9B2.6.

Limitations

This procedure is basically limited to small hydrocarbons and the nonhydrocarbon hydrate formers—nitrogen, carbon dioxide, and hydrogen sulfide. Non-hydrate formers, such as hydrogen and hydrocarbons heavier than and including *n*-butane, may also be present and are treated simply as components of the gas mixture.

The procedure is applicable to mixtures of water, hydrocarbons, and the related non-hydrocarbons which exhibit one vapor phase, one water-rich liquid phase, and the hydrate phase. It cannot be used for fully condensed systems.

The correlation has been tested against nine pure-component and 25 multicomponent systems. (A binary mixture of water and a hydrate former is considered a pure-component system.) The procedure is applicable to hydrocarbon and hydrogen sulfide pure-component systems but not to nitrogen and carbon dioxide systems. It is most reliable for multicomponent systems in which the concentrations of the nonhydrocarbons are less than about 50 percent. The correlation is most accurate at pressures up to about 10,000 pounds per square inch absolute, above which convergence is slow and not always achieved.

Because of the complex nature of the procedure, the convergence routine used is very important and may influence the success or failure of the computer program. Several different techniques should be available to guarantee convergence.

Based on limited data, the procedure is usually reliable for calculating hydrate phase composition. However, it should be used with caution for components whose gas-phase compositions are less than 20 percent.

Reliability

For pressure prediction in pure component systems, an average error of 29 percent can be expected, excluding isobutane. The error in pressure prediction for isobutane is 120 percent. The average error in temperature prediction for pure component systems is less than 10 F.

For multicomponent systems, an average error of 25.0 percent can be expected for pressure prediction. An average error in temperature prediction of 3.8 F may be expected.

Use this procedure with caution for the calculation of hydrate phase composition and *K* values, since insufficient data are available to predict the expected error. In addition, no data are available to determine which of the methods (i.e., this procedure or Figures 9B1.4 through 9B1.12) is correct.

Special Comments

Ongoing studies are being done to further improve the Kihara parameters in Table 9B2.4. The user is advised to refer to current literature to obtain the most recent values for those parameters.

Literature Source

This procedure is basically from W. R. Parrish and J. M. Prausnitz, *Ind. Eng. Chem. Proc. Des. Develop.* 11 26 (1972), and has been modified and adapted for use in this book.

CHAPTER 10

SURFACE AND INTERFACIAL TENSION

10-0 INTRODUCTION

Surface Tension

The molecules at a liquid-gas interface are acted upon by unbalanced forces of attraction whose net inward force tends to minimize the surface area of the liquid. The work required to expand the surface area by 1 square centimeter is called the surface free energy. The opposing force in the surface of the liquid acts parallel to the plane of the surface and is called the surface tension.

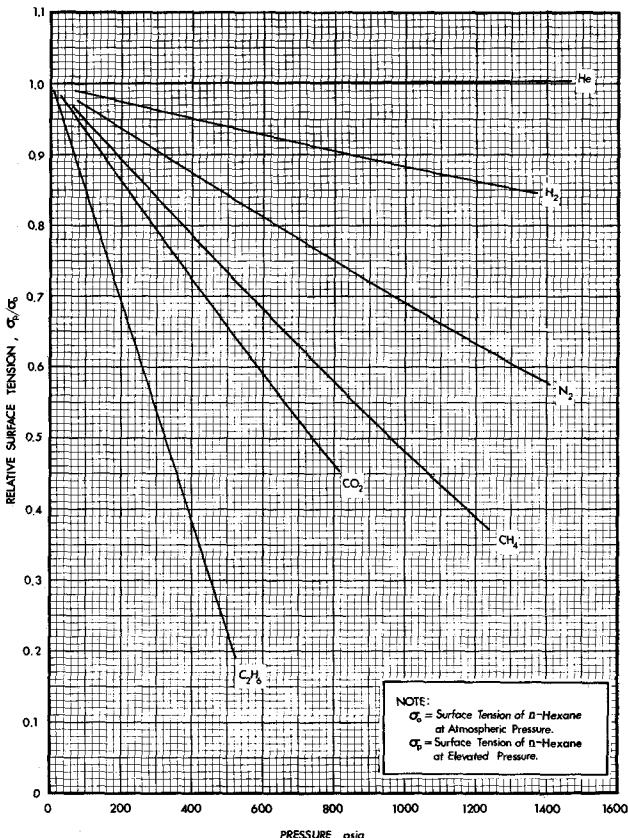
A knowledge of surface tension behavior is becoming increasingly important where foaming, wetting, emulsification, and droplet formation are encountered. Specifically, surface tension data are used in designing bubble caps, trays, and towers for distillation and extraction units.

Pure Hydrocarbons: The surface tensions of pure hydrocarbons may be obtained from the low- and high-temperature nomographs, Figures 10A1.1 and 10A1.2, respectively. The grid coordinates and temperature limits are listed in Table 10A1.3. These nomographs are based mainly on data from API Research Project 44 (2a) with temperature limits extended using independent experimental data. All values are for the air-saturated liquid at 1 atmosphere, with the exception of methane, propane, *n*-butane, isobutane, and *n*-pentane, which are for the liquid in equilibrium with its vapor under a higher (saturation) pressure.

For compounds not appearing in Table 10A1.3, a list of group contribution values for calculating parachors is given in Procedure 10A1.4. From the parachor, molecular weight, and density of the material, the surface tension may be calculated using the relationship of Sugden (118a), Procedure 10A1.4. A quick and accurate estimate may be obtained from Figure 10A1.5, which correlates reduced temperature and Watson characterization factors to the surface tension.

Pressure Effect: By the phase rule, the effect of pressure on the surface tension of a liquid can be studied only if two components are present (with one component, pressure—that is, vapor pressure—fixed for a given temperature). The effect of pressure, therefore, is inseparable from the effects of solubility and adsorption. Very few studies have been performed in this area, and no general correlations exist.

Due to the solubility effect (increasing pressure generally results in increased gas solubility), the surface

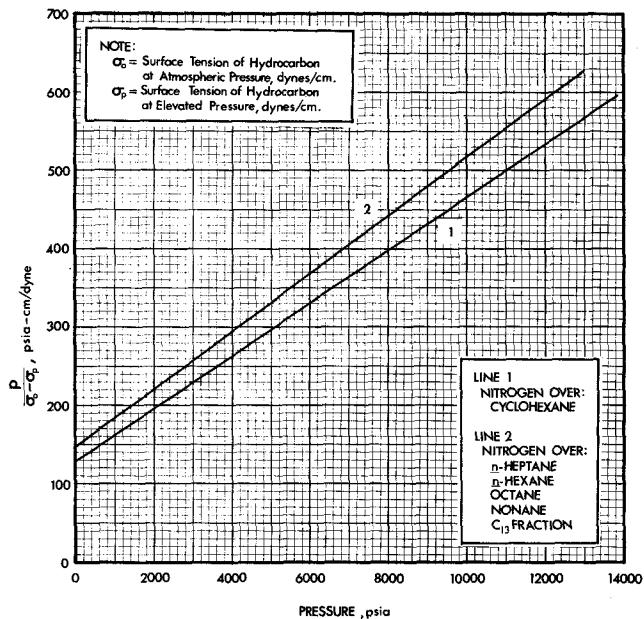


Source: Slowinski, et al., *J. Phys. Chem.* 61 808 (1957).

Figure 10-0.1—Effect of Pressure on Surface Tension of *n*-Hexane at 25 C For Various Gases

tension would be expected to decrease with increasing pressure. This has been proven theoretically (35c) and verified by various researchers. Slowinski et al. (39c) were first to report that, in general, the higher the critical temperature (or boiling point) of the gas, the greater the decrease in surface tension with increasing pressure. Their results for the surface tension of *n*-hexane against several gases are shown in Figure 10-0.1. In terms of increasing critical temperature (or boiling point), this ordering effect is largely supported by independent data (14c, 31c, 43c) and may be visualized as an increased solubility effect.

A relation between surface tension and pressure (16c) for a greater range of pressure than that of Figure 10-0.1 is presented in Figure 10-0.2. As can be seen, the relation is independent of the hydrocarbon for various paraffins under nitrogen. It was also shown (16c) that the surface tensions of *n*-hexane and *n*-nonane increase



Source: Gielessen and Schmatz, *Z. Physik. Chem. (Frankfurt)* 27 157 (1961).

Figure 10-0.2—Effect of Pressure on Surface Tension of Several Nitrogen-Hydrocarbon Systems at 22°C

with increasing pressure when helium is the overlying gas.

It would be erroneous to extend these results beyond the specific systems that have been studied. For example, where the two components have comparable volatilities, these results may not follow.

Defined Mixtures: The surface tension of a mixture of known composition may be predicted by either of two methods, depending on the system pressure. For systems below or near atmospheric pressure, the method of Morgan and Griggs (28b), Procedure 10A2.1, may be used. For systems above atmospheric pressure, the method of Weinaug and Katz (43b), Procedure 10A2.2, should be employed.

Crude Oils and Petroleum Fractions: Two methods for estimating the surface tension of crude oils and petroleum fractions are included. Procedure 10A3.1 estimates these values graphically by a modified use of Figure 10A1.5 and should be used as a desk method. When large amounts of data must be evaluated, Procedure 10A3.2 can be used with the aid of a computer to calculate the surface tension values.

Nonhydrocarbons: The surface tension of pure nonhydrocarbons may be predicted with good accuracy from Figure 10A4.1. The grid coordinates and temperature limits that accompany this figure are given in Table 10A4.2. Additional nonhydrocarbons and data sources are presented in Table 10A4.3. The grid coordinates for these substances may be determined by plot-

ting data from the sources given. For substances that do not appear in either Table 10A4.2 or Table 10A4.3, surface tension values may be obtained using Procedure 10A1.4 and the group contributions therein.

Interfacial Tension

In order for an interface to exist in a binary liquid system, the two compounds must be partially or totally immiscible. At the interface, the interfacial tension, or free energy, results from a complex balance of attractive and repulsive forces acting within each bulk phase and across the interface. These forces, dispersion, induction, dipole-dipole interactions, and hydrogen bonding, vary with temperature, pressure, solubility, and the size and geometric arrangement of the molecules.

Most correlations attempt to predict the interfacial tension from the properties of the bulk phases with some allowance for the interaction between liquids. However, many researchers agree that there exist monolayers on each side of the interface that exhibit distinctly different properties from those of the bulk phase, and that govern the interfacial tension.

Much research has been done on such monolayers, especially through the use of surfactants. When minute amounts of certain compounds are introduced into a bulk phase, the composition of the monolayers, and thus the interfacial tension, changes dramatically. This area is beyond the scope of this chapter. Knowledge of interfacial tensions has been of particular importance to many liquid-liquid mass transfer operations and is of increasing importance to enhanced oil recovery.

Hydrocarbon-Water Interfaces: In pure hydrocarbon-water systems the mutual solubilities are relatively low, and several correlations accurately predict the interfacial tension from bulk properties. If the interfacial tension at or near ambient conditions is known, Procedure 10B1.1 estimates the interfacial tension of any hydrocarbon-water system. In this method, the liquid-liquid interaction is accounted for by the dispersion forces within each phase. The dispersion forces within the hydrocarbon phase are assumed to be equal to the surface tension, while those for water must be calculated for each system.

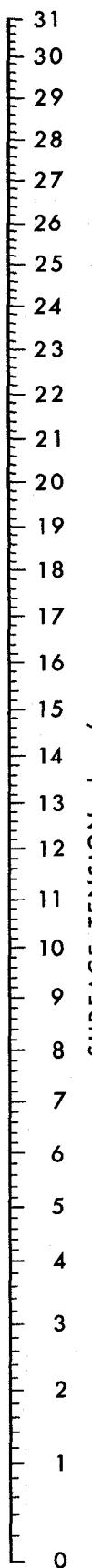
Procedure 10B1.3 is an alternate method for estimation of interfacial tension for hydrocarbon-water systems using only the surface tension of each pure liquid phase. This method is used only when dispersion constants are not obtainable.

Temperature Effect: Although both temperature and pressure affect the interfacial tension between two liquids, temperature variations produce much larger

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changes than do pressure variations. These changes occur due to the influence of temperature on mutual solubilities, which alters the composition of the mono-

layers and thus the interfacial tension. Both Procedures 10B1.1 and 10B1.3 compensate for temperature changes; neither compensates for pressure changes.



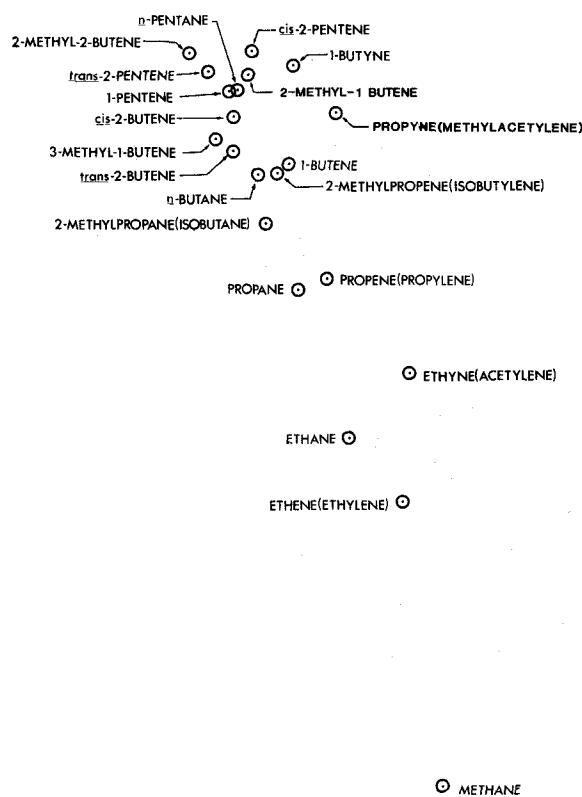
NOTE:

Temperature Limits for this Figure
are given in Table 10A1.3.

Do Not Extrapolate

FIGURE 10A1.1
SURFACE TENSION
OF PURE
LIQUID HYDROCARBONS
AT ONE ATMOSPHERE
LOW-TEMPERATURE RANGE

AP TECHNICAL DATA BOOK
MARCH 1982
Approved: RPD & TED



COMMENTS ON FIGURE 10A1.1**Purpose**

Surface tension-temperature data are presented for pure hydrocarbons. For higher molecular weight hydrocarbons, use Figure 10A1.2.

Limitations

The valid temperature range for each hydrocarbon is given in Table 10A1.3.

Reliability

Values taken from this nomograph are accurate to within 0.5 dyne per centimeter.

Literature Sources

The nomograph was prepared using data from the references noted in Table 10A1.3.

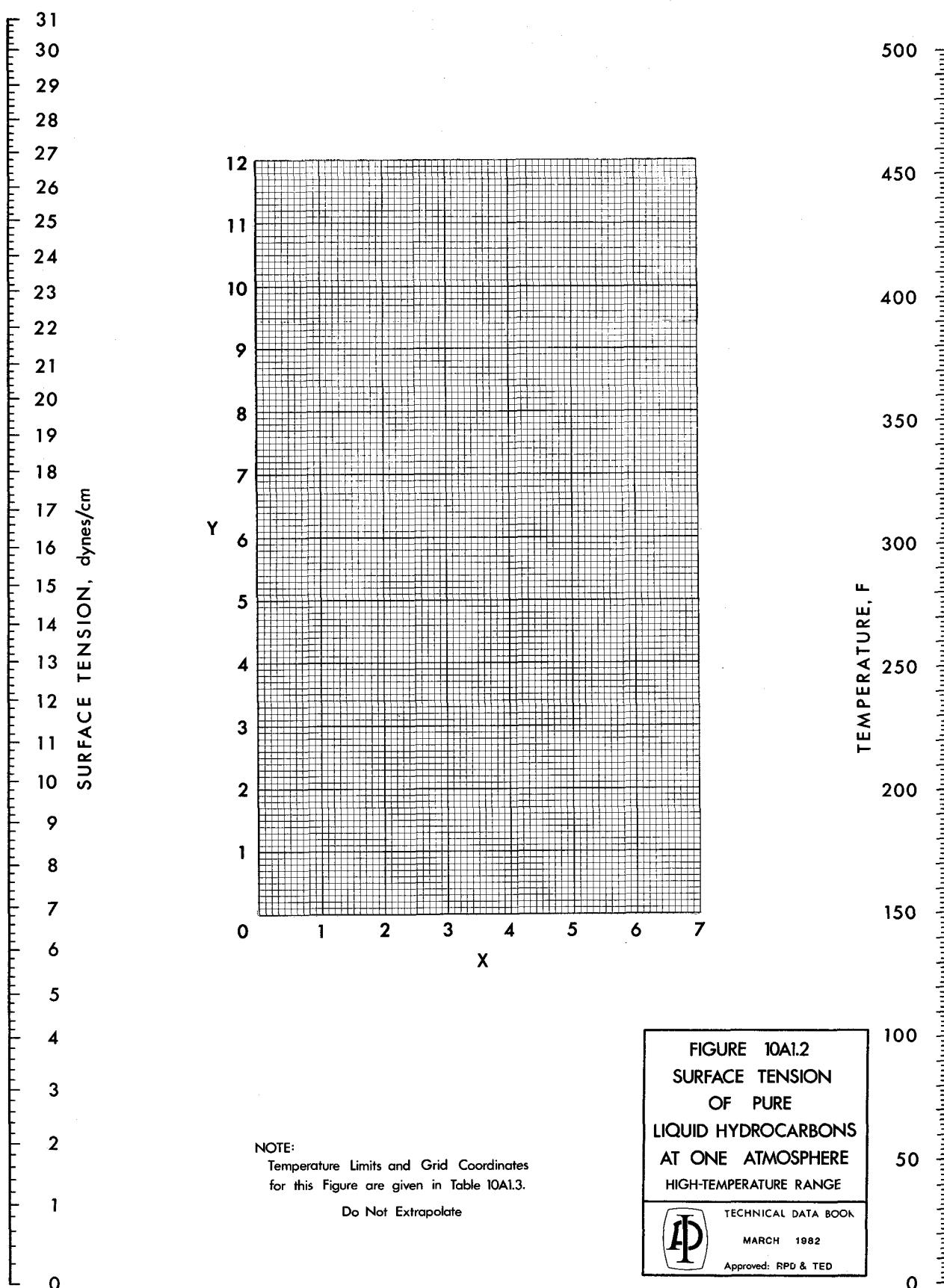
Example

Find the surface tension of *n*-butane at -10 F.

From Table 10A1.3, -10 F is within the valid temperature range for *n*-butane.

A straight line through the temperature scale at -10 F and the pivot point intersects the surface tension scale at 17.6 dynes per centimeter.

The experimental value (2a) is 17.62 dynes per centimeter.



COMMENTS ON FIGURE 10A1.2**Purpose**

Surface tension-temperature data are presented for pure hydrocarbons. For lower molecular weight hydrocarbons, use Figure 10A1.1.

Limitations

The valid temperature range for each hydrocarbon is given in Table 10A1.3, along with the necessary grid coordinates.

Reliability

Values taken from this nomograph are accurate to within 0.5 dyne per centimeter.

Literature Sources

The nomograph was prepared using data from the references noted in Table 10A1.3.

Example

Find the surface tension of ethylbenzene at 180 F.

Table 10A1.3 shows that 180 F is within the temperature limits for the compound. The X-Y coordinates are 2.76 and 5.85, respectively. This locates the pivot point on the grid.

A straight line through the pivot point and temperature scale at 180 F intersects the surface tension scale at 22.4 dynes per centimeter.

The experimental value (2a) is 22.6 dynes per centimeter.

PROCEDURE 10A1.4

ESTIMATION OF SURFACE TENSION FROM THE PARACHOR

Discussion

For compounds that are not included in Table 10A1.3 because of the absence of experimental data, surface tension values may be estimated using the equation:

$$\sigma = \left[\frac{P}{M} (\rho_L - \rho_V) \right]^4 \quad (10A1.4-1)$$

Where:

σ = surface tension, in dynes per centimeter.

P = parachor, sum of group contributions.

M = molecular weight.

ρ_L = saturated liquid density at the system temperature, in grams per milliliter.

ρ_V = saturated vapor density at the system temperature, in grams per milliliter.

The group contributions for calculating the parachor are listed in the following tabulation:

Group	Contribution	Group	Contribution
CH_2 in $-(\text{CH}_2)_n$:		Single bond	0.0
$n < 12$	40.0	Semipolar bond	0.0
$n > 12$	40.3	Singlet linkage	-9.5
C	9.0	Hydrogen bridge	-14.4
H	15.5	Chain branching, per branch	-3.7
H in OH	10.0	Secondary-secondary	
H in HN	12.5	adjacency	-1.6
O	19.8	Secondary-tertiary	
O_2 in esters	54.8	adjacency	-2.0
N	17.5	Tertiary-tertiary	
S	49.1	adjacency	-4.5
P	40.5	Alkyl groups:	
F	26.1	1-Methylethyl	133.3
Cl	55.2	1-Methylpropyl	171.9
Br	68.0	1-Methylbutyl	211.7
I	90.3	2-Methylpropyl	173.3
Ethylenic bond:		1-Ethylpropyl	209.5
Terminal ^a	19.1	1,1-Dimethylethyl	170.4
2,3-Position	17.7	1,1-Dimethylpropyl	207.5
3,4-Position ^b	16.3	1,2-Dimethylpropyl	207.9
Triple bond	40.6	1,1,2-Trimethylpropyl	243.5
Carbonyl bond in ketones		Ring closure:	
RCOR':		3-Membered ring	12.5
Total C = 3	22.3	4-Membered ring	6.0
4	20.0	5-Membered ring	3.0
5	18.5	6-Membered ring	0.8
6	17.3	7-Membered ring	4.0
7	17.3	Position differences in	
8	15.1	benzene:	
9	14.1	Ortho-Meta	1.8—3.4
10	13.0	Meta-Para	0.2—0.5
11	12.6	Ortho-Para	2.0—3.8

^aUse this value for double bonds in cyclic compounds.

^bUse 16.3 for double bonds in the 3,4- or higher positions.

Procedure

Step 1: Obtain the molecular weight from Chapter 1 and the saturated vapor and liquid densities from Chapter 6.

Step 2: From the preceding tabulation, obtain the various contributions that are required to form the desired molecule. Sum the contributions to derive a value for the parachor.

Step 3: Calculate the surface tension using equation (10A1.4-1).

COMMENTS ON PROCEDURE 10A1.4

Purpose

An equation is presented for calculating the surface tension of pure components under a wide variety of conditions for compounds not included in Table 10A1.3.

Limitations

Methane and ethane surface tensions should not be predicted by this method as errors of 15–20 percent result. The equation is not accurate above reduced temperatures of 0.90.

Reliability

Surface tensions are predicted by this method with an average error of 2.3 percent.

Literature Sources

The equation was developed by Sugden, *J. Chem. Soc.* **125** 32 (1924). Group contributions for calculating parachors are from Quayle, *Chem. Rev.* **53** 439 (1953).

Example

Calculate the surface tension of ethylbenzene at 180 F.

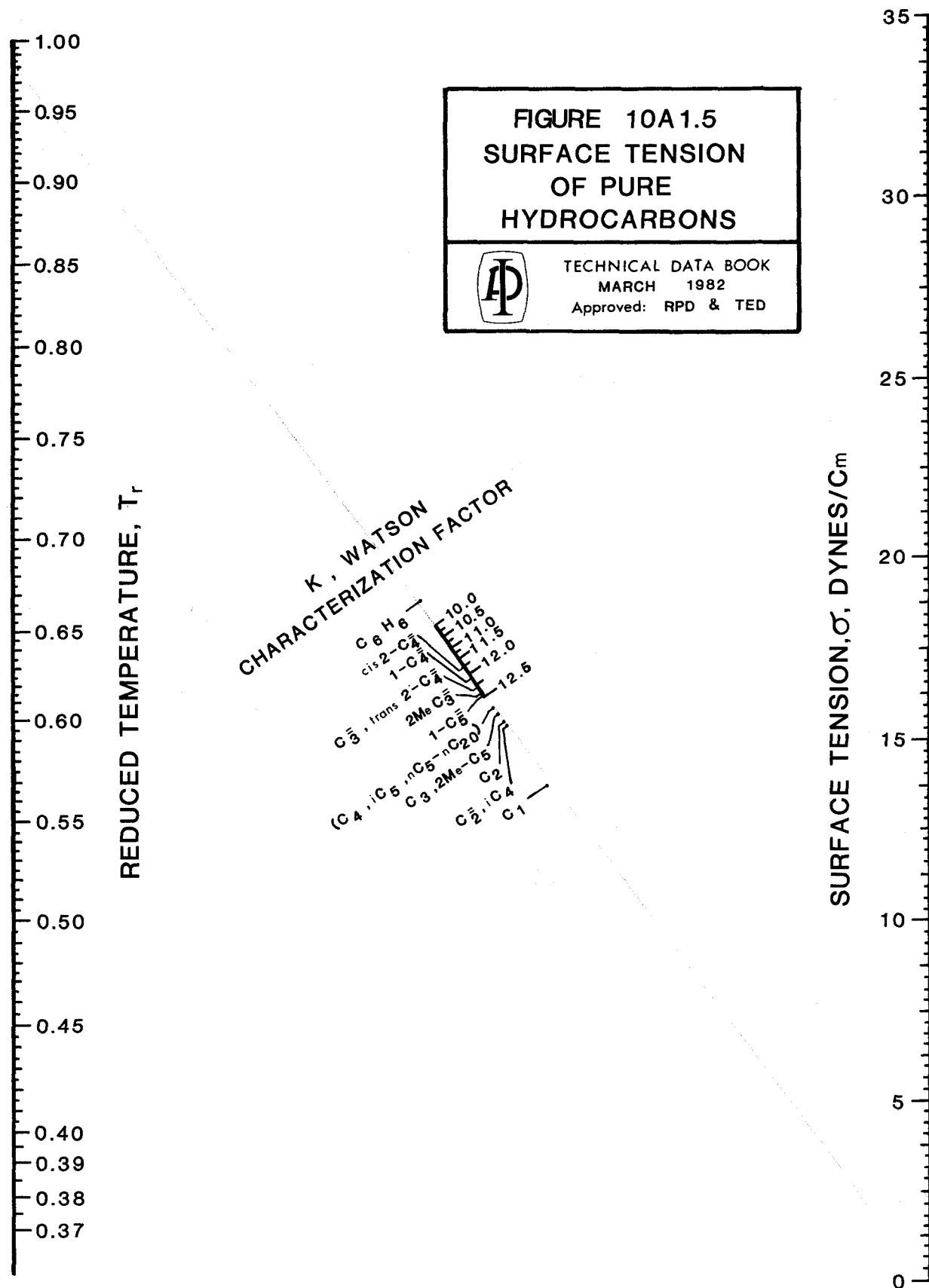
From Chapter 1, the molecular weight is 106.2, and, from Chapter 6, the saturated liquid and vapor densities are 0.812 grams per milliliter and 0.00063 grams per milliliter, respectively. The parachor is calculated from the contributions in the preceding tabulation:

7 Carbon atoms, (7) (9.0)	= 63.0
8 Hydrogen atoms, (8) (15.5)	= 124.0
3 Ethylenic bonds, (3) (19.1)	= 57.3
1 Six-member ring closure, (1) (0.8)	= 0.8
1 —CH ₂ — group, (1) (40.0)	= 40.0
Total	= 285.1

From equation (10A1.4-1),

$$\sigma = \left[\left(\frac{285.1}{106.20} \right) (0.812 - 0.00063) \right]^4 = 22.5 \text{ dynes per centimeter}$$

The experimental value (2a) is 22.6 dynes per centimeter.



COMMENTS ON FIGURE 10A1.5

Purpose

Figure 10A1.5 is presented as a desk method for the estimation of the surface tensions of pure hydrocarbons at the corresponding vapor pressure for temperatures above the normal boiling point. It is the most accurate method available for predicting methane and ethane surface tensions.

Procedure

Step 1: Obtain the critical temperature of the hydrocarbon from Chapter 1.

Step 2: Calculate the reduced temperature.

Step 3: If a point for the hydrocarbon is not presented on the nomograph, obtain the Watson characterization factor from Chapter 2.

Step 4: Determine the surface tension from Figure 10A1.5.

Limitations

This method is only accurate at the vapor pressure of the system. Do not extrapolate along either ordinates or the diagonal. The method should not be used for condensed ring aromatic compounds.

Reliability

Pure component surface tensions are estimated with an average error of 2.5 percent.

Literature Source

This nomograph was developed by Hadden and presented in *Hydrocarbon Processing* 45 [10] 161 (1966).

Example

Calculate the surface tension of methane at -199 F.

From Chapter 1, the critical temperature of methane is -116.67 F. The reduced temperature is calculated as:

$$T_r = (-199 + 459.6)/(-116.6 + 459.6) = 0.76$$

Notice that a point for a C₁ hydrocarbon is given in Figure 10A1.5. A straight line through that point and the left-hand scale at $T_r = 0.76$ projects through the surface tension scale at 6.80 dynes per centimeter. The experimental value (51a) is 7.28 dynes per centimeter.

PROCEDURE 10A2.1**SURFACE TENSION OF DEFINED HYDROCARBON MIXTURES AT LOW PRESSURES****Discussion**

For mixtures of known composition at or below atmospheric pressure, surface tensions may be calculated using the following equation:

$$\sigma_m = \sum_{i=1}^n x_i \sigma_i \quad (10A2.1-1)$$

Where:

σ_m = mixture surface tension, in dynes per centimeter.

σ_i = surface tension at the desired temperature for component i , in dynes per centimeter.

x_i = mole fraction of component i in liquid.

Subscripts i and m refer to pure component i and the n -component mixture, respectively.

Procedure

Step 1: Obtain the surface tensions of the pure components using Figure 10A1.1 or 10A1.2 or Procedure 10A1.4.

Step 2: Calculate the surface tension of the mixture using equation (10A2.1-1).

COMMENTS ON PROCEDURE 10A2.1**Purpose**

An equation is presented for calculating the surface tension of hydrocarbon mixtures of known composition at or below atmospheric pressure.

Limitations

The method is not accurate above atmospheric pressure. The equation is not applicable when one of the pure components is a gas at the operating temperature and pressure (use Procedure 10A2.2). The method is not accurate for systems involving nonhydrocarbons, particularly when the difference in surface tensions of the pure substances exceeds 10 dynes per centimeter.

Reliability

Surface tensions calculated by this method are accurate to within an average deviation of 2-7 percent. The amount of error varies depending upon the relative differences between the hydrocarbons in the mixture. Mixtures composed of hydrocarbons of greatly differing nature will produce larger errors than the average. Alkane-alkane and aromatic-aromatic mixtures average errors of less than 2 percent, while aromatic-alkane mixtures average errors of 7 percent or more. Mixtures of naphthalenes and either aromatics or alkanes produce average errors of 3 percent.

Literature Source

The method was developed by Morgan and Griggs *J. Am. Chem. Soc.* **39** 2261 (1917).

Example

Calculate the surface tension of a mixture containing 37.9 mole percent benzene in cyclohexane at 77 F and 1 atmosphere.

From Figure 10A1.2, at 77 F the surface tension of benzene is 28.2 dynes per centimeter and that of cyclohexane is 24.3 dynes per centimeter.

Using equation (10A2.1-1),

$$\sigma_m = (0.379) (28.2) + (0.621) (24.3) = 25.8 \text{ dynes per centimeter}$$

The experimental value (17b) is 25.4 dynes per centimeter.

PROCEDURE 10A2.2**SURFACE TENSION OF DEFINED HYDROCARBON MIXTURES AT HIGH PRESSURES****Discussion**

For mixtures of known composition at high pressures, surface tensions may be calculated using the following equation:

$$\sigma_m = \left\{ \sum_{i=1}^n \left[P_i \left(\frac{\rho_L}{M_L} x_i - \frac{\rho_V}{M_V} y_i \right) \right] \right\}^4 \quad (10A2.2-1)$$

Where:

σ_m = surface tension of the mixture, in dynes per centimeter.

n = number of components in the mixture.

P_i = parachor for component i .

ρ_L = density of the liquid mixture, in grams per milliliter.

ρ_V = density of the vapor mixture, in grams per milliliter.

M_L = molecular weight of the liquid mixture.

M_V = molecular weight of the vapor mixture.

x_i = mole fraction of component i in liquid.

y_i = mole fraction of component i in vapor.

This method is especially useful for computer applications where a large number of surface tension values are needed, and where the required parameters for equation (10A2.2-1) must also be calculated. When equation (10A2.2-1) is applied to data near or below atmospheric pressure, the vapor term, $(\rho_V/M_V) y_i$, may be neglected with little loss in accuracy.

Procedure

Step 1: If required, calculate vapor and liquid compositions from Chapter 8.

Step 2: Estimate the saturated liquid density of the mixture (and vapor density, if required) from Chapter 6.

Step 3: Calculate the parachor for each term using Procedure 10A1.4.

Step 4: Calculate the average molecular weight of the saturated liquid and vapor phases.

Step 5: Calculate the surface tension of the mixture using equation (10A2.2-1).

COMMENTS ON PROCEDURE 10A2.2

Purpose

An equation is presented for calculating the surface tension of hydrocarbon mixtures of known composition at variable temperatures and pressures.

Limitations

For hydrocarbon mixtures that contain methane, this procedure is applicable only when the vapor and liquid densities for use in equation (10A2.2-1) either are experimentally determined or can be estimated by very accurate methods. A small error in either term will often produce deviations of several hundred percent in the calculated surface tension. Procedures of Chapter 6 may be used for vapor density prediction with reasonable accuracy. Methane liquid densities predicted by methods of Chapter 6, however, are usually high by as much as 50 percent. Private communications have noted that a more accurate answer for methane systems will result if, prior to use of the method, a constant-temperature flash calculation at fixed liquid mole fraction methane is carried out with an appropriate equation of state to estimate the methane vapor mole fraction, liquid density, and vapor density.

The procedure should not be used for mixtures containing biphenyl (or similar compounds).

Reliability

An average error of 3 percent is incurred by use of this method for mixtures not containing methane. For methane-containing mixtures for which accurate compositions and densities are available, an average error of 8 percent applies. Small errors in parameters may decrease the reliability of the method.

Literature Source

The method was developed by Weinaug and Katz, *Ind. Eng. Chem.* **35** 239 (1943).

Example

Calculate the surface tension of a methane-propane mixture at 50 F and 1109 pounds per square inch absolute. The mole fraction of methane is known to be 0.418 in the liquid and 0.788 in the vapor, and the densities of the saturated phases are 0.393 grams per milliliter for the liquid and 0.112 grams per milliliter for the vapor.

Using Procedure 10A1.4, the methane parachor is 72.6 and that for propane is 150.8. The average molecular weights are next calculated using pure-component values from Chapter 1:

$$M_L = (0.418)(16.04) + (0.582)(44.10) = 32.37$$

$$M_V = (0.788)(16.04) + (0.212)(44.10) = 21.99$$

Using equation (10A2.2-1),

$$\begin{aligned} \sigma_m &= \left\{ 72.6 \left[\left(\frac{0.393}{32.37} \right)(0.418) - \left(\frac{0.112}{21.99} \right)(0.788) \right] \right. \\ &\quad \left. + 150.8 \left[\left(\frac{0.393}{32.37} \right)(0.582) - \left(\frac{0.112}{21.99} \right)(0.212) \right] \right\}^4 \end{aligned}$$

$$= 0.922 \text{ dynes per centimeter}$$

The experimental value (43b) is 0.98 dynes per centimeter.

PROCEDURE 10A3.1

SURFACE TENSION OF PETROLEUM FRACTIONS

Discussion

For petroleum fractions at temperatures above the normal boiling point, surface tensions can be estimated by the following procedure.

Procedure

Step 1: If the critical temperature of the fraction is not known, obtain a pseudocritical temperature from Chapter 4.

Step 2: Calculate the reduced temperature.

Step 3: Calculate the Watson characterization factor from its definition in Chapter 2.

Step 4: Calculate the surface tension using Figure 10A1.5.

10A3.1

COMMENTS ON PROCEDURE 10A3.1

Purpose

This procedure is presented as a desk method for predicting the surface tension of petroleum fractions and crude oils at temperatures (and corresponding vapor pressures) above the normal boiling point.

Limitations

This procedure is not applicable to coal liquids.

Reliability

The surface tension values predicted by this method are, on the average, 10 percent greater than the experimental values.

Literature Source

The nomograph was developed by Hadden and presented in *Hydrocarbon Processing* **45** [10], 161 (1966).

Example

Calculate the surface tension of Crude Oil #19 (32c). The API gravity is known to be 41.6 and the kinematic viscosity at 100 F is 2.22 centistokes.

Using Figure 11A4.1, the Watson *K* is calculated to be 11.96.

Using the API gravity and this Watson *K* factor, Figure 2B6.1 predicts the mean average boiling point to be 482 F. From this boiling point the methods of Chapter 4 yield an estimated pseudocritical temperature of 1278 R. $T_r = 560/1278 = 0.44$.

Figure 10A1.5 estimates the surface tension of this crude oil to be 27.6 dynes per centimeter. An experimental value (32c) is 28.5 dynes per centimeter.

PROCEDURE 10A3.2**ALTERNATE COMPUTER METHOD FOR SURFACE TENSION OF PETROLEUM FRACTIONS****Discussion**

This method is useful for predicting the surface tension of crude oils and petroleum fractions of unknown composition. Although Procedure 10A3.1 predicts a slightly more accurate value, the following equation readily adapts to computer applications.

$$\sigma = 673.7 [(T_c - T)/T_c]^{1.232}/K \quad (10A3.2-1)$$

Where:

- σ = surface tension of the liquid, in dynes per centimeter.
- T_c = critical or pseudocritical temperature, in degrees Rankine.
- T = temperature of system, in degrees Rankine.
- K = Watson characterization factor.

Procedure

Step 1: Calculate the Watson characterization factor by methods of Chapter 2. If the boiling point of the liquid is not known, predict the mean average boiling point by methods of Chapter 2.

Step 2: If the critical temperature is not known, obtain a pseudocritical temperature from Chapter 4.

Step 3: Calculate the surface tension of the system using equation (10A3.2-1).

COMMENTS ON PROCEDURE 10A3.2**Purpose**

An equation is presented as an alternate computer method to predict the surface tension of petroleum fractions.

Limitations

This method should not be applied to coal liquids. Since equation (10A3.2-1) contains no terms to correct for pressure changes, it will give higher errors at pressures above about 500 pounds per square inch absolute.

Reliability

Values calculated by this method showed an average error of 10.7 percent.

Literature Source

The equation was presented in an unpublished report (Technical Report No. 52-53R of the Shell Development Company) by Sanborn and Evans, 1953.

Example

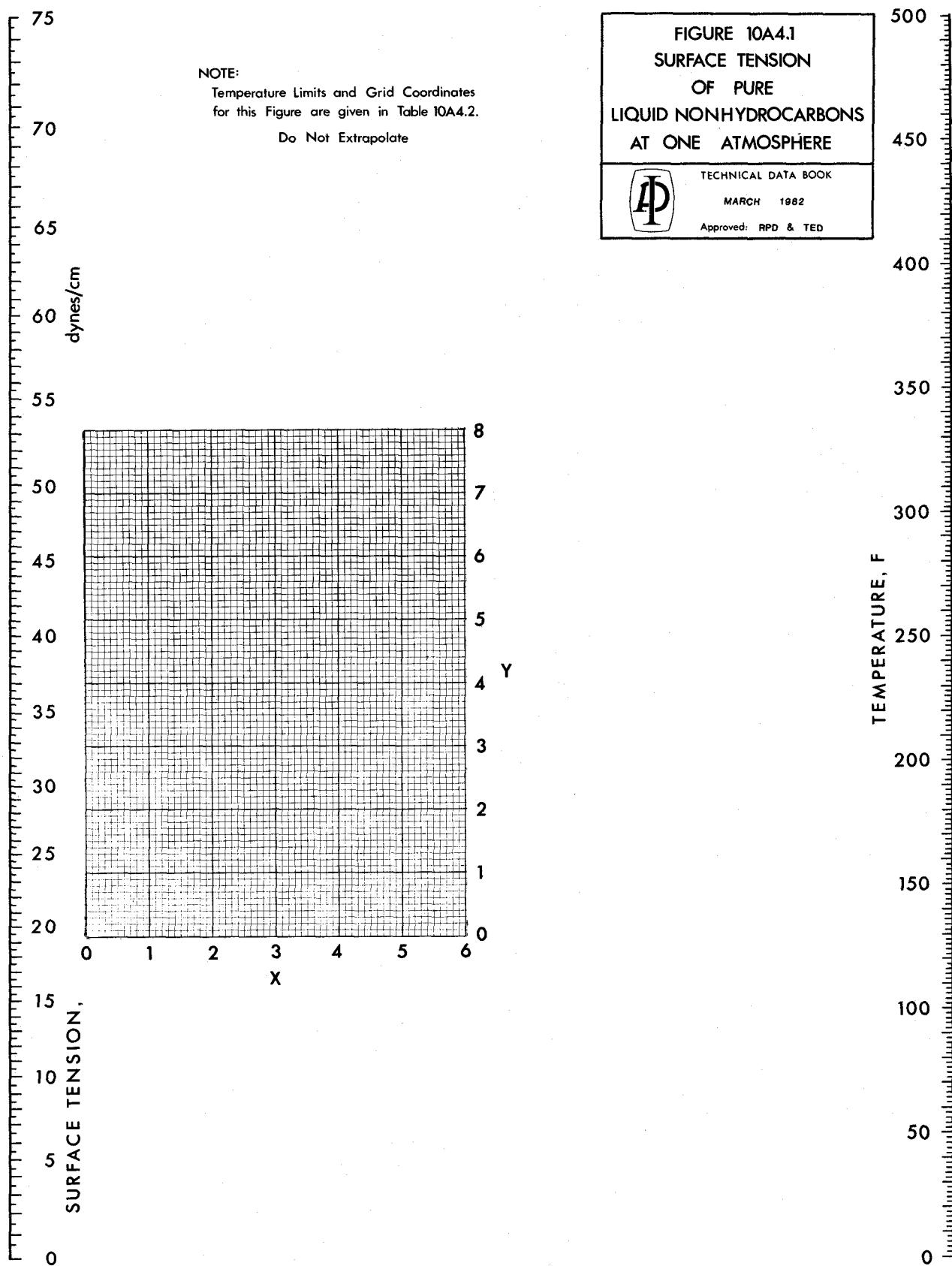
Calculate the surface tension of Crude Oil #2180 (19c) at 60 F, given: API gravity = 43.3, and molecular weight = 252.

From Chapter 2, the mean average boiling point is 560 F, and Watson *K* is 12.4. The pseudocritical temperature is estimated to be 1334 R from Chapter 4.

From equation 10A3.2-1:

$$\begin{aligned}\sigma &= 673.7 [\{ 1334 - (60 + 459.6) \} / 1334]^{1.232} / 12.4 \\ &= 29.6 \text{ dynes per centimeter}\end{aligned}$$

An experimental value (19c) is 28.7 dynes per centimeter.



COMMENTS ON FIGURE 10A4.1**Purpose**

Surface tension-temperature data are presented for pure nonhydrocarbons.

Limitations

The acceptable temperature range for each nonhydrocarbon is given in Table 10A4.2, along with the necessary grid coordinates. Table 10A4.3 lists sources of data for estimating grid coordinates for other compounds.

Reliability

Values taken from this nomograph show an average error of 1.7 percent.

Literature Sources

The nomograph was prepared using data from the references noted in Table 10A4.2.

Example

Find the surface tension of propionic acid at 187 F.

Table 10A4.2 shows that this temperature is within the acceptable range. The *X-Y* coordinates are 2.40 and 0.68, respectively.

A straight line through 187 F and the pivot point intersects the surface tension scale at 20.1 dynes per centimeter.

The experimental value (128a) is 20.16 dynes per centimeter.

PROCEDURE 10B1.1**INTERFACIAL TENSION BETWEEN HYDROCARBONS AND WATER****Discussion**

The following method reliably estimates the interfacial tension between a hydrocarbon and water. If dispersion constants are not available or calculable, use Procedure 10B1.3.

$$\sigma_{HW} = \sigma_H + \sigma_W - 2(\sigma_W^d \sigma_H)^{1/2} \quad (10B1.1-1)$$

Where:

σ_{HW} = interfacial tension between the liquid phases, in dynes per centimeter.

σ_i = surface tension of pure liquid component i at temperature and pressure of system, in dynes per centimeter; H = hydrocarbon, W = water.

σ_W^d = the dispersion constant in water in dynes per centimeter (from Table 10B1.2).

Procedure

Step 1: Obtain experimental values for the surface tension of the hydrocarbon phase or calculate it by methods of Section 10A1.

Step 2: Obtain a value for the surface tension of water from Table 10B1.4.

Step 3: Obtain a value of σ_W^d from Table 10B1.2. If none is recorded for the hydrocarbon, σ_W^d may be calculated from equation (10B1.1-1) if a value of the interfacial tension is known at or near ambient temperature and pressure.

Step 4: Calculate the interfacial tension using equation (10B1.1-1) at the temperature and pressure of the system.

COMMENTS ON PROCEDURE 10B1.1

Purpose

This procedure is presented as a general method to calculate values of interfacial tension between water and hydrocarbon phases.

Limitations

This method should be used only when the dispersion constant is known or can be calculated from ambient temperature and pressure data.

Although equation (10B1.1-1) is accurate at reduced pressures as great as 40, it should not be used in the range $0.65 < P_r < 1.35$.

Reliability

When this procedure was applied to systems at ambient or low pressures, an average error of 2.6 percent resulted. With high-pressure systems the average error was 5.9 percent.

Literature Source

This method was developed by Fowkes in *J. Phys. Chem.* **67**, 2538 (1963).

Example 1: Ambient Pressure Case

Calculate the interfacial tension between ethylbenzene and water at 176 F (80 C) and atmospheric pressure. The surface tension of ethylbenzene is given by the source (I25) as 22.30 dynes per centimeter. From Table 10B1.4, the surface tension of pure water is 64.01 dynes per centimeter, and from Table 10B1.2, σ_w^d is 34.73 dynes per centimeter.

Using equation (10B1.1-1),

$$\sigma_{HW} = 22.30 + 64.01 - 2(34.73 \times 22.30)^{1/2} = 30.65 \text{ dynes per centimeter}$$

The experimental value (I30) is 30.70 dynes per centimeter.

Example 2: High Pressure Case

Calculate the interfacial tension between *n*-decane and water at 212 F (100C) and 5145 pounds per square inch absolute.

Using Procedure 10A1.4, the surface tension of *n*-decane at these conditions is 31.10 dynes per centimeter. Assuming the pressure has little effect on the surface tension of water, that value is given as 61.06 dynes per centimeter in Table 10B1.4. From Table 10B1.2, σ_w^d is 21.00 dynes per centimeter.

Using equation (10B1.1-1),

$$\sigma_{HW} = 31.10 + 61.06 - 2(21.00 \times 31.10)^{1/2} = 41.05 \text{ dynes per centimeter}$$

The experimental value (I33) is 42.20 dynes per centimeter.

PROCEDURE 10B1.3

ALTERNATE METHOD FOR INTERFACIAL TENSION BETWEEN HYDROCARBONS AND WATER

Discussion

The interfacial tension between a hydrocarbon and water may be estimated by the following equation in cases where dispersion constants are not available or calculable and Procedure 10B1.1 is hence not applicable.

$$\sigma_{HW} = \sigma_H + \sigma_W - 1.10 (\sigma_H \sigma_W)^{1/2} \quad (10B1.3-1)$$

Where:

σ_{HW} = interfacial tension between the hydrocarbon and water phases, in dynes per centimeter.

σ_i = surface tension of pure component i at system conditions, in dynes per centimeter; H = hydrocarbon, W = water.

Procedure

Step 1: Obtain the pure component surface tension of each liquid phase. The surface tension of water may be interpolated from Table 10B1.4. For the hydrocarbon phase, literature values should be available (2a), or Procedure 10A1.4 or Figure 10A1.5 will accurately estimate the surface tension.

Step 2: Calculate the interfacial tension using equation (10B1.3-1).

COMMENTS ON PROCEDURE 10B1.3

Purpose

This procedure is presented for the estimation of the interfacial tension between hydrocarbon and water liquid phases.

Limitations

This method is primarily applicable to saturated hydrocarbons which contain five or more carbon atoms. The accuracy of this procedure decreases rapidly when the reduced temperature of the hydrocarbon phase exceeds 0.53, although it is accurate with hydrocarbon reduced pressure values as high as 40.

Reliability

For saturated hydrocarbons the interfacial tension values calculated by this method will be accurate to within an average error of 2.0 percent when used with systems at ambient pressures. When it is applied to high pressure systems, an average error of 7 percent can be expected. For all hydrocarbons the average errors increase to 12 percent at ambient conditions and to 200 percent at high pressures.

Literature Source

This method was developed by Good and Elbing, *Ind. Eng. Chem.* **62** 3, 54 (1970).

Example 1: Ambient Pressure Case

Find the interfacial tension between ethylbenzene and water at 176 F (80 C). The surface tension of ethylbenzene is given by the source (I25) as 22.30 dynes per centimeter. From Table 10B1.4, the surface tension of pure water is 64.01 dynes per centimeter.

$$\sigma_{HW} = 22.30 + 64.01 - (1.10) (22.30 \times 64.01)^{1/2} = 44.75 \text{ dynes per centimeter}$$

The experimental value (I30) is 30.70 dynes per centimeter.

Example 2: High Pressure Case

Determine the interfacial tension between *n*-decane and water at 212 F (100 C) and 5145 pounds per square inch absolute.

Using Procedure 10A1.4, the surface tension of *n*-decane at these conditions is calculated to be 31.1 dynes per centimeter. The surface tension of the water phase is assumed to be that of pure water at this temperature and ambient pressure. From Table 10B1.4, the surface tension of water is 61.06 dynes per centimeter.

Using equation (10B1.3-1),

$$\sigma_{HW} = 31.10 + 61.06 - (1.10) (31.10 \times 61.06)^{1/2} = 44.23 \text{ dynes per centimeter}$$

The experimental value (I33) is 42.20 dynes per centimeter.

Note that both examples are identical to those given in Procedure 10B1.1, in which both predictions were close to the experimental value. For Procedure 10B1.3, Example 1 shows a high error, as ethylbenzene is not a saturated hydrocarbon, while Example 2 shows very good predictive accuracy.

CHAPTER 11

VISCOSITY

11-0 INTRODUCTION

Viscosity is a measure of the ability of a fluid to resist shear. When the shear stress on any differential volume element of flowing fluid is proportional to the velocity gradient in the direction perpendicular to the direction of flow, the fluid is called a Newtonian fluid.

The methods presented in this chapter are for Newtonian fluids and should not be expected to maintain their accuracy for non-Newtonian fluids. Almost all gases and most hydrocarbon liquids are Newtonian fluids. Very heavy asphalts with low UOP K's exhibit non-Newtonian behavior. Some other common non-Newtonian fluids are polymers, pastes, slurries, waxy oils, and some silicate esters.

Viscosity is a function of temperature, pressure, and molecular species. For non-Newtonian fluids, the viscosity is also a function of the local velocity gradient.

The absolute viscosity is defined as the shear stress at a point divided by the velocity gradient at that point. The unit of absolute viscosity is the poise, which is equal to 1 gram per (centimeter)(second).

The kinematic viscosity is defined as the ratio of the absolute viscosity to the density, both at the same temperature and pressure. The unit of kinematic viscosity corresponding to the poise is the stoke, which is equal to 1 square centimeter per second. The conversion from absolute to kinematic viscosity is given by the following equation:

$$v = \frac{\mu}{\rho} \quad (11-0.1)$$

Where:

- | | |
|----------|--|
| v = | kinematic viscosity, in stokes |
| μ = | absolute viscosity, in poises |
| ρ = | density, in vacuo, in grams per cubic centimeter |

The units centipoise (0.01 poise) and centistoke (0.01 stoke) are used most frequently.

Saybolt Universal viscosity is the efflux time in seconds for a 60-milliliter sample to flow through a standard orifice in the bottom of a tube. Saybolt Furol viscosity is determined in the same manner as Saybolt Universal viscosity except that a larger orifice is used. The orifice and tube geometry are specified in standards of the American Society for Testing and Materials.

Viscosity of Liquid Systems

Conversions between the more common engineering units of viscosity are given in Chapter 1. Conversions of kinematic viscosity data to Saybolt Universal seconds and to Saybolt Furol seconds are given in Procedures 11A1.1 and 11A1.2, respectively. The relationships between other viscosity scales and kinematic viscosity are shown in Procedure 11A1.6.

The viscosity-temperature behavior for approximately 300 pure liquid hydrocarbons can be determined from the correlating equation given in Procedure 11A2.1. Using viscosity data at the two temperatures, the viscosity-temperature behavior can be estimated using Procedure 11A4.4. Viscosity data at 100 F and 210 F are given in Chapter 1 for a number of hydrocarbons and the more common nonhydrocarbons. The viscosities of compounds for which no experimental data exist can be estimated by a group contribution method given in Procedure 11A2.3. Liquid viscosities of defined mixtures can be predicted with Procedure 11A3.1.

Several methods are presented to determine the viscosity-temperature relationship for petroleum fractions. Procedure 11A4.1 can be used to calculate viscosity if a measured viscosity at 100 F is known.

Procedure 11A4.2 can be used to predict liquid viscosity if no experimental measurements are available. Procedure 11A4.2 predicts the viscosity at two temperatures, 100 F and 210 F. The viscosity at any other temperature can then be determined by using Procedure 11A4.4. Procedure 11A4.5 is used to mathematically estimate the viscosity of liquid blends of petroleum fractions. Procedure 11A4.6 is used to determine the viscosity of multicomponent blends of pure hydrocarbons with petroleum fractions or multicomponent blends of petroleum fractions.

There is no general method for predicting the effect of pressure on the liquid viscosity of all types of hydrocarbons. For low-molecular-weight hydrocarbons, Procedure 11A5.1 may be used to predict viscosity at elevated pressures provided the critical pressure, critical temperature, and acentric factor are known, and provided either a value of the viscosity at the critical point or a liquid viscosity value at another temperature and pressure is known. Procedure 11A5.5 is given to estimate the effect of pressure on the viscosity of high-molecular-weight pure and mixed hydrocarbons. Procedure 11A5.5 should be used for the effect of pressure on the viscosity of petroleum fractions.

The viscosity index of an oil is an empirical number indicating the effect of a change in temperature on viscosity. It can be calculated using Procedure 11A6.1. The liquid viscosity of pure and mixed hydrocarbons containing dissolved gases is given by Procedure 11A7.1.

Viscosity of Gaseous Systems

In contrast with the viscosities of liquids, viscosities of gases increase with increasing temperature and with increasing pressure.

The viscosities predicted by the methods of this chapter should not be used at pressures below approximately 0.2 pound per square inch absolute.

The viscosity-temperature behavior for approximately 300 pure gaseous hydrocarbons can be determined from the correlating equation given in Procedure 11B1.1. The viscosities of other pure gases at reduced pressures below 0.6 are estimated by Procedure 11B1.3.

The viscosities of mixtures of known composition at reduced pressures below 0.6 are estimated by Procedure 11B2.1 in conjunction with Procedure 11B1.1 or Procedure 11B1.3. A more rapid but less precise approximation is given by Procedure 11B3.1. Procedure 11B3.1 is not recommended except as a rough approximation for gaseous hydrocarbon mixtures of undefined composition.

For reduced pressures above 0.6, the effect of pressure on viscosity can be estimated using Procedure 11B4.1.

Viscosity of Nonhydrocarbons

The viscosity of liquid and gaseous hydrogen is plotted in Figure 11C1.1. Procedure 11C1.2 correlates the effect of pressure on the viscosity of nonhydrocarbon gases. Procedures 11B2.1 and 11B4.1 are also applicable for calculating the viscosities of gaseous mixtures containing nonhydrocarbons at low and high pressure, respectively.

Summary of Viscosity Calculation Methods

Figure 11-0.1 gives a schematic diagram showing which procedure(s) should be used for calculating hydrocarbon viscosities for any particular case.

Computerized Subroutines Available in Chapter 16

Chapter 16 of the API Technical Data Book contains subprograms for all the predictive methods in Chapter 11. The subprograms are written in standard Fortran code and can be incorporated into computer

PROCEDURE 11A1.1**CONVERSION OF KINEMATIC VISCOSITY TO SAYBOLT UNIVERSAL VISCOSITY****Discussion**

The following equations are to be used to convert kinematic viscosity data in centistokes at any temperature to Saybolt Universal viscosity in Saybolt Universal seconds (SUS) at the same temperature.

For kinematic viscosities less than 75 centistokes at 100 F, Table 11A1.2 applies.

For kinematic viscosities less than 75 centistokes at temperature t , Table 11A1.2 gives an *equivalent* Saybolt Universal viscosity, which must be corrected by factor A obtained from Table 11A1.3. Equation (11A1.1-2) applies.

$$SUS_t = (SUS_{eq})(A) \quad (11A1.1-1)$$

Where:

SUS_t = Saybolt University viscosity at t , in seconds.

SUS_{eq} = equivalent Saybolt Universal viscosity at t , in seconds (from Table 11A1.2). At 100 F the equivalent Saybolt Universal viscosity is equal to the actual Saybolt Universal viscosity.

t = temperature, in degrees Fahrenheit.

A = multiplier used in Equation (11A1.1-1) when the kinematic viscosity at t is less than 75 centistokes (from Table 11A1.3).

For kinematic viscosities greater than 75 centistokes, Equation (11A1.1-2) applies.

$$SUS_t = v_t B \quad (11A1.1-2)$$

Where:

v_t = kinematic viscosity at t , in centistokes.

B = multiplier used in Equation (11A1.1-2) when the kinematic viscosity at t is greater than 75 centistokes (from Table 11A1.3).

For computer use, the Saybolt Universal viscosities at 100 F may be calculated by Equation (11A1.1-3), and those at a temperature t by Equation (11A1.1-4). These equations are valid both above and below 75 centistokes.

$$SUS_{eq} = 4.6324v_t + \frac{[1.0+0.03264v_t]}{[3930.2+262.7v_t+23.97v_t^2+1.646v_t^3]*10^{-5}} \quad (11A1.1-3)$$

$$SUS_t = [1+0.000061(t-100)]SUS_{eq} \quad (11A1.1-4)$$

Procedure

Step 1: Find the equivalent Saybolt Universal viscosity from the kinematic viscosity in centistokes at t , from Table 11A1.2 or from Equation (11A1.1-3). If the equation is used, go to Step 3.

Step 2: If the kinematic viscosity at t is less than 75.0 centistokes, use Equation (11A1.1-1) to convert to Saybolt Universal viscosity. Factor A is determined from Table 11A1.3. If the kinematic viscosity is greater than 75.0 centistokes, use Equation (11A1.1-2) to convert to Saybolt Universal viscosity. Factor B is obtained from Table 11A1.3.

Step 3: Use Equation (11A1.1-4) to convert the equivalent Saybolt Universal viscosity to the actual Saybolt Universal viscosity at temperature, t .

COMMENTS ON PROCEDURE 11A1.1

Purpose

This procedure is given for converting kinematic viscosity in centistokes to Saybolt Universal viscosity in seconds. Tables 11A1.2 and 11A1.3 are part of this procedure.

Reliability

In the range of 70F to 300F, the average deviation between calculated and experimental Saybolt Universal viscosities is 0.17 percent, and the maximum deviation is 0.5 percent.

Special Comment

Expanded versions of the table are available as ASTM D 2161-82 (see Literature Source).

Literature Source

The procedure and tables were adapted from ASTM D 2161-82, *Standard Method for Conversion of Kinematic Viscosity to Saybolt Universal Viscosity or to Saybolt Furol Viscosity* (6).

Examples

- A. Estimate the Saybolt Universal viscosity in seconds at 200F for an oil having a kinematic viscosity of 53.00 centistokes at 200F.

From Table 11A1.2, $SUS_{eq} = 246$ seconds. From Table 11A1.3, $A = 1.006$.

From Equation (11A1.1-1), the Saybolt Universal viscosity at 200 F = $(246)(1.006) = 247$ seconds.

- B. Estimate the Saybolt Universal viscosity at 0F for an oil having a kinematic viscosity of 90.00 centistokes at 0F.

Because the kinematic viscosity is greater than 75 centistokes, Equation (11A1.1-2) must be used.

From Table 11A1.3, $B = 4.604$.

From Equation (11A1.1-2), Saybolt Universal viscosity at 0 F = $(90.00)(4.604) = 414.4$ seconds.

TABLE 11A1.2

CONVERSION OF KINEMATIC VISCOSITY TO AN UNCORRECTED SAYBOLT UNIVERSAL VISCOSITY
(Part of Procedure 11A1.1)

Kinematic Viscosity (centistokes)	Equivalent Saybolt Universal Viscosity (seconds)	Kinematic Viscosity (centistokes)	Equivalent Saybolt Universal Viscosity (seconds)	Kinematic Viscosity (centistokes)	Equivalent Saybolt Universal Viscosity (seconds)	Kinematic Viscosity (centistokes)	Equivalent Saybolt Universal Viscosity (seconds)
1.82	32.0	5.80	44.9	14.40	75.1	23.00	110.6
1.84	32.1	6.00	45.6	14.60	75.8	23.20	111.5
1.86	32.1	6.20	46.2	14.80	76.6	23.40	112.4
1.88	32.2	6.40	46.9	15.00	77.4	23.60	113.2
1.90	32.3	6.60	47.5	15.20	78.2	23.80	114.1
1.92	32.3	6.80	48.1	15.40	79.0	24.00	115.0
1.94	32.4	7.00	48.8	15.60	79.8	24.20	115.9
1.96	32.5	7.20	49.4	15.80	80.6	24.40	116.7
1.98	32.5	7.40	50.1	16.00	81.4	24.60	117.6
2.00	32.6	7.60	50.7	16.20	82.2	24.80	118.5
2.10	32.9	7.80	51.4	16.40	83.0	25.00	119.4
2.20	33.3	8.00	52.1	16.60	83.8	25.50	121.6
2.30	33.6	8.20	52.7	16.80	84.6	26.00	123.7
2.40	34.0	8.40	53.4	17.00	85.4	26.50	126.0
2.50	34.3	8.60	54.1	17.20	86.2	27.00	128.2
2.60	34.6	8.80	54.7	17.40	87.0	27.50	130.4
2.70	35.0	9.00	55.4	17.60	87.8	28.00	132.6
2.80	35.3	9.20	56.1	17.80	88.7	28.50	134.8
2.90	35.6	9.40	56.8	18.00	89.5	29.00	137.0
3.00	36.0	9.60	57.5	18.20	90.3	29.50	139.3
3.10	36.3	9.80	58.1	18.40	91.1	30.00	141.5
3.20	36.6	10.00	58.8	18.60	92.0	30.50	143.8
3.30	36.9	10.20	59.5	18.80	92.8	31.00	146.0
3.40	37.3	10.40	60.2	19.00	93.6	31.50	148.2
3.50	37.6	10.60	60.9	19.20	94.5	32.00	150.5
3.60	37.9	10.80	61.7	19.40	95.3	32.50	152.7
3.70	38.2	11.00	62.4	19.60	96.1	33.00	155.0
3.80	38.6	11.20	63.1	19.80	97.0	33.50	157.2
3.90	38.9	11.40	63.8	20.00	97.8	34.00	159.5
4.00	39.2	11.60	64.5	20.20	98.7	34.50	161.8
4.10	39.5	11.80	65.3	20.40	99.5	35.00	164.0
4.20	39.8	12.00	66.0	20.60	100.4	35.50	166.3
4.30	40.2	12.20	66.7	20.80	101.2	36.00	168.6
4.40	40.5	12.40	67.5	21.00	102.1	36.50	170.8
4.50	40.8	12.60	68.2	21.20	102.9	37.00	173.1
4.60	41.1	12.80	69.0	21.40	103.8	37.50	175.4
4.70	41.4	13.00	69.7	21.60	104.6	38.00	177.6
4.80	41.8	13.20	70.5	21.80	105.5	38.50	179.9
4.90	42.1	13.40	71.2	22.00	106.3	39.00	182.2
5.00	42.4	13.60	72.0	22.20	107.2	39.50	184.5
5.20	43.0	13.80	72.7	22.40	108.1	40.00	186.8
5.40	43.7	14.00	73.5	22.60	108.9	40.50	189.0
5.60	44.3	14.20	74.3	22.80	109.8	41.00	191.3

NOTE: The equivalent Saybolt Universal viscosity is equal to the Saybolt Universal viscosity at 100 F. At other temperatures, the equivalent Saybolt Universal viscosity must be corrected using equation (11A1.1-1).

PROCEDURE 11A1.4**CONVERSION OF KINEMATIC VISCOSITY TO SAYBOLT FUROL VISCOSITY****Discussion**

The following procedure is to be used to convert kinematic viscosity data at 122F and 210F in centistokes to Saybolt Furol viscosity at 122F and 210F in Saybolt Furol seconds.

The conversion of kinematic viscosity to Saybolt Furol viscosity may be made using the following equations, which are valid for all values of kinematic viscosity.

$$SFS_{122F} = 0.4717 v_{122F} + \frac{13,924}{v_{122F}^2 - 72.59 v_{122F} + 6816} \quad (11A1.4-1)$$

$$SFS_{210F} = 0.4792 v_{210F} + \frac{5610}{v_{210F}^2 + 2130} \quad (11A1.4-2)$$

Procedure

Calculate the Saybolt Furol viscosity at 122F from Equation (11A1.4-1) or at 210F from Equation (11A1.4-2) given the kinematic viscosity at 122F or 210F respectively.

COMMENTS ON PROCEDURE 11A1.4

Purpose

This procedure is given for converting kinematic viscosity in centistokes at 122F and 210F to the equivalent Saybolt Furol viscosity in Saybolt Furol seconds.

Reliability

Errors between calculated and experimental Saybolt Furol viscosities average 0.3 percent.

Literature Source

The procedure was adapted from ASTM D 2161-82, *Standard Method for Conversion of Kinematic Viscosity to Saybolt Universal Viscosity or to Saybolt Furol Viscosity* (6).

Examples

A. Estimate the Saybolt Furol viscosity in seconds at 122F and 210F for an oil having a kinematic viscosity of 300 centistokes at 122F and of 100 centistokes at 210F.

1. Determine SFS_{122F} using Equation (11A1.4-1).

$$SFS_{122F} = (0.4717 * 300) + \frac{13,924}{300^2 - (72.59 * 300) + 6816} = 141.5 \text{ seconds}$$

2. Determine SFS_{210F} using Equation (11A1.4-2)

$$SFS_{210F} = (0.4792 * 100) + \frac{5610}{100^2 + 2130} = 48.4 \text{ seconds}$$

TABLE 11A1.5
CONVERSION OF KINEMATIC VISCOSITY TO SAYBOLT FUROL VISCOSITY
(Part of Procedure 11A1.4)

Kinematic Viscosity (centistokes)	Saybolt Furol Viscosity		Kinematic Viscosity (centistokes)	Saybolt Furol Viscosity		Kinematic Viscosity (centistokes)	Saybolt Furol Viscosity	
	at 122 F	at 210 F		at 122 F	at 210 F		at 122 F	at 210 F
48	25.1	—	125	60.0	60.2	350	165.2	167.8
49	25.6	—	130	62.3	62.6	355	167.6	170.2
50	26.0	25.2	135	64.6	65.0	360	169.9	172.6
51	26.5	25.6	140	66.9	67.3	365	172.3	174.9
52	27.0	26.1	145	69.2	69.7	370	174.6	177.3
53	27.4	26.5	150	71.5	72.1	375	177.0	179.7
54	27.9	27.0	155	73.8	74.5	380	179.4	182.1
55	28.3	27.4	160	76.1	76.9	385	181.7	184.5
56	28.8	27.9	165	78.5	79.3	390	184.1	186.9
57	29.2	28.4	170	80.8	81.6	395	186.4	189.3
58	29.7	28.8	175	83.1	84.0	400	188.8	191.7
59	30.1	29.3	180	85.4	86.4	405	191.1	194.1
60	30.6	29.7	185	87.8	88.8	410	193.5	196.5
61	31.1	30.2	190	90.1	91.2	415	195.8	198.9
62	31.5	30.6	195	92.4	93.6	420	198.2	201
63	32.0	31.1	200	94.8	96.0	425	201	204
64	32.4	31.6	205	97.1	98.4	430	203	206
65	32.9	32.0	210	99.4	100.8	435	205	208
66	33.3	32.5	215	101.8	103.1	440	208	211
67	33.8	33.0	220	104.1	105.5	445	210	213
68	34.2	33.4	225	106.5	107.9	450	212	216
69	34.7	33.9	230	108.8	110.3	455	215	218
70	35.1	34.3	235	111.2	112.7	460	217	220
71	35.6	34.8	240	113.5	115.1	465	219	223
72	36.0	35.3	245	115.9	117.5	470	222	225
73	36.5	35.7	250	118.2	119.9	475	224	228
74	36.9	36.2	255	120.5	122.3	480	226	230
75	37.4	36.7	260	122.9	124.7	485	229	232
76	37.8	37.1	265	125.2	127.1	490	231	235
78	38.7	38.1	270	127.6	129.5	495	234	237
80	39.6	39.0	275	129.9	131.9	500	236	240
82	40.5	39.9	280	132.3	134.2	505	238	242
84	41.4	40.9	285	134.6	136.6	510	241	244
86	42.3	41.8	290	137.0	139.0	515	243	247
88	43.2	42.7	295	139.3	141.4	520	245	249
90	44.1	43.7	300	141.7	143.8	525	248	252
92	45.0	44.6	305	144.0	146.2	530	250	254
94	45.9	45.6	310	146.4	148.6	535	252	256
96	46.8	46.5	315	148.8	151.0	540	255	259
98	47.7	47.4	320	151.1	153.4	545	257	261
100	48.6	48.4	325	153.5	155.8	550	259	264
105	50.9	50.7	330	155.8	158.2	555	262	266
110	53.2	53.1	335	158.2	160.6	560	264	268
115	55.4	55.5	340	160.5	163.0	565	267	271
120	57.7	57.8	345	162.9	165.4	570	269	273

PROCEDURE 11A1.6
VISCOSITY CONVERSION

Discussion

The following equation, (11A1.6-1), is to be used to convert Redwood No. 1 viscosity at 140F, Redwood No. 2 viscosity, Engler viscosity, Saybolt Furol viscosity at 122F, Saybolt Furol viscosity at 210F, or Saybolt Universal viscosity to kinematic viscosity, in centistokes.

$$v = FR - \frac{GR}{R^3 + H} \quad (11A1.6-1)$$

Where:

v = kinematic viscosity, in centistokes.

R = desired property to be converted, as talked about in the discussion, in degrees or seconds.

F,G,H = constants given in the following tabulation:

	Redwood No.1 at 140F	Redwood No.2	Engler Degrees	Saybolt Furol at 122F	Saybolt Furol at 210F	Equivalent Saybolt Universal
F	0.244	2.44	7.60	2.12	2.09	0.22
G	8,000	3,410	18.0	1,000	2,088	7,336
H	12,500	9,550	1.7273	8,001	5,187	12,813
Range of R (seconds or degrees)	>35	>31	>1.000	>25	>25	>32

In order to do calculations with Saybolt Universal viscosity at temperatures other than 100 F, a conversion must be made from Equivalent Saybolt Universal viscosity to Saybolt Universal viscosity at temperature, t. This conversion can be done through the use of Equation (11A1.6-2).

$$SUS_{eq} = \frac{SUS_t}{[1.0 + 0.000061(t - 100)]} \quad (11A1.6-2)$$

Where:

SUS_{eq} = equivalent Saybolt Universal viscosity at t, in seconds.

SUS_t = Saybolt Universal viscosity at t, in seconds.

t = temperature, in degrees Fahrenheit.

Procedure

Step 1: Look up the appropriate constants for the desired property in the table above. If the desired property is the Saybolt Universal viscosity, make sure to make the conversion to the equivalent Saybolt Universal viscosity by using Equation (11A1.6-2).

Step 2: Calculate the kinematic viscosity, in centistokes, using the correct constants in Equation (11A1.6-1).

COMMENTS ON PROCEDURE 11A1.6

Purpose

This procedure is given for converting Redwood, Engler, Saybolt Furol, and Saybolt Universal viscosities, in seconds and degrees, to kinematic viscosity, in centistokes.

Reliability

The estimated reliability of the equations are within 1 percent.

Special Comments

The conversion of kinematic viscosity data to Saybolt Universal and Saybolt Furol viscosities are given in Procedures 11A1.1 and 11A1.2 respectively.

The conversion of kinematic viscosity to Redwood No. 1 viscosity at 140F, Redwood No. 2 viscosity, or to Engler viscosity can be made using Equation (11A1.6-3).

$$R = A v + \frac{1}{B + C v + D v^2 + E v^3} \quad (11A1.6-3)$$

Where:

R = flow time, in seconds or Engler degrees.

v = kinematic viscosity, in centistokes.

A through E = constants given in the following tabulation:

	Redwood No.1 at 140F	Redwood No.2	Engler Degrees
A	4.0984	0.40984	0.13158
B	0.038014	0.38014	1.1326
C	0.001919	0.01919	0.0104
D	0.0000278	0.000278	0.00656
E	0.00000521	0.0000521	0.0
Range of v (centistokes)	>4.0	>73	>1.0

Literature Sources

The conversion of kinematic viscosity to Redwood No. 1 at 140F was taken from *IP Standards for Petroleum and Its Products, Part 1, Sect. 2-Appendix B* (1969).

Equation (11A1.6-2) was adapted from Procedure 11A1.1

Equations (11A1.6-1) and (11A1.6-3) were adapted from O'Donnell, *Mater. Res. Std. 9 [5] 25* (1969).

Examples

A. Find the kinematic viscosity of an oil having a Saybolt Universal viscosity of 300 seconds at 200 degrees Fahrenheit.

1. Convert the Saybolt Universal viscosity to the equivalent Saybolt Universal viscosity by using Equation (11A1.6-2). For this particular problem, $t = 200F$ and $SUS_t = 300$ seconds.

$$SUS_{eq} = \frac{300}{[1.0 + 0.000061 (200 - 100)]} = 298 \text{ seconds}$$

2. Select the appropriate constants for equivalent Saybolt Universal viscosity.

$$\begin{aligned} F &= 0.22 \\ G &= 7,336 \\ H &= 12,813 \end{aligned}$$

3. Use these constants in Equation (11A1.3-1) to find the kinematic viscosity, in centistokes.

$$v = 298 F - \frac{298 G}{298^3 + H} = 65.48 \text{ centistokes}$$

B. Find the Redwood No. 1 viscosity at 140F of an oil having a kinematic viscosity of 70 centistokes.

1. Look up the appropriate constants for converting kinematic viscosity to Redwood No. 1 viscosity at 140F.

$$\begin{aligned} A &= 4.0984 \\ B &= 0.038014 \\ C &= 0.001919 \\ D &= 0.0000278 \\ E &= 0.00000521 \end{aligned}$$

2. Use these constants in Equation (11A1.6-3) to find the Redwood No. 1 viscosity at 140F, in seconds.

$$T = A(70) + \frac{1}{B + C(70) + D(70^2) + E(70^3)} = 287.4 \text{ seconds}$$

PROCEDURE 11A2.1**CORRELATION FOR THE LIQUID VISCOSITY OF PURE COMPOUNDS
AT LOW PRESSURE****Discussion**

The following equation is recommended for calculating the liquid viscosity of pure compounds over a specified temperature range at low pressure.

$$\mu = 1000 \exp (A + B/T + C \ln T + DT^E) \quad (11A2.1-1)$$

Where:

μ = absolute viscosity of liquid, in centipoises.

T = temperature, in degrees Rankine.

A through E = correlation coefficients from Table 11A2.2.

Procedure

Step 1: Locate the coefficients for the desired compound in Table 11A2.2. Check to see if the temperature is within the specified range of the correlation.

Step 2: Calculate the liquid viscosity from Equation (11A2.1-1).

COMMENTS ON PROCEDURE 11A2.1

Purpose

This procedure is used to calculate the liquid viscosity of pure compounds as a function of temperature at low pressure. Table 11A2.2 lists coefficients for 300 pure compounds.

Limitations

This procedure is valid only over the temperature range listed in Table 11A2.2 for each compound. The average error over the entire temperature range is less than 5 percent and generally better than 2 percent.

The correlations only are valid for low pressure liquids. Procedures 11A5.1 or 11A5.7 can be used to correct the viscosity for high pressure.

Literature Sources

Procedure 11A2.1 was developed by the project staff at The Pennsylvania State University.

Example

Determine the liquid viscosity of n-decane at 104 F.

1. Obtain the necessary coefficients from Table 11A2.2.

$$\begin{aligned} A &= -16.911 \\ B &= 2761.2 \\ C &= 0.7511 \\ D &= 0 \\ E &= 0 \end{aligned}$$

2. Convert the temperature from Fahrenheit to Rankine.

$$T = 104 + 459.67 = 563.67 \text{ R}$$

This value is within the correlation temperature range of 438 to 807 Rankine.

3. Using Equation (11A2.1-1).

$$\begin{aligned} \mu &= 1000 \exp [-16.911 + 2761.2/563.67 + 0.7511 \ln (563.67)] \\ \mu &= 0.707 \text{ centipoise} \end{aligned}$$

The experimental value is 0.696 centipoise.

PROCEDURE 11A2.3

LIQUID VISCOSITY OF PURE HYDROCARBONS AT LOW PRESSURE

Discussion

The following group contribution method is to be used to estimate the viscosity of pure liquid hydrocarbons at low pressures:

$$\log \mu = B \left[\frac{1.8}{T} - \frac{1}{T_o} \right] \quad (11A2.3-1)$$

Where:

μ = absolute viscosity of liquid, in centipoises.

T = temperature, in degrees Rankine.

B and T_o are obtained in the following manner:

$$N^* = N + \sum_i n_i \Delta N_i \quad (11A2.3-2)$$

Where:

N^* = equivalent chain length.

N = actual number of carbon atoms in the molecule.

ΔN_i = structural contributions of group i, which can be found in Table 11A2.4.

n_i = number of times a functional group appears in a molecule.

$$T_o = 28.86 + 37.439 N^* - 1.3547 N^{*2} + 0.02076 N^{*3} \quad N^* \leq 20 \quad (11A2.3-3)$$

$$T_o = 238.59 + 8.164 N^* \quad N^* > 20 \quad (11A2.3-4)$$

$$B_a = B_a + \sum_i n_i \Delta B_i \quad (11A2.3-5)$$

$$B_a = 24.79 + 66.885 N^* - 1.3171 N^{*2} - 0.00377 N^{*3} \quad N^* \leq 20 \quad (11A2.3-6)$$

$$B_a = 530.59 + 13.740 N^* \quad N^* > 20 \quad (11A2.3-7)$$

ΔB_i represents the contributions of group i, which can be found in Table 11A2.4

NOTE: If the structural or functional group ΔN_i appears n_i times in the molecule, $n_i \Delta N_i$ corrections must be added, while the ΔB_i contribution is applied only a single time.

Procedure

Step 1: Compute ΔN_i from Table 11A2.4.

Step 2: Calculate N^* using ΔN_i and Equation (11A2.3-2).

Step 3: Calculate T_o using Equation (11A2.3-3) for $N^* \leq 20$ or Equation (11A2.3-4) for $N^* > 20$.

Step 4: Calculate B_a using Equation (11A2.3-6) for $N^* \leq 20$ or Equation (11A2.3-7) for $N^* > 20$.

Step 5: Compute ΔB_i using N^* and Table 11A2.4.

Step 6: Calculate B using ΔB_i and Equation (11A2.3-5).

Step 7: Calculate the liquid viscosity using equation (11A2.3-1).

COMMENTS ON PROCEDURE 11A2.3

Purpose

Procedure 11A2.3 is a general method for estimating the liquid viscosity of pure hydrocarbons when there is no experimental viscosity data known for the substance.

Limitations

This method should not be used for reduced temperatures that exceed 0.7 (approximately the normal boiling point).

Reliability

Equation (11A2.3-1) gave an average error of 12 percent for the 1700 data points evaluated. Large errors usually result for the first member of a homologous series.

Literature Sources

The equations and contribution factors were taken from Van Veltzen, Cardozo, and Langenkamp, *Ind. Eng. Chem. Fundam.*, 11 20 (1972), and from Van Veltzen, Cardozo and Langenkamp, "Liquid Viscosity and Chemical Constitution of Organic Compounds: A New Correlation and a Compilation of Literature Data," Euratom 4735e, Joint Nuclear Research Center, Ispra Establishment, Italy (1972).

Example

Determine the viscosity of *cis*-1,4-dimethylcyclohexane at 32F.

1. There are two functional groups in *cis*-1,4-dimethylcyclohexane, namely, cyclohexane and *n*-alkanes. $N = 8$.
2. From Table 11A2.4, ΔN_i is 1.48 for cyclohexane and 0 for *n*-alkanes.
3. N^* can be found from Equation (11A2.3-3):

$$N^* = 8 + 1.48 + 0 + 2 = 9.48$$

4. T_o can then be calculated using Equation (11A2.3-3) because $N^* \leq 20$:

$$T_o = 28.86 + 37.439 (9.48) - 1.3547 (9.48^2) + 0.02076 (9.48^3) = 279.72$$

5. B_a can be found using Equation (11A2.3-6) because $N^* \leq 20$:

$$B_a = 24.79 + 66.885 (9.48) - 1.3173 (9.48^2) - 0.00377 (9.48^3) = 537.26$$

6. Using Table 11A2.4 and the value for N^* calculated in Step 3, ΔB_i can be determined:

$$\Delta B_i = -272.85 + 25.041 (9.48) = -35.46 \quad \text{for cyclohexane}$$

$$\Delta B_i = 0 \quad \text{for } n\text{-alkanes}$$

7. The value for B can be determined using Equation (11A2.3-5):

$$B = 537.26 + (-35.46) = 501.80$$

8. The viscosity can finally be calculated using Equation (11A2.3-1):

$$\log \mu = 501.80 \left(\frac{1.8}{32 + 459.67} + \frac{1}{279.72} \right) = 0.043$$

$$\mu = 1.104 \text{ centipoises}$$

The experimental value for the liquid viscosity at 32F is 1.224 centipoises.

PROCEDURE 11A3.1**LIQUID VISCOSITIES OF DEFINED MIXTURES
AT LOW PRESSURES****Discussion**

Equation (11A3.1-1) is to be used to estimate the viscosity of defined liquid mixtures. Although Procedure 11A4.4 is preferable for blending complex hydrocarbon mixtures when the viscosities of the component liquids are known at two temperatures, this procedure can be used when the components are similar in molecular weight and general character.

$$\mu_m = \left(\sum_{i=1}^n x_i \mu_i^{1/3} \right)^3 \quad (11A3.1-1)$$

Where:

μ_m = viscosity of the mixture, in centipoises.

μ_i = viscosity of component i, in centipoises.

n = number of components in the mixture.

x_i = mole fraction of component i.

Procedure

Step 1: Find the liquid viscosities of the individual components at the desired temperature and pressure from the Procedures of 11A2 and 11A5.

Step 2: Convert the concentration units to mole fractions. Molecular weights and densities of pure compounds are given in Chapter 1. The molecular weights of petroleum fractions are given by the methods outlined in Chapter 2, and densities are given by the methods outlined in Chapter 6.

Step 3: Obtain the viscosity of the mixture from Equation (11A3.1-1).

COMMENTS ON PROCEDURE 11A3.1

Purpose

This procedure is given for estimating the liquid viscosity of defined hydrocarbon mixtures.

Limitations

This procedure requires the viscosities of all components at the same temperature and pressure. Results for a blend of two liquids of dissimilar character will give high or low results, depending on the viscosity of the liquid with the lowest viscosity-temperature coefficient. This method is not recommended for blending petroleum fractions or hydrocarbon mixtures of undefined composition. Procedure 11A4.5 should be used for these blends. If one component is above its critical temperature, then treat as a dissolved gas and use procedure 11A7.1.

Reliability

The average error for this method is 5.7% based on 1300 data points. Errors are usually 3% or less for systems of the same chemical family (e.g., paraffin-paraffin). Errors from 10% to 15% can be expected for mixtures of paraffins with aromatics or paraffins with naphthenes.

Literature Source

Equation (11A3.1-1) was adapted from Kendall and Monroe, *J. Am. Chem. Soc.* **39** 1787 (1917).

Examples

- A. Estimate the liquid viscosity of a mixture containing 29.57 mole percent *n*-hexadecane, 35.86 mole percent benzene, and 34.57 mole percent *n*-hexane at 77 F and 14.7 pounds per square inch absolute.

From Procedure 11A2.1, the viscosity of *n*-hexane is 0.30 centipoise, *n*-hexadecane is 3.03 centipoise, and of benzene is 0.60 centipoise. All at the stated conditions.

$$\begin{aligned}\mu_m &= [(0.2957)(3.03)^{1/3} + (0.3586)(0.60)^{1/3} + (0.3457)(0.30)^{1/3}]^3 \\ &= [(0.2957)(1.447) + (0.3586)(0.8434) + (0.3457)(0.6694)]^3 \\ &= [(0.4279) + (0.3024) + (0.2314)]^3 = 0.89 \text{ centipoise}\end{aligned}$$

The experimental value is 0.891 centipoise.

- B. Estimate the viscosity of a mixture containing 25 mole percent propane, 50 mole percent *n*-pentane, and 25 mole percent cyclohexane at 160 F and 5000 pounds per square inch absolute.

1. The viscosities of the individual compounds at 5000 psia may be found by Procedure 11A5.1. The following tabulation gives the critical temperatures, critical pressures, and acentric factors (from Chapter 1):

11A3.1

Component	Critical Temperature (F)	Critical Pressure (psia)	Acentric Factor
Propane	206.0	616.1	0.1523
<i>n</i> -Pentane	385.8	488.8	0.2515
Cyclohexane	536.8	591.0	0.2096

2. From Table 11A5.2, the critical viscosity of propane is 0.0237 centipoise and of *n*-pentane is 0.0255 centipoise. From these values the viscosity at 5000 pounds per square inch absolute and 160 F calculated by Procedure 11A5.1 for propane is 0.109 centipoise and for *n*-pentane is 0.218 centipoise.

3. The viscosity of cyclohexane at 14.7 pounds per square inch absolute and 160 F from Procedure 11A2.1 is 0.455 centipoise. At 5000 pounds per square inch absolute and 160 F, using Procedure 11A5.1, its viscosity is 0.630 centipoise.

4. Finally find the viscosity of the mixture, simply apply Equation (11A3.1-1):

$$\begin{aligned}\mu_m &= [(0.25)(0.109)^{1/3} + (0.50)(0.218)^{1/3} + (0.25)(0.630)^{1/3}]^3 \\ &= [(0.25)(0.478) + (0.50)(0.602) + (0.25)(0.857)]^3 \\ &= 0.256 \text{ centipoise}\end{aligned}$$

PROCEDURE 11A4.1**CORRELATION FOR THE LIQUID VISCOSITY OF PETROLEUM FRACTIONS
AT LOW PRESSURE****Discussion**

The equations below can be used to calculate the liquid viscosity of petroleum fractions at any temperature and low pressure given an experimental viscosity at 100 F.

$$\log(v) = B \left[\frac{559.67}{(T + 459.67)} \right]^S - 0.86960 \quad (11A4.1-1)$$

Where:

v = kinematic viscosity at temperature T, in centistokes.

T = temperature, in degrees Fahrenheit.

v_0 = measured kinematic viscosity at 100 F, in centistokes.

B = $\log(v_0) + 0.86960$ (11A4.1-2)

S = $0.28008 \log(v_0) + 1.8616$ (11A4.1-3)

Procedure

Step 1: Calculate the constants B and S using the experimentally measured kinematic viscosity at 100 F and Equations (11A4.1-2) and (11A4.1-3).

Step 2: Calculate the liquid viscosity from Equation (11A4.1-1).

COMMENTS ON PROCEDURE 11A4.1**Purpose**

Procedure 11A4.1 is a correlation for predicting the liquid viscosity of petroleum fractions as a function of temperature at low pressure from a measured viscosity at 100 F.

Limitations

This procedure requires a measured kinematic viscosity at 100 F. The correlation is only valid for low pressures. After calculating the viscosity at low pressure, Procedure 11A5.5 can be used to correct the viscosity to any elevated pressure. This procedure should only be used at temperatures where the material is a liquid.

Reliability

The average error was approximately 5.6% when tested for 1300 data points. The method works best for light, paraffinic fractions with API gravities in excess of 30 degrees API. The method degrades substantially for much heavier fractions.

Literature Sources

The procedure is from Singh, Mutyala and Puttagunta, *Hydrocarbon Processing*, 69(9), 39 (1990).

Example

Estimate the liquid viscosity of a Sumatran crude at 210 F. The viscosity of this crude is 1.38 centistokes at 100 F.

1. Determine B from Equation (11A4.1-2),

$$\begin{aligned} B &= \log (1.38) + 0.86960 \\ B &= 1.0095 \end{aligned}$$

Determine S from Equation (11A4.1-3),

$$\begin{aligned} S &= 0.28008 \log (1.38) + 1.8616 \\ S &= 1.9008 \end{aligned}$$

2. Use Equation (11A4.1-1) to calculate the viscosity at 210 F.

$$\begin{aligned} \log (v) &= 1.0095 [559.67/(210 + 459.67)]^{1.9008} - 0.86960 \\ \log (v) &= -0.1518 \\ v &= 0.705 \text{ centistokes} \end{aligned}$$

The experimental value is 0.668 centistokes.

COMMENTS ON PROCEDURE 11A4.2

Purpose

Procedure 11A4.2 is presented to predict the liquid viscosity of a petroleum fraction as a function of temperature at low pressure. This procedure also can be used for whole crudes or any other petroleum based liquid. The procedure can also be used for coal liquids.

Limitations

The procedure is intended for use near atmospheric pressure. Procedure 11A5.5 can be used to correct for pressure above atmospheric. The procedure is restricted to Newtonian fluids and should only be used at temperatures where the material is a liquid.

Equations (11A4.2-1) through (11A4.2-6) should be used for petroleum liquids that fall within the range of applicability depicted graphically in Figure 11A4.3. Figure 11A4.3 shows the range of model applicability as a function of Watson K and API gravity. The model should not be used for any data that lie within the crosshatched areas A & B. The procedure was tested for fluids that had an average boiling point between 150 F and 1200 F and API gravities between 0 and 75 degrees API. The procedure should be used with care outside of these boiling point and API gravity ranges. If no experimental data exist and one desires to predict the viscosity of a petroleum fraction that falls outside of the range of model applicability as described in Figure 11A4.3, then the predictive method by Twu (Ind. Eng. Chem. Process Des. Dev., 24(4), 1287 1985) is the next best alternative.

Reliability

When tested against over 7000 data points, the procedure gave an overall average error of 14%. Better results were obtained for light and intermediate fractions than for heavy fractions. For petroleum liquids with an API gravity greater than 30, the average error improves to 8%. For coal liquids, the average error was 35% for 252 data points. The error improves to 8% for coal liquids with an API gravity greater than 30.

Literature Sources

Equations (11A4.2-1) through (11A4.2-6) are from Fitzgerald, D. J., private communication to API Technical Data Committee.

Example

A. For a petroleum fraction having an API gravity of 33.4 and a mean average boiling point of 598.7 F,

- A. Estimate the viscosity at 100 F
- B. Estimate the viscosity at 210 F
- C. Estimate the viscosity at 140 F.

1. Convert the API gravity to specific gravity using Equation (11A4.2-5). Convert the boiling point from degrees Fahrenheit to degrees Rankine.

$$\text{specific gravity} = \frac{141.5}{(33.4 + 131.5)} = 0.8581$$

11A4.2

$$T_b = 598.7 + 459.67 = 1058.37 \text{ R} \quad K = \frac{(1058.37)^{1/3}}{.8581} = 11.87$$

2. Use Equations (11A4.2-1) through (11A4.2-5) to calculate the viscosity at 100 F.

$$\begin{aligned}\log v_{\text{ref}} &= -1.35579 + 8.16059 \times 10^{-4} (1058.37) + 8.38505 \times 10^{-7} (1058.37)^2 \\ v_{\text{ref}} &= 2.80 \text{ centistokes} \\ A_1 &= 34.9310 - 8.84387 \times 10^{-2} (1058.37) + 6.73513 \times 10^{-5} (1058.37)^2 \\ &\quad - 1.01394 \times 10^{-8} (1058.37)^3 \\ A_1 &= 4.753 \\ A_2 &= -2.92649 + 6.98405 \times 10^{-3} (1058.37) - 5.09947 \times 10^{-6} (1058.37)^2 \\ &\quad + 7.49378 \times 10^{-10} (1058.37)^3 \\ A_2 &= -0.3585 \\ \log v_{\text{cor}} &= 4.753 - 0.3585 (11.870) \\ v_{\text{cor}} &= 3.14 \text{ centistokes} \\ v_{100} &= 2.80 + 3.14 = 5.94 \text{ centistokes}\end{aligned}$$

The experimental value is 5.59 centistokes.

3. Use Equation (11A4.2-6) to calculate the viscosity at 210 F.

$$\begin{aligned}\log v_{210} &= -1.92353 + 2.41071 \times 10^{-4} (1058.37) + 0.511300 \log (1058.37 \times 5.94) \\ \log v_{210} &= 0.2738 \\ v_{210} &= 1.88 \text{ centistokes}\end{aligned}$$

The experimental value is 1.81 centistokes.

4. Use Procedure 11A4.4 to calculate the viscosity at 140 F. Plotting the calculated viscosities at 100 and 210 F, the viscosity at 140 F is 3.6 centistokes from Procedure 11A4.4. The experimental value is 3.37 centistokes.

Alternatively, using Equations (11A4.4-1) through (11A4.4-5) the viscosity is calculated to be 3.58 centistokes.

- B. For a coal liquid fraction having an API gravity of 4.70 and a mean average boiling point of 647.3 F, calculate the kinematic viscosity at 304 F.

1. Convert the API gravity to specific gravity using Equation (11A4.2-7). Convert the boiling point from degrees Fahrenheit to degrees Rankine.

$$\text{specific gravity} = \frac{141.5}{(4.70 + 131.5)} = 1.0389$$

$$T_b = 647.3 + 459.67 = 1106.97 \text{ R} \quad K = \frac{(1106.97)^{1/3}}{1.0389} = 9.955$$

2. Use Equations (11A4.2-1) through (11A4.2-5) to calculate the viscosity at 100 F.

$$\begin{aligned}\log v_{\text{ref}} &= -1.35579 + 8.16059 \times 10^{-4} (1106.97) + 8.38505 \times 10^{-7} (1106.97)^2 \\ v_{\text{ref}} &= 3.76 \text{ centistokes} \\ A_1 &= 34.9310 - 8.84387 \times 10^{-2} (1106.97) + 6.73513 \times 10^{-5} (1106.97)^2 \\ &\quad - 1.01394 \times 10^{-8} (1106.97)^3 \\ A_1 &= 5.809 \\ A_2 &= -2.92649 + 6.98405 \times 10^{-3} (1106.97) - 5.09947 \times 10^{-6} (1106.97)^2 \\ &\quad + 7.49378 \times 10^{-10} (1106.97)^3 \\ A_2 &= -0.4277\end{aligned}$$

$$\begin{aligned}\log v_{\text{cor}} &= 5.809 - 0.4277 (9.955) \\ v_{\text{cor}} &= 35.58 \text{ centistokes} \\ v_{100} &= 3.76 + 35.58 = 39.34 \text{ centistokes}\end{aligned}$$

3. Use Equation (11A4.2-6) to calculate the viscosity at 210 F.

$$\begin{aligned}\log v_{210} &= -1.92353 + 2.41071 \times 10^{-4} (1106.97) \\ &\quad + 0.511300 \log (1106.97 \times 39.34) \\ v_{210} &= 5.19 \text{ centistokes}\end{aligned}$$

4. With the viscosities calculated in steps 2 and 3 above, the viscosity is estimated to be 2.15 centistokes at 304 F from Procedure 11A4.4. Alternatively, using Equations (11A4.4-1) through (11A4.4-5) the viscosity is calculated to be 2.12 centistokes. The experimental value is 1.78 centistokes at 304 F.

- C. Calculate the kinematic viscosity at 100 F for two Middle Eastern crude fractions having the following properties:

Fraction	API Gravity	Mean Average Boiling Point, F
1	47.40	382.10
2	13.80	1113.20

1. For crude fraction number one,

$$\begin{aligned}SG &= 141.5/(47.40 + 131.5) = 0.7909 \\ T_b &= 382.10 + 459.67 = 841.77 \quad K = \frac{(841.77)^{1/3}}{.7909} = 11.93 \\ \log v_{\text{ref}} &= -1.35579 + 8.16059 \times 10^{-4} (841.77) + 8.38505 \times 10^{-7} (841.77)^2 \\ v_{\text{ref}} &= 0.842 \text{ centistokes} \\ A_1 &= 34.9310 - 8.84387 \times 10^{-2} (841.77) + 6.73513 \times 10^{-5} (841.77)^2 \\ &\quad - 1.01394 \times 10^{-8} (841.77)^3 \\ A_1 &= 2.162 \\ A_2 &= -2.92649 + 6.98405 \times 10^{-3} (841.77) - 5.09947 \times 10^{-6} (841.77)^2 \\ &\quad + 7.49378 \times 10^{-10} (841.77)^3 \\ A_2 &= -0.214 \\ \log v_{\text{cor}} &= 2.162 - 0.214 (11.93) \\ v_{\text{cor}} &= 0.406 \text{ centistokes} \\ v_{100} &= 0.842 + 0.406 = 1.248 \text{ centistokes}\end{aligned}$$

The experimental value is 1.29 centistokes

2. For crude fraction number two,

$$\begin{aligned}SG &= 141.5/(13.80 + 131.5) = 0.9738 \\ T_b &= 1113.20 + 459.67 = 1572.87 \quad K = \frac{(1572.87)^{1/3}}{.9738} = 11.94 \\ v_{\text{ref}} &= 100 \text{ centistokes} \\ \log v_{\text{cor}} &= 22.996 - 1.641 (11.94)\end{aligned}$$

11A4.2

$$\begin{aligned}v_{\text{cor}} &= 2526 \text{ centistokes} \\v_{100} &= 100 + 2526 = 2626 \text{ centistokes}\end{aligned}$$

The experimental value is 2130 centistokes.

11A4.4

PROCEDURE 11A4.4

TEMPERATURE VARIATION OF LIQUID VISCOSITY

Discussion

Equations (11A4.4-1) through (11A4.4-5) are to be used to estimate the liquid viscosity of a petroleum liquid providing two other viscosities are known at two separate temperatures.

$$v = Z - 0.7 - \exp [-0.7487 - 3.295 (Z - 0.7) + 0.6119 (Z - 0.7)^2 - 0.3193 (Z - 0.7)^3] \quad (11A4.4-1)$$

Where:

$$Z = \text{antilog} [\text{antilog} [\log \log Z_2 + B (\log T - \log T_1)]] \quad (11A4.4-2)$$

and,

$$B = (\log \log (Z_1) - \log \log (Z_2)) / (\log T_1 - \log T_2) \quad (11A4.4-3)$$

and,

$$Z_1 = v_1 + 0.7 + \exp [-1.47 - 1.84 v_1 - 0.51 v_1^2] \quad (11A4.4-4)$$

and,

$$Z_2 = v_2 + 0.7 + \exp [-1.47 - 1.84 v_2 - 0.51 v_2^2] \quad (11A4.4-5)$$

and,

Where:

v = kinematic viscosity at temperature T , in centistokes

T = required temperature, in degrees Rankine

v_1 = kinematic viscosity at temperature T_1 , in centistokes

v_2 = kinematic viscosity at temperature T_2 , in centistokes

$T_1 T_2$ = reference temperature corresponding to v_1 and v_2 , in degrees Rankine

Procedure

Step 1: Calculate the constants Z_1 and Z_2 using Equations (11A4.4-4) and (11A4.4-5) respectively.

Step 2: Calculate the constant B using Z_1 and Z_2 from step 1 and Equation (11A4.4-3).

Step 3: Calculate the constant Z using Equation (11A4.4-2).

Step 4: Calculate the kinematic viscosity of the petroleum liquid using Equation (11A4.4-1).

COMMENTS ON PROCEDURE 11A4.4

Purpose

Procedure 11A4.4 is a convenient means for estimating the liquid viscosity of a petroleum liquid at any temperature within a limited range, provided viscosities at two temperatures are known.

Limitations

Procedure 11A4.4 should be used only in the temperature range where the hydrocarbon is a liquid. Thermal cracking in oils at temperatures greater than about 475 F makes viscosities predicted at these temperatures unreliable.

This procedure is suitable only for Newtonian fluids. Caution should be applied when using this procedure in regions far removed from the experimental values.

Reliability

At low temperatures, deviations can be quite large. Some polymers, waxy oils, and some silicate esters have significantly higher viscosities than are predicted by this procedure. Deviations are greater the higher the aromaticity. Some high-molecular-weight pure compounds, as well as some superrefined mineral oils, have significantly lower viscosities at low temperature than those predicted. Average error in viscosity of pure compounds is less than 4 percent. The assumption of linearity is very good between 32 F and 212 F. Predicted values of the viscosity will always be at temperatures above 212 F, with the deviation increasing as the temperature is increased. Such deviations are greater for aromatic stocks than for paraffinic stocks. Errors greater than those stated may occur when interpolation is made over more than one order of magnitude in viscosity.

Special Comments

The following charts, which are described in ASTM D 341-93, are available from the American Society for Testing and Materials:

ASTM Chart	Kinematic Viscosity Range (centistokes)	Temperature Range	Size (inches)
I	0.3 to 20×10^6	-70 to +307 C	27 x 32
II	0.18 to 6.5	-70 to +370 C	27 x 32
III	0.3 to 20×10^6	-70 to +370 C	8.5 x 11
IV	0.18 to 6.5	-70 to +370 C	8.5 x 11
V	0.3 to 20×10^6	-100 to +700 F	27 x 32
VI	0.18 to 3.0	-100 to +700 F	21 x 32
VII	$3.0 \text{ to } 0.2 \times 10^6$	-40 to +150 C	8.5 x 11

Literature Source

The charts are published as an adjunct to ASTM D 341-93 by the American Society for Testing and Materials, Philadelphia, Pennsylvania. Equations 11A4.4-1 through 11A4.4-5 are from ASTM D 341-93.

Examples

- A. Find the viscosity of an oil at 150 F whose viscosity at 100 F and 210 F is 200 centistokes and 20 centistokes, respectively.

ASTM Chart V (see special comments) could be used for this calculation. This shows that the viscosity at 150 F is 57.5 centistokes.

- B. Find the viscosity of 2-methylnonane at 68 F.

From Procedure 11A2.1, the viscosity of 2-methylnonane at 32 F is 1.644 centistokes and at 104 F is 0.925 centistokes.

Alternatively, using Equations (11A4.4-1) through (11A4.4-5),

$$1. T_1 = 32 + 459.67 = 491.67 \text{ R}$$

$$T_2 = 104 + 459.67 = 563.67 \text{ R}$$

$$v_1 = 1.644 \text{ centistokes}$$

$$v_2 = 0.925 \text{ centistoke}$$

2. Calculate Z_1 and Z_2 using Equations (11A4.4-4) and (11A4.4-5), respectively.

$$Z_1 = 1.644 + 0.7 + \exp[-1.47 - 1.84(1.644) - 0.51(1.644)^2]$$

$$Z_1 = 2.3468$$

$$Z_2 = 0.925 + 0.7 + \exp[-1.47 - 1.84(0.925) - 0.51(0.925)^2]$$

$$Z_2 = 1.6521$$

3. Calculate B from Equation (11A4.4-3).

$$B = [\log(\log 2.3468) - \log(\log 1.6521)] / [\log 491.67 - \log 563.67]$$

$$B = -3.8791$$

4. Calculate Z from Equation (11A4.4-2).

$$Z = \text{antilog} \left[\text{antilog} \left[\log(\log 2.3468) + (-3.8791) (\log(68 + 459.67) - \log 491.67) \right] \right]$$

$$Z = 1.9127$$

5. Calculate the viscosity at 68 F from Equation (11A4.4-1).

$$v = 1.9127 - 0.7 - \exp[-0.7487 - 3.295(1.9127 - 0.7)$$

$$+ 0.6119(1.9127 - 0.7)^2 - 0.3193(1.9127 - 0.7)^3]$$

$$v = 1.201 \text{ centistokes}$$

The experimental value is 1.199 centistokes.

Where:

- T_H = temperature where the viscosity of the heavy component equals the viscosity of the light component at T_2 , in degrees Rankine.
 T_y = temperature of blend at constant viscosity, in degrees Rankine.

Step 6: Knowing the blend viscosity at T_x and T_y , calculate for the blend the parameters m and b in Equation (11A4.5-1).

Step 7: Determine the viscosity of the blend at any temperature using Equation (11A4.5-1) and m and b from Step 6.

COMMENTS ON PROCEDURE 11A4.5

Purpose

This procedure is used to estimate the viscosity of blends of petroleum liquids. The procedure may also be used to estimate the viscosity of blends of pure compounds, although Procedure 11A3.1 is preferred for estimating the viscosity of mixtures of pure compounds.

Limitations

This procedure is to be used at low pressure. Procedure 11A5.3 can be used to correct the viscosity from low to high pressure.

Reliability

The average error was 3.3% for approximately 300 blends. This error increases to approximately 11.1% if one component is a very light oil and one component is a very heavy oil. The technique can be extended to ternary blends. The average deviation was 9.9% for 20 ternary blends.

Special Comment

This procedure has been computerized and is listed as VIS25 of Chapter 16.

Literature Source

This procedure was developed by Twu and Bulls, *Hydrocarbon Processing*, 60(4), 217 (1981).

Example

Find the kinematic viscosity of a blend of two crude oils at 104 F. The crude oils have the following data:

	T ₁ , F	viscosity, centistokes	T ₂ , F	viscosity, centistokes
component 1	50	14.22	122	4.85
component 2	50	163.40	122	24.98

The blend is 60% by weight component 1 and 40% by weight component 2.

1. Designate component 1 as the light oil (subscript L) and component 2 as the heavy oil (subscript H). Calculate m_L and b_L for the light oil from the two viscosity-temperature data points and using Equation (11A4.5-1).

$$T_1 = 50 + 459.67 = 509.67 \text{ R} \quad T_2 = 122 + 459.67 = 581.67 \text{ R}$$

$$\ln [\ln (14.22 + 0.7)] = m_L (\ln 509.67) + b_L$$

$$\ln [\ln (4.85 + 0.7)] = m_L (\ln 581.67) + b_L$$

Solving simultaneously,

$$m_L = -3.4474$$

$$b_L = 22.4845$$

Repeat for the heavy oil,

$$m_H = -3.4206$$

$$b_H = 22.9525$$

2. Use Equation (11A4.5-1) and b_L and m_L to find the temperature, T_L , of the light component having the same viscosity as the heavy component at temperature T_1 .

$$\ln [\ln (163.40 + 0.7)] = -3.4474 \ln T_L + 22.4845$$

$$T_L = 423.91 \text{ R}$$

3. Determine the temperature T_x of the blend at constant viscosity (i.e., 163.40 centistokes) using Equation (11A4.5-2).

$$\ln T_x = 0.6 (\ln 423.91) + 0.4 (\ln 509.67)$$

$$T_x = 456.33 \text{ R}$$

4. Use Equation (11A4.5-1) and b_H and m_H to find the temperature, T_H , of the heavy component having the same viscosity as the light component at T_2 .

$$\ln [\ln (4.85 + 0.7)] = -3.4206 \ln T_H + 22.9525$$

$$T_H = 701.05 \text{ R}$$

5. Determine the temperature, T_y , of the blend at constant viscosity (i.e., 4.85 centistokes) using Equation (11A4.5-3).

$$\ln T_y = 0.6 (\ln 581.67) + 0.4 (\ln 701.05)$$

$$T_y = 626.76$$

6. Now use the blend data,

$$\begin{aligned} T_x &= 456.33 \text{ R} \\ T_y &= 626.76 \text{ R} \end{aligned}$$

$$\begin{aligned} v_1 &= 163.4 \text{ centistokes} \\ v_2 &= 4.85 \text{ centistokes} \end{aligned}$$

and Equation (11A4.5-1) to estimate m and b for the blend.

$$\ln [\ln (163.4 + 0.7)] = m \ln (456.33) + b$$

$$\ln [\ln (4.85 + 0.7)] = m \ln (626.76) + b$$

Solving simultaneously,

$$m = -3.4360$$

$$b = 22.6687$$

7. Now use Equation (11A4.5-1) to estimate the blend viscosity at 104 F.

$$\ln [\ln (v + 0.7)] = -3.4360 \ln (459.67 + 104) + 22.6687$$

$$v = 11.10 \text{ centistokes}$$

This compares to an experimental value of 10.79 centistokes.

PROCEDURE 11A4.6**LIQUID VISCOSITY BLENDING OF MULTICOMPONENT MIXTURES
OF DEFINED AND UNDEFINED COMPOUNDS****Discussion**

Equation (11A3.1-1) can also be used to predict the viscosity of mixtures of defined and undefined components. These mixtures can be multicomponent mixtures of pure hydrocarbons with petroleum fractions or multicomponent mixtures of petroleum fractions.

Procedure

Step 1: Find the liquid viscosities of the individual components at the desired temperature and atmospheric pressure. If experimental data is not available, Procedure 11A2.1 or Procedure 11A2.3 can be used to predict the viscosity of pure compounds. The viscosity of undefined mixtures (i.e. petroleum or coal fractions) can be predicted by Procedures 11A4.1 or 11A4.2.

Step 2: If the mixture is at a pressure above atmospheric, the viscosity predicted in step 1 can be adjusted for pressure using either Procedure 11A5.1 or Procedure 11A5.5.

Step 3: Convert the viscosity from kinematic to absolute for any components as necessary. Densities are given by the methods outlined in Chapter 6.

Step 4: Convert the concentration units to mole fractions. Molecular weights and densities of pure compounds are given in Chapter 1. The Molecular weights of petroleum fractions are given by the methods outlined in Chapter 2, and the densities are given by the methods outlined in Chapter 6.

Step 5: Obtain the viscosity of the mixture from Equation (11A3.1-1).

COMMENTS ON PROCEDURE 11A4.6

Purpose

This procedure is given for estimating the liquid viscosity of multicomponent mixtures of pure hydrocarbons with crude oils and petroleum fractions. The procedure can also be used for multicomponent mixtures of petroleum fractions.

Limitations

All of the components must be a liquid at the temperature and pressure of interest. The viscosity of all components must be calculated at the same temperature and pressure. Procedure 11A7.1 may be used to correct for a dissolved gas. No experimental data were available to test the reliability of the method.

Literature Source

Equation (11A3.1-1) was adapted from Kendall and Munroe, J. Am. Chem. Soc., 39 1787 (1917).

Example

- A. Estimate the liquid viscosity at 100 F and 1 atmosphere pressure of a mixture containing 20 weight percent n-hexane, 40 weight percent of a petroleum fraction having an API gravity of 43.6 and a mean average boiling point of 397.1 F, and 40 weight percent of a second petroleum fraction having an API gravity of 22.6 and a mean average boiling point of 828.3 F.

1. Find the viscosities of the individual components at 100 F. For n-hexane use Procedure 11A2.1,

$$\text{viscosity of n-hexane} = 0.2644 \text{ centipoise}$$

for the two petroleum fractions use Procedure 11A4.2,

$$\text{viscosity of 43.6 API fraction} = 1.409 \text{ centistokes}$$

$$\text{viscosity of 22.6 API fraction} = 66.31 \text{ centistokes}$$

2. Convert the viscosity of the petroleum fractions from kinematic to absolute values. Using Procedure 6A3.5 for the 43.6 API fraction,

$$\text{density at } 100 \text{ F} = 49.07 \text{ lb/ft}^3$$

$$\text{correct density units to gm/cc} = 49.07 \times 0.016018 = 0.7860 \text{ gm/cc}$$

$$\text{absolute viscosity (cP)} = \text{Kinematic Viscosity (Cst)} \times \text{Density (gm/cc)}$$

$$= 1.409 \times 0.7860$$

$$= 1.107 \text{ centipoise}$$

Repeating for the 22.6 API fraction,

$$\text{absolute viscosity} = 59.75 \text{ centipoise}$$

3. Convert the concentrations from weight fraction to mole fraction. The molecular weight for n-hexane is given in Chapter 1. The molecular weight for the petroleum fractions can be calculated from the procedures of Chapter 2.

<u>Compound</u>	<u>Wt. Frac.</u>	<u>MW</u>	<u>Moles</u>	<u>MoleFrac.</u>
n-hexane	0.2	86.18	0.00232	0.4021
43.6 API Fraction	0.4	163	0.00245	0.4246
22.6 API Fraction	0.4	400	0.00100	0.1733
Total Moles			0.00577	1.0000

The number of moles is obtained by dividing the weight fraction by the molecular

11A4.6

weight.

- 4. Use Equation (11A3.1-1) to calculate the viscosity of the mixture.**

$$\begin{aligned} &= [(0.4021)(0.2644)^{1/3} + (0.4246)(1.107)^{1/3} + (0.1733)(59.75)^{1/3}]^3 \\ &= 2.60 \text{ centipoise} \end{aligned}$$

PROCEDURE 11A4.6**LIQUID VISCOSITY BLENDING OF MULTICOMPONENT MIXTURES
OF DEFINED AND UNDEFINED COMPOUNDS****Discussion**

Equation (11A3.1-1) can also be used to predict the viscosity of mixtures of defined and undefined components. These mixtures can be multicomponent mixtures of pure hydrocarbons with petroleum fractions or multicomponent mixtures of petroleum fractions.

Procedure

Step 1: Find the liquid viscosities of the individual components at the desired temperature and atmospheric pressure. If experimental data is not available, Procedure 11A2.1 or Procedure 11A2.3 can be used to predict the viscosity of pure compounds. The viscosity of undefined mixtures (i.e. petroleum or coal fractions) can be predicted by Procedures 11A4.1 or 11A4.2.

Step 2: If the mixture is at a pressure above atmospheric, the viscosity predicted in step 1 can be adjusted for pressure using either Procedure 11A5.1 or Procedure 11A5.5.

Step 3: Convert the viscosity from kinematic to absolute for any components as necessary. Densities are given by the methods outlined in Chapter 6.

Step 4: Convert the concentration units to mole fractions. Molecular weights and densities of pure compounds are given in Chapter 1. The Molecular weights of petroleum fractions are given by the methods outlined in Chapter 2, and the densities are given by the methods outlined in Chapter 6.

Step 5: Obtain the viscosity of the mixture from Equation (11A3.1-1).

COMMENTS ON PROCEDURE 11A4.6

Purpose

This procedure is given for estimating the liquid viscosity of multicomponent mixtures of pure hydrocarbons with crude oils and petroleum fractions. The procedure can also be used for multicomponent mixtures of petroleum fractions.

Limitations

All of the components must be a liquid at the temperature and pressure of interest. The viscosity of all components must be calculated at the same temperature and pressure. Procedure 11A7.1 may be used to correct for a dissolved gas. No experimental data were available to test the reliability of the method.

Literature Source

Equation (11A3.1-1) was adapted from Kendall and Munroe, J. Am. Chem. Soc., 39 1787 (1917).

Example

- A. Estimate the liquid viscosity at 100 F and 1 atmosphere pressure of a mixture containing 20 weight percent n-hexane, 40 weight percent of a petroleum fraction having an API gravity of 43.6 and a mean average boiling point of 397.1 F, and 40 weight percent of a second petroleum fraction having an API gravity of 22.6 and a mean average boiling point of 828.3 F.

1. Find the viscosities of the individual components at 100 F. For n-hexane use Procedure 11A2.1,

$$\text{viscosity of n-hexane} = 0.2644 \text{ centipoise}$$

for the two petroleum fractions use Procedure 11A4.2,

$$\text{viscosity of 43.6 API fraction} = 1.409 \text{ centistokes}$$

$$\text{viscosity of 22.6 API fraction} = 66.31 \text{ centistokes}$$

2. Convert the viscosity of the petroleum fractions from kinematic to absolute values.

Using Procedure 6A3.5 for the 43.6 API fraction,

$$\text{density at } 100 \text{ F} = 49.07 \text{ lb/ft}^3$$

$$\text{correct density units to gm/cc} = 49.07 \times 0.016018 = 0.7860 \text{ gm/cc}$$

$$\text{absolute viscosity (cP)} = \text{Kinematic Viscosity (Cst)} \times \text{Density (gm/cc)}$$

$$= 1.409 \times 0.7860$$

$$= 1.107 \text{ centipoise}$$

Repeating for the 22.6 API fraction,

$$\text{absolute viscosity} = 59.75 \text{ centipoise}$$

3. Convert the concentrations from weight fraction to mole fraction. The molecular weight for n-hexane is given in Chapter 1. The molecular weight for the petroleum fractions can be calculated from the procedures of Chapter 2.

<u>Compound</u>	<u>Wt. Frac.</u>	<u>MW</u>	<u>Moles</u>	<u>MoleFrac.</u>
n-hexane	0.2	86.18	0.00232	0.4021
43.6 API Fraction	0.4	163	0.00245	0.4246
22.6 API Fraction	0.4	400	<u>0.00100</u>	<u>0.1733</u>
Total Moles			0.00577	1.0000

The number of moles is obtained by dividing the weight fraction by the molecular

weight.

4. Use Equation (11A3.1-1) to calculate the viscosity of the mixture.

$$\begin{aligned} &= [(0.4021)(0.2644)^{1/3} + (0.4246)(1.107)^{1/3} + (0.1733)(59.75)^{1/3}]^3 \\ &= 2.60 \text{ centipoise} \end{aligned}$$

11A5.1

For $0.45 \leq P_r \leq 0.75$

$f_1 = -0.2462$	$f_2 = -0.3199$	$f_3 = 4.7217$
$g_1 = 0.0484$	$g_2 = 17.0626$	$g_3 = -1.9831$
$h_1 = 0.0$	$h_2 = 0.0$	$h_3 = 19.2008$
$i_1 = 0.0$	$i_2 = 0.0$	$i_3 = -1.7595$
$j_1 = -0.7275$	$j_2 = -0.0695$	$j_3 = 65.5728$
$k_1 = -0.0588$	$k_2 = 0.1267$	$k_3 = 0.6110$
$l_1 = 0.0079$	$l_2 = -0.0101$	$l_3 = -19.1590$

For $0.75 < P_r \leq 1.00$

$f_1 = -0.0214$	$f_2 = -0.3588$	$f_3 = 3.7166$
$g_1 = 0.0484$	$g_2 = 5.0537$	$g_3 = -2.5689$
$h_1 = 0.0$	$h_2 = 0.0$	$h_3 = 52.1358$
$i_1 = 0.0$	$i_2 = 0.0$	$i_3 = 0.3514$
$j_1 = -0.1827$	$j_2 = -0.1321$	$j_3 = -13.0750$
$k_1 = -0.0183$	$k_2 = 0.0204$	$k_3 = 0.6358$
$l_1 = 0.0090$	$l_2 = -0.0075$	$l_3 = -56.6687$

If the critical viscosity of the compound is known,

$$\mu = \mu_r \mu_c \quad (11A5.1-6)$$

If the critical viscosity of the compound is not known but the viscosity at one reference temperature and pressure is known,

$$\mu = \mu_r \frac{\mu_o}{\mu_{ro}} \quad (11A5.1-7)$$

where:

μ_r = reduced viscosity, μ/μ_c

μ = viscosity in centipoises

μ_c = critical viscosity, in centipoises

μ_{ro} = reduced viscosity at the reference temperature and pressure, μ_o/μ_c

μ_o = viscosity at a reference temperature and pressure, in centipoises

Procedure

- Step 1:* Obtain the critical temperature and pressure from Chapter 1 and the acentric factor from Chapter 2. In addition, obtain either the critical viscosity from Table 11A5.6 or a reference point value of atmospheric liquid viscosity from 11A2, preferably near the temperature under study.

Step 2: Calculate the reduced temperature and pressure at which the viscosity is required.

Step 3: Obtain the correlation terms $\mu_r^{(0)}$ and $\mu_r^{(1)}$ from Equations (11A5.1-2) through (11A5.1-5), or by using Tables 11A5.2 and 11A4.3, an approximation of $\mu_r^{(0)}$ and $\mu_r^{(1)}$ can be attained.

Step 4: Calculate the reduced viscosity using Equation (11A5.1-1).

Step 5: If a critical viscosity value is available, proceed to Step 6, otherwise proceed to Step 7.

Step 6: Calculate the viscosity using Equation (11A5.1-2).

Step 7: Calculate the reference reduced viscosity, μ_o/μ_c .

Step 8: Calculate the viscosity using Equation (11A5.1-3).

COMMENTS ON PROCEDURE 11A5.1

Purpose

Procedure 11A5.1 is to be used to predict the effect of pressure on the liquid viscosity of low-molecular-weight hydrocarbons. Compounds containing fewer than 20 carbon atoms are treated as low-molecular-weight hydrocarbons.

Limitations

To apply the method, either a critical viscosity or a viscosity at some known temperature and pressure is required.

Reliability

This procedure yielded an average error of 5 percent before a regression was performed to convert it to an equivalent format from a graphical one. The average error for the regression was slightly higher than 8 percent.

Literature Source

Private communication, Graboski and Braun, The Pennsylvania State University, University Park, Pennsylvania, 1969.

Examples

A. Estimate the viscosity of n-pentane at 3000 pounds per square inch absolute and 200 F.

1) From Chapter 1, the critical temperature is 385.7 F, the critical pressure is 488.8 pounds per square inch absolute, and the molecular weight is 72.15. For the condition specified,

$$P_r = \frac{3000}{488.8} = 6.14$$

$$T_r = \frac{200 + 459.7}{385.7 + 459} = 0.78$$

2) From Chapter 2, $\omega = 0.2515$; from Table 11A5.6, $\mu_c = 0.0255$ centipoise.

3) From Equations (11A5.1-2) and (11A5.1-3), $\mu_r^{(0)} = 5.20$ and from Equations (11A5.1-4) and (11A5.1-5), $\mu_r^{(1)} = 1.89$.

4) Calculate the reduced viscosity using Equation (11A5.1-1).

$$\mu_r = 5.20 + (0.2515)(1.89) = 5.68$$

5) The viscosity is calculated using Equation (11A5.1-6).

$$\mu = (5.68)(0.0255) = 0.145 \text{ centipoise}$$

The experimental value is 0.166 centipoise.

B. Estimate the viscosity of n-decane at 280 F and 1500 pounds per square inch absolute. The value at 1 atmosphere and 280 F for the viscosity n-decane is 0.2720 centipoise.

- 1) From Chapter 1, the critical pressure is 306 pounds per square inch absolute and the critical temperature is 652.1 F. For the condition specified

$$P_r = \frac{1500}{306} = 4.90$$

$$T_r = \frac{280 + 459.7}{652.1 + 459.7} = 0.665$$

- 2) From Equations (11A5.1-2) and (11A5.1-3), $\mu_r^{(0)} = 8.04$ and from Equations (11A5.1-4) and (11A5.1-5), $\mu_r^{(1)} = 4.91$.

- 3) The reduced viscosity is then calculated using Equation (11A5.1-1) with the value $\omega = 0.4923$ obtained from Chapter 1.

$$\mu_r = 8.04 + (.4923)(4.91) = 10.46$$

- 4) The conditions of 1 atmosphere and 280 F are close to saturation and the reference viscosity may be assumed to be the saturation value. From Equations (11A5.1-2) and (11A5.1-3), $\mu_r^{(0)} = 7.25$ and from Equations (11A5.1-4) and (11A5.1-5) $\mu_r^{(1)} = 4.15$ at the saturation condition (1 atmosphere)

- 5) The reduced viscosity at the reference condition is calculated using Equation (11A5.1-1).

$$\mu_{r0} = 7.25 + (0.4923)(4.15) = 9.29$$

- 6) The viscosity is calculated using equation (11A5.1-7)

$$\mu = 10.46 \frac{0.2720}{9.29} = 0.306$$

The experimental value is 0.310 centipoise.

PROCEDURE 11A5.5**LIQUID VISCOSITY OF HIGH-MOLECULAR-WEIGHT PURE AND
MIXED HYDROCARBONS AT HIGH PRESSURE****Discussion**

The following equation should be used to estimate the effect of pressure on viscosity of high-molecular-weight pure hydrocarbons and their mixtures.

$$\log \frac{\mu_p}{\mu_a} = \frac{P}{1000} (-0.0102 + 0.04042\mu_a^{0.181}) \quad (11A5.5-1)$$

Where:

μ_p = viscosity at given temperature and pressure, in centipoises.

μ_a = viscosity at given temperature and 1 atmosphere, in centipoises.

p = pressure, in pounds per square inch gage.

Procedure

Step 1: Obtain the atmospheric-pressure viscosity of the fluid.

Step 2: If the oil is gas-free, go to Step 3. If the oil contains a dissolved gas, apply Procedure 11A7.1 to obtain the viscosity of the solution at saturated conditions for the same quantity of dissolved gas. Compute the pressure as the difference between the desired pressure and that of the bubble point of the mixture. Use the viscosity of the solution at its bubble point as the reference viscosity for the calculation.

Step 3: Apply Equation (11A5.5-1) to obtain the viscosity at the elevated pressure.

Purpose

This procedure is presented for estimating the pressure effect on liquid viscosity of high-molecular-weight hydrocarbons and mixtures of hydrocarbons of undefined composition at high pressures. Compounds containing 20 or more carbon atoms are usually treated as high-molecular-weight hydrocarbons.

Limitations

The method should not be applied for pressures greater than 20,000 pounds per square inch.

Reliability

The average error between calculated and experimental viscosities was determined to be 9.5 percent for the 1279 data points evaluated.

Literature Source

Equation (11A5.5-1) is a modified form of the original equation presented by Kouzel, *Hydrocarbon Process. Petrol. Refiner* 44 [3] 120 (1965). New constants for Equation (11A5.5-1) were determined at The Pennsylvania State University using currently available data.

Example

Estimate the viscosity of the extract portion of a lubricating oil at 9940.0 pounds per square inch absolute and 120.2 F. The viscosity at 120.2 F and 1 atmosphere is 52.70 centipoises.

From Equation (11A5.5-1),

$$\log \frac{\mu_p}{52.70} = \frac{(9940 - 14.7)}{1000} [-0.0102 + 0.04042 (52.70)^{0.181}]$$
$$= 0.721$$
$$\mu_p = 277.2 \text{ centipoises}$$

The experimental value is 281 centipoises.

PROCEDURE 11A6.1**VISCOSITY INDEX FROM KINEMATIC VISCOSITY****Discussion**

The viscosity index is an empirical number indicating the effect of changes in temperature on the viscosity of an oil. A low viscosity index signifies a relatively large change of viscosity with temperature. This procedure was taken directly from ASTM D 2770-86. Two methods are involved: Method A applies only to oils having a viscosity index between 0 and 100; whereas, Method B applies to oils having a viscosity index greater than 100.

Method A (for viscosity indexes of 100 or less):

$$\text{Viscosity index} = \frac{L - U}{L - H} \times 100 \quad (11A6.1-1)$$

Where:

- L = viscosity at 40 C of a reference oil of 0 viscosity index and having the same viscosity at 100 C as the oil whose viscosity index is to be calculated, in centistokes.
- U = viscosity at 40 C of the oil whose viscosity index is to be calculated, in centistokes.
- H = viscosity at 40 C of a reference oil of 100 viscosity index and having the same viscosity at 100 C as the oil whose viscosity index is to be calculated, in centistokes.

If the kinematic viscosity of the oil at 100 C is below 70.0 centistokes, the values of L and H can be read from Table 11A6.2. If the kinematic viscosity at 100 C is above 70.0 and the viscosity index is below 100, then the values of L and H are calculated from the following equations:

$$L = 0.8353 Y^2 + 14.67Y - 216 \quad (11A6.1-2)$$

$$H = 0.1684 Y^2 + 11.85Y - 97 \quad (11A6.1-3)$$

Where:

- Y = kinematic viscosity at 100 C of the oil whose viscosity index is to be calculated, in centistokes.

Method B (for viscosity indexes above 100):

$$\text{Viscosity index} = \frac{(\text{antilog } N) - 1}{0.00715} + 100.0 \quad (11A6.1-4)$$

Where:

- N = power required to raise the viscosity of the oil at 100 C to equal the ratio of H and U.

$$N = \frac{\log H - \log U}{\log Y} \quad (11A6.1-5)$$

Procedure

Method A (for viscosity indexes of 100 or less):

Step 1: If the kinematic viscosity of the oil at 100 C is less than 70.0, centistokes obtain the L and H from Table 11A6.2. If not, calculate L and H from Equations (11A6.1-2) and (11A6.1-3), respectively.

Step 2: Calculate the viscosity index from Equation (11A6.1-1).

Method B (for viscosity indexes above 100):

Step 1: If the kinematic viscosity of the oil at 100 C is less than 70.0 centistokes, obtain H from

Table 11A6.2. If not, calculate H from Equation (11A6.1-3).

Step 2: Calculate N from Equation (11A6.1-5).

Step 3: Calculate the viscosity index from Equation (11A6.1-4).

COMMENTS ON PROCEDURE 11A6.1

Purpose

This procedure is given for calculating the viscosity index of oils.

Limitations

Saybolt viscosity should not be used for calculating the viscosity index. Instead, use kinematic viscosity, in centistokes. (A trial-and-error solution must be used to determine whether Method A or Method B is valid.) Viscosity index values that are somewhat greater than 100 will not differ significantly whether calculated by Method A or Method B. The viscosity index should be reported to the nearest whole number. The viscosity index is not defined for oils with a kinematic viscosity less than 2.0 centistokes at 100 C.

Special Comments

The results obtained from the calculation of viscosity index from kinematic viscosities at 40 and 100 C are virtually the same as those obtained from the former viscosity index system using kinematic viscosities determined at 100 and 210 F.

Literature Source

The procedure and tables were adapted from ASTM D 2770-86, *Standard Practice for Calculating Viscosity Index from Kinematic Viscosity at 40 and 100 C.*

Examples

A. Calculate the viscosity index of an oil having a kinematic viscosity of 73.30 centistokes at 40 C and 8.86 centistokes at 100 C.

Assume the viscosity index to be between 0 and 100 and use Method A.

From Table 11A6.2, L = 119.94 and H = 69.48.

Using Equation (11A6.1-1),

$$\text{Viscosity index} = \frac{119.94 - 73.30}{119.94 - 69.48} \times 100 = 92.43$$

Thus, Method A was the appropriate choice. The viscosity index should be reported as 92.

B. Calculate the viscosity index of an oil whose kinematic viscosity is 5000 centistokes at 40 C and 100 centistokes at 100 C.

Because the change in viscosity is large, assume Method A applies.

Using Equations (11A6.1-2) and (11A6.1-3), respectively.

$$L = (0.8353)(100)^2 + 14.67(100) - 216 = 9604$$

$$H = (0.1684)(100)^2 + (11.85)(100) - 97 = 2772$$

Using Equation (11A6.1-1),

$$\text{Viscosity index} = \frac{9604 - 5000}{9604 - 2772} \times 100 = 67.39$$

Since the result is less than 100, Method A was the appropriate choice. The viscosity index should be reported as 67.

C. Calculate the viscosity index of an oil whose kinematic viscosity is 22.83 centistokes at 40 C and 5.05 centistokes at 100 C.

Assume Method A applies. From Table 11A6.2, L = 41.11 and H = 28.98. Using Equation (11A6.1-1),

$$\text{Viscosity index} = \frac{41.11 - 22.83}{41.11 - 28.98} \times 100 = 150.7$$

The viscosity index is greater than 100, so Method B must be used. Using Equation (11A6.1-5),

$$N = \frac{\log 28.98 - \log 22.83}{\log 5.05} = 0.1473$$

From Equation (11A6.1-4),

$$\text{Viscosity index} = \frac{1.404 - 1}{0.00715} + 100 = 156.5$$

The viscosity index should be reported as 157.

D. Calculate the viscosity index of an oil whose kinematic viscosity is 1500 centistokes at 40 C and 100 centistokes at 100 C.

Assume Method B is appropriate.

Using Equations (11A6.1-3) and (11A6.1-5), respectively.

$$H = (0.1684)(100)^2 + (11.85)(100) - 97 = 2772$$

$$N = \frac{\log 2772 - \log 1500}{\log 100} = 0.1334$$

Using Equation (11A6.1-4),

$$\text{Viscosity index} = \frac{1.360 - 1}{0.00715} + 100 = 150.3$$

Since the result is greater than 100, Method B was the correct procedure. The viscosity index should be reported as 150.

Table 11A6.2

**Reference Values For Viscosity Index
(Part of Procedure 11A6.1)**

Kinematic Viscosity at 100°C., L H cSt (mm²/s)			Kinematic Viscosity at 100°C., L H cSt (mm²/s)			Kinematic Viscosity at 100°C., L H cSt (mm²/s)			Kinematic Viscosity at 100°C., L H cSt (mm²/s)			Kinematic Viscosity at 100°C., L H cSt (mm²/s)				
2.00	7.994	6.394	7.00	78.00	48.57	12.0	201.9	108.0	17.0	369.4	180.2	24.0	683.9	301.8	42.5	
2.10	8.640	6.894	7.10	80.25	49.61	12.1	204.8	109.4	17.1	373.3	181.7	24.2	694.5	305.6	43.0	
2.20	9.309	7.410	7.20	82.39	50.69	12.2	207.8	110.7	17.2	377.1	183.3	24.4	704.2	309.4	43.5	
2.30	10.00	7.944	7.30	84.53	51.78	12.3	210.7	112.0	17.3	381.0	184.9	24.6	714.9	313.0	44.0	
2.40	10.71	8.496	7.40	86.66	52.88	12.4	213.6	113.3	17.4	384.9	186.5	24.8	725.7	317.0	44.5	
2.50	11.45	9.063	7.50	88.85	53.98	12.5	216.6	114.7	17.5	388.9	188.1	25.0	736.5	320.9	45.0	
2.60	12.21	9.647	7.60	91.04	55.09	12.6	219.6	116.0	17.6	392.7	189.7	25.2	747.2	324.9	45.5	
2.70	13.00	10.25	7.70	93.20	56.20	12.7	222.6	117.4	17.7	396.7	191.3	25.4	758.2	328.8	46.0	
2.80	13.80	10.87	7.80	95.43	57.31	12.8	225.7	118.7	17.8	400.7	192.9	25.6	769.3	332.7	46.5	
2.90	14.63	11.50	7.90	97.72	58.45	12.9	228.8	120.1	17.9	404.6	194.6	25.8	779.7	336.7	47.0	
3.00	15.49	12.15	8.00	100.0	59.60	13.0	231.9	121.5	18.0	408.6	196.2	26.0	790.4	340.5	47.5	
3.10	16.36	12.82	8.10	102.3	60.74	13.1	235.0	122.9	18.1	412.6	197.8	26.2	801.6	344.4	48.0	
3.20	17.26	13.51	8.20	104.6	61.89	13.2	238.1	124.2	18.2	416.7	199.4	26.4	812.8	348.4	48.5	
3.30	18.18	14.21	8.30	106.9	63.05	13.3	241.2	125.6	18.3	420.7	201.0	26.6	824.1	352.3	49.0	
3.40	19.12	14.93	8.40	109.2	64.18	13.4	244.3	127.0	18.4	424.9	202.6	26.8	835.5	356.4	49.5	
3.50	20.09	15.66	8.50	111.5	65.32	13.5	247.4	128.4	18.5	429.0	204.3	27.0	847.0	360.5	50.0	
3.60	21.08	16.42	8.60	113.9	66.48	13.6	250.6	129.8	18.6	433.2	205.9	27.2	857.5	364.6	50.5	
3.70	22.09	17.19	8.70	116.2	67.64	13.7	253.8	131.2	18.7	437.3	207.6	27.4	869.0	368.3	51.0	
3.80	23.13	17.97	8.80	118.5	68.79	13.8	257.0	132.6	18.8	441.5	209.3	27.6	880.6	372.3	51.5	
3.90	24.19	18.77	8.90	120.9	69.94	13.9	260.1	134.0	18.9	445.7	211.0	27.8	892.3	376.4	52.0	
4.00	25.32	19.56	9.00	123.3	71.10	14.0	263.3	135.4	19.0	449.9	212.7	28.0	904.1	380.6	52.5	
4.10	26.50	20.37	9.10	125.7	72.27	14.1	266.6	136.8	19.1	454.2	214.4	28.2	915.8	384.6	53.0	
4.20	27.75	21.21	9.20	128.0	73.42	14.2	269.8	138.2	19.2	458.4	216.1	28.4	927.6	388.8	53.5	
4.30	29.07	22.05	9.30	130.4	74.57	14.3	273.0	139.6	19.3	462.7	217.7	28.6	938.6	393.0	54.0	
4.40	30.48	22.92	9.40	132.8	75.73	14.4	276.3	141.0	19.4	467.0	219.4	28.8	951.2	396.6	54.5	
4.50	31.96	23.81	9.50	135.3	76.91	14.5	279.6	142.4	19.5	471.3	221.1	29.0	963.4	401.1	55.0	
4.60	33.52	24.71	9.60	137.7	78.08	14.6	283.0	143.9	19.6	475.7	222.8	29.2	975.4	405.3	55.5	
4.70	35.13	25.63	9.70	140.1	79.27	14.7	286.4	145.3	19.7	479.7	224.5	29.4	987.1	409.5	56.0	
4.80	36.79	26.57	9.80	142.7	80.46	14.8	289.7	146.8	19.8	483.9	226.2	29.6	998.9	413.5	56.5	
4.90	38.50	27.53	9.90	145.2	81.67	14.9	293.0	148.2	19.9	488.6	227.7	29.8	1011	417.6	57.0	
5.00	40.23	28.49	10.0	147.7	82.87	15.0	296.5	149.7	20.0	493.2	229.5	30.0	1023	421.7	57.5	
5.10	41.99	29.46	10.1	150.3	84.08	15.1	300.0	151.2	20.2	501.5	233.0	30.5	1055	432.4	58.0	
5.20	43.76	30.43	10.2	152.9	85.30	15.2	303.4	152.6	20.4	510.8	236.4	31.0	1086	443.2	58.5	
5.30	45.53	31.40	10.3	155.4	86.51	15.3	306.9	154.1	20.6	519.9	240.1	31.5	1119	454.0	59.0	
5.40	47.31	32.37	10.4	158.0	87.72	15.4	310.3	155.6	20.8	528.8	243.5	32.0	1151	464.9	59.5	
5.50	49.09	33.34	10.5	160.6	88.95	15.5	313.9	157.0	21.0	538.4	247.1	32.5	1184	475.9	60.0	
5.60	50.87	34.32	10.6	163.2	90.19	15.6	317.5	158.6	21.2	547.5	250.7	33.0	1217	487.0	60.5	
5.70	52.64	35.29	10.7	165.8	91.40	15.7	321.1	160.1	21.4	556.7	254.2	33.5	1251	498.1	61.0	
5.80	54.42	36.26	10.8	168.5	92.65	15.8	324.6	161.6	21.6	566.4	257.8	34.0	1286	509.6	61.5	
5.90	56.20	37.23	10.9	171.2	93.92	15.9	328.3	163.1	21.8	575.6	261.5	34.5	1321	521.1	62.0	
6.00	57.97	38.19	11.0	173.9	95.19	16.0	331.9	164.6	22.0	585.2	264.9	35.0	1356	532.5	62.5	
6.10	59.74	39.17	11.1	176.6	96.45	16.1	335.5	166.1	22.2	595.0	268.6	35.5	1391	544.0	63.0	
6.20	61.52	40.15	11.2	179.4	97.71	16.2	339.2	167.7	22.4	604.3	272.3	36.0	1427	555.6	63.5	
6.30	63.32	41.13	11.3	182.1	98.97	16.3	342.9	169.2	22.6	614.2	275.8	36.5	1464	567.1	64.0	
6.40	65.18	42.14	11.4	184.9	100.2	16.4	346.6	170.7	22.8	624.1	279.6	37.0	1501	579.3	64.5	
6.50	67.12	43.18	11.5	187.6	101.5	16.5	350.3	172.3	23.0	633.6	283.3	37.5	1538	591.3	65.0	
6.60	69.16	44.24	11.6	190.4	102.8	16.6	354.1	173.8	23.2	643.4	286.8	38.0	1575	603.1	65.5	
6.70	71.29	45.33	11.7	193.3	104.1	16.7	358.0	175.4	23.4	653.8	290.5	38.5	1613	615.0	66.0	
6.80	73.48	46.44	11.8	196.2	105.4	16.8	361.7	177.0	23.6	663.3	294.4	39.0	1651	627.1	66.5	
6.90	75.72	47.51	11.9	199.0	106.7	16.9	365.6	178.6	23.8	673.7	297.9	39.5	1691	639.2	67.0	
													40.0	1730	651.8	67.5
													40.5	1770	664.2	68.0
													41.0	1810	676.6	68.5
													41.5	1851	689.1	69.0
													42.0	1892	701.9	69.5
													70.0	4905	1558	

PROCEDURE 11A7.1

LIQUID VISCOSITY OF PURE AND MIXED HYDROCARBONS CONTAINING DISSOLVED GASES

Discussion

The following equation is to be used for estimating the effect of dissolved gas on the viscosity of liquid hydrocarbons at 100 F and the saturation pressure:

$$\frac{\mu_m}{\mu_a} = \frac{0.294(\text{GLR}) + 137.0\mu_a^{1/3} + 538.4}{[\mu_a^{1/3}(137.0 + 0.871(\text{GLR})) + 538.4]} \quad (11A7.1-1)$$

Where:

- μ_m = viscosity of saturated liquid at 100 F and the saturation pressure, in centipoises.
- μ_a = viscosity of gas-free liquid at 100 F and 1 atmosphere, in centipoise.
- GLR = gas-to-liquid ratio, in cubic feet of gas per barrel of liquid evaluated at 60 F and 1 atmosphere.

In order to apply this at temperatures other than 100 F, the following relation is to be used:

$$\log \mu_t = -1.209 + \left[\frac{1.209 + \log (\mu_m)}{t + 139} \right] \times 239 \quad (11A7.1-2)$$

Where:

- μ_t = viscosity at the desired temperature, in centipoises.
- t = temperature, in degrees Fahrenheit.

Procedure

Step 1: Calculate the volume of gas dissolved per volume of gas-free liquid at 60 F and 1 atmosphere pressure. If the gas-to-liquid ratio is in cubic feet of gas per cubic foot of liquid, multiply this figure by 5.615 to obtain the defined units for gas-to-liquid ratio, GLR.

Step 2: Obtain the viscosity of gas-free liquid at 100 F and 1 atmosphere. If an experimental value is not available, Procedure 11A2.1 or Procedure 11A2.3 can be used to predict the viscosity of pure compounds. For petroleum fractions, Procedure 11A4.2 can be used to predict viscosity. For a defined mixture of pure compounds, Procedure 11A3.1 should be used to predict the viscosity. For a blend of petroleum fractions, Procedure 11A4.5 may be used, and Procedure 11A4.6 should be used to predict the viscosity if the blend contains pure components.

Step 3: Use Equation (11A7.1-1) to calculate the viscosity at 100 F. Use Equation (11A7.1-2) to calculate the viscosity at temperatures other than 100 F.

COMMENTS ON PROCEDURE 11A7.1

Purpose

Procedure 11A7.1 is to be used to estimate the viscosity of a hydrocarbon liquid containing dissolved gases at the saturation pressure. The procedure can be used for dissolved gases that are pure components, defined mixtures, or undefined mixtures (i.e., natural gas).

Limitations

Equation (11A7.1-2) should not be used above 500 F. This correlation was developed from data on liquid hydrocarbons containing dissolved gases, such as N₂, CO₂, CH₄ and light hydrocarbons only. The method is valid for saturation pressures up to 5000 psia. The method should not be used to predict the viscosity of mixtures at pressures far above the bubble point pressure.

For mixtures at pressures far above the bubble point pressure, Procedure 11A5.3 can be used to predict the viscosity if the bubble point pressure is at or near atmospheric pressure. If the bubble point pressure is not near atmospheric pressure, then the alternate computer procedure SUPERTRAPP could be used to predict the viscosity of the dissolved gas mixtures at pressures greatly exceeding the bubble point.

Reliability

The average error in viscosity calculation is approximately 15% for 227 data points. The method was evaluated for the light hydrocarbon gases, methane, ethane, propane, and the nonhydrocarbon gases, carbon dioxide, helium, and nitrogen at gas-to-liquid ratios up to 1000 cubic feet per barrel.

Literature Source

Private communication from Kouzel, Union Oil Co. of California, Brea, California, 1982.

Example

A. Estimate the viscosity of a saturated solution of methane in a paraffin oil (crystal oil) at 130 F and 400 psia. Gas-to-liquid ratio, GLR, is 54.55 cubic feet of gas per barrel of liquid. The viscosity of the gas-free oil at 100 F is 28.38 centipoises. From Equation (11A7.1-1),

$$\begin{aligned} \frac{\mu_m}{28.38} &= \frac{0.294(54.55) + 137.0(28.38)^{1/3} + 538.4}{(28.38)^{1/3}[137.0 + 0.871(54.55)] + 538.4}^3 \\ &= 0.6886 \\ \mu_m &= 19.54 \text{ centipoises} \end{aligned}$$

From Equation (11A7.1-2),

$$\begin{aligned} \log \mu_t &= -1.209 + \left[\frac{1.209 + \log(19.54)}{130 + 139} \right] \times 239 \\ &= 1.012 \end{aligned}$$

$$\mu_t = 10.28 \text{ centipoises}$$

The experimental value is 10.72 centipoises.

B. Estimate the viscosity of a saturated solution of 30 mole percent methane and 70 mole percent n-decane at 100 F. The saturation pressure of the mixture is approximately 1000 psia. The density of methane vapor is 0.00264 lb mol per cubic foot at 60 F and 1 atmosphere pressure. The density of n-decane liquid at 60 F is 0.3219 lb mol per cubic foot. The viscosity of n-decane is 0.728 centipoise at 100 F and 1 atmosphere pressure.

Calculate the gas-to-liquid ratio, GLR,

$$\text{GLR} = \frac{\left(\frac{1}{0.00264 \text{ lb mol/ft}^3} \right) (0.3)}{\left(\frac{1}{0.3219 \text{ lb mol/ft}^3} \right) (0.7)} = 52.3 \frac{\text{cubic feet of gas}}{\text{cubic feet of liquid}}$$

$$\text{GLR} = 52.3 \times 5.615 = 293.7 \text{ cubic feet of gas/barrel of liquid}$$

From Equation (11A7.1-1),

$$\frac{\mu_m}{0.728} = \frac{0.294 (293.7) + 137.0 (0.728)^{1/3} + 538.4}{(0.728)^{1/3} [137.0 + 0.871 (293.7)] + 538.4}^3$$

$$\mu_m = 0.430 \text{ centipoise}$$

The experimental value is 0.518 centipoise.

PROCEDURE 11B1.1**CORRELATION FOR THE VAPOR VISCOSITY
OF PURE COMPOUNDS AT LOW PRESSURE****Discussion**

The following equation is recommended for calculating the vapor viscosity of any pure compound over a specific temperature range.

$$\mu = \frac{1000 A T^3}{\left(1 + \frac{C}{T} + \frac{D}{T^2}\right)} \quad (11B1.1-1)$$

Where:

μ = absolute viscosity of vapor, in centipoise.

T = temperature, in degrees Rankine.

A,B,C,D = correlation coefficients from Table 11B1.2.

Procedure

Step 1: Locate the coefficients for the desired compound in Table 11B1.2. Check to see if the temperature is within the specified range of the correlation.

Step 2: Calculate the vapor viscosity from Equation (11B1.1-1).

COMMENTS ON PROCEDURE 11B1.1

Purpose

This correlation is used to calculate the vapor viscosity of pure components as a function of temperature. Table 11B1.2 lists coefficients for 300 pure compounds.

Limitations

This procedure is valid only over the specified temperature range listed in Table 11B1.2 for each pure component. The average error over the entire temperature range is less than 5% and generally better than 2%. The correlations only are valid at reduced pressures less than 0.6.

Literature Sources

Procedure 11B1.1 was developed by the project staff at The Pennsylvania State University.

Example

Determine the vapor viscosity of n-hexane at 121.95 F and 14.7 psia.

1. Convert temperature to Rankine and check to see if this temperature is contained within the range given in Table 11B1.2.

$$T = 121.95 + 459.67 = 581.62 \text{ R}$$

This temperature is within the specified range of 320 to 1800 Rankine.

2. Obtain the values for the coefficients A, B, C, and D from Table 11B1.2.

$$A = 1.1553 \times 10^{-7}$$

$$B = 0.70740$$

$$C = 282.78$$

$$D = 0.0$$

3. Use Equation (11B1.1-1) and the coefficients to calculate the vapor viscosity at the specified temperature.

$$\mu = 1000 (1.1553 \times 10^{-7})(581.62)^{0.7074} / [1 + 282.73/581.62]$$

$$\mu = 7.02 \times 10^{-3} \text{ centipoise}$$

The experimental value is 7.14×10^{-3} centipoise.

11B1.2

TABLE 11B1.2

API No.	NAME	COEFFICIENTS FOR PROCEDURE 11B1.1				TEMPERATURE		
		A	B	C	D	MIN	MAX	Q
794	OXYGEN	7.906E-07	5.634E-01	1.733E+02	0.000E+00	98	2700	x
781	HYDROGEN	1.201E-07	6.850E-01	-1.06E+00	4.536E+02	25	5400	x
845	WATER	4.152E-07	6.778E-01	1.525E+03	-2.40E+05	492	1932	x
792	NITROGEN DIOXIDE	3.565E-08	9.222E-01	-5.13E+02	2.411E+05	540	1800	x
790	NITRIC OXIDE	1.086E-06	5.123E-01	2.257E+02	0.000E+00	198	2700	x
791	NITROUS OXIDE	1.610E-06	4.642E-01	5.503E+02	0.000E+00	328	1800	x
771	AMMONIA	2.352E-08	9.806E-01	5.544E+01	0.000E+00	352	1800	x
777	CHLORINE	1.681E-07	7.423E-01	1.769E+02	0.000E+00	360	1800	x
783	HYDROGEN CHLORIDE	3.321E-07	6.702E-01	2.839E+02	0.000E+00	360	1800	x
786	HYDROGEN SULFIDE	3.223E-08	1.017E+00	6.703E+02	-2.08E+05	450	864	x
789	NITROGEN	4.588E-07	6.081E-01	9.848E+01	0.000E+00	114	3546	x
774	CARBON MONOXIDE	8.133E-07	5.338E-01	1.705E+02	0.000E+00	123	2250	x
775	CARBON DIOXIDE	1.639E-06	4.600E-01	5.220E+02	0.000E+00	350	2700	x
796	SULFUR DIOXIDE	4.792E-07	6.112E-01	3.906E+02	0.000E+00	356	1800	x
797	SULFUR TRIOXIDE	3.116E-06	3.845E-01	8.462E+02	0.000E+00	536	1250	x
770	AIR	1.059E-06	5.039E-01	1.949E+02	0.000E+00	144	3600	x
PARAFFINS								
1	METHANE	3.715E-07	5.901E-01	1.903E+02	0.000E+00	163	1800	x
2	ETHANE	1.737E-07	6.799E-01	1.780E+02	0.000E+00	163	1800	x
3	PROPANE	1.670E-07	6.861E-01	3.227E+02	-2.67E+04	154	1800	x
4	n-BUTANE	1.528E-07	6.944E-01	4.099E+02	-4.73E+04	243	1800	x
5	ISOBUTANE	5.090E-07	5.214E-01	4.122E+02	0.000E+00	270	1800	x
6	n-PENTANE	3.853E-08	8.476E-01	7.510E+01	0.000E+00	258	1800	x
7	ISOPENTANE	8.782E-07	4.572E-01	6.527E+02	-1.61E+04	204	1800	x
8	NEOPENTANE	3.484E-07	5.678E-01	3.832E+02	0.000E+00	462	1800	x
9	n-HEXANE	1.155E-07	7.074E-01	2.828E+02	0.000E+00	320	1800	p
10	2-METHYLPENTANE	8.548E-07	4.537E-01	6.745E+02	0.000E+00	215	1800	p
11	3-METHYLPENTANE	1.157E-06	4.251E-01	8.213E+02	0.000E+00	198	1800	p
12	2,2-DIMETHYLBUTANE	1.296E-07	6.826E-01	1.841E+02	0.000E+00	314	1800	x
13	2,3-DIMETHYLBUTANE	5.035E-07	5.254E-01	5.018E+02	0.000E+00	261	1800	x
14	n-HEPTANE	4.100E-08	8.284E-01	1.544E+02	0.000E+00	329	1800	x
15	2-METHYLHEXANE	7.748E-07	4.561E-01	6.476E+02	0.000E+00	279	1800	p
16	3-METHYLHEXANE	3.264E-07	5.548E-01	3.791E+02	0.000E+00	277	1800	p
17	3-ETHYLPENTANE	5.050E-07	5.148E-01	5.634E+02	0.000E+00	660	1800	p
18	2,2-DIMETHYLPENTANE	3.202E-07	5.676E-01	4.147E+02	0.000E+00	634	1800	p
19	2,3-DIMETHYLPENTANE	3.657E-07	5.446E-01	4.093E+02	0.000E+00	288	1800	p
20	2,4-DIMETHYLPENTANE	1.251E-07	6.761E-01	1.805E+02	0.000E+00	277	1800	x
21	3,3-DIMETHYLPENTANE	7.050E-07	4.817E-01	6.937E+02	0.000E+00	647	1800	p
22	2,2,3-TRIMETHYLBUTANE	1.796E-09	1.222E+00	-2.23E+02	0.000E+00	618	963	x
23	n-OCTANE	1.806E-08	9.292E-01	9.916E+01	0.000E+00	389	1800	x
24	2-METHYLHEPTANE	3.221E-07	5.535E-01	4.000E+02	0.000E+00	295	1800	x
25	3-METHYLHEPTANE	5.925E-06	2.145E-01	1.468E+03	0.000E+00	275	1800	x
26	4-METHYLHEPTANE	3.578E-06	2.726E-01	1.180E+03	0.000E+00	274	1800	x
27	3-ETHYLHEXANE	2.678E-07	5.744E-01	3.528E+02	0.000E+00	705	1800	p
28	2,2-DIMETHYLHEXANE	1.479E-06	3.847E-01	9.515E+02	0.000E+00	684	1800	p
29	2,3-DIMETHYLHEXANE	3.200E-07	5.616E-01	4.408E+02	0.000E+00	700	1800	p
30	2,4-DIMETHYLHEXANE	1.053E-06	4.216E-01	7.987E+02	0.000E+00	689	1800	p
31	2,5-DIMETHYLHEXANE	6.333E-07	4.783E-01	6.199E+02	0.000E+00	688	1800	p
32	3,3-DIMETHYLHEXANE	2.126E-07	6.021E-01	2.851E+02	0.000E+00	693	1800	p
33	3,4-DIMETHYLHEXANE	4.741E-07	5.177E-01	5.603E+02	0.000E+00	704	1800	p
34	2-METHYL-3-ETHYLPENTANE	4.152E-07	5.252E-01	4.585E+02	0.000E+00	700	1800	p
35	3-METHYL-3-ETHYLPENTANE	3.661E-07	5.514E-01	4.923E+02	0.000E+00	328	1800	p
36	2,2,3-TRIMETHYLPENTANE	3.383E-07	5.509E-01	4.027E+02	0.000E+00	290	1800	p
37	2,2,4-TRIMETHYLPENTANE	7.140E-08	7.460E-01	1.303E+02	0.000E+00	298	1800	x
38	2,3,3-TRIMETHYLPENTANE	6.168E-07	4.931E-01	6.685E+02	0.000E+00	698	1800	p
39	2,3,4-TRIMETHYLPENTANE	5.017E-07	5.142E-01	5.859E+02	0.000E+00	696	1800	p
40	2,2,3,3-TETRAMETHYLBUTANE	6.062E-07	5.026E-01	6.845E+02	0.000E+00	673	1800	p
41	n-NONANE	6.564E-08	7.730E-01	3.969E+02	0.000E+00	395	1800	x
42	2-METHYLOCTANE	4.037E-07	5.195E-01	4.837E+02	0.000E+00	347	1800	p
43	3-METHYLOCTANE	3.622E-07	5.315E-01	4.430E+02	0.000E+00	298	1800	p
44	4-METHYLOCTANE	2.319E-07	5.848E-01	3.310E+02	0.000E+00	288	1800	p
45	3-ETHYLHEPTANE	3.530E-07	5.401E-01	4.572E+02	0.000E+00	285	1800	p
46	2,2-DIMETHYLHEPTANE	4.868E-07	5.009E-01	5.200E+02	0.000E+00	288	1800	p
47	2,6-DIMETHYLHEPTANE	3.669E-07	5.276E-01	4.248E+02	0.000E+00	306	1800	p

PROCEDURE 11B1.3**VISCOSITY OF PURE GASES AT LOW PRESSURE****Discussion**

The following equation is used to predict the pure component viscosity of hydrocarbon gases at low pressure. Separate equations are also provided for hydrogen.

$$\mu = N\xi \quad (11B1.3-1)$$

Where:

$$\xi = 5.4403 \frac{T_c^{16}}{M^{1/2} P_c^{23}} \quad (11B1.3-2)$$

For hydrocarbons, calculate N using

$$N = 3.400 \times 10^{-4} T_r^{0.94} \quad \text{for } T_r \leq 1.5 \quad (11B1.3-3)$$

$$N = 1.778 \times 10^{-4} (4.58 T_r - 1.67)^{0.625} \quad \text{for } T_r > 1.5 \quad (11B1.3-4)$$

For hydrogen, calculate viscosity, μ , using

$$\mu = 3.700 \times 10^{-5} T^{0.94} \quad \text{for } T_r \leq 1.5 \quad (11B1.3-5)$$

$$\mu = 9.071 \times 10^{-4} ((7.639 \times 10^{-2})T - 1.67)^{0.625} \quad \text{for } T_r > 1.5 \quad (11B1.3-6)$$

Where:

μ = vapor viscosity, in centipoise.

T_c = critical temperature, in degrees Rankine.

T = temperature, in degrees Rankine.

P_c = critical pressure, in psia.

M = molecular weight

Procedure

Step 1: Obtain the critical temperature, critical pressure and molecular weight from Chapter 1.

Step 2: Calculate ξ using Equation (11B1.3-2).

Step 3: Determine the reduced temperature, T_r .

Step 4: Use the appropriate equation, either (11B1.3-3) or (11B1.3-4) to calculate N.

Step 5: Calculate the vapor viscosity using Equation (11B1.3-1). For hydrogen, omit steps 1 through 4 and use Equations (11B1.3-5) or (11B1.3-6) to calculate the viscosity.

COMMENTS ON PROCEDURE 11B1.3

Purpose

Procedure 11B1.3 is used to estimate the viscosity of hydrogen and pure component hydrocarbon gases.

Limitations

This procedure should be used for reduced pressures less than 0.6. Procedure 11B4.1 should be used for higher reduced pressures.

Reliability

The procedure produced an average error of 3.0% for 800 data points. The error was higher, between 5% and 10% for n-alkanes larger than n-decane.

Literature Source

Equations 11B1.3-1 through 11B1.3-6 are from Stiel and Thodos, *AIChE J.*, 7(4) 611 (1961).

Example

- A. Determine the vapor viscosity of propane at 176 F and 14.7 psia.

1. Find the critical temperature, critical pressure and molecular weight from Chapter 1.

$$T_c = 206 \text{ F}$$

$$P_c = 616 \text{ psia}$$

$$M = 44.1$$

2. Calculate ξ using Equation (11B1.3-2).

$$\xi = 5.4403 \frac{(206 + 459.67)^{1/6}}{(44.10)^{1/2} (616)^{2/3}}$$

$$\xi = 0.03344$$

3. Calculate the reduced temperature T_r .

$$T_r = \frac{T}{T_c} = \frac{(176 + 459.67)}{(206 + 459.67)} = 0.9549$$

4. Since $T_r < 1.5$, use Equation (11B1.3-3) to calculate N.

$$N = 3.400 \times 10^{-4} (0.9549)^{0.94} = 3.256 \times 10^{-4}$$

5. Calculate the viscosity using Equation (11B1.3-1).

$$\mu = \frac{N}{\xi} = \frac{3.256 \times 10^{-4}}{0.03344} = 0.0097 \text{ centipoise}$$

The experimental value is 0.0095 centipoise.

- B. Determine the vapor viscosity of methane at 543 F and 14.7 psia.

1. Find the critical temperature, critical pressure and molecular weight from Chapter 1.

$$T_c = -116.67 \text{ F}$$

$$P_c = 667 \text{ psia}$$

$$M = 16.04$$

2. Calculate ξ using Equation (11B1.3-2).

$$\xi = 5.4403 \frac{(-116.67 + 459.67)^{16}}{(16.04)^{12}(667)^{23}}$$

$$\xi = 0.0471$$

3. Calculate the reduced temperature T_r .

$$T_r = \frac{T}{T_c} = \frac{(543 + 459.67)}{(-116.67 + 459.67)} = 2.923$$

4. Since $T_r > 1.5$, use Equation (11B1.3-4) to calculate N.

$$N = 1.778 \times 10^{-4} (4.58 (2.923) - 1.67)^{0.625}$$

$$N = 8.279 \times 10^{-4}$$

5. Calculate the viscosity using Equation (11B1.3-1).

$$\mu = \frac{N}{\xi} = \frac{8.279 \times 10^{-4}}{0.04710} = 0.0176 \text{ centipoise}$$

The experimental value is 0.0181 centipoise.

PROCEDURE 11B2.1

VISCOSITY OF GASEOUS MIXTURES AT LOW PRESSURE

Discussion

Equation (11B2.1-1) is to be used for estimating the viscosity of a gaseous mixture of defined composition at reduced pressures below 0.6 and at any temperature. Viscosities of the pure components are required at the same conditions.

$$\mu_m = \sum_{i=1}^n \frac{\mu_i}{1 + \sum_{\substack{i=1 \\ j=1}}^n \phi_{ij} \frac{x_i}{x_j}} \quad (11B2.1-1)$$

$$\phi_{ij} = \frac{\left[1 + \left(\frac{\mu_i}{\mu_j} \right)^{1/2} \left(\frac{M_i}{M_j} \right)^{1/4} \right]^2}{\sqrt{8} \left[1 + \frac{M_i}{M_j} \right]^{1/2}} \quad (11B2.1-2)$$

Where:

- μ_m = viscosity of mixture, in centipoises.
- μ_i = viscosity of component i, in centipoises.
- μ_j = viscosity of component j, in centipoises.
- n = number of components in the mixture.
- x_i = mole fraction of component i.
- x_j = mole fraction of component j.
- ϕ_{ij} = interaction parameter for component i with respect to component j.
- M_i = molecular weight of component i.
- M_j = molecular weight of component j.

This method is applicable to gas mixtures containing hydrocarbons, hydrogen, and other common non-polar gases.

Procedure

- Step 1: Obtain the molecular weight of each component from Chapter 1.
- Step 2: Obtain the viscosity of each component at the temperature of the mixture using Procedure 11B1.1 or Procedure 11B1.3.
- Step 3: Obtain the interaction parameters from Equation (11B2.1-2).
- Step 4: Calculate the viscosity of the mixture using Equation (11B2.1-1).

COMMENTS ON PROCEDURE 11B2.1

Purpose

Equation (11B2.1-1) is used to calculate the viscosity of a low-pressure gaseous mixture of defined composition using pure-component viscosities at the same temperature.

Limitations

Below reduced pressures of 0.6, Equation (11B2.1-1) should be used. At reduced pressures greater than 0.6, Procedure 11B4.1 should be used for adjusting the viscosity of gas mixtures.

Reliability

Equation (11B2.1-1) yields average deviations of about 3 percent for the 364 points evaluated. Evaluations showed nearly equal reliability for binary and multicomponent mixtures. The equation is applicable to nonpolar, nonhydrocarbon gas mixtures as well as to hydrocarbon mixtures.

Literature Sources

Equations (11B2.1-1) and (11B2.1-2) were given by Bromley and Wilke, *Ind. Eng. Chem.* **43** 1641 (1951).

Examples

A. Calculate the viscosity of a mixture containing 58.18 mole percent hydrogen and 41.82 mole percent propane at 77 F and 14.7 pounds per square inch absolute.

From Procedure 11B1.3, the viscosity of propane is 0.00822 centipoise and, from Figure 11C1.1, the viscosity of hydrogen is 0.00891 centipoise. The molecular weights, M, from Chapter 1 are 2.02 for hydrogen and 44.10 for propane.

From Equation (11B2.1-2) the following values for ϕ_{ij} may be obtained where component 1 corresponds to hydrogen and component 2 corresponds to propane:

Interaction	μ/μ_j	M/M_j	ϕ_{ij}
1-2	1.09	0.046	3.59
2-1	0.92	21.8	0.15

For a binary system, Equation (11B2.1-2) is

$$\begin{aligned} \mu_m &= \frac{\mu_1}{1 + \phi_{1-2} \frac{x_2}{x_1}} + \frac{\mu_2}{1 + \phi_{2-1} \frac{x_1}{x_2}} \\ &= \frac{0.00891}{1 + (3.59) \left(\frac{0.4182}{0.5818} \right)} + \frac{0.00822}{1 + (0.15) \left(\frac{0.5818}{0.4182} \right)} \\ &= 0.0024885 + 0.0068008 = 0.009289 \text{ centipoise} \end{aligned}$$

The experimental value is 0.009240 centipoise.

B. Calculate the viscosity of a mixture at 85 F and 14.7 pounds per square inch absolute containing the following substances. The molecular weights and pure component viscosities are available in Chapters 1 and 11.

Component	x (mole percent)	μ (centipoise)	M
1. Methane	95.6	0.01125	16.04
2. Ethane	3.6	0.00950	30.07
3. Propane	0.5	0.00840	44.10
4. Nitrogen	0.3	0.01790	28.01

Since there are four components, $n(n-1) = 4(3) = 12$ interaction parameters are necessary.

Interaction

(ij)	μ_i/μ_j	M_i/M_j	ϕ_{ij}	$\phi_{ij}(x_j/x_i)$	$\sum \phi_{ij}(x_j/x_i)$
1-2	1.18	0.53	1.48	0.056	
1-3	1.34	0.36	1.88	0.010	0.069
1-4	0.63	0.57	1.03	0.003	
2-1	0.84	1.87	0.66	17.53	
2-3	1.13	0.68	1.29	0.18	17.77
2-4	0.53	1.07	0.72	0.06	
3-1	0.75	2.75	0.51	97.51	
3-2	0.88	1.47	0.77	5.54	103.39
3-4	0.47	1.57	0.57	0.34	
4-1	1.59	1.75	0.94	299.54	
4-2	1.88	0.93	1.48	17.76	320.50
4-3	2.13	0.64	1.92	3.20	

The viscosity of the mixture may be calculated using Equation (11B2.1-1)

$$\mu_m = \frac{0.01125}{1+0.069} + \frac{0.00950}{1+17.77} + \frac{0.00840}{1+103.39} + \frac{0.01790}{1+320.50}$$

$$= 0.01117 \text{ centipoise}$$

The experimental value is 0.1120 centipoise.

PROCEDURE 11B3.1**VISCOSITY OF GASEOUS UNDEFINED
MIXTURES AT LOW PRESSURE****Discussion**

Equation (11B3.1-1) should be used to calculate the viscosities of gaseous hydrocarbon mixtures of undefined composition at reduced pressures not greater than 0.6.

$$\mu = A + \sqrt{T} (B - C\sqrt{MW}) + D \times MW \quad (11B3.1-1)$$

where:

μ = absolute viscosity of the mixture, in centipoise

A = -0.0092696

B = 0.0010310

C = 4.4507×10^{-5}

D = 1.1249×10^{-5}

T = temperature in degrees Rankine

MW = molecular weight

Procedure

Step 1: Obtain the molecular weight of the hydrocarbon from experimental data or by using procedures outlined in Chapter 2.

Step 2: Using the molecular weight from Step 1 and the temperature of the mixture, calculate the absolute viscosity using Equation (11B3.1-1).

COMMENTS ON PROCEDURE 11B3.1

Purpose

Procedure 11B3.1 is to be used to estimate the viscosities of gaseous hydrocarbon mixtures of undefined composition at reduced pressures not exceeding 0.6.

Limitations

This procedure should be used only if the required data are not available to use Procedure 11B2.1.

Reliability

An average error of 6 percent and a maximum error of 22 percent were observed using Equation 11B3.1-1 on all available viscosity data. The correlation was developed for paraffin vapors. The errors varied greatly between different compounds. However, for general use, a minimum average error of 6 percent should be expected.

Special Comments

If the molecular weight of the mixture is not known, it can be roughly estimated. The uncertainty introduced by the estimation will be overshadowed by the uncertainty of the method.

The procedure can be used for hydrogen-hydrocarbon mixtures with average molecular weights greater than 16. For molecular weights less than 16, use Procedure 11B2.1.

The effect of pressure on the viscosity of mixture of undefined composition may be obtained by estimating T_c and P_c from the methods given in Chapter 4 and then using Procedure 11B4.1.

Literature Source

This Procedure was adapted from Bircher and Katz, *Trans AIME* 155 246 (1944).

Example

Estimate the viscosity of a mixture at 100 F with a molecular weight of 250.

By using Equation (11B3.1-1)

$$\mu = -0.0092696 + \sqrt{(100 + 459.67)(0.0010310 - 4.4507 \times 10^{-5}\sqrt{250})} + 1.1249 \times 10^{-5} \times 250$$

$$\mu = 0.1019 \text{ centipoise}$$

PROCEDURE 11B4.1**VISCOSITY OF PURE HYDROCARBON GASES
AND THEIR GASEOUS MIXTURES AT HIGH PRESSURE****Discussion**

Equation (11B4.1-1) is to be used for estimating the effect of pressure on gas viscosity. The equation may be applied at all pressures above the critical temperature. Below the critical temperature, the pressure must be less than the saturation pressure.

$$(\mu - \mu_0)\xi = 10.8 \times 10^{-4} [\exp(1.439\rho_r) - \exp(-1.11\rho_r^{1.88})] \quad (11B4.1-1)$$

$$\xi = 5.440 \frac{T_c^{16}}{M^{1/2} p_c^{23}} \quad (11B4.1-2)$$

Where:

- μ = viscosity, in centipoises.
- μ_0 = viscosity at low pressure, in centipoises.
- ρ_r = reduced density, ρ/ρ_c .
- ρ = density, in pounds per cubic foot.
- ρ_c = critical density, $1/V_c$, in pounds per cubic foot.
- V_c = critical volume, in cubic feet per pound.
- T_c = critical temperature, in degrees Rankine.
- M = molecular weight
- p_c = critical pressure, in pounds per square inch absolute.

For a mixture, the pseudocritical temperature, pseudocritical pressure, and mixture molecular weight are necessary. The following are summaries of the definition:

$$T_{pc} = \sum_{i=1}^n x_i T_{ci} \quad (11B4.1-3)$$

Where:

- T_{pc} = pseudocritical temperature, in degrees Rankine.
- n = number of components in the mixture.
- x_i = mole fraction of component i.
- T_{ci} = critical temperature of component i, in degrees Rankine.

$$p_{pc} = \sum_{i=1}^n x_i p_{ci} \quad (11B4.1-4)$$

Where:

- p_{pc} = pseudocritical pressure, in pounds per square inch absolute.
- p_{ci} = critical pressure of component i.

$$M_m = \sum_{i=1}^n x_i M_i$$

Where:

M_m = molecular weight of mixture.

M_i = molecular weight of component i.

Procedure

Step 1: Obtain the critical temperatures, critical pressures, critical volumes, and molecular weights from Chapter 1. Obtain the viscosity of the gas components at low pressure from Procedure 11B1.1, or Procedure 11B1.3 may also be used to predict the pure component viscosity.

For a pure compounds, proceed to Step 2; for a mixture, proceed to Step 4.

Step 2: Calculate the value of ξ using Equation (11B4.1-2).

Step 3: Obtain the density of the gas from the procedures of Chapter 6 and calculate the reduced density from this and from the critical volume obtained in Step 1. Proceed to Step 8.

Step 4: Calculate the low-pressure viscosity of the mixture using Procedure 11B2.1.

Step 5: Calculate the pseudocritical temperature and pseudocritical pressure using Equations (11B4.1-3) and (11B4.1-4) and the molecular weight using Equation (11B4.1-5).

Step 6: Calculate the value of ξ using Equation (11B4.1-2) with these pseudocritical values and the molecular weight.

Step 7: Calculate the density of the gas at the critical point and at the temperature and pressure of the gas mixture using the procedures of Chapter 6. Calculate the reduced density.

Step 8: Calculate the viscosity of the gas using Equation (11B4.1-1).

COMMENTS ON PROCEDURE 11B4.1

Purpose

This procedure is presented for estimating the viscosities of gases and gas mixtures at high pressures (reduced pressures greater than 0.6) using the low-pressure viscosity as calculated from the preceding methods for the base value.

Limitations

The procedure should not be applied to nonhydrocarbon gases (O_2 , N_2 , CO_2 , etc.).

The equation may be applied at all pressures above the critical temperature. Below the critical temperature it may be applied up to the saturation pressure.

Reliability

Errors between calculated and experimental viscosities are about 5.3 percent using the method. Nonhydrocarbons show larger average deviations (9 percent). If experimental densities are used, the error can be expected to be reduced by about 0.5 percent. The method has approximately the same accuracy for mixtures as for pure compounds provided the molecular weight range is narrow.

Literature Sources

The forms of Equation (11B4.1-1) and (11B4.1-2) were originally suggested by Eakin and Ellington, *J. Petrol. Technol.* 15 [2] 210 (1963) [Eakin, Ph.D. dissertation, Illinois Institute of Technology, Chicago, Illinois (1962)] and were modified by Jossi et al., *AIChE Journal* 8 59 (1962). The final form of Equation (11B4.1-1) and its application to mixtures was given by Dean and Stiel, *AIChE Journal* 11 526 (1965).

Example

Calculate the viscosity of a mixture containing 60 mole percent methane and 40 mole percent propane at 1500 pounds per square inch absolute and 257 F.

From Procedure 11B2.1, the viscosity of the mixture at 1 atmosphere is calculated to be 0.0123 centipoise.

From Chapter 1, the critical pressures, critical temperatures, and molecular weights are obtained.

Component	Critical Pressure (pounds per square inch absolute)	Critical Temperature (F)	Molecular Weight
Methane	667.04	-116.66	16.04
Propane	616.13	206.02	44.10

Hence, the pseudocritical properties and molecular weight of the mixture are as follows:

$$T_{pc} = (0.60)(459.7 - 116.66) + (0.40)(459.7 + 206.02) = 472.09 R$$

$$p_{pc} = (0.60)(667.04) + (0.40)(616.13) = 646.68 \text{ pounds per square inch absolute}$$

$$M_m = (0.60)(16.04) + (0.40)(44.10) = 27.264$$

Using Equation (11B4.1-2),

$$\eta \xi = \frac{5.440 \times (472.09)^{16}}{(27.264)^{12}(647.7)^{23}} = 0.0388$$

From Chapter 6, the reduced density is calculated.

$$\rho_r = 0.5283$$

Using Equation (11B4.1-1),

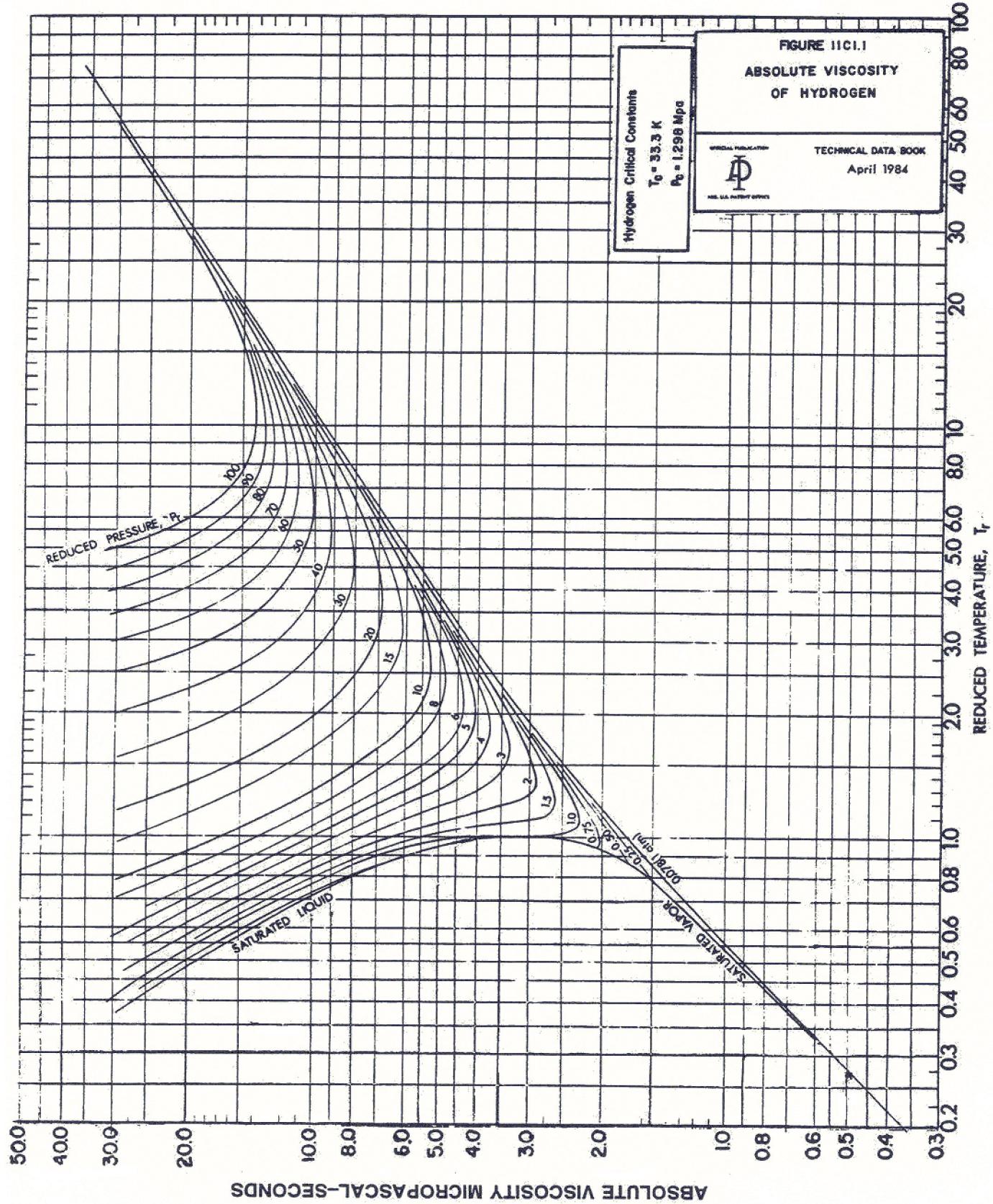
$$\begin{aligned} (\mu - \mu_o) \xi &= 10.8 \times 10^{-5} \{ \exp[(1.439)(0.5283)] - \exp[-1.11(0.5283)^{1.858}] \} \\ &= 1.5405 \times 10^{-4} \\ (\mu - \mu_o) &= 3.970 \times 10^{-3} \text{ centipoise} \end{aligned}$$

Given that μ_o is 0.0123 centipoise,

$$\mu = 0.01627 \text{ centipoise}$$

The experimental value is 0.01670 centipoise.

11C1.1



COMMENTS ON FIGURE 11C1.1**Purpose**

Figure 11C1.1 is to be used to estimate the viscosity of gaseous and liquid hydrogen.

Limitations

At temperatures above 5000 F, hydrogen dissociates into atomic hydrogen. Figure 11C1.1 does not make a correction for this change in structure. Also, the figure is based on a limited amount of experimental high-pressure data.

Reliability

An average error of 3 percent can be expected at atmospheric pressure with increasing errors as the pressure increases.

Literature Source

The figure was taken from Stiel and Thodos, *Ind. Eng. Chem. Fundamentals* 2 233 (1963).

Example

Estimate the viscosity of hydrogen at 570 F and 14.7 pounds per square inch absolute.

From Figure 11C1.1, the critical temperature of hydrogen is 59.9 R and the critical pressure is 188.2 pounds per square inch absolute.

$$T_r = \frac{570 + 459.7}{59.9} = \frac{1029.7}{59.9} = 17.19$$

$$p_r = \frac{14.7}{188.2} = 0.078$$

From Figure 11C1.1, the viscosity is estimated to be 0.0135 centipoise.

The experimental value is 0.0138 centipoise.

PROCEDURE 11C1.2

VISCOSEITY OF GASEOUS NONHYDROCARBONS
AT HIGH PRESSURE

Discussion

Equations (11C1.2-1) and (11C1.2-2) should be used to calculate the viscosity of gaseous nonhydrocarbons at high pressure.

$$\frac{\mu}{\mu_0} = A_1 \left(\frac{h}{P_r} \right) + A_2 \left(\frac{k}{P_r^1} + \frac{m}{P_r^2} + \frac{n}{P_r^3} \right) \quad (11C1.2-1)$$

$$A_1 = \left(a_1 T_r^{b_1} + c_1 T_r^{d_1} + e_1 T_r^{f_1} + g_1 \right) \quad (11C1.2-2)$$

$$\begin{aligned} a_1 &= 83.8970 \\ b_1 &= 0.0105 \\ c_1 &= 0.6030 \\ d_1 &= -0.0822 \\ e_1 &= 0.9017 \\ f_1 &= -0.1200 \\ g_1 &= -85.3080 \end{aligned}$$

$$\begin{aligned} a_2 &= 1.5140 \\ b_2 &= -11.3036 \\ c_2 &= 0.3018 \\ d_2 &= -0.6856 \\ e_2 &= 2.0636 \\ f_2 &= -2.7611 \\ g_2 &= 0 \end{aligned}$$

$$\begin{aligned} h &= 1.5071 \\ j &= -0.4487 \\ k &= 11.4789 \\ l &= 0.2606 \\ m &= -12.6843 \\ n &= 0.1773 \\ p &= 1.6953 \\ q &= -0.1052 \end{aligned}$$

where:

- $\frac{\mu}{\mu_0}$ = viscosity ratio
- μ = viscosity at T and P, in centipoises
- μ_0 = viscosity at T and 1 atmosphere of pressure, in centipoises
- T = temperature, in degrees Rankine
- T_c = critical temperature, in degrees Rankine
- T_r = reduced temperature = T/T_c
- P = pressure, in pounds per square inch absolute
- P_c = critical pressure, in pounds per square inch absolute
- P_r = reduced pressure = P/P_c
- A_1, A_2, \dots, Q = constants as defined in above table

Once the viscosity ratio is calculated, the viscosity for the gaseous nonhydrocarbon can be calculated using Equation (11C1.2-3).

$$\mu = (\mu/\mu_0) \cdot \mu_0 \quad (11C1.2-3)$$

where:

- μ = viscosity at T and P, in centipoises
- $\frac{\mu}{\mu_0}$ = viscosity ratio
- μ_0 = viscosity at T and 1 atmosphere of pressure, in centipoises

Procedure

Step 1: Calculate values for the reduced temperature and reduced pressure for the gaseous non-hydrocarbon using methods outlined in Chapter 4.

Step 2: Using the values for T_r and P_r from Step 1, calculate the viscosity ratio using Equations (11C1.2-1) and (11C1.2-2).

Step 3: Calculate the viscosity of the nonhydrocarbon by using Equation (11C1.2-3).

COMMENTS ON PROCEDURE 11C1.2

Purpose

Procedure 11C1.2 is presented for estimating the viscosities of gaseous nonhydrocarbons at high pressures ($P_r > 0.6$) using low-pressure input viscosities from the preceding methods. Procedure 11B4.1 is not recommended for hydrocarbons, although this method is also applicable as shown by example B.

Reliability

Procedure 11C1.2 yielded an average error of 4.4 percent before a regression was performed. The average error for the regression was slightly higher than 7 percent.

Special Comment

For pressures below the lower limit of Procedure 11C1.2 (i.e. $P_r < 0.6$), the gas may be assumed to be ideal and the preceding methods outlined in Chapter 11 may be used without correcting for the pressure.

Literature Source

Procedure 11C1.2 was adapted from a figure from Carr, et al., *Chem. Eng. Prog. Symp. Ser. No. 16* 51 91 (1955).

Examples

A. Calculate the viscosity of nitrogen at -58.0 F and 1677.0 pounds per square inch absolute.

1) From Figure 11C1.2, the viscosity of nitrogen at 1 atmosphere and -58.0 F is 0.0144 centipoise.

2) From Chapter 1, for nitrogen

$$\begin{aligned} P_c &= 493.1 \text{ pounds per square inch absolute} \\ T_c &= -232.5 \text{ F} \end{aligned}$$

For the conditions given, the reduced temperature and pressure are as follows:

$$P_r = \frac{1677.0}{493.1} = 3.4$$

$$T_r = \frac{-58.0 + 459.7}{-232.5 + 459.7} = 1.767$$

3) Using the reduced conditions and Equations (11C1.2-1) and (11C1.2-2), the viscosity ratio, μ/μ_o , is found to be 1.41.

4) Using Equation (11C1.2-3), the viscosity at the desired temperature and pressure is

$$\mu = \left(\frac{\mu}{\mu_o} \right) \mu_o = (1.41)(0.0144)$$

$$= 0.0203 \text{ centipoise}$$

The experimental value is 0.01869 centipoise.

B. Calculate the viscosity of a mixture containing 60 mole percent methane and 40 mole percent propane at 1500 pounds per square inch absolute and 257 F.

1) From Procedure 11B2.1, the viscosity at the mixture at 1 atmosphere is calculated to be 0.0123 centipoise.

2) From Chapter 1, the critical pressures and temperature are obtained.

Component	Critical Pressure (pounds per square inch absolute)	Critical Temperature (F)
Methane	667.8	-116.6
Propane	616.3	206.0

$$P_r = \frac{1500}{(0.60)(667.8)+(0.40)(616.3)} = 2.32$$

$$T_r = \frac{257 + 459.7}{(0.60)(-116.6 + 459.7) + (0.40)(206.0 + 459.7)} = 1.52$$

3) Using the reduced conditions and Equations (11C1.2-1) and (11C1.2-2), the viscosity ratio, μ/μ_o , is found to be 1.41.

4) Using Equation (11C1.2-3), the viscosity at the desired temperature and pressure is

$$\mu = \mu/\mu_o \cdot \mu_o = (1.41)(0.0123) = 0.0173 \text{ centipoise}$$

The experimental value is 0.0167 centipoise.

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CHAPTER 12

THERMAL CONDUCTIVITY

12-0 INTRODUCTION

Thermal conductivity is that physical property which describes the ease with which heat can flow by conduction through a quiescent solid, liquid, or gaseous layer of a substance. It is defined as the proportionality constant, k , in, Fourier's law of heat conduction, in Btu per (hr)(sq ft)(deg F) per ft. The variation of thermal conductivity for different temperatures, pressures, chemical compositions, and physical states may be viewed in a general and simplified manner by considering the orderliness of the substance. For a single chemical compound, the order and, hence, thermal conductivity increases in the sequence: vapor, liquid, amorphous solid, crystal. Although this is largely true for intersubstance comparisons also, there are exceptions. For instance, gaseous hydrogen has a higher thermal conductivity than does liquid benzene, and water has a higher thermal conductivity than does wood.

The thermal conductivity of most liquids decreases with increasing temperature. This is primarily a function of density (and order); however, the velocity of sound likewise decreases with temperature for organic liquids. For some liquids, the velocity of sound increases with temperature. This effect may overshadow the effect of density, resulting in a rise in conductivity with a rise in temperature. For water, the conductivity first rises to a maximum and then falls with increasing temperature.

Inasmuch as a low-pressure gas is almost completely disordered, decreasing order with increasing temperature is not a strong factor. The thermal conductivity of such a gas is instead a strong function of viscosity and heat capacity at constant volume. Accordingly, it increases with temperature as do these two properties.

The thermal conductivity of all nonmetallic materials increases with pressure (and order). A detailed treatment of various pressure regions is not as simple as a mere density function might indicate. At higher pressure, anomalies appear in the temperature function.

By disturbing the order of a material, impurities have disproportionate effects in reducing conductivities. Accordingly, hydrocarbon liquid and gas mixtures do not usually obey simple mixing rules.

Thermal conductivities of substances are required in correlations and design methods for heat transfer operations. The thermal conductivity may be used directly or in dimensionless numbers such as the Prandtl, Nusselt, and Graetz numbers. Unfortunately, some of the design correlations involving these dimensionless numbers were based on questionable experimental data. The user should be aware of this when designing for crucial service.

In this chapter, means are provided for estimating the required thermal conductivities in the liquid and gas phases for pure and mixed hydrocarbons and for nonhydrocarbon gases. When considering the use of new thermal conductivity data versus the use of recommended correlations, vapor-phase data obtained by a conscientious investigator almost always are reliable; whereas liquid data obtained before the introduction of transient measurement techniques may very well be in considerable error. Experimental problems with simultaneous convective heat transfer have a much stronger effect on the results for liquids than on those for vapors.

The various methods for determining the thermal conductivity of hydrocarbons and their

mixtures are listed in Table 12-0.1 and Figure 12-0.2.

Liquid Systems

The thermal conductivities of liquids are independent of pressure (relative to the accuracy of existing data and correlations) below approximately 500 pounds per square inch absolute and decrease linearly as temperature increases from the freezing point to the normal boiling point. This linearity is believed to continue to a reduced temperature of approximately 0.8, where thermal conductivity begins to decrease more rapidly as the critical point is approached (159). Data for the conductivities at the freezing and normal boiling points, which were selected on the basis of reliability, are given in Procedure 12A1.1. A value at an intermediate temperature may be obtained by linear interpolation.

Procedure 12A1.2 provides a general but slightly less accurate method for calculating the thermal conductivity of pure hydrocarbons below a pressure of 500 pounds per square inch absolute and a reduced temperature of 0.8. Procedure 12A1.3 can be used to obtain the thermal conductivity of liquid hydrocarbons at the higher reduced temperatures and at any pressure.

For mixtures of known composition at any temperature and pressure, Procedure 12A2.1 includes a mixing rule involving conductivities of the pure components at the same conditions. Procedure 12A3.1 allows estimation of low-pressure thermal conductivities of undefined liquid hydrocarbons and should be used only when Procedure 12A2.1 or Procedure 12A3.2 cannot be applied. Procedure 12A3.2 calculates the low-pressure thermal conductivities of characterized undefined liquid hydrocarbons and gives better accuracy than Procedure 12A3.1. Procedure 12A3.3 allows estimation of low-pressure thermal conductivities of petroleum fractions blended with defined light hydrocarbon liquid mixtures. Procedure 12A4.1 is a correction for obtaining high-pressure conductivities from the previously obtained low-pressure values.

Gaseous Systems

The thermal conductivity of an ideal gas is independent of pressure. Pure-component vapor thermal conductivities can be calculated analytically as a function of temperature by using Procedure 12B1.1. When required data are unavailable, Procedure 12B1.2 should be used to estimate ideal gas thermal conductivity values for pure components.

For mixtures of known composition, the thermal conductivities of the pure components should be blended at the desired conditions as outlined in Procedure 12B2.1. Procedure 12B3.1 provides a means of estimating the ideal gas thermal conductivity of undefined hydrocarbon mixtures. Procedure 12B4.1 is a correction to be applied to the ideal gas thermal conductivity estimates from the earlier correlations for the effect of high pressure.

The thermal conductivity of pure gaseous hydrogen is given in Procedure 12C1.4. For defined mixtures of hydrogen with hydrocarbons, use the given mixing rules and Procedure 12A2.1 for liquids or Procedure 12B2.1 for gases. For mixtures of hydrogen with petroleum fractions, use these same mixing rules, treating the entire hydrocarbon portion as a pseudocomponent. The hydrocarbon input data are available from Procedure 12A3.1 for liquids or Procedure 12B3.1 for vapors, and the pressure correction (where necessary) should be applied before blending.

Thermal conductivities of other pure nonhydrocarbon gases are obtained by Procedure 12C1.1

through Procedure 12C1.3, Procedure 12C1.5, Fig. 12C1.6, Procedure 12C1.7, Figures 12C1.8 and 12C1.9, and Procedures 12C1.10 and 12C1.11. The same procedures that apply to hydrogen should be appropriate for these gases.

Commercial Computer Methods for Liquid and Vapor Thermal Conductivities

The SUPERTRAPP software package developed at and available from NIST (National Institute of Standards and Technology) is a commercially available software package. The method is based on corresponding states principles. It is capable of predicting the thermal conductivity of nonpolar pure fluids and mixtures over the temperature range of 40 - 1800 Rankine and the pressure range of 0 - 43500 psia. The available SUPERTRAPP database contains 116 compounds although new compounds may be added to the database. The absolute minimum information required for a new compound is the critical temperature, pressure, and volume, the molecular weight, and the normal boiling point; liquid density and vapor pressure data could also be added to improve the accuracy of the method. The main advantage of this commercial software is its ability to handle fluids over wide temperature and pressure ranges in one method.

Another software package for the prediction of thermal conductivity of liquid petroleum fractions is under development at NIST.

TABLE 12-0.1 - THERMAL CONDUCTIVITY OF HYDROCARBONS

Hydrocarbons	Pressure (psia)	Temperature*	Method	Notes
Pure Liquids	<500	T_f to T_b	Procedure 12A1.1	-
	<500	$0.25 < T_r < 0.8$	Procedure 12A1.2	Use only when Procedure 12A1.1 inapplicable
	<500	$0.8 < T_r < 1.0$	Procedure 12A1.3	-
	≥ 500	$T_r < 1.0$	Procedure 12A4.1	Input from Procedures 12A1.1 or 12A1.2
Known Liquid Mixtures	All	All	Procedure 12A2.1	Input from methods above, <i>not</i> Procedure 12A3.1
Liquid Petroleum Fractions	All	-58 to 752 F	Procedure 12A3.1	Used only for non-characterized fractions. For pressures greater than 500 psia, apply Procedure 12A4.1 to correct the pressure
	All	-58 to 752 F	Procedure 12A3.2	Used only for characterized fraction. For pressures greater than 500 psia, apply Procedure 12A4.1 to correct the pressure
Liquid Petroleum Fraction Blended With Light Liquid Hydrocarbon Mixture	All	-58 to 752 F	Procedure 12A3.3	For pressures greater than 500 psia, apply Procedure 12A4.1 to correct the pressure
Pure Gases	≤ 50	As shown	Procedure 12B1.1	-
	≤ 50	All	Procedure 12B1.2	Use only when Procedure 12B1.1 does not apply
	> 50	All	Procedure 12B4.1	Input from above
Known Gas Mixtures	All	All	Procedure 12B2.1	For pressures greater than 50 psia, apply Procedure 12B4.1 to correct the pressure
Petroleum Fraction Vapors	All	-60 to 600F	Procedure 12B3.1	For pressures greater than 50 psia, apply Procedure 12B4.1 to correct the pressure

* T_f =freezing point; T_b =normal boiling point; T_r =reduced temperature (T/T_c); T = temperature; and T_c =critical temperature.

Figure 12-0.2 Hydrocarbon Thermal Conductivity Calculation Procedure

	Freezing Point ^a	Thermal Conductivity at Freezing Point ^b	Normal Boiling Point ^c	Thermal Conductivity at Normal Boiling Point ^d
2-Methylpropene.....	-220.61	0.1083	19.58	0.06773
1-Hexene.....	-219.57	0.1024	146.26	0.06205
<i>trans</i> -2-Hexene.....	-207.36	0.09564	154.17	0.06357
1-Heptene.....	-181.98	0.09644	200.55	0.06029
<i>trans</i> -2-Heptene.....	-165.06	0.09322	208.31	0.06156
<i>trans</i> -3-Heptene.....	-213.93	0.09684	204.21	0.06159
1-Octene.....	-151.06	0.08981	250.32	0.06066
<i>trans</i> -2-Octene.....	-125.86	0.09081	257.00	0.06022
1-Nonene.....	-114.47	0.09052	296.36	0.05333
1-Decene.....	-87.27	0.08830	339.08	0.05554
Cyclohexene.....	-154.26	0.09548	181.35	0.06740
2-Methyl-1,3-butadiene.....	-220.00 ^e	0.1049 ^f	93.30	0.06817
Benzene.....	41.95	0.08631	176.16	0.07313
Methylbenzene (Toluene).....	-138.95	0.09336	231.13	0.06452
Ethylbenzene.....	-138.91	0.09106	277.16	0.05921
1,2-Dimethylbenzene (<i>o</i> -Xylene)....	-13.31	0.08263	291.97	0.06009
1,3-Dimethylbenzene (<i>m</i> -Xylene)....	-54.13	0.08525	282.42	0.05979
1,4-Dimethylbenzene (<i>p</i> -Xylene)....	55.87	0.07664	281.05	0.05958
<i>n</i> -Propylbenzene.....	-147.28	0.08827	318.63	0.05856
Isopropylbenzene.....	-140.82	0.08588	284.00 ^g	0.05736 ^h
1,2,4-Trimethylbenzene.....	-46.88	0.08322	336.88	0.05726
1,3,5-Trimethylbenzene.....	-48.51	0.08703	328.53	0.06028
<i>n</i> -Butylbenzene.....	-126.13	0.08672	361.95	0.05530
<i>tert</i> -Butylbenzene.....	-72.18	0.07534	336.47	0.05534
Biphenyl.....	156.60	0.08021	491.00	0.06393
<i>o</i> -Terphenyl.....	133.16	0.07687	639.50	0.05927
<i>m</i> -Terphenyl.....	188.33	0.07814	710.33	0.06650
<i>p</i> -Terphenyl.....	413.33	0.07480	708.80	0.06256

^aT_f, deg F.^bK_f, Btu per (hr)(sq ft)(deg F) per ft.^cT_b, deg F.^dK_b, Btu per (hr)(sq ft)(deg F) per ft.^eT_l, lower limit of the temperature range, deg F.^fK_l, thermal conductivity at the lower limit of the temperature range, Btu per (hr)(sq ft)(deg F) per ft.^gT_u, upper limit of the temperature range, deg F.^hK_u, thermal conductivity at the upper limit of the temperature range, Btu per (hr)(sq ft)(deg F) per ft.

Procedure

Step 1: From the preceding tabulation, obtain the thermal conductivities of the compound at the freezing point and the normal boiling point.

Step 2: Calculate the thermal conductivity of the liquid by linearly interpolating between these values.

COMMENTS ON PROCEDURE 12A1.1

Purpose

Procedure 12A1.1 is presented to calculate the thermal conductivities of pure liquid hydrocarbons at pressures lower than 500 pounds per square inch absolute from available experimental data. For higher pressures, the correction in Fig. 12A4.1 should be applied. This procedure is not applicable above the normal boiling point, where Procedure 12A1.3 should be used. Within its range of applicability, this procedure is somewhat more accurate than is Procedure 12A1.2.

Limitations

Within a few degrees of freezing point, the thermal conductivity rises more sharply than indicated by the simple interpolation relationship because of clustering of the molecules in anticipation of solidification. This phenomenon can usually be safely ignored in calculation.

Do not extrapolate the data to temperatures above the normal boiling point.

Reliability

Average deviations of values calculated by this procedure from experimental data are less than 5 percent.

Literature Sources

The entries in the tabulation were derived from data from the following sources:

Methane (13,14,86,147)	Cyclohexane (43,56,107,156,167)
Propane (18,129,145,153)	Methylcyclohexane (17,82,124,156)
<i>n</i> -Butane (18)	2-Methylpropene (43,152)
2-Methylpropane (58)	1-Hexene (18,43,110)
<i>n</i> -Pentane (14,15,18,122,142,154,155)	<i>trans</i> -2-Hexene (142,155,157)
<i>n</i> -Hexane (9,18,56,75,82,124,142,144, 157,168)	1-Heptene (18,108)
2-Methylpentane (157)	<i>trans</i> -2-Heptene (157)
3-Methylpentane (157)	<i>trans</i> -3-Heptene (156)
2,2-Dimethylbutane (157)	1-Octene (109,157)
2,3-Dimethylbutane (157)	<i>trans</i> -2-Octene (157)
<i>n</i> -Heptane (9,10,18,56,82,105,105,120 124,139,142,155,157)	1-Nonene (103)
2,4-Dimethylpentane (156)	1-Decene (103)
<i>n</i> -Octane (18,19,56,116,120,124,142, 144,157,168)	Cyclohexene (43,142,155,156)
2,2,4-Trimethylpentane (19,92,124,142, 155,157)	2-Methyl-1,3-butadiene (18)
<i>n</i> -Nonane (18,19,45,141,142,144,157)	Benzene (17,27,48,56,77,92,120,131,140, 159,167,175)
2,2,5-Trimethylhexane (124,157)	Methylbenzene (10,18,38,41,45,47,53, 83,105,118,120,124,131,132,133, 136,140,171,175,185)
<i>n</i> -Decane (9,17,18,25,45,56,82,114, 116,157,168)	Ethylbenzene (56,136,140)
<i>n</i> -Dodecane (56,156,168)	1,2-Dimethylbenzene (<i>o</i> -Xylene) (8,45,56, 124,136,140,171)
<i>n</i> -Tridecane (101)	1,3-Dimethylbenzene (<i>m</i> -Xylene) (8,56,136, 142,155,171)
<i>n</i> -Tetradecane (15,19,102,156,180)	1,4-Dimethylbenzene (<i>p</i> -Xylene) (3,8,56, 120,136,142,155,171)
<i>n</i> -Pentadecane (15,98,180)	<i>n</i> -Propylbenzene (46)
<i>n</i> -Hexadecane (15,98,156,180)	Isopropylbenzene (46,56,88,142,155,156)
<i>n</i> -Heptadecane (100,111,134)	1,2,4-Trimethylbenzene (135)
<i>n</i> -Octadecane (100,111,134,156)	1,3,5-Trimethylbenzene (135,140)
<i>n</i> -Nonadecane (98,100,115)	<i>n</i> -Butylbenzene (136,156)
<i>n</i> -Eicosane (138)	<i>tert</i> -Butylbenzene (135)
Heneicosane (138)	Biphenyl (47,184)
Docosane (98,138)	<i>o</i> -Terphenyl (48)
Tricosane (138)	<i>m</i> -Terphenyl (48)
Tetracosane (98,138)	<i>p</i> -Terphenyl (48)
Cyclopentane (43,124,156)	
Methylcyclopentane (17,142,154,156)	

Example

Find the thermal conductivity of *n*-hexane at 68 F and atmospheric pressure.

From the preceding tabulation, $k_f = 0.09375$ at $T_f = -139.58$ F and $k_b = 0.06022$ at $T_b = 155.71$ F. Interpolating linearly,

$$k = 0.09375 - \frac{68 - (-139.58)}{155.71 - (-139.58)} (0.09375 - 0.06022)$$

$$k = 0.09375 - 0.02357 = 0.07018 \text{ Btu per (hr)(sq ft)(deg F) per ft}$$

The experimental value (18) is 0.07032 Btu per (hr)(sq ft)(deg F) per ft.

PROCEDURE 12A1.2

THERMAL CONDUCTIVITY OF PURE LIQUID HYDROCARBONS AT LOW PRESSURES, GENERALIZED METHOD

Discussion

The following equation is to be used to obtain the thermal conductivity of pure liquid hydrocarbons at pressures below 500 pounds per square inch absolute and at reduced temperatures between 0.25 and 0.80:

$$K = \frac{CM^n}{V_m} \left[\frac{3+20(1-T_r)^{2/3}}{3+20\left(1-\frac{527.67}{T_c}\right)^{2/3}} \right] \quad (12A1.2-1)$$

Where:

- k = thermal conductivity, in Btu per (hr)(sq ft)(deg F) per ft.
- C = coefficient obtained from the tabulation below.
- n = coefficient obtained from the tabulation below.
- M = molecular weight
- V_m = molar volume at 68 F, in cubic feet per lb-mole.
- T_r = reduced temperature, T/T_c .
- T = temperature, in degrees Rankine.
- T_c = critical temperature, in degrees Rankine.

	n	C
For unbranched, straight chain hydrocarbon:	1.001	1.676×10^{-3}
For branched and cyclic hydrocarbons:	0.7717	4.079×10^{-3}

Procedure

- Step 1:* Obtain the critical temperature, T_c , and the molecular weight from Chapter 1.
- Step 2:* Calculate the reduced temperature ($T_r = T/T_c$).
- Step 3:* Determine the coefficients n and C from the preceding tabulation.
- Step 4:* Determine the density of the hydrocarbon at 68 F according to the methods in Chap. 6.
- Step 5:* Determine the molar volume at 68 F by dividing the molecular weight by the density of the hydrocarbon.
- Step 6:* Calculate the thermal conductivity by using equation (12A1.2-1).

COMMENTS ON PROCEDURE 12A1.2

Purpose

When Procedure 12A1.1 is applicable, it should be used in preference. Procedure 12A1.2 is presented to calculate the thermal conductivity of pure liquid hydrocarbons as a function of temperature at pressures less than 500 pounds per square inch absolute. For higher pressures, apply the correction outlined in Figure 12A4.1.

Limitations

Equation (12A1.2-1) is not accurate for pressures greater than 500 pounds per square inch absolute or at reduced temperatures less than 0.25 or greater than 0.80. At reduced temperatures greater than 0.80, Procedure 12A1.3 should be used.

Reliability

The equation yields data with an average error of 5 percent and a maximum error of 20 percent from experimental values.

Literature Sources

This procedure is based on methods presented by Pachaiyappan, Ibrahim, and Kuloor, *Chem. Eng.* 74[4] 140 (1967) and Riedel, *Chem.-Ingr.-Tech.* 21 349 (1949).

Example

Calculate the thermal conductivity of liquid *n*-butylbenzene at 140 F and 1 atm.

From Chapter 1 the molecular weight is 134.22 and the critical temperature is 729.32 F. The reduced temperature is therefore $\frac{140 + 459.67}{729.32 + 459.67} = 0.5044$. For *n*-butylbenzene, the coefficients n and C from the tabulation are 0.7717 and 4.079×10^{-3} , respectively. From Chapter 6, the density at 68 F is 53.76 lb per cu ft. The molar volume at 68 F is therefore $134.22/53.76 = 2.497$ cu ft per lb-mol.

The thermal conductivity is calculated next from equation (12A1.2-1):

$$K = \left[\frac{(4.079 \times 10^{-3})(134.22)^{0.7717}}{2.497} \right] \left[\frac{3 + 20(1 - 0.5044)^{2/3}}{3 + 20 \left(1 - \frac{527.67}{(729.32 + 459.67)} \right)^{2/3}} \right]$$

$$K = 0.06730 \text{ Btu per (hr)(sq ft)(deg F) per ft}$$

The experimental value (136) at these conditions is 0.06830 Btu per (hr)(sq ft)(deg F) per ft.

PROCEDURE 12A1.3

THERMAL CONDUCTIVITY OF PURE LIQUID HYDROCARBONS ABOVE THE NORMAL BOILING POINT AND AT ALL PRESSURES

Discussion

The thermal conductivities of liquid hydrocarbons at temperatures greater than the normal boiling point and at any pressure are to be obtained from the following equations:

$$k = \frac{-1.884 \times 10^{-6} P_r^2 + 1.442 \times 10^{-3} P_r + \alpha \exp(\beta P_r)}{\lambda} \quad (12A1.3-1)$$

Where,

$$\alpha = \frac{7.137 \times 10^{-3}}{\beta^{3.322}} \quad (12A1.3-2)$$

$$\beta = 0.40 + \frac{0.986}{\exp(0.58 \lambda)} \quad (12A1.3-3)$$

$$\lambda = \frac{T_c^{1/6} M^{1/2}}{(P_c/14.696)^{2/3}} \quad (12A1.3-4)$$

k =thermal conductivity, in Btu per (hr)(sq ft)(deg F) per ft.

ρ_r =reduced density, $\rho/\rho_c=\rho V_c$.

ρ =density, in pounds per cubic foot.

ρ_c =critical density, in pounds per cubic foot.

V_c =critical volume, in cubic feet per pound.

T_c =critical temperature, in degrees Rankine.

M =molecular weight.

P_r =reduced pressure, P/P_c .

P_c =critical pressure, in psia.

P =pressure, in psia.

Procedure

Step 1: Obtain the critical temperature, critical pressure, critical volume, and molecular weight from Chapter 1.

Step 2: Calculate the reduced pressure, $P_r=P/P_c$.

Step 3: Determine λ from equation (12A1.3-4).

Step 4: Determine the density of the hydrocarbon according to the methods of Chapter 6 and obtain the reduced density, $\rho_r=\rho V_c$.

Step 5: Calculate β by using equation (12A1.3-3) and α by using equation (12A1.3-2).

Step 6: Calculate the thermal conductivity by using equation (12A1.3-1).

12A1.3

COMMENTS ON PROCEDURE 12A1.3

Purpose

Procedure 12A1.3 is presented to calculate the thermal conductivity of pure liquid hydrocarbons above the normal boiling point and at any pressure.

Limitations

At temperatures below the normal boiling point. Procedure 12A1.1 or 12A1.2 should be used with a pressure correction obtained from Figure 12A4.1 if required.

Reliability

Average errors of 8 percent can be expected, with maximum errors of -32 percent.

Literature Source

The procedure is adapted from Kanitkar and Thodos, *Can. J. Chem. Eng.* 47 427 (1969).

Example

Calculate the thermal conductivity of liquid *n*-heptane at 320 F and 197.4 atm.

From Chapter 1, the critical temperature is 512.69 F, the critical pressure is 397.41 psia, the critical volume is 0.0684 cu ft per lb, and the molecular weight is 100.2. The reduced pressure is $197.4 / (397.41 / 14.696) = 7.30$, and from equation (12A1.3-4):

$$\lambda = \frac{(512.69 + 459.67)^{1/6}(100.2)^{1/2}}{(397.41 / 14.696)^{2/3}}$$

$$\lambda = 3.497$$

From chapter 6, the density is determined to be 37.93 lb per cu ft, and the reduced density is therefore $(37.93)(0.0684) = 2.594$. By using equations (12A1.3-3) and (12A1.3-2), the values of β and α are calculated as follows:

$$\beta = 0.40 + \frac{0.986}{\exp[(0.58)(3.497)]}$$

$$\beta = 0.5297$$

$$\alpha = \frac{7.137 \times 10^{-3}}{(0.5297)^{3.322}}$$

$$\alpha = 0.05892$$

The thermal conductivity is then calculated by using equation (12A1.3-1):

$$k = \frac{(-1.884 \times 10^{-6})(7.30)^2 + (1.442 \times 10^{-3})(7.30) + 0.05892 \exp[(0.5297)(2.594)]}{3.497}$$

$$k = 0.06956 \text{ Btu per (hr)(sq ft)(deg F) per ft}$$

The experimental value (106) at these conditions is 0.06379 Btu per (hr)(sq ft)(deg F) per ft.

Procedure

- Step 1:* From Chap. 1, determine the molecular weight of each component of the mixture, and from Procedure 12A1.1 or 12A1.2, determine the thermal conductivity of each component at the conditions desired for the mixture.
- Step 2:* From Chap. 6, determine the density of each component of the mixture.
- Step 3:* Calculate the molar volume of each component as the molecular weight divided by the density.
- Step 4:* Calculate k_{ij} by using equation (12A2.1-2).
- Step 5:* Calculate the volume fraction of each component of the mixture by using equation (12A2.1-3) and check to determine that the sum of all the pure component volume fractions total 1, according to equation (12A2.1-4).
- Step 6:* Calculate the thermal conductivity of the mixture by using equation (12A2.1-1).

COMMENTS ON PROCEDURE 12A2.1

Purpose

Procedure 12A2.1 is presented for calculating the thermal conductivity of liquid hydrocarbon mixtures of known composition at any temperature and pressure from the pure-component data under the same conditions.

Reliability

Average deviations of values calculated by this procedure from experimental data are approximately 5 percent. Errors will rarely exceed 15 percent for hydrocarbons systems for which reliable pure-component input conductivities are available.

Special Comments

Procedures 12A1.1 and 12A1.2 should be used to obtain the pure-component input data for this procedure. For high pressures, the correction outlined in Figure 12A4.1 must be applied. To get pure-component conductivities near the critical point, use Procedure 12A1.3.

Although not recommended when the mixture composition is known, Figure 12A3.1 may be used for fast but less accurate estimates of mixture thermal conductivities. Figure 12A3.1 is the only method available to be used for a liquid mixture containing a component that is above its critical temperature.

Literature Source

The procedure is adapted from Li, *AIChE Journal* 22 927 (1976).

Example

Calculate the thermal conductivity of a 68-mole percent *n*-heptane-32-mole percent cyclopentane (i-j) mixture at 32 F and 1 atm. The experimental thermal conductivities of *n*-heptane and cyclopentane at these conditions (124) are 0.07639 and 0.08130 Btu per (hr)(sq ft)(deg F) per ft, respectively.

From Chapter 1, the molecular weights are 100.2 for *n*-heptane and 70.13 for cyclopentane. The density of *n*-heptane at these conditions is 43.85 lb per cu ft, and the density of cyclopentane is 47.60 lb per cu ft according to the methods of chapter 6. The molar volumes are determined to be (100.2/43.85)=2.285 cu ft per lb-mole for *n*-heptane and (70.13/47.60)=1.473 cu ft per lb-mol for cyclopentane. From equation (12A2.1-2), the value of k_{ij} is calculated as follows:

$$k_{ij} = 2 \left(\frac{1}{0.07639} + \frac{1}{0.08130} \right)^{-1}$$

$$k_{ij} = 0.07877 \text{ Btu per (hr)(sq ft)(deg F) per ft}$$

The volume fractions of the pure components are determined by using equation 912A2.1-3):

$$\text{*n*-heptane: } \phi_i = \frac{(0.68)(2.285)}{(0.68)(2.285) + (0.32)(1.473)} = 0.7672$$

12A2.1

$$\text{cyclopentane: } \phi_f = \frac{(0.32)(1.473)}{(0.68)(2.285) + (0.32)(1.473)} = 0.2328$$

As a check, the sum of the volume fraction is $(0.7672+0.2328)=1.0$, as required by equation (12A2.1-4).

The thermal conductivity of the mixture is calculated by using equation 912A2.1-5):

$$k_m = (0.7672)^2(0.07639) + 2(0.7672)(0.2328)(0.07877) + (0.2328)^2(0.08130)$$
$$k_m = 0.07751 \text{ Btu per (hr)(sq ft)(deg F) per ft}$$

The experimental value (124) at these conditions is 0.07714 Btu per (hr)(sq ft)(deg F) per ft.

PROCEDURE 12A3.1**THERMAL CONDUCTIVITY OF UNCHARACTERIZED LIQUID
PETROLEUM FRACTIONS AT LOW PRESSURES****Discussion**

The following equation is to be used to obtain the thermal conductivity of uncharacterized liquid petroleum fractions at low pressures and temperatures between 0-600 degrees Fahrenheit.

$$K = 0.07577 - 4.1 \times 10^{-5}T \quad (12A3.1-1)$$

Where:

K = thermal conductivity, in BTU per (hr)(sqft)(deg F) per ft.

T = temperature, in degrees Fahrenheit

Procedure

Step 1: Calculate the thermal conductivity of the fraction using equation (12A3.1-1).

COMMENTS ON PROCEDURE 12A3.1

Purpose

Procedure 12A3.1 allows quick estimation of thermal conductivity at low pressure as a function of temperature for any liquid hydrocarbon, although the procedure was developed for petroleum fractions. For pressures above 500 pounds per square inch absolute, correct the value from this procedure by using Procedure 12A4.1.

Limitations

This procedure is an oversimplification, inasmuch as molecular type and weight have not been correlated. Accordingly, Procedure 12A2.1 should be used in preference for mixtures for which the composition is known.

Reliability

Average errors of 10 percent can be expected from Procedure 12A3.1, with maximum errors of 40 percent.

Literature Sources

This Procedure is the best representative of data from the following sources: 11, 16, 41, 43, 51, 57, 65, 80, 127, 128, 130, 141, 170, 174.

Example

Calculate the thermal conductivity of atmospheric pressure of a liquid petroleum fraction with temperature of 550.6 F.

The thermal conductivity is calculated from equation (12A3.1-1)

$$K = 0.07577 - 4.1 \times 10^{-5} \cdot 550.6$$

$$K = 0.05320 \text{ BTU per (hr)(sqft)(deg F) per ft}$$

PROCEDURE 12A3.2**THERMAL CONDUCTIVITY OF LIQUID PETROLEUM FRACTIONS AT LOW PRESSURES****Discussion**

The following equation is to be used to obtain the thermal conductivity of characterized liquid petroleum fractions at low pressures.

$$k = \text{MeABP}^{0.2904} \cdot (9.961 \times 10^{-3} - 5.364 \times 10^{-6} \cdot T) \quad (12A3.2-1)$$

Where:

k = thermal conductivity, in Btu per (hr)(sq ft)(deg F) per ft.

MeABP = mean average boiling point, in degrees Rankine.

T = temperature, in degrees Fahrenheit.

Procedure

Step 1: Calculate the thermal conductivity of the fraction by using equation (12A3.2-1).

COMMENTS ON PROCEDURE 12A3.2

Purpose

Procedure 12A3.2 is presented to calculate the thermal conductivity of characterized liquid petroleum fractions at any temperature and low pressures.

Reliability

Average deviations of values calculated by this procedure from experimental data are approximately 6 percent, maximum deviations are 24 percent.

Special Comments

This procedure only applies to liquid petroleum fractions that are fully characterized, if the mean average boiling point is not known, it could be estimated by any two of the following characterization properties: Watson characterization factor, K, aniline point, carbon-to-hydrogen weight ratio, molecular weight by using Figure 2B6.1 of Chapter 2.

This procedure is applicable in the MeABP range of 607 R to 1545 R.

For mixtures that are not characterized at all, Fig. 12A3.1 should be used.

For high pressures, the correction outlined in Figure 12A4.1 must be applied.

Literature Source

This procedure was developed at The Pennsylvania State University.

Example

Calculate the thermal conductivity of a liquid petroleum fraction with mean average boiling point of 646.74 R at the temperature of 71.87 F.

The thermal conductivity is calculated from equation (12A3.2.1):

$$k = (646.74)^{0.2904} \cdot (9.961 \times 10^{-3} - 5.364 \times 10^{-6} \cdot 71.87)$$

$$k = 0.06272 \text{ Btu per (hr)(sq ft)(deg F) per ft}$$

The experiment value (127) at these conditions is 0.06402 Btu per (hr)(sq ft)(deg F) per ft.

PROCEDURE 12A3.3

THERMAL CONDUCTIVITY OF LIQUID PETROLEUM FRACTION BLENDED WITH DEFINED LIGHT HYDROCARBON LIQUID MIXTURES

Discussion

This procedure is used for the calculation of the thermal conductivity of a liquid petroleum fraction blended with a light hydrocarbon liquid mixture. Use equation (12A3.1-1) or equation (12A3.2-1) to obtain the thermal conductivity of the liquid petroleum fraction. Use Procedure 12A2.1 to obtain the thermal conductivity of the light hydrocarbon liquid mixtures. Then treat the light hydrocarbon liquid mixtures and the petroleum fractions as pseudocomponents, using Procedure 12A2.1 to calculate the thermal conductivity of the whole blend.

Procedure

- Step 1:* Obtain the thermal conductivity of the liquid petroleum fraction by using equation (12A3.1) or equation (12A3.2-1).
- Step 2:* Obtain the thermal conductivity of the defined light hydrocarbon liquid mixture by using Procedure 12A2.1 steps 1 through 6.
- Step 3:* Consider the liquid petroleum fraction and the light hydrocarbon liquid mixtures as pseudocomponents, and obtain the thermal conductivity of the blend by using Procedure 12A2.1 steps 1 through 6.

COMMENTS ON PROCEDURE 12A3.3

Purpose

Procedure 12A3.3 is presented to calculate the thermal conductivity of liquid petroleum fractions blended with defined light hydrocarbon liquid mixtures.

Example

Calculate the thermal conductivity of a mixture containing 60-mole percent liquid petroleum fraction with a mean average boiling point of 646.74 R and a specific gravity of 0.698 blended with 15-mole percent n-pentane(1), 10-mole percent n-hexane(2), and 15% benzene(3) at 60 F and 1 atm.

The molecular weight of the petroleum fraction is 94.257 as calculated from Chapter 2, the density is calculated as $(0.698)(62.27)=43.46$ lb per ft³, thus the molar volume is $(43.46)^{-1}(94.257)=2.1688$ ft³ per lbmol.

The thermal conductivity of the petroleum fraction is calculated from equation (12A3.1-1):

$$k = 0.07577 - 4.1 \times 10^{-5} (60.0)$$

$$k = 0.07331 \text{ Btu per (hr)(sq ft)(deg F) per (ft)}$$

The thermal conductivity of the defined light hydrocarbon liquid mixture (the molar fractions are normalized as 37.5 mole percent n-pentane, 25.0 mole percent n-hexane, and 37.5 mole percent benzene in order to treat the defined mixture as a pseudocomponent) is calculated from Procedure 12A2.1. From Procedure 12A1.1, the liquid thermal conductivities of n-pentane, n-hexane and benzene are 0.06772, 0.07109 and 0.08454 Btu per (hr)(sq ft)(deg F) per ft, respectively at the specified conditions. From Procedure 6A2.13 and Procedure 6A3.1 of Chapter 6, the molar volumes are determined to be 1.831 ft³/lbmol for n-pentane, 2.066 ft³/lbmol for n-hexane, 1.418 ft³/lbmol for benzene, and 1.7346 ft³/lbmol for the mixture. From equation (12A2.1-2), the values of k_{ij} is calculated as follows:

$$k_{12} = 2\left(\frac{1}{0.06772} + \frac{1}{0.07109}\right)^{-1} = 0.06936$$

$$k_{13} = 2\left(\frac{1}{0.06772} + \frac{1}{0.08454}\right)^{-1} = 0.07520$$

$$k_{23} = 2\left(\frac{1}{0.07109} + \frac{1}{0.08454}\right)^{-1} = 0.07723$$

The volume fractions of the pure components are determined by using equation (12A2.1-3):

$$\text{n-pentane: } \theta_1 = \frac{(0.375)(1.831)}{(0.375)(1.831)+(0.25)(2.066)+(0.375)(1.418)} = 0.3958$$

$$\text{n-hexane: } \theta_2 = \frac{(0.25)(2.066)}{(0.375)(1.831)+(0.25)(2.066)+(0.375)(1.418)} = 0.2977$$

$$\text{benzene: } \theta_3 = \frac{(0.375)(1.418)}{(0.375)(1.831)+(0.25)(2.066)+(0.375)(1.418)} = 0.3065$$

The thermal conductivity of the mixture is calculated by using equation (12A2.1-1):

$$k_m = \sum \sum \theta_i \theta_j k_{ij} = \theta_1^2 k_1 + \theta_2^2 k_2 + \theta_3^2 k_3 + 2\theta_1 \theta_2 k_{12} + 2\theta_1 \theta_3 k_{13} + 2\theta_2 \theta_3 k_{23}$$

$$k_m = (0.3958)^2(0.06772) + (0.2977)^2(0.07109) + (0.3065)^2(0.08454) + 2(0.3958)(0.2977)(0.06936)$$

$$+ 2(0.3958)(0.3065)(0.07520) + 2(0.2977)(0.3065)(0.07723)$$

$$k_m = 0.07354 \text{ Btu per (hr)(sq ft)(deg F) per (ft)}$$

The petroleum fraction(i) and the defined hydrocarbon liquid mixture(j) are treated as two pseudocomponents, and Procedure 12A2.1 is applied again to calculate the thermal conductivity of the blend. From equation (12A2.1-2), the values of k_{ij} is calculated as follows:

$$k_{ij} = 2\left(\frac{1}{0.07331} + \frac{1}{0.07354}\right)^{-1} = 0.07342$$

The volume fractions of the pseudocomponents are determined by using equation (12A2.1-3):

$$\text{liquid petroleum fraction: } \theta_i = \frac{(0.6)(2.1688)}{(0.6)(2.1688) + (0.4)(1.7346)} = 0.6522$$

$$\text{defined hydrocarbon liquid mixture: } \theta_j = \frac{(0.4)(1.7346)}{(0.6)(2.1688) + (0.4)(1.7346)} = 0.3478$$

The thermal conductivity of the blend is calculated by using equation (12A2.1-5):

$$k_m = (0.6522)^2(0.07331) + 2(0.6522)(0.3478)(0.07342) + (0.3478)^2(0.07354)$$

$$k_m = 0.07339 \text{ Btu per (hr)(sq ft)(deg F) per (ft)}$$

**PROCEDURE 12A4.1
THERMAL CONDUCTIVITY OF LIQUID HYDROCARBONS
AT HIGH PRESSURES**

Discussion

The following equations are to be used to obtain thermal conductivity for liquid hydrocarbons in the reduced temperature range 0.4-0.8 and pressures greater than 500 pounds per square inch absolute:

$$k_2 = k_1 \frac{C_2}{C_1} \quad (12A4.1-1)$$

$$C = 17.77 + 0.065 P_r - 7.764 T_r - \frac{2.065 T_r^2}{\exp(0.2 P_r)} \quad (12A4.1-2)$$

Where:

- k_2 = thermal conductivity at the desired temperature and pressure, in Btu per (hr)(sq ft) (deg F) per ft.
- k_1 = thermal conductivity at the same temperature and another pressure (usually atmospheric), in Btu per (hr)(sq ft)(deg F) per ft.
- C_1, C_2 = conductivity factors calculated from equation (12A4.1-2) corresponding to the reduced conditions applicable to k_1 and k_2 , respectively.
- P_r = reduced pressure P/P_c
- P = pressure, in pounds per square inch absolute
- P_c = critical pressure, in pounds per square inch absolute
- T_r = reduced temperature, T/T_c
- T = temperature, in degrees Rankine
- T_c = critical temperature in degrees Rankine

Procedure

- Step 1:* From Chapter 1 determine the critical temperature and critical pressure, then calculate the reduced temperature and reduced pressure.
- Step 2:* If the reduced temperature falls within the range .4-.8 then calculate C_1 and C_2 from equation (12A4.1-2).
- Step 3:* Find a literature value for the thermal conductivity of the liquid at the same temperature and different pressure.
- Step 4:* Calculate k_2 from equation (12A4.1-1).

COMMENTS ON PROCEDURE 12A4.1

Purpose

Procedure 12A4.1 is presented for estimating the effect of pressure on the thermal conductivities of liquid hydrocarbons when the pressure is greater than 500 pounds per square inch absolute.

Reliability

The average error in the pressure correction alone is approximately 5 percent, with a maximum error of 25 percent. The final thermal conductivity, k_2 , also is subject to error from the input value, k_1 .

Literature Source

The procedure was adapted from Lenoir, *Petroleum Refiner* 36[8] 162 (1957).

Example

Calculate the thermal conductivity of liquid toluene at 87.5 F and 22,044 psia. From Chapter 1, the critical temperature is 1065.22 R and the critical pressure is 595.90 psia. A literature value (53) for the thermal conductivity of the liquid at 87.5 F and 14.696 psia is $k = 0.07425$ Btu per (hr)(sq ft)(deg F) per ft. For this condition the reduced temperature is

$$\frac{87.5 + 459.67}{1065.22} = 0.5136 \text{ and the reduced pressure } P_{r_1} = \frac{14.696}{595.90} = 0.0247 . \text{ The reduced}$$

temperature falls within the range of .4 to .8. Using equation (12A4.1-2) the conductivity factor

$$C_1 = 17.77 + 0.065 * 0.024662 - 7.764 * 0.513646 - \frac{2.054 * 0.513646^2}{\exp(0.2 * 0.024662)} = 13.2444 .$$

For the evaluated pressure condition, the reduced temperature is also 0.5136 and the reduced pressure P_{r_2} is $\frac{22044}{595.90} = 36.993$. Using equation (12A4.1-2) the conductivity factor

$$C_2 = 17.77 + 0.065 * 36.993 - 7.764 * .513646 - \frac{2.054 * 0.5136^2}{\exp(0.2 * 36.993)} = 16.1863 .$$

By using equation (12A4.1-1), $k_2 = k_1 (C_2/C_1) = \frac{(0.07425)*(16.1863)}{13.2444} = 0.09074$ Btu per (hr)(sq ft)(deg F) per ft. An experimental value (53) is 0.09435 Btu per (hr)(sq ft)(deg F) per ft.

PROCEDURE 12B1.1
THERMAL CONDUCTIVITY OF PURE HYDROCARBON
GASES AT LOW PRESSURE

Discussion

The following equation is recommended for predicting the thermal conductivity of pure hydrocarbon gases at pressures below 50 pounds per square inch absolute:

$$k = A + BT + CT^2 \quad (12B1.1-1)$$

Where:

- k = thermal conductivity, in Btu per (hr)(sq ft)(deg F) per ft.
- T = temperature, in degrees Fahrenheit.
- A, B, C = derived coefficients

The values of the coefficients A, B, and C are tabulated below for a number of compounds. The temperature range of the data with which the coefficients were derived also is given.

	AX10 ³	B X 10 ⁵	C X 10 ⁸	Temperature Range (deg F)
Methane.....	16.77	4.358	1.335	-285 to 980
Ethane.....	8.74	4.343	1.364	32 to 850
Propane.....	7.54	3.362	1.971	-40 to 1000
<i>n</i> -Butane.....	6.91	2.809	2.841	32 to 340
<i>n</i> -Pentane.....	6.76	2.337	2.778	32 to 340.
<i>n</i> -Hexane.....	6.42	2.214	2.180	32 to 770
<i>n</i> -Heptane.....	4.95	2.444	1.685	220 to 790
<i>n</i> -Octane.....	3.59	2.710	1.175	290 to 750
<i>n</i> -Nonane.....	3.60	2.453	1.237	350 to 760
<i>n</i> -Decane.....	0.72	3.200	0.470	350 to 760
<i>n</i> -Undecane.....	1.77	2.461	1.111	390 to 750
<i>n</i> -Dodecane.....	-0.84	3.190	0.405	470 to 740
<i>n</i> -Tridecane.....	0.22	2.714	0.637	490 to 740
<i>n</i> -Tetradecane.....	-4.02	3.810	-0.233	525 to 720
<i>n</i> -Pentadecane.....	-4.30	3.850	-0.450	560 to 700
<i>n</i> -Hexadecane.....	-6.79	4.350	-0.828	590 to 700
2-Methylpropane.....	7.17	2.849	3.131	32 to 212
2-Methylbutane.....	7.92	0.774	8.393	120 to 212
Ethene.....	9.33	3.231	2.139	-140 to 600
Propene.....	7.23	3.296	1.442	70 to 700

1-Butene.....	7.72	1.475	6.590	70 to 212
1-Hexene.....	5.14	2.802	1.311	170 to 650
1-Heptene.....	4.13	3.049	0.693	212 to 670
1-Octene.....	3.79	2.904	0.606	280 to 430
Ethyne.....	10.98	2.531	2.038	32 to 400
Cyclopropane.....	8.09	1.083	7.526	120 to 300
Cyclohexane.....	4.50	2.414	2.572	210 to 680
Benzene.....	2.58	3.235	0.160	210 to 740
Toluene.....	0.94	4.005	-0.275	300 to 730
Ethylbenzene.....	-0.49	4.039	-0.231	360 to 760
1,2-Dimethylbenzene (<i>o</i> -Xylene)...	5.16	2.964	0.095	370 to 790
1,3-Dimethylbenzene (<i>m</i> -Xylene)...	6.96	1.520	1.880	410 to 800
1,4-Dimethylbenzene (<i>p</i> -Xylene)...	1.64	3.418	0.241	350 to 780
<i>n</i> -Propylbenzene.....	-0.42	4.276	1.266	360 to 650
Isopropylbenzene.....	-4.64	7.580	-2.036	360 to 660

Procedure

For the desired compound, obtain the appropriate coefficients from the given tabulation and use equation (12B1.1-1) to calculate the thermal conductivity at the temperature of interest.

COMMENTS ON PROCEDURE 12B1.1

Purpose

Procedure 12B1.1 is presented to calculate the thermal conductivities of pure hydrocarbon gases at pressures below 50 pounds per square inch absolute. For higher pressures, the correction from Procedure 12B4.1 should be applied. Within its range of applicability, this procedure is somewhat more accurate than is Procedure 12B1.2.

Limitations

This method is intended for use only within the specified temperature regions.

Reliability

Average deviations of values calculated by this procedure from experimental data are less than 5 percent.

Literature Sources

The entries in the tabulation were derived from data from the following sources:

Methane (22,28,50,55,61,62,67,69,70,72, 74,84,85,94,147,148,149,160,164, 165,176,183)	<i>n</i> -Hexadecane (104,169)
Ethane (23,31,40,62,67,69,70,71,72,155, 162,179,183)	2-Methylpropane (67,85,125)
Propane (24,67,71,85,129,153,162,164, 179,183)	2-Methylbutane (67,125-176)
<i>n</i> -Butane (21,66,67,85,117,125,161,162, 164,177)	Ethene (28,62,64,67,74,112,161,162,183)
<i>n</i> -Pentane (20,67,85,164)	Propene (67,112,113,126,161,162)
<i>n</i> -Hexane (31,67,68,85,87,178,179)	1-Butene (126,162,177)
<i>n</i> -Heptane (67,103,169)	1-Hexane (110,112,113)
<i>n</i> -Octane (67,103)	1-Heptene (108,112,113)
<i>n</i> -Nonane (103,104)	1-Octene (112,113)
<i>n</i> -Decane (104,114)	Ethyne (99,184)
<i>n</i> -Undecane (103,104,111,169)	Cyclopropane (67,126,179)
<i>n</i> -Dodecane (104)	Cyclohexane (12,31,68,107,178,179)
<i>n</i> -Tridecane (104)	Benzene (4,31,68,178,179)
<i>n</i> -Tetradecane (103,104,169)	Methylbenzene (Toluene)(1)
<i>n</i> -Pentadecane (104)	Ethylbenzene (5)
	1,2-Dimethylbenzene (<i>o</i> -Xylene) (2)
	1,3-Dimethylbenzene (<i>m</i> -Xylene) (2)
	1,4-Dimethylbenzene (<i>p</i> -Xylene) (3)
	<i>n</i> -Propylbenzene (46)
	Isopropylbenzene (46)

Example

Find the thermal conductivity of 1-heptene at 268 F and 1 atm.

From the preceding tabulation, $A = 4.13 \times 10^{-3}$, $B = 3.049 \times 10^{-5}$, $C = 0.693 \times 10^{-8}$. The thermal conductivity then is calculated by using equation 912B1.4-1):

$$k = 4.13 \times 10^{-3} + (3.049 \times 10^{-5}) (268) + (0.693 \times 10^{-8})(268)^2$$

$$k = 0.01280 \text{ Btu per (hr)(sq ft)(deg F) per ft.}$$

An experimental value (113) is 0.01309 Btu per (hr)(sq ft)(deg F) per ft.

PROCEDURE 12B1.2

THERMAL CONDUCTIVITY OF PURE HYDROCARBON GASES AT LOW PRESSURES, GENERALIZED METHOD

Discussion

The following equations are to be used to obtain the thermal conductivity of pure hydrocarbon gases at pressures below 50 pounds per square inch absolute.

For methane and cyclic compounds at reduced temperatures less than 1.0:

$$k = 1.188 \times 10^{-3} \frac{T_r C_p}{\lambda} \quad (12B1.2-1)$$

For methane and cyclic compounds at reduced temperatures greater than 1.0 and for all other compounds at any temperature:

$$k = (2.67 \times 10^{-4} (14.52 T_r - 5.14)^{2/3} \frac{C_p}{\lambda}) \quad (12B1.2-2)$$

$$\lambda = T_c^{1/6} M^{1/2} \left(\frac{14.696}{P_c} \right)^{2/3} \quad (12B1.2-3)$$

Where:

k = thermal conductivity, in Btu per (hr)(sq ft)(deg F) per foot.

T_r = reduced temperature, T/T_c .

T = temperature, in degrees Rankine.

T_c = critical temperature, in degrees Rankine.

C_p = isobaric heat capacity, in Btu per (lb-mole)(deg R).

M = molecular weight.

p_c = critical pressure, psia.

Procedure

Step 1: Obtain the critical temperature, T_c , the critical pressure p_c , and molecular weight, M , from Chapter 1.

Step 2: Calculate λ from equation (12B1.2-3).

Step 3: Calculate the reduced temperature ($T_r = T/T_c$).

Step 4: Obtain the isobaric heat capacity according to the method of Chapter 7 and convert to a Btu per (lb-mole)(deg R) basis.

Step 5: Depending on the reduced temperature and compound type, calculate the thermal conductivity using either equation (12B1.2-1) or equation (12B1.2-2).

COMMENTS ON PROCEDURE 12B1.2

Purpose

Procedure 12B1.2 is presented to calculate the thermal conductivity of pure hydrocarbon gases at pressures less than 50 pounds per square inch absolute. For higher pressures, apply the correction outlined in Procedure 12B4.1. When Procedure 12B1.1 is applicable, it should be used in preference to this procedure.

Reliability

This procedure yields average errors of 5 percent and maximum errors of 40 percent.

Literature Source

This procedure is adapted from Misic and Thodos, *AICHE Journal* 7 264 (1961).

Example

Calculate the thermal conductivity of 2-methylbutane at 212 F and 1 atm.

From Chapter 1, the critical temperature is 369.1 F, the critical pressure is 498.38 psia, and the molecular weight is 72.15. The value of λ is therefore:

$$\lambda = \frac{(369.1 + 459.67)^{1/6}(72.15)^{1/2}}{(490.38/14.696)^{2/3}}$$

$$\lambda = 2.512$$

The reduced temperature is $\frac{(212 + 459.67)}{369.1 + 459.7} = 0.810$. From Chapter 7, the isobaric heat capacity is 34.49 Btu per (lb-mole)(deg R).

The thermal conductivity for 2-methylbutane is then calculated by using equation (12B1.2-2):

$$k = (2.67 \times 10^{-4}) [(14.52) (0.810) - 5.14]^{2/3} \frac{34.49}{2.512}$$

$$k = 0.01293 \text{ Btu per (hr)(sq ft)(deg F) per ft.}$$

An experimental value (124) at these conditions is 0.01333 Btu per (hr)(sq ft)(deg F) per ft.

PROCEDURE 12B2.1

THERMAL CONDUCTIVITIES OF DEFINED MIXTURES OF HYDROCARBON GASES

Discussion

The following equations are to be used to predict the thermal conductivity of vapor mixtures of known composition at any conditions of temperature and pressure. The conductivities of the pure components are required at the same conditions.

$$k_m = \sum_{i=1}^n \frac{k_i}{\frac{1}{y_i} \sum_{j=1}^n A_{ij} y_j} \quad (12B2.1-1)$$

Where:

- k_m = thermal conductivity of the mixture, in Btu per (hr)(sq ft)(deg F) per ft.
- k_i = thermal conductivity of component i, in Btu per (hr)(sq ft)(deg F) per ft.
- n = number of components in the mixture.
- y_i, y_j = mole fractions of components i and j.

$$A_{ij} = \frac{1}{4} \left\{ 1 + \left[\frac{\mu_i \left(\frac{M_j}{M_i} \right)^{3/4}}{\mu_j \left(\frac{M_i}{M_j} \right)} \frac{\left(1 + \frac{S_i}{T} \right)}{\left(1 + \frac{S_j}{T} \right)} \right]^{1/2} \right\} \frac{\left(1 + \frac{S_{ij}}{T} \right)}{\left(1 + \frac{S_i}{T} \right)} \quad (12B2.1-2)$$

$$S_i, S_j \text{ (Sutherland Constants)} = 1.5 T_b \quad (12B2.1-3)$$

$$S_i, S_j = 142^\circ R \text{ for hydrogen, deuterium, and helium.} \quad (12B2.1-4)$$

$$S_{ij} = \sqrt{S_i S_j} \quad (12B2.1-5)$$

Note that $A_{ij} \neq A_{ji}$.

Where:

- μ_i, μ_j = viscosities of components i and j, in centipoises.
- M_i, M_j = molecular weights of components i and j.
- T_b = normal boiling point, in degrees Rankine.
- T = temperature, in degrees Rankine.

This method is also applicable to mixtures of nonhydrocarbons, including hydrogen.

Procedure

- Step 1:* Obtain the molecular weights and normal boiling points of the pure components of the mixture from Chap. 1 and calculate the thermal conductivities by using Procedure 12B1.1 or 12B1.2. If the values are required at elevated pressures, use Procedure 12B4.1 to correct for the effect of pressure.
- Step 2:* Calculate S_i , S_j , and S_{ij} from equations (12B2.1-3) and (12B2.1-4).
- Step 3:* Obtain the pure component viscosities using the method of Chap. 11.
- Step 4:* From equation (12B2.1-2), calculate the factors A_{ij} .
- Step 5:* Obtain the thermal conductivity of the mixture from equation (12B2.1-1).

COMMENTS ON PROCEDURE 12B2.1

Purpose

Equation (12B2.1-1) is used to calculate the thermal conductivity of a gaseous mixture for which the composition is known, using pure-component conductivities under the same conditions.

Reliability

Equation (12B2.1-1) yields average errors of approximately 5 percent and maximum errors of 40 percent when compared with the available data.

Special Comments

Equation (12B2.1-1) also will yield reliable results for many nonhydrocarbon systems, including mixtures containing polar compounds.

For mixtures of quantum gases (hydrogen, helium, and neon) and hydrocarbons where the fraction of the quantum gas is known but the composition of the hydrocarbon portion is not, use Procedure 12B3.1 to obtain a k_1 for the entire hydrocarbon portion of the mixture, which is then treated as a pseudocomponent in this procedure.

Although not recommended when the mixture composition is known, Procedure 12B3.1 may be used for fast but less accurate estimates of mixture thermal conductivities.

Literature Source

This procedure is adapted from Lindsay and Bromley, *Ind. Eng. Chem.* **42** 1508 (1950).

Example

Calculate the thermal conductivity of a 29.96-mole percent *n*-pentane(1) - 70.04-mole percent *n*-hexane(2) mixture at 212 F and 1 atm. The experimental thermal conductivities of *n*-pentane and *n*-hexane at these conditions (42) are 0.01280 and 0.01165 Btu per (hr)(sq ft)(deg F) per ft, respectively.

The molecular weights and normal boiling points are taken from Chapter 1.

n-pentane: M = 72.15; T_b = 96.93 F

n-hexane: M = 86.18; T_b = 155.71 F

The Sutherland constant of *n*-pentane is S₁ = 1.5(96.93+459.67) = 834.9 R and the Sutherland constant of *n*-hexane is S₂ = 1.5(155.71+459.67) = 923.07 R. The factor S₁₂ = S₁₂ is therefore $\sqrt{(834.9)(923.07)} = 877.88$. From Chapter 11, the viscosities of *n*-pentane and *n*-hexane are determined to be 0.008631 and 0.008129 centipoise, respectively. By using equation (12B2.1-2), the factors A_{ij} are calculated as follows:

$$A_{11} = A_{22} = 1.0$$

$$A_{12} = \frac{1}{4} \left\{ 1 + \left[\frac{0.008631}{0.008129} \left(\frac{86.18}{72.15} \right)^{3/4} \left(\frac{1 + \frac{834.9}{212 + 459.67}}{1 + \frac{923.07}{212 + 459.67}} \right)^{1/2} \right]^2 \left(\frac{1 + \frac{877.88}{212 + 459.67}}{1 + \frac{834.9}{212 + 459.67}} \right) \right\}$$

$$A_{12} = 1.102$$

$$A_{12} = \frac{1}{4} \left\{ 1 + \left[\frac{0.008129}{0.008631} \left(\frac{72.15}{86.18} \right)^{3/4} \frac{\left(1 + \frac{923.07}{212+459.67} \right)}{\left(1 + \frac{834.9}{212+459.67} \right)} \right]^{1/2} \right\}^2 \left(\frac{1 + \frac{877.88}{212+459.67}}{1 + \frac{923.07}{212+459.67}} \right)$$

$$A_{21} = 0.9087$$

The mixture's thermal conductivity is calculated next by using equation (12B2.1-1):

$$k_m = \frac{0.01280}{\frac{1}{0.2996}[(1.0)(0.2996) + (1.102)(0.7004)]} + \frac{0.01165}{\frac{1}{0.7004}[(0.9087)(0.2996) + (1.0)(0.7004)]}$$

$$k_m = 0.01197 \text{ Btu per (hr)(sq ft)(deg F) per ft}$$

An experimental value (42) is 0.001188 Btu per (hr)(sq ft)(deg F) per ft.

PROCEDURE 12B3.1**THERMAL CONDUCTIVITY OF PETROLEUM FRACTION
VAPORS AT LOW PRESSURES****Discussion**

The following equation is to be used to estimate the thermal conductivity between a temperature range of 0-1000 degrees F and a molecular weight range of 15-150 g/mol.

$$k = A + \frac{B}{MW} + \frac{C}{MW^2} + T \left(D + \frac{E}{MW} + \frac{F}{MW^2} \right) \quad (12B3.1-1)$$

Where:

k	=	thermal conductivity at T in BTU per (hr)(sq ft)(deg F) per ft
T	=	temperature, in degrees Fahrenheit
MW	=	molecular weight
A	=	0.0013349
B	=	0.24628
C	=	1.1493
D	=	3.2768×10^{-5}
E	=	4.1881×10^{-5}
F	=	0.0018427

Procedure

- Step 1:* After knowing the temperature and molecular weight, check to see if they fall in the specified range.
- Step 2:* Plug in the values for the constants A-F, the values for T and MW and calculate the thermal conductivity from equation (12B3.1-1).

COMMENTS ON PROCEDURE 12B3.1

Purpose

Procedure 12B3.1 is to be used for estimation of the thermal conductivity of hydrocarbon vapor mixtures of undefined composition at low pressures where the vapor may be considered to be an ideal gas. Procedure 12B1.2 is more accurate and is preferable when the input data are available. For higher pressures, apply the pressure correction, Procedure 12B4.1.

Limitations

This method is an oversimplification which should be used only when other methods of the chapter are inapplicable. Procedure 12B3.1 must not be used for mixtures containing quantum gases (hydrogen, helium, or neon).

Reliability

This procedure is in error by an average of 10 percent except for mixtures containing appreciable quantities of hydrogen, helium, or neon where an average error of 25 percent is obtained. No data for petroleum fraction vapors are available for comparison.

Literature Source

This procedure is a regression of a figures which is a similar figure presented by Maxwell. "Data Book on Hydrocarbons." 215. D. Van Nostrand Company, Inc., Princeton, New Jersey (1950), based on thermal conductivity data of defined vapor mixtures from the following sources: 26, 28, 29, 40, 42, 52, 59, 60, 89, 125, 126, 149, 164, 183.

Example

Calculate the thermal conductivity of a petroleum fraction vapor at a low pressure and a temperature of 455 F which has a molecular weight of 138 g/mol. The thermal conductivity is calculated from equation (12B3.1-1)

$$k = 0.0013349 + \frac{0.24628}{138} + \frac{1.1493}{138^2} + 455 \left(3.2768 \times 10^{-5} + \frac{4.1881 \times 10^{-5}}{138} + \frac{0.0018427}{138^2} \right)$$

$$k = 0.01828 \text{ BTU per (hr)(sq ft)(deg F) per ft.}$$

PROCEDURE 12B4.1

THERMAL CONDUCTIVITY OF PURE HYDROCARBON GASES AT HIGH PRESSURES

Discussion

The following equations are to be used to predict the effect of pressure on the thermal conductivity of hydrocarbon gases when the pressure is greater than 50 pounds per square inch absolute:

$$\frac{k}{k^*} = \frac{C_v}{C_v^*} \left(\frac{k}{k^*} \right)^* + \frac{C_v^*}{C_v} \left(\frac{k}{k^*} \right)^* \quad (12B4.1-1)$$

Where:

- k = thermal conductivity at temperature and pressure of interest, in Btu per (hr)(sq ft) (deg F) per ft.
- k^* = thermal conductivity at temperature of interest but at a low pressure (usually atmospheric, in Btu per (hr)(sq ft)(deg F) per ft).
- C_v = isochoric heat capacity of the real gas, in Btu per (lb-mole) (deg F).
- C_v^* = translational isochoric heat capacity of the real gas to be calculated from equation (12B4.1-7), in Btu per (lb-mole)(deg F).
- C_v^* = internal isochoric heat capacity of the real gas, $C_v - C_v^*$, in Btu per (lb-mole)(deg F).
- $(k/k^*)^*$ = translational contribution to the thermal conductivity ratio which is given analytically as a function of T_r and p_r as equation (12B4.1-2).
- $(k/k^*)^*$ = internal contribution to the thermal conductivity ratio which is given analytically as a function of T_r and P_c as equation (12B4.1-5) for noncyclic hydrocarbons and as equation (12B4.1-6) for cyclic hydrocarbons.
- T_r = reduced temperature, T/T_c .
- T = temperature, in degrees Rankine.
- T_c = critical temperature, in degrees Rankine.
- p_r = reduced pressure, p/p_c .
- p = pressure, in pounds per square inch absolute.
- p_c = critical pressure, in pounds per square inch absolute.

$$(k/k^*)^* = 1.0 + \left(\frac{4.18}{T_r^4} + 0.537 \frac{P_r}{T_r^2} \right) [1.0 - \exp(AP_r^B)] + 0.510 \frac{P_r}{T_r^3} \exp(AP_r^B) \quad (12B4.1-2)$$

Where:

$$A = -0.0617 \exp \left(\frac{1.91}{T_r^9} \right) \quad (12B4.1-3)$$

$$B = 2.29 \exp \left(\frac{1.34}{T_r^{16}} \right) \quad (12B4.1-4)$$

For noncyclic hydrocarbons:

$$(k/k^*)_{\text{noncyclic}} = 1.0 + \frac{1.0}{T_r^5} \left(\frac{P_r^4}{2.44 T_r^{20} + P_r^4} \right) + 0.012 \frac{P_r}{T_r} \quad (12B4.1-5)$$

For cyclic hydrocarbons:

$$(k/k^*)_{\text{cyclic}} = 1.0 + \frac{0.520}{T_r^4} \left(\frac{P_r^5}{5.38 + P_r^5} \right) + 0.009 \frac{P_r}{T_r} \quad (12B4.1-6)$$

The isochoric heat capacity, C_v , can be obtained according to the methods of Chapter 7. The translational heat capacity can be calculated from the following equation:

$$C_v' = 4.965 - R \left[1 + \left(\frac{\tilde{C}_v^\circ - \tilde{C}_v}{R} \right)^{(o)} \right] \quad (12B4.1-7)$$

Where:

R = gas constant = 1.986 Btu per (lb-mole)(deg R).

$\left(\frac{\tilde{C}_v^\circ - \tilde{C}_v}{R} \right)^{(o)}$ = effect of pressure on isochoric heat capacity for the simple fluid which is obtained from Chapter 7.

The internal heat capacity, C_v'' , is then calculated as the difference between the total isochoric heat capacity and the translational capacity, $C_v'' = C_v - C_v'$.

Procedure

- Step 1: Obtain the critical temperature, T_c , and the critical pressure, p_c , from Chapter 1 and determine the thermal conductivity of the low-pressure gas from Procedure 12B1.1 or 12B1.2.
- Step 2: Calculate the reduced temperature and the reduced pressure.
- Step 3: From Chapter 7, obtain the isochoric heat capacity, C_v , and $\left(\frac{\tilde{C}_v^\circ - \tilde{C}_v}{R} \right)^{(o)}$. Use equation (12B4.1-7) to calculate the translational heat capacity, C_v' , and then obtain the internal capacity, $C_v'' = C_v - C_v'$.
- Step 4: Calculate the coefficients A and B from equations (12B4.1-3) and (12B4.1-4) and use these values in equation (12B4.1-2) to determine the translational contribution to the thermal conductivity ratio, (k/k^*) .
- Step 5: Depending on compound type, use either equation (12B4.1-5) or (12B4.1-6) to calculate the internal contribution to the thermal conductivity ratio, (k/k^*) .
- Step 6: Obtain the thermal conductivity ratio from equation (12B4.1-1) and multiply the result by the low-pressure vapor thermal conductivity, k^* , to determine the thermal conductivity of the dense gas.

COMMENTS ON PROCEDURE 12B4.1

Purpose

Procedure 12B4.1 is presented for estimating a correction to the low-pressure thermal conductivity of hydrocarbons in the dense-gas region.

Reliability

Average errors between calculated and experimental thermal conductivities of dense gases are 10 percent except in the critical region, where 20-percent errors should be expected and errors as high as 70 percent can occur.

Literature Source

This procedure is adapted from Crooks, M.S. thesis. The Pennsylvania State University, University Park, Pennsylvania (1978).

Example

Calculate the vapor-phase thermal conductivity of n-heptane at 472 F and 1450 psia.

From Chapter 1, the critical temperature of n-heptane is 512.69 F and the critical pressure is 397.41 psia. By using Procedure 12B1.4, $k^*(572 \text{ F}, 1 \text{ atm}) = 0.02444 \text{ Btu per (hr)(sq ft)(deg F) per ft}$. The reduced temperature is $(572 + 459.67)/(512.69 + 459.67) = 1.061$, and the reduced pressure is $1450/397.41 = 3.65$. From Chapter 7, the total isochoric heat capacity is determined to be 66.52 Btu per (lb-mole)(deg F) and $\left(\frac{\bar{C}_v^\circ - \bar{C}_v}{R}\right)^{(o)}$ is -0.409. The translational isochoric heat capacity is calculated by using equation (12B4.1-7):

$$C_v' = 4.965 = 1.986 [1 + (-0.409)]$$

$$C_v' = 3.79 \text{ Btu per (lb-mole)(deg F)}$$

The internal isochoric heat capacity is therefore $(66.52 - 3.79) = 62.73 \text{ Btu per (lb-mole)(deg F)}$. The coefficients A and B are calculated by using equations (12B4.1-3) and (12B4.1-4):

$$A = -0.0617 \exp \left[\frac{1.91}{(1.061)^9} \right] = 0.189$$

$$B = -2.29 \exp \left[\frac{1.34}{(1.061)^{16}} \right] = 3.85$$

By using equation (12B4.1-2):

$$(k/k^*)' = 1.0 + \left[\frac{4.18}{(1.061)^4} + 0.537 \frac{(3.65)}{(1.061)^2} \right] [1.0 - \exp(-0.189 (3.65)^{3.85})] + 0.510 \frac{3.65}{(1.061)^3} \exp(-0.189 (3.65)^{3.85})$$

$$(k/k^*) = 1.0 + 5.04 + 0.0 = 6.04$$

Because n-heptane is noncyclic, equation 912B4.1-5) is used to calculate the internal contribution to the thermal conductivity ratio:

$$(k/k^*)^* = 1.0 + \frac{1.0}{(1.061)^5} \left[\frac{3.65)^4}{2.44(1.061)^{20} + (3.65)^4} \right] + \frac{3.65}{1.061}$$

$$(k/k^*)^* = 1.0 + 0.712 + 0.041 = 1.753$$

Therefore, using equation (12B4.1-1):

$$(k/k^*) = \frac{3.79}{66.52}(6.04) + \frac{62.73}{66.52}(1.753) = 1.997$$

The actual high-pressure thermal conductivity is $(1.997)(0.02444) = 0.04881$ Btu per (hr)(sq ft)(deg F) per ft.

An experimental value (106) is 0.04813 Btu per (hr)(sq ft)(deg F) per ft.

PROCEDURE 12C1.1**THERMAL CONDUCTIVITY OF SELECTED NONHYDROCARBONS****Discussion**

The following equation is to be used to obtain the thermal conductivity of selected nonhydrocarbons at various temperatures and pressures.

$$k = A + BT + CT^2 + DP + E \frac{P}{T^{1.2}} + \frac{F}{(0.4P - 0.001T)^{0.015}} + G \ln P \quad (12C1.1-1)$$

Where:

k = thermal conductivity in BTU per (hr)(sq ft)(deg F) per foot

T = temperature in degrees Rankine

P = pressure in pounds per square inch absolute

Procedure

Step 1: Obtain the constants for equation (12C1.1-1) from Table 12C1.2.

Step 2: Check to see if the desired temperature and pressure are within the limitations of the equation.

Step 3: Calculate the thermal conductivity using equation (12C1.1-1).

COMMENTS ON PROCEDURE 12C1.1

Purpose

Procedure 12C1.1 is to be used to estimate the thermal conductivity of selected nonhydrocarbons at various temperatures and pressures.

Limitations

	Temperature Range (deg. R)	Pressure Range (psia)
Nitrogen	460 to 2,460	15 to 10,000
Carbon Monoxide	460 to 2,460	15 to 10,000
Oxygen	460 to 2,460	15 to 15,000
Hydrogen	260 to 2,260	15 to 10,000
Sulfur Dioxide (gas)	960 to 2,460	15 to 10,000
Hydrogen Sulfide	460 to 2,460	Atmospheric
Sulfur Trioxide	460 to 2,460	Atmospheric

Procedure 12C1.1 is not recommended outside of the above ranges.

Reliability

The error for the data before regression did not exceed five percent. The average error for the regression was:

	Number of Tested Points	Average Absolute % Error
Nitrogen	155	1.69
Carbon Monoxide	229	1.81
Oxygen	151	1.88
Hydrogen	77	1.72
Sulfur Dioxide (gas)	96	2.98
Hydrogen Sulfide	11	<0.5
Sulfur Trioxide	11	3.81

Literature Source

Hydrogen - Schaefer and Thodos, *Ind. Eng. Chem.* **60** 1585 (1958).

Oxygen, Nitrogen, Carbon Monoxide - Stiel and Thodos, *The Prediction of Transport Properties of Pure Gaseous and Liquid Substances, in Progress in International Research on Thermodynamic and Transport Properties*, Chapter 31, ASME, 1962.

Sulfur Dioxide - Institute of Gas Technology Data Book.

Sulfur Trioxide, Hydrogen Sulfide - Daubert, T. E., Danner, R. P., *Data Compilation: Tables of Properties of Pure Compounds*, American Institute of Chemical Engineers, New York (extant 1995).

Example

Calculate the thermal conductivity of oxygen at 984.67 degrees Rankine and 6075.0 pounds per square inch absolute.

Obtain the constants for oxygen from Table 12C1.2. They are:

$$A = 5.950 \times 10^{-4}$$

$$B = 1.710 \times 10^{-5}$$

$$C = 0.000$$

$$D = -2.100 \times 10^{-8}$$

$$E = 5.869 \times 10^{-3}$$

$$F = 6.995 \times 10^{-3}$$

$$G = 0.000$$

Check to see if the temperature and pressure are within the limitations for oxygen.

Limitations for oxygen are:

$$T (R) 460 \text{ to } 2,460$$

$$P (\text{psia}) 15 \text{ to } 15,000$$

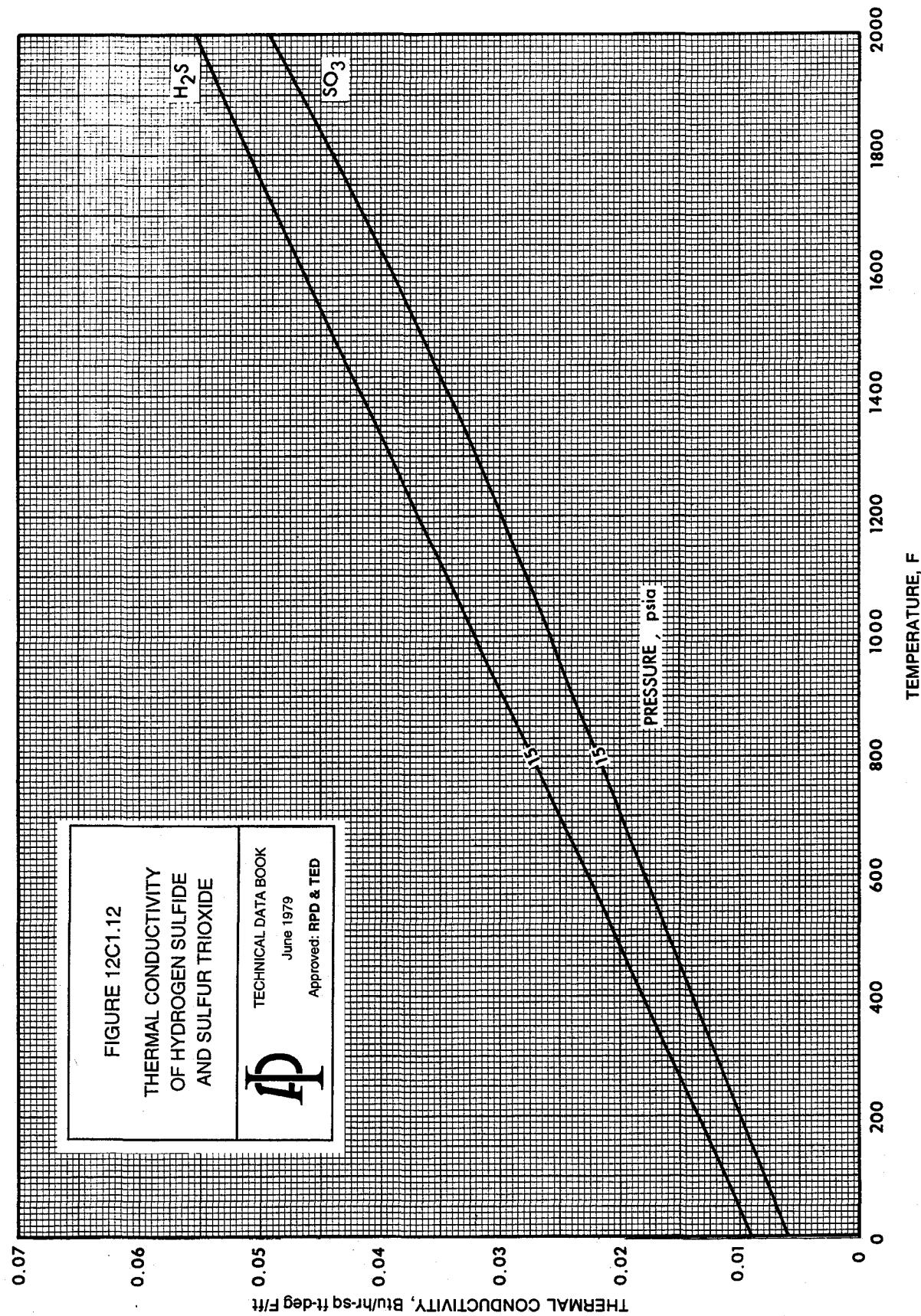
The temperature and pressure fall within the limitations.

Calculate the thermal conductivity of oxygen using equation (12C1.1-1).

$$k = A + B \times 984.67 + C \times 984.67^2 + D \times 6075.0 + E \frac{6075.0}{984.67^{1.2}} + F \ln (6075.0) + G \ln (6075.0)$$

$$(12C1.1-1)$$

The calculated thermal conductivity is 0.03265 BTU per (hr)(sq ft)(deg F) per foot.



COMMENTS ON FIG. 12C1.3 THROUGH 12C1.12 |

Purpose

Thermal conductivity data for 10 common nonhydrocarbon gases are presented for available temperature and pressure ranges.

Reliability

The maximum error for all atmospheric pressure data was slightly less than 5 percent with a mean error for individual gases from 1.5 to 3.0 percent. High-pressure data errors did not exceed 5 percent.

Literature Sources

Hydrogen—Schaefer and Thodos, *Ind. Eng. Chem.* **50** 1585 (1958).

Oxygen, nitrogen, carbon monoxide, carbon dioxide, water, ammonia—Stiel and Thodos, "The Prediction of the Transport Properties of Pure Gaseous and Liquid Substances," in *Progress in International Research on Thermodynamic and Transport Properties*, Chapter 31, ASME, 1962.

Sulfur dioxide, sulfur trioxide, hydrogen sulfide—Institute of Gas Technology Data Book.

CHAPTER 13

DIFFUSIVITY

13-0 INTRODUCTION

Diffusion of mass is the dissipation of a concentration (or chemical potential) gradient by molecular transport without overall mass flow. The diffusion coefficient is the proportionality constant between the diffusion rate and the concentration gradient causing diffusion. It is generally defined by Fick's first law for unidirectional, binary-system diffusion. This equation, which follows, is valid only in nonturbulent systems:

$$W_1 = -D_{1,2} \frac{dC_1}{dL} \quad (13-0.1)$$

Where:

W_1 = molar flow of species 1, in pound-mole per (hour) (square feet).

$D_{1,2}$ = diffusion coefficient of species 1 in 2, in square feet per hour.

C_1 = concentration of species 1, in pound-mole per cubic feet.

L = distance, in feet.

On differentiation, the rate of change of local concentration with time (Fick's second law) results:

$$\frac{dC_1}{dt} = D_{1,2} \frac{d^2C_1}{dL^2} \quad (13-0.2)$$

where t = time, in hours. Although other diffusion coefficients have been defined, the Fick diffusion coefficient is the most common measure of diffusional tendency. Accordingly, only Fick ordinary diffusion coefficients are predicted by the methods in this chapter.

The primary application of diffusion coefficients in chemical engineering calculations is in the Schmidt number, $\mu/\rho D$, which is used generally to correlate mass transfer properties. The equations are useful in reaction rate calculations for which the rate of diffusion to a catalyst is important.

Unfortunately, experimental diffusion coefficients are usually not precise, particularly in the liquid phase. The correlations that were developed from these data necessarily reflect this experimental uncertainty. Although the reliability quotations for the correlations in this edition are not low, they are superior to those quoted in the last edition. The estimated diffusion coefficients are suitable for most engineering applications.

Liquid Systems

Because no single correlation is satisfactory for estimating properties for all systems involving liquid solutions, two correlations are presented for the estimation of diffusion coefficients in dilute binary liquid mixtures. In some molecules, uneven spatial distribution of electronic charges about the positively charged nucleus gives these molecules permanent dipoles. These molecules are, by definition, polar. Typical polar compounds include acetone, acetaldehyde, and methyl ether. The dipole-dipole interaction from these permanent dipole moments is not always an adequate description of the interactions between polar molecules because other localized effects do occur. For instance, the molecules of some pure polar liquids such as water, carboxylic acids, and alcohols occur in aggregated forms due to specific forces such as hydrogen bonding. These compounds are called associating compounds.

Symmetrical molecules, such as carbon tetrachloride, benzene, and methane, have dipole moments of zero. These substances are called nonpolar molecules. Using these definitions, Procedure 13A1.1 is presented for the estimation of diffusion coefficients in binary nonpolar liquid systems at high dilution of the solute. Procedure 13A1.3 is given for the estimation of diffusion coefficients in binary systems at high dilution of the solute when either the solvent is polar (or associating) and the solute is nonpolar, or both components are polar (or associating). Procedure 13A1.5 and 13A2.1 are presented as the recommended methods for estimating diffusivities in concentrated solutions and liquid mixtures of more than two components, respectively. These procedures are semiempirical in nature; the more theoretical methods are not sufficiently accurate for general utility.

Gaseous Systems

Two semiempirical correlations are given for estimating diffusion coefficients in low-pressure binary gaseous systems. Procedure 13B1.1 is recommended for binary hydrocarbon-hydrocarbon systems and Procedure 13B1.2 is recommended for estimating diffusion coefficients in binary air-hydrocarbon systems.

A correction chart for high pressures, Figure 13B1.4, is more empirical in nature and is retained from the last edition. This pressure correction term, although based on very few data, predicts diffusion coefficient values that are suitable for most engineering applications. The binary gaseous diffusion coefficients can be combined, using Procedure 13B2.1 to obtain a multicomponent diffusion

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coefficient value that is satisfactory for most engineering applications.

Gas-Liquid Systems

Procedure 13C1.1 is recommended for estimating the diffusion coefficients of dissolved gases diffusing into

liquids. It is the same method used in Procedure 13A1.1. The correlation was developed for use with gas-liquid systems and with nonpolar liquid-liquid systems (at high dilution of the solute).

PROCEDURE 13A1.1**DIFFUSION COEFFICIENTS IN BINARY NONPOLAR LIQUID SYSTEMS AT HIGH DILUTION OF THE SOLUTE****Discussion**

The following equation is recommended for estimating diffusion coefficients in binary nonpolar liquid systems at high dilution of the solute.

$$D_{1,2} = 5.922 \times 10^{-8} \frac{T \bar{R}_2}{\mu \bar{R}_1^{2/3}} \quad (13A1.1-1)$$

Where:

$D_{1,2}$ = diffusion coefficient of solute (component 1) in solvent (component 2), in square feet per hour.

T = temperature, in degrees Kankine.

μ = viscosity of solution (considered as pure solvent), in centipoise.

\bar{R}_2 = radius of gyration of solvent, in angstrom units.

\bar{R}_1 = radius of gyration of solute, in angstrom units.

Procedure

Step 1: Obtain \bar{R}_1 and \bar{R}_2 from Table 13A1.2. In the absence of experimental data, estimate μ using the procedures of Chapter 11.

Step 2: Calculate $D_{1,2}$ from equation (13A1.1-1).

13A1.1

COMMENTS ON PROCEDURE 13A1.1

Purpose

Procedure 13A1.1 is presented primarily for the estimation of diffusion coefficients in dilute (less than 5 mole percent solute) binary nonpolar liquid solutions (for example, solutions of hydrocarbons and carbon tetrachloride/hydrocarbons). Indirectly, it is also used to estimate diffusion coefficients in nonpolar concentrated solutions (with Procedure 13A1.5) and *nonpolar* multicomponent liquid solutions (with Procedure 13A2.1).

Limitations

Equation (13A1.1-1) was developed from hydrocarbon/hydrocarbon and hydrocarbon/carbon tetrachloride data at a solute concentration less than 5 mole percent. For systems involving water and other polar or associating compounds, use Procedure 13A1.3.

Reliability

For the systems to which this equation applies, experimental data are reproduced to within an average of 16 percent with occasional errors of 30 percent. Umesi (11) has shown that this equation gives good results for polar solutes diffusing into nonpolar solvents. For polar-polar systems, however, the calculated coefficients tend to be 15 to 50 percent too low.

Special Comments

For concentrated solutions (more than 5 mole percent solute) the coefficients from this procedure must be combined using Procedure 13A1.5. For multicomponent solutions the use of Procedure 13A2.1 is recommended. A table of R values is given in Reid et al. (7) for 250 compounds.

Literature Source

Equation (13A1.1-1) was developed by Umesi (M.S. Thesis, The Pennsylvania State University, 1980).

Example

Estimate the diffusion coefficient of *n*-decane in a binary liquid solution of *n*-decane and *n*-heptane at 77 F.

The viscosity of the solution (considered as the viscosity of pure *n*-heptane) at 77 F is 0.3984 centipoise.

From Table 13A1.2, the radius of gyration of *n*-heptane is 4.2665 Å and that of *n*-decane is 5.5390 Å. The diffusion coefficient is calculated using equation (13A1.1-1).

$$D_{1,2} = \frac{(5.922 \times 10^{-8})(77 + 459.7)(4.2665)}{(0.3984)(5.5390)^{3/2}} = 1.09 \times 10^{-4} \text{ sq ft per hr}$$

An experimental value of 1.19×10^{-4} square feet per hour is available. The predicted value represents an absolute deviation of 8.4 percent from the experimental value.

PROCEDURE 13A1.3**DIFFUSION COEFFICIENTS IN BINARY POLAR OR ASSOCIATING LIQUID SYSTEMS AT HIGH DILUTION OF THE SOLUTE****Discussion**

The following equation is recommended for estimating diffusion coefficients in dilute binary liquid systems involving polar or associating solvents. The equation may be used directly or approximated conveniently with the nomograph in Figure 13A1.4.

$$D_{1,2} = 1.59 \times 10^{-7} \frac{(\phi_2 M_2)^{1/2} T}{\mu (V_1)^{0.6}} \quad (13A1.3-1)$$

Where:

ϕ_2 = association parameter for the solvent.

M_2 = molecular weight of the solvent.

V_1 = molar volume of solute at the normal boiling point, given by $V_1 = 0.285 V_{c1}^{1.048}$, in cubic centimeter per gram mole.

V_{c1} = critical volume, in cubic centimeter per gram mole.

μ = viscosity of the pure solvent, in centipoise.

T = temperature, in degrees Rankine.

Procedure

Step 1: Obtain M_2 and V_{c1} from Chapter 1 and V_1 from the equation given above. In the absence of experimental data, estimate μ using the procedures of Chapter 11.

Step 2: Determine the association parameter, ϕ_2 , for the solvent from the tabulation below:

	ϕ_2
Ethyl Alcohol	1.5
Methyl Alcohol	1.9
Water	2.6
Other Associating Solvents	1.0–2.6

Step 3: Obtain $D_{1,2}$ directly from equation (13A1.3-1) or with nomograph, Figure 13A1.4.

COMMENTS ON PROCEDURE 13A1.3

Purpose

Procedure 13A1.3 is presented primarily for the estimation of diffusion coefficients in dilute (less than 5 mole percent solute) polar or associating binary liquid solutions. Those coefficients are also required to estimate diffusivities in polar or associating concentrated solutions (with Procedure 13A1.5) and polar or associating multicomponent liquid solutions (with Procedure 13A2.1).

Limitations

For most associating systems other than methanol, ethanol, and water, the association parameter is arbitrarily assigned according to an estimate of the degree of association of the solvent (see step 2). The diffusion coefficient estimated with this equation is not very accurate when more than 5 mole percent solute is present in the solution.

Reliability

Equation (13A1.3-1) reproduces experimental data of associating binary liquid systems with an average deviation of 20 percent, with occasional errors of 35 percent. It should not be used for systems in which the solvent is a hydrocarbon because calculated coefficients are too small when compared to the experimental values. Higher errors occur when the diffusing molecule is much smaller than the solvent.

Special Comments

For concentrated solutions (more than 5 mole percent solute) of polar or associating systems, the coefficients from this procedure must be combined using Procedure 13A1.5. For multicomponent solutions of polar or associating systems, Procedure 13A2.1 is appropriate.

Literature Sources

Equation (13A1.3-1) was developed by Wilke and Chang, *AIChE Journal* **1** 264 (1955). The correlation between molar volume at the normal boiling point and the critical molar volumes was developed by Tyn and Calus, *Processing* **21** [4] 16 (1975).

Example

Estimate the diffusion coefficient of benzene in a binary liquid solution of benzene and water at 68 F.

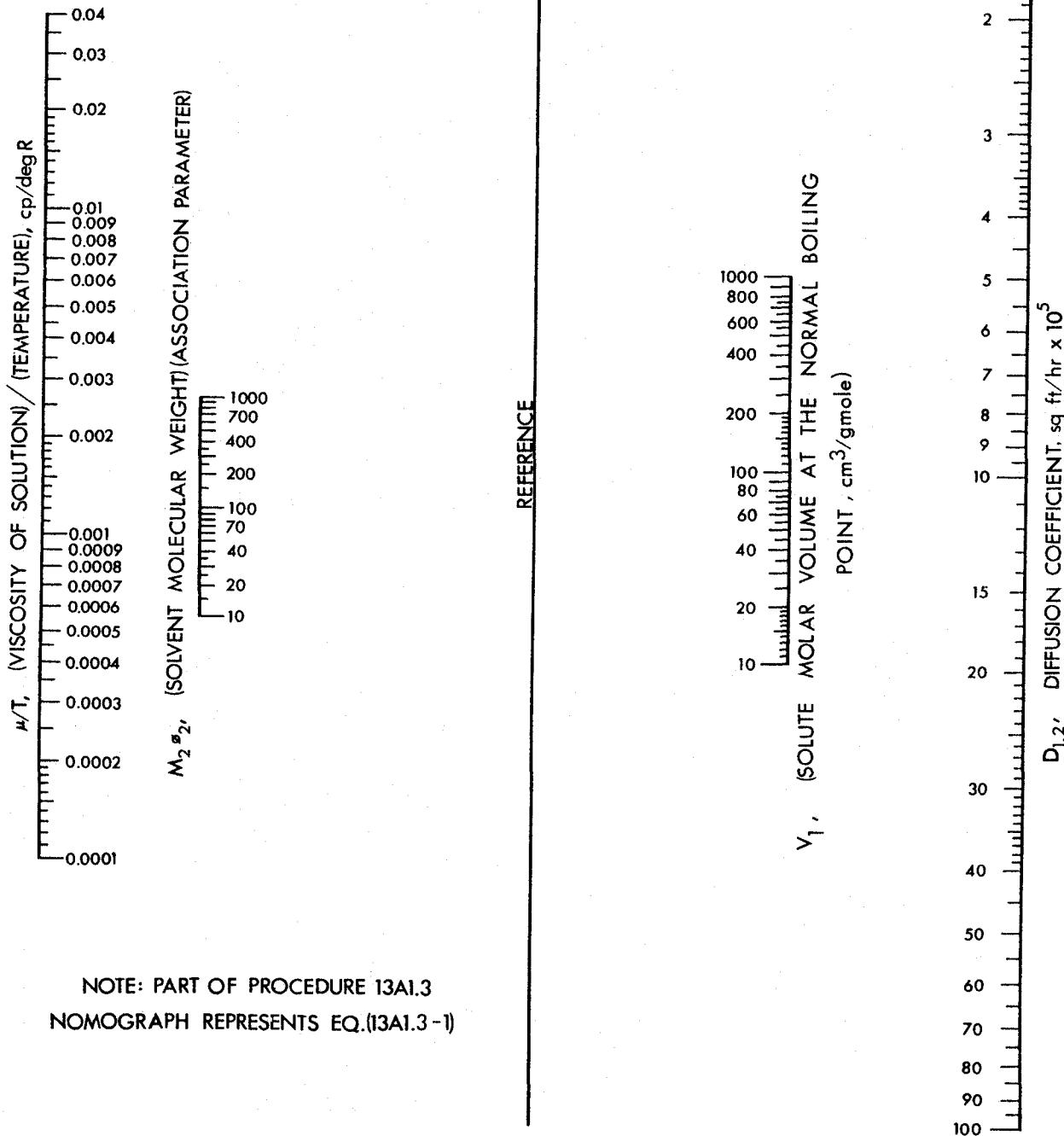
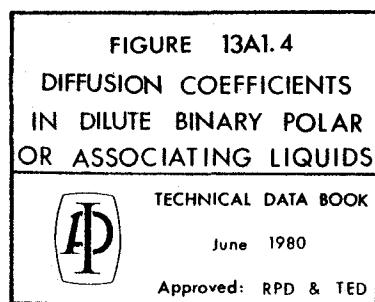
The viscosity of the solution (considered as the viscosity of pure water) at 68 F is 0.95 centipoise.

From Chapter 1, $M_2 = 18.015$. The molar volume of benzene at the normal boiling point is $96.35 \text{ cm}^3/\text{gmole}$. For water, the association factor is 2.6. The diffusion coefficient is calculated using equation (13A1.3-1).

$$D_{1,2} = \frac{1.59 \times 10^{-7} (2.6 \times 18.015)^{1/2} (68 + 459.7)}{0.95 (96.35)^{0.6}}$$

$$= 3.90 \times 10^{-5} \text{ square feet per hour}$$

An experimental value of 4.57×10^{-5} square feet per hour is available; an absolute deviation of 14.7 percent.



COMMENTS ON FIGURE 13A1.4**Purpose**

Figure 13A1.4 is a convenient representation of equation (13A1.3-1) for estimating diffusion coefficients in dilute (less than 5 mole percent solute) polar or associating binary liquid solutions.

Limitations

For most associating systems other than methanol, ethanol, and water, the association parameter has to be arbitrarily assigned according to an estimate of the degree of association of the solvent (see step 2 of Procedure 13A1.3). The diffusion coefficient estimated with this equation is not very accurate when more than 5 mole percent solute is present in the solution.

Notation

μ = viscosity of solution (considered as pure solvent), in centipoise.

T = temperature, in degrees Rankine.

M_2 = molecular weight of solvent.

ϕ_2 = association parameter for the solvent.

V_1 = solute molar volume at the normal boiling point, in cubic centimeters per gmole.

$D_{1,2}$ = diffusion coefficient of solute (component 1) in solvent (component 2), in square feet per hour.

Reliability

Figure 13A1.4 is a representation of equation (13A1.3-1) which reproduces experimental data for polar or associating binary liquid systems to an average deviation of 25 percent, with occasional errors of 50 percent. An additional uncertainty of approximately 5 percent is introduced with the nomograph. This figure should not be used for systems in which the solvent is a hydrocarbon.

Special Comments

For concentrated solutions (more than 5 mole percent solute) of polar or associating systems, the coefficients from this figure must be combined using Procedure 13A1.5. For multicomponent solutions of polar or associating systems, Procedure 13A2.1 is necessary.

Literature Source

This nomograph was adapted from Kuong, *Chem. Eng.* **68** [12] 258 (1961).

Example

Estimate the diffusion coefficient of benzene in a binary liquid solution of benzene and water at 68 F. To obtain a solution, follow the steps outlined in Procedure 13A1.3 with the values of the parameters as given. The nomograph parameters are calculated below:

$$\frac{\mu}{T} = \frac{0.95}{527.7} = 0.00180 \frac{\text{centipoise}}{\text{degrees Rankine}}$$

$$\phi_2 M_2 = 46.84$$

$$V_1 = 96.38 \text{ cm}^3/\text{gmole}$$

Connect 0.00180 on the $\frac{\mu}{T}$ scale of Figure 13A1.4 with 46.84 on the $\phi_2 M_2$ scale, and locate a point on the reference line. Connect this reference line with 96.38 on the V_1 scale and read the diffusion coefficient on the $D_{1,2}$ scale.

The estimated coefficient is 4.02×10^{-5} square feet per hour which compares favorably with the value of 3.90×10^{-5} square feet per hour calculated from equation (13A1.3-1). The experimental value is 4.57×10^{-5} square feet per hour.

PROCEDURE 13A1.5
DIFFUSION COEFFICIENTS IN CONCENTRATED
BINARY NONPOLAR LIQUID SYSTEMS

Discussion

For concentrated binary liquid solutions (more than 5 mole percent solute), Procedures 13A1.1 and 13A1.3 are not accurate. The following equation should be used:

$$D_{1,m} = x_1 D_{2,1}^{\circ} + (1 - x_1) D_{1,2}^{\circ} \quad (13A1.5-1)$$

Where:

D = diffusion coefficient ($D_{1,m}$ for the concentrated solution, and $D_{1,2}^{\circ}$ and $D_{2,1}^{\circ}$ for the dilute solution), in square feet per hour.

x = mole fraction.

Subscripts 1 and 2 = species 1 and 2.

There are no viscosity terms, only mole fractions of the components and diffusion coefficients of one component in the other as the concentration of the diffusing component approaches zero.

Procedure

Step 1: If experimental data are not available, estimate the dilute binary coefficients with Procedure 13A1.1 or 13A1.3 (depending on the chemical nature of the system).

Step 2: Calculate the binary diffusion coefficient in the concentrated mixture using equation (13A1.5-1).

13A1.5

COMMENTS ON PROCEDURE 13A1.5

Purpose

Equation (13A1.5-1) is a correction applied to dilute solution diffusion coefficients when dealing with concentrated binary solutions (more than 5 mole percent solute).

Limitations and Reliability

In addition to being entirely empirical, equation (13A1.5-1) is based on very few data. Use of it for solutions containing polar or associating compounds may result in substantial error. However, when used for hydrocarbon systems in conjunction with Procedure 13A1.1, experimental data are reproduced with an average deviation of 14.0 percent.

Literature Source

Equation (13A1.5-1) was developed by Caldwell and Babb, *J. Phys. Chem.* **60** 51 (1956) and cited by Sanchez and Clifton, *Ind. Eng. Chem. Fundam.* **16** 318 (1977).

Example

Estimate the diffusion coefficient of methylbenzene (1) in a binary liquid solution composed of 0.40 mole fraction methylbenzene and 0.60 mole fraction cyclohexane (2) at 104 F and 14.7 pounds per square inch absolute.

The dilute binary solution diffusion coefficients are obtained from Procedure 13A1.1 as 7.32×10^{-5} square feet per hour for methylbenzene in cyclohexane at 104 F and 1.14×10^{-4} square feet per hour for cyclohexane in methylbenzene at 104 F (see Procedure 13A1.1).

The concentrated solution diffusion coefficient is then calculated using equation (13A1.5-1):

$$\begin{aligned} D_{1,m} &= [0.40 (11.4) + 0.60 (7.32)] \times 10^{-5} \\ &= 8.95 \times 10^{-5} \text{ square feet per hour} \end{aligned}$$

An experimental value of 8.76×10^{-5} square feet per hour is available. This represents an absolute deviation of 2.2 percent.

PROCEDURE 13A2.1**DIFFUSION COEFFICIENTS IN MULTICOMPONENT LIQUID SYSTEMS****Discussion**

The following equation estimates diffusion coefficients in multicomponent liquid systems consisting of nonpolar components from the binary coefficients of the component pairs (with reference to the dilute solute) in the mixture:

$$D_{1,m} \mu_m = (D_{1,2}^\infty \mu_2)^{x_2} (D_{1,3}^\infty \mu_3)^{x_3} \dots \quad (13A2.1-1)$$

Where:

$D_{1,m}$ = diffusion coefficient for the diffusion of solute 1 with reference to the multicomponent mixture, in square feet per hour.

$D_{1,j}^\infty$ = diffusion coefficient of the binary pairs ($j = 2, 3, \dots$) at infinite dilution of the solute, in square feet per hour (obtained from Procedure 13A1.1 or 13A1.3).

x_j = mole fraction of component j in the mixture.

μ_j = viscosity of component j , in centipoise.

μ_m = viscosity of mixture, in centipoise.

The binary pairs referred to are the solute and individual components of the mixture. This formulation assumes that the solute is dilute and that there are no concentration gradients for the solvent species. One can, therefore, speak of a single solute diffusivity $D_{1,m}$ with respect to the mixture.

Procedure

Step 1: If experimental data are not available, estimate the dilute binary diffusion coefficients with Procedures 13A1.1 or 13A1.3 (depending on the chemical nature of the system).

Step 2: Obtain the pure-component and mixture viscosities from Chapter 11 if no experimental viscosity values are available.

Step 3: Using equation (13A2.1-1), calculate the mixture diffusion coefficient (i.e., the single solute diffusivity with respect to the mixture).

COMMENTS ON PROCEDURE 13A2.1**Purpose**

Equation (13A2.1-1) is recommended for the estimation of diffusion coefficients in multicomponent liquid systems from the binary coefficients of the component pairs (see Procedure 13A1.1).

Limitations and Reliability

Equation (13A2.1-1) has a semiempirical basis but has been tested with very few data points for nonpolar systems involving three components. Use of the equation for solutions containing polar or associating compounds may result in substantial errors.

Literature Source

Equation (13A2.1-1) was developed by Leffler and Cullinan, *Ind. Eng. Chem. Fundam.* **9** 88 (1970).

Example

Estimate the diffusion coefficient of methylbenzene in a mixture consisting of 0.786 *n*-hexane and 0.214 cyclohexane at 77 F. The viscosity of *n*-hexane at 77 F is 0.2985 centipoise, that of cyclohexane at 77 F is 0.898 centipoise. The mixture viscosity which may be estimated from the recommendations of Chapter 11 is 0.3918 centipoise. The infinite dilute solution binary diffusion coefficients are obtained from Procedure 13A1.1 as 1.78×10^{-4} square feet per hour for methylbenzene in *n*-hexane at 77 F and 5.08×10^{-5} square feet per hour for methylbenzene in cyclohexane at 77 F.

The multicomponent diffusion coefficient is then calculated using equation (13A2.1-1):

$$D_{1,m} = \frac{\{(1.78 \times 10^{-4})(0.2985)\}^{0.786} \{(5.08 \times 10^{-5})(0.898)\}^{0.214}}{0.3918}$$

$$= 1.31 \times 10^{-4} \text{ square feet per hour}$$

An experimental value of 1.59×10^{-4} square feet per hour is available.

PROCEDURE 13B1.1**DIFFUSION COEFFICIENTS IN BINARY GAS SYSTEMS AT
LOW PRESSURES—HYDROCARBON/HYDROCARBON SYSTEMS****Discussion**

The following equation is recommended for estimating diffusion coefficients in binary gas systems of hydrocarbon-hydrocarbon components at pressures less than 500 pounds per square inch absolute.

$$D_{1,2} = \frac{0.1014 T^{1.5} \left\{ \frac{1}{M_1} + \frac{1}{M_2} \right\}^{0.5}}{p \{ V_1^{\frac{1}{3}} + V_2^{\frac{1}{3}} \}^2} \quad (13B1.1-1)$$

Where:

M_1 = molecular weight of solute.

M_2 = molecular weight of solvent.

T = temperature, in degrees Rankine.

$D_{1,2}$ = diffusion coefficient of component 1 in component 2, in square feet per hour.

p = pressure, in pounds per square inch absolute.

V_i = molar volume of solute at the normal boiling point, given by $V_i = 0.285 V_{ci}^{1.048}$ ($i = 1, 2$) in cm^3/gmole .

Procedure

Step 1: From Chapter 1, obtain the molecular weights, M_1 , M_2 and the critical volumes V_{c1} and V_{c2} .

Step 2: Calculate the molar volume at the normal boiling point.

Step 3: With the temperature and pressure known, calculate the diffusion coefficient using equation (13B1.1-1).

COMMENTS ON PROCEDURE 13B1.1

Purpose

Procedure 13B1.1 is presented primarily to estimate diffusion coefficients in binary vapor systems consisting of hydrocarbon-hydrocarbon components at pressures less than 500 pounds per square inch absolute.

Limitations

Equation (13B1.1-1) is not accurate for pressures greater than 500 pounds per square inch absolute. The constant gives the best fit to the data available and hence is restricted to systems consisting of hydrocarbon-hydrocarbon components.

Reliability

Equation (13B1.1-1) is an empirical equation which does not require use of the collision diameter that is generally associated with more theoretical methods based on the kinetic theory of gases. Nevertheless, it reproduces experimental hydrocarbon-hydrocarbon diffusivity data to an average deviation of not more than 4 percent. Also, the parameters associated with equation (13B1.1-1) are easier to obtain than those associated with more theoretical methods.

Special Comments

If the desired pressure is greater than 500 pounds per square inch absolute, use a convenient low pressure in equation (13B1.1-1) and apply the pressure correction (Figure 13B1.4) to the resulting diffusion coefficients. For diffusion in a multicomponent vapor, combine the binary coefficients using Procedure 13B2.1. For systems involving air, use Procedure 13B1.2.

Literature Sources

Equation (13B1.1-1) was developed by Gilliland, *Ind. Eng. Chem.* **26** 681 (1934). The correlation between the molar volume at the normal boiling point and the critical molar volume was developed by Tyn and Calus, *Processing* **21** [4] 16 (1975).

Example

Estimate the diffusion coefficient of *n*-hexane vapor diffusing into methane at 50 F and 14.7 pounds per square inch absolute pressure.

From Chapter 1, the molecular weights are: *n*-hexane (M_1) = 86.18; methane (M_2) = 16.04. The critical molar volumes are *n*-hexane (V_{c1}) = 370.17 cm³/gmole; methane (V_{c2}) = 99.23 cm³/gmole. The molar volumes at the normal boiling points are *n*-hexane (V_1) = 140.13 cm³/gmole; methane (V_2) = 35.27 cm³/gmole.

The diffusion coefficient is calculated using equation (13B1.1-1):

$$D_{1,2} = \frac{0.1014 (50 + 459.7)^{1.5} \left[\frac{1}{86.18} + \frac{1}{16.04} \right]^{0.5}}{14.7 [(140.13)^{1/3} + (35.27)^{1/3}]^2}$$

$$= 0.301 \text{ square feet per hour}$$

An experimental value of 0.2914 square feet per hour is available. This estimated value represents a deviation of 3.3 percent from the experimental value.

PROCEDURE 13B1.2**DIFFUSION COEFFICIENTS IN BINARY GAS SYSTEMS
AT LOW PRESSURES—AIR/HYDROCARBON SYSTEMS****Discussion**

The following equation is recommended for the estimation of diffusion coefficients in binary gas systems of air-hydrocarbon components at pressures less than 500 pounds per square inch absolute.

$$D_{1,2} = \frac{0.0204 T^{1.75} \left\{ \frac{1}{M_1} + \frac{1}{M_2} \right\}^{0.5}}{p [(\sum_1 v_i)^{1/2} + (\sum_2 v_i)^{1/2}]^2} \quad (13B1.2-1)$$

Where:

$\Sigma_j v_i$ = sum of atomic diffusion volumes of component j (see Table 13B1.3).

T = temperature, in degrees Rankine.

p = pressure, in pounds per square inch absolute.

$D_{1,2}$ = diffusion coefficient of component 1 in component 2, in square feet per hour.

Procedure

Step 1: From Chapter 1, obtain the molecular weights, M_1 and M_2 .

Step 2: From Table 13B1.3, obtain $\Sigma_j v_i$.

Step 3: With the temperature and pressure known, calculate the diffusion coefficient using equation (13B1.2-1).

COMMENTS ON PROCEDURE 13B1.2

Purpose

Procedure 13B1.2 is presented primarily for the estimation of diffusion coefficients in binary vapor systems consisting of air-hydrocarbon components at pressures less than 500 pounds per square inch absolute.

Limitations

Equation (13B1.2-1) is not accurate for pressures greater than 500 pounds per square inch absolute. The constants were chosen to give the best fit to the data used in the development of the correlation. Thus, the results can be no more reliable than the diffusion data.

Reliability

Its empirical nature notwithstanding, equation (13B1.2-1) reproduces experimental air-hydrocarbon diffusivity data with an average deviation of not more than 9 percent. The nature of the atomic and structural diffusion volumes is such that diffusion coefficients in a wider range of nonhydrocarbon systems can also be estimated.

Special Comments

If the desired pressure is greater than 500 pounds per square inch absolute, use a convenient low pressure in equation (13B1.2-1) and apply the pressure correction (Figure 13B1.4) to the resulting diffusion coefficients. For diffusion in a multicomponent vapor, combine the binary coefficients using Procedure 13B2.1. For hydrocarbon-hydrocarbon systems, use Procedure 13B1.1.

Literature Sources

Equation (13B1.2-1) and Table 13B1.3 were developed by Fuller, Schettler, and Giddings, *Ind. Eng. Chem.* **58** 19(1966).

Example

Estimate the diffusion coefficient of benzene vapor diffusing into air at 86 F and 14 pounds per square inch absolute pressure.

From Chapter 1, the molecular weights are benzene (M_1) = 78.11; air (M_2) = 28.86. From Table 13B1.3, the diffusion volumes are:

$$\sum_1 v_i (\text{benzene}) = 6 (16.5) + 6 (1.98) - 1 (20.2) = 90.68$$

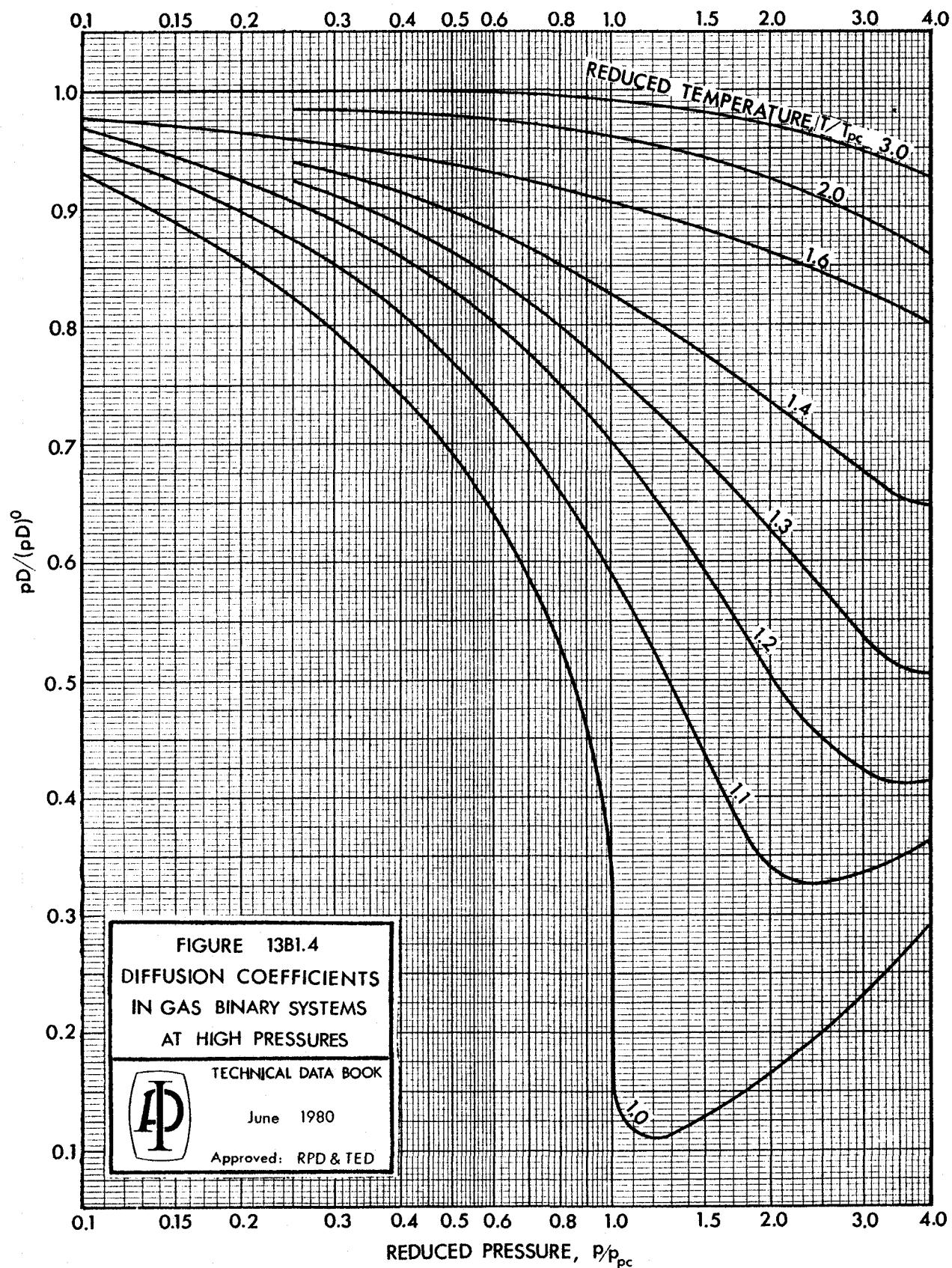
$$\sum_2 v_i (\text{air}) = 20.1$$

The diffusion coefficient of benzene vapor in air at 86 F and 14.7 pounds per square inch absolute is calculated using equation (13B1.2):

$$D_{1,2} = 0.0204 \frac{(86 + 459.7)^{1.75} \left\{ \frac{1}{78.11} + \frac{1}{28.86} \right\}^{0.5}}{14.7 [(90.68)^{1/3} + (20.1)^{1/3}]^2}$$

$$= 0.358 \text{ square feet per hour}$$

An experimental value of 0.357 square feet per hour is available. This estimated value represents a deviation of 0.28 percent.



COMMENTS ON FIGURE 13B1.4

Figure 13B1.4 is presented for estimating the effect of pressure on binary gas diffusion coefficients when the desired pressure is greater than 500 pounds per square inch. It is applicable to both hydrocarbon/hydrocarbon systems and air/hydrocarbon systems.

Limitations

This figure is based on very few experimental data.

Reliability

Published experimental data are not available to evaluate the figure. The estimated reliability is 50 percent.

Notation

$pD_{1,2}$ = product of the pressure and binary diffusion coefficient at a pressure greater than 500 pounds per square inch absolute.

$(pD_{1,2})^\circ$ = same product at a convenient pressure below 500 pounds per square inch absolute in consistent units.

p = pressure of the system, in pounds per square inch absolute.

p_{pc} = pseudocritical pressure of the mixture, in pounds per square inch absolute.

T = temperature of the mixture, in degrees Rankine.

T_{pc} = pseudocritical temperature of the mixture, in degrees Rankine.

Special Comments

In the absence of experimental data, use Procedure 13B1.1 or Procedure 13B1.2 (depending on the type of system) to determine $(pD_{1,2})^\circ$. For a multicomponent mixture at high pressure, the binary diffusion coefficients from this figure should be used in conjunction with Procedure 13B2.1.

Literature Sources

This figure was developed by Slattery and Bird, *AIChE Journal* 4 137 (1958) and reproduced in Bird et al., *Transport Phenomena*, John Wiley and Sons, Inc., New York (1960).

Example

Estimate the diffusion coefficient of *n*-hexane vapor diffusing into methane at 50 F and 600 pounds per square inch absolute.

In the absence of experimental data, calculate the diffusion coefficient for *n*-hexane in methane at 50 F and a convenient pressure less than 500 pounds per square inch absolute using Procedure 13B1.1. From the example of Procedure 13B1.1, $D_{1,2}^\circ = 0.301$ square centimeter per second at 14.7 pounds per square inch absolute. The pseudocritical properties of the predominantly methane mixture are taken as 343 R and 667 pounds per square inch absolute. The reduced pressure is therefore 0.8995 and the reduced temperature is 1.486. From Figure 13B1.4,

$$\left\{ \frac{(pD_{1,2})}{(pD_{1,2})^\circ} \right\} = 0.86$$

The desired coefficient is:

$$\begin{aligned} D_{1,2} &= (0.86) (pD_{1,2})^\circ / p \\ &= \frac{(0.86) (14.7) (0.301)}{600} \\ &= 0.0063 \text{ square feet per hour.} \end{aligned}$$

PROCEDURE 13B2.1
DIFFUSION COEFFICIENTS IN MULTICOMPONENT GAS SYSTEMS

Discussion

The following equation is recommended for the estimation of diffusion coefficients in multicomponent gaseous systems from the binary coefficients of the component pairs in the mixture:

$$D_{1, 2, 3, \dots, n} = \frac{1 - y_1}{\frac{y_2}{D_{1, 2}} + \frac{y_3}{D_{1, 3}} + \dots + \frac{y_n}{D_{1, n}}} \quad (13B2.1-1)$$

Where:

$D_{1, 2, 3, \dots, n}$ = diffusion coefficient of component 1 in the n -component mixture, in square feet per hour.

$D_{1, i}$ = binary diffusion coefficient of component 1 in component i , in square feet per hour ($i \neq 1$).

y_i = mole fraction of component i in the mixture.

Procedure

Step 1: Obtain all the necessary gas binary diffusion coefficients. In the absence of experimental data use the procedures of section 13B1.

Step 2: Calculate the multicomponent diffusivity using equation (13B2.1-1).

13B2.1

COMMENTS ON PROCEDURE 13B2.1

Purpose

This procedure is useful for estimating diffusion coefficients in multicomponent vapor systems from the binary coefficients of the component pairs in the mixture.

Limitations

Equation (13B2.1-1) is based on very few experimental data for vapor systems, most of which are nonhydrocarbons (usually hydrogen).

Reliability

Few published experimental data are available to evaluate equation (13B2.1-1). It is estimated that approximately 5 percent uncertainty is added to errors in the binary coefficients when using this equation.

Literature Source

Equation (13B2.1-1) was developed by Wilke, *Chem. Eng. Progr.* **46** 95 (1950).

Example

Estimate the diffusion coefficient of *n*-hexane at 50 F and 14.7 pounds per square inch absolute pressure in a gaseous mixture containing 0.01 mole fraction *n*-hexane, 0.03 mole fraction propane, and 0.96 mole fraction methane.

The diffusion coefficients of *n*-hexane in propane and *n*-hexane in methane are first calculated using Procedure 13B1.1. From the example for Procedure 13B1.1, $D_{c_6, c_1} = 0.3010$ square feet per hour. Similarly, $D_{c_6, c_3} = 0.1662$ square feet per hour.

The multicomponent diffusion coefficient is determined using equation (13B2.1-1):

$$D_{c_6, c_3, c_1} = \frac{(1 - 0.01)}{\left(\frac{0.03}{0.1662}\right) + \left(\frac{0.96}{0.3010}\right)}$$
$$= 0.294 \text{ square feet per hour}$$

PROCEDURE 13C1.1**DIFFUSION COEFFICIENTS OF DISSOLVED GASES IN LIQUIDS****Discussion**

The following equation is recommended for estimating diffusion coefficients of dissolved gases diffusing into liquids. It is the same equation used in Procedure 13A1.1. It was developed for use in both gas-liquid and dilute binary liquid systems.

$$D_{1,2} = 5.922 \times 10^{-8} \frac{T \bar{R}_2}{\mu \bar{R}_1^{2/3}} \quad (13C.1-1)$$

Where:

$D_{1,2}$ = diffusion coefficient of solute (component 1) in solvent (component 2), in square feet per hour.

T = temperature, in degrees Rankine.

μ = viscosity of solution (considered as pure solvent), in centipoise.

\bar{R}_2 = radius of gyration of solvent, in angstrom units.

\bar{R}_1 = radius of gyration of solute, in angstrom units.

Procedure

Step 1: Obtain \bar{R}_1 and \bar{R}_2 from Table 13A1.2. In the absence of experimental data, estimate μ using the procedures of Chapter 11.

Step 2: Calculate $D_{1,2}$ from equation (13C1.1-1).

COMMENTS ON PROCEDURE 13C1.1

Purpose

Procedure 13C1.1 is presented primarily for the estimation of diffusion coefficients of gases diffusing into nonpolar liquids.

Limitations and Reliability

Equation (13C1.1-1) was developed from hydrocarbon/hydrocarbon and hydrocarbon/carbon tetrachloride data. It is based on relatively few experimental data points. For the systems studied, an average deviation of 16 percent was obtained with occasional errors of 25 percent. It is not intended to be used for the diffusion of acid gases into liquids. The coefficients predicted for these systems are too small — generally by 40 to 50 percent.

Source of Equation

Equation (13C1.1-1) was developed by Umesi (M.S. Thesis, The Pennsylvania State University, 1980).

Example

Estimate the diffusion coefficient of methane diffusing into *n*-hexane at 86 F.

From Chapter 11, the viscosity of the solution (considered as the viscosity of pure *n*-hexane) at 86 F is 0.2820 centipoise.

From Table 13A1.2, the radius of gyration of *n*-hexane, \bar{R}_2 , is 3.812 Å and that of methane, \bar{R}_1 , is 1.1234 Å. The diffusion coefficient is calculated using equation (13C1.1):

$$D_{1,2} = \frac{5.922 \times 10^{-8} (86 + 459.7) (3.812)}{(0.282) (1.1234)^{2/3}} \\ = 4.04 \times 10^{-4} \text{ square feet per hour}$$

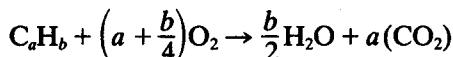
An experimental value of 3.95×10^{-4} square feet per hour is available. This estimated value represents a deviation of 2.28 percent from the experimental value.

CHAPTER 14

COMBUSTION

14-0 INTRODUCTION

The heat of combustion of a substance is the heat evolved when that substance is converted to its final oxidation products by means of molecular oxygen. The following reaction represents the complete combustion of a hydrocarbon:



The standard heat of combustion is defined as the change in enthalpy resulting from the combustion of a substance, in the state that is normal at 77 F and atmospheric pressure, beginning and ending at a temperature of 77 F. The gross heat of combustion is the same as the standard heat of combustion except that the combustion begins and ends at 60 F rather than 77 F. The normal state for the water formed by the reaction is liquid in both cases.

The difference between the standard and the gross heats of combustion is the difference between the sensible heat changes of the products and the reactants from 60 F to 77 F. This sensible heat difference is usually negligible in comparison with the heats of combustion, so the gross and standard heats of combustion are approximately equal.

The net heat of combustion is the heat evolved in a combustion beginning and ending at 60 F with products of gaseous water and carbon dioxide. Therefore,

$$\Delta H = Q - c\lambda_{H_2O} \quad (14-0.1)$$

Where:

ΔH = net heat of combustion, in British thermal units per pound of fuel.

Q = gross heat of combustion, in British thermal units per pound of fuel.

c = pounds of water formed per pound of fuel consumed.

λ_{H_2O} = heat of vaporization of water at 60 F and at its vapor pressure, in British thermal units per pound of fuel.

Pure Compounds

Net and gross heats of combustion are tabulated for many pure hydrocarbons in Tables 14A1.1 and 14A1.2. Procedure 14A1.3 may be used in determining the heats

of combustion for mixed liquid fuels, including synthetic fuels and petroleum fractions.

Inasmuch as combustion reactions proceed with a decrease in enthalpy, the enthalpy change is negative in sign. However, the heat of combustion is defined as the heat evolved; therefore, the values for heat of combustion in this chapter and Chapter 1 are positive. In all cases, complete combustion (to carbon dioxide) is assumed.

Refinery Gases and Fuel Oils

In most applications, the molecular oxygen necessary for combustion is supplied as air. To ensure complete combustion, excess air is commonly added. The following equation relates the heat available from combustion of a given fuel gas, when the flue gases exit at any temperature, t , to the gross heat of combustion and the composition of the flue gas. Excess air increases the negative term on the right-hand side of the equation, thereby decreasing the available heat, $(H_t - H_{60})$:

$$(H_t - H_{60}) = Q - \sum_{i=1}^n d_i(H_t - H_{60})_i \quad (14-0.2)$$

Where:

$(H_t - H_{60})$ = heat available from combustion when the fuel is charged at 60 F and the flue gases exit at t F, in British thermal units per pound of fuel.

$(H_t - H_{60})_i$ = total enthalpy change of flue gas component i from 60 F to t F, in British thermal units per pound of fuel.

n = total number of components in flue gas.

d_i = pounds of flue gas component i per pound of fuel consumed.

For water, $(H_t - H_{60})_{H_2O}$ contains both the sensible heat from 60 F to t F and the heat of vaporization. Equation (14-0.2) was used to develop Figures 14B1.1 through 14B1.7 for various refinery gases and fuel oils.

Equation (14-0.2) is a statement of the law of Hess: Enthalpy is a function of the state and not of the path used to reach the state. Therefore, the heat available from the combustion of a given fuel that is initially at 60 F with a given amount of air is a function only of the flue gas temperature (i.e., the final state).

TABLE 14-0.1
LIQUID AND GASEOUS FUELS

Liquid Fuels			
Gravity (Degrees API)	Sulfur (Percent by Weight)	Inerts (Percent by Weight)	Carbon-to- Hydrogen Weight Ratio
0	2.95	1.15	8.80
5	2.35	1.00	8.55
10	1.80	0.95	8.06
15	1.35	0.85	7.69
20	1.00	0.75	7.65
25	0.70	0.70	7.17
30	0.40	0.65	6.79
35 ^a	0.30	0.60	6.50

Gaseous Fuels

Nominal High ^b Heating Value (British Thermal Units per Cubic Foot at 60F)	Actual Heat of Combustion				Sulfur (Percent by Weight) ^c	Inert Gases (Percent by Weight) ^d	Molecular Weight of Hydrocarbon Portion
	Gross (British Thermal Units per Cubic Foot at 60 F)	Gross (British Thermal Units per Pound)	Net (British Thermal Units per Pound)	Net (British Thermal Units per Pound)			
1,000	1,037	21,800	19,700	—	4.72	5.38	16.5
1,200	1,248	21,600	—	—	3.88	4.42	20.4
1,400	1,458	21,500	—	—	3.32	3.78	24.3
1,600	1,669	21,300	19,400	—	2.90	3.30	28.2
1,800	1,879	21,000	—	—	2.52	2.88	32.1
2,000	2,090	20,800	—	—	2.29	2.61	36.1

^aAbove 35°API, the correction for impurities in Procedure 14A1.3 is negligible and the equations represent pure paraffins (carbon-to-hydrogen weight ratio is $12.0n/2n + 2$, where n is the number of carbon atoms in the hydrocarbon).

^bThe nominal high heating value is an approximate gross heat of combustion.

^cEquivalent to 2.5 mole percent hydrogen sulfide.

^dEquivalent to 1.25 mole percent carbon dioxide and 1.25 mole percent air.

Flue Gases

The enthalpies of common flue gas components are plotted in Figures 14C1.1 and 14C1.2. The enthalpy basis (enthalpy is zero for the ideal gas at 60 F) is more convenient for combustion calculations than the basis used in the rest of this book. These enthalpies may be used in equation (14-0.2) with Table 14A1.1 heats of combustion to calculate the heat available from combustion as a function of temperature for pure hydrocarbons.

Figures 14B1.1 through 14B1.7 (see Table 14-0.1) were prepared for various liquid and gaseous fuels containing arbitrary amounts of impurities.

Most procedures include corrections to be used when the composition of the fuel differs appreciably from those previously tabulated.

The weight ratio of flue gas to fuel, for refinery gases and fuel oil, can be determined as a function of percent excess air by making a simple material balance. Equating the weight of the fuel minus the inert plus air to the weight of the flue gas gives the following relation for fuel oil:

$$\frac{\text{lb flue gas}}{\text{1 lb fuel}} = \frac{64.1x_{ws}}{32.1} + \frac{44.0(\text{C/H})(1 - x_{ws} - x_{wi})}{12.0(\text{C/H} + 1)} + \frac{18.0(1 - x_{ws} - x_{wi})}{2(\text{C/H} + 1)} + \left[\frac{x_{ws}}{32.1} + \frac{(\text{C/H})(1 - x_{ws} - x_{wi})}{12.0(\text{C/H} + 1)} + \frac{1 - x_{ws} - x_{wi}}{4(\text{C/H} + 1)} \right] \left[\frac{(79)(28.0)}{21} + \frac{(29.0)(\% \text{ Ex Air})}{21} \right] \quad (14-0.3)$$

Where:

x_{ws} = weight fraction of sulfur.
 x_{wi} = weight fraction of inerts.

C/H = carbon-to-hydrogen weight ratio.
% Ex Air = mole percent of excess air.

The mole percent of carbon dioxide in the flue gas may be obtained by a similar material balance. The percent carbon dioxide on a water-free basis is given as

$$\% \text{ CO}_2 = \frac{(C/H)(1 - x_{ws} - x_{wi})}{(12.0)(C/H + 1) \left\{ \frac{x_{ws}}{32.1} + \frac{(C/H)(1 - x_{ws} - x_{wi})}{12.0(C/H + 1)} + \left(\frac{79}{21} + \frac{\% \text{ Ex Air}}{21} \right) \right\} \left[\frac{x_{ws}}{32.1} + \frac{(C/H)(1 - x_{ws} - x_{wi})}{12.0(C/H + 1)} + \frac{(1 - x_{ws} - x_{wi})}{4(C/H + 1)} \right]} \quad (14-0.4)$$

For refinery gases, calculations should account for the fact that inert gases (in this case, carbon dioxide and air) appear in the flue gas. Equations (14-0.3) and (14-0.4) are based on data given by Maxwell (4), and assumes average impurities as given in Table 14-0.1.

Coal

ASTM D 388 (1) gives the heating value ranges for

the various grades of coal, as reproduced in Table 14-0.2.

Procedure 14D1.1 is used to compute the gross and net calorific values of coal. These heating values are a function of the ultimate analysis and moisture percentage of the coal.

TABLE 14-0.2
CLASSIFICATION OF COAL BY RANK

Class	Group	Agglomerating Character ^a	Fixed Carbon Limits, % ^b		Volatile Matter Limits, % ^b		Gross Calorific Value Limits, Btu/lb ^c	
			≥	<	>	≤	≥	<
Anthracitic	Meta-anthracite	N	98	—	—	2	—	—
	Anthracite	N	92	98	2	8	—	—
	Semianthracite ^d	N	86	92	8	14	—	—
Bituminous	Low-volatile bituminous	CA ^e	78	86	14	22	—	—
	Medium-volatile bituminous	CA ^e	69	78	22	31	—	—
	High-volatile A bituminous	CA ^e	—	69	31	—	14,000 ^f	—
	High-volatile B bituminous	CA ^e	—	—	—	—	13,000 ^f	14,000
	High-volatile C bituminous	CA ^e	—	—	—	—	11,500	13,000
		A	—	—	—	—	10,500	11,500
Subbituminous	Subbituminous A	N	—	—	—	—	10,500	11,500
	Subbituminous B	N	—	—	—	—	9,500	10,500
	Subbituminous C	N	—	—	—	—	8,300	9,500
Lignitic	Lignite A	N	—	—	—	—	6,300	8,300
	Lignite B	N	—	—	—	—	—	6,300

NOTE: This table is adapted and republished by permission of ASTM from ASTM D 388, "Standard Classification of Coals by Rank," 1983 Annual Book of ASTM Standards, Volume 05.05. This classification does not include a few coals, principally nonbanded varieties, that have unusual physical and chemical properties and come within the limits of fixed carbon or calorific value of the high-volatile bituminous and subbituminous ranks. All of these coals either contain less than 48 percent dry, mineral-matter-free fixed carbon or have more than 15,500 British thermal units per pound on the moist, mineral-matter-free basis.

^a A = agglomerating; CA = commonly agglomerating; N = nonagglomerating.

^b Dry, mineral-matter-free basis.

^c Moist, mineral-matter-free basis, moist referring to coal containing its natural inherent moisture but not including visible water on the surface of the coal.

^d If agglomerating, classify in low-volatile group of the bituminous class.

^e It is recognized that there may be nonagglomerating varieties in these groups of the bituminous class, and there are notable exceptions in high-volatile C bituminous group.

^f Coals having 69 percent or more fixed carbon on the dry, mineral-matter-free basis should be classified according to fixed carbon, regardless of calorific value.

PROCEDURE 14A1.3

HEATS OF COMBUSTION OF PETROLEUM FRACTIONS AND SYNTHETIC FUELS

Discussion

The following equation is used to predict the gross heat of combustion of petroleum fractions and synthetic fuels:

$$-\Delta H_{c,60}^* = 17,672 + 66.6G - 0.316G^2 - 0.0014G^3 \quad (14A1.3-1)$$

Where:

$-\Delta H_{c,60}^*$ = gross heat of combustion at 60 F, in British thermal units per pound.

G = API gravity.

If water is present in the fuel or if impurities are significantly different from those given in the Introduction, the following equation should be used to correct for it:

$$-\Delta H_{c,60} = (-\Delta H_{c,60}^*) - 0.01(-\Delta H_{c,60}^*)(\% \text{ H}_2\text{O} + \% \text{ S}_e + \% \text{ Inerts}_e) + 40.5(\% \text{ S}_e) \quad (14A1.3-2)$$

Where:

$-\Delta H_{c,60}$ = corrected gross heat of combustion, in British thermal units per pound.

% H_2O = weight percent of water in the fuel.

% S_e = weight percent of sulfur in the fuel minus the average weight percent (given in the Introduction).

% Inerts_e = weight percent of inerts in the fuel minus the average weight percent (given in the Introduction).

The net heat of combustion is obtained from equation (14A1.3-3).

$$-\Delta H_{c,60}^* (\text{net}) = 16,796 + 54.5G - 0.217G^2 - 0.0019G^3 \quad (14A1.3-3)$$

Where:

$-\Delta H_{c,60}^* (\text{net})$ = heat of combustion at 60 F, in British thermal units per pound.

$$-\Delta H_{c,60} (\text{net}) = [-\Delta H_{c,60}^* (\text{net})] - 0.01[-\Delta H_{c,60}^* (\text{net})](\% \text{ H}_2\text{O} + \% \text{ S}_e + \% \text{ Inerts}_e) + 40.5(\% \text{ S}_e) - 10.53(\% \text{ H}_2\text{O}) \quad (14A1.3-4)$$

Where:

$-\Delta H_{c,60} (\text{net})$ = corrected net heat of combustion at 60 F, in British thermal units per pound.

Procedure

Step 1: Obtain the API gravity and the impurity and moisture weight percents of the petroleum fraction or synthetic fuel.

Step 2: Use equations (14A1.3-1) and (14A1.3-2) to calculate the gross heat of combustion.

Step 3: Calculate the net heat of combustion from equations (14A1.3-3) and (14A1.3-4).

14A1.3

COMMENTS ON PROCEDURE 14A1.3

Purpose

Procedure 14A1.3 is a method to estimate heats of combustion of petroleum liquids and synthetic fuels.

Reliability

Gross heats of combustion estimated by this procedure have an average error of 180 British thermal units per pound of fuel. An average deviation of 205 British thermal units per pound of fuel was obtained for predicted net heat of combustion values.

Literature Sources

Equations (14A1.3-1) and (14A1.3-3) were developed using the figure given by J. B. Maxwell, *Data Book on Hydrocarbons*, D. Van Nostrand Company, Inc., Princeton, N.J. (1950). Equations (14A1.3-2) and (14A1.3-4) were given in *Standard Design Data*, Foster Wheeler Corporation, New York (1960).

Example

Determine the gross and net heats of combustion of an 11.3°API fuel oil that contains 1.49 weight percent sulfur, 1.67 weight percent inerts and 0.30 weight percent water.

The average percent of sulfur in an 11.3°API fuel on which equations (14A1.3-1) and (14A1.3-3) are based is 1.68 by interpolation from the table in the Introduction, so % S_e = 1.49 - 1.68 = -0.19. Similarly, the average inerts content for the basis fuel is 0.92, so % Inerts_e = 1.67 - 0.92 = 0.75.

The gross heat of combustion can now be calculated from equations (14A1.3-1) and (14A1.3-2).

$$-\Delta H_{c,60}^* = 17,672 + 66.6(11.3) - 0.316(11.3)^2 - 0.0014(11.3)^3 \\ = 18,382$$

$$-\Delta H_{c,60} = 18,382 - (0.01)(18,382)(0.3 - 0.19 + 0.75) + 40.5(-0.19) \\ = 18,216 \text{ British thermal units per pound of fuel}$$

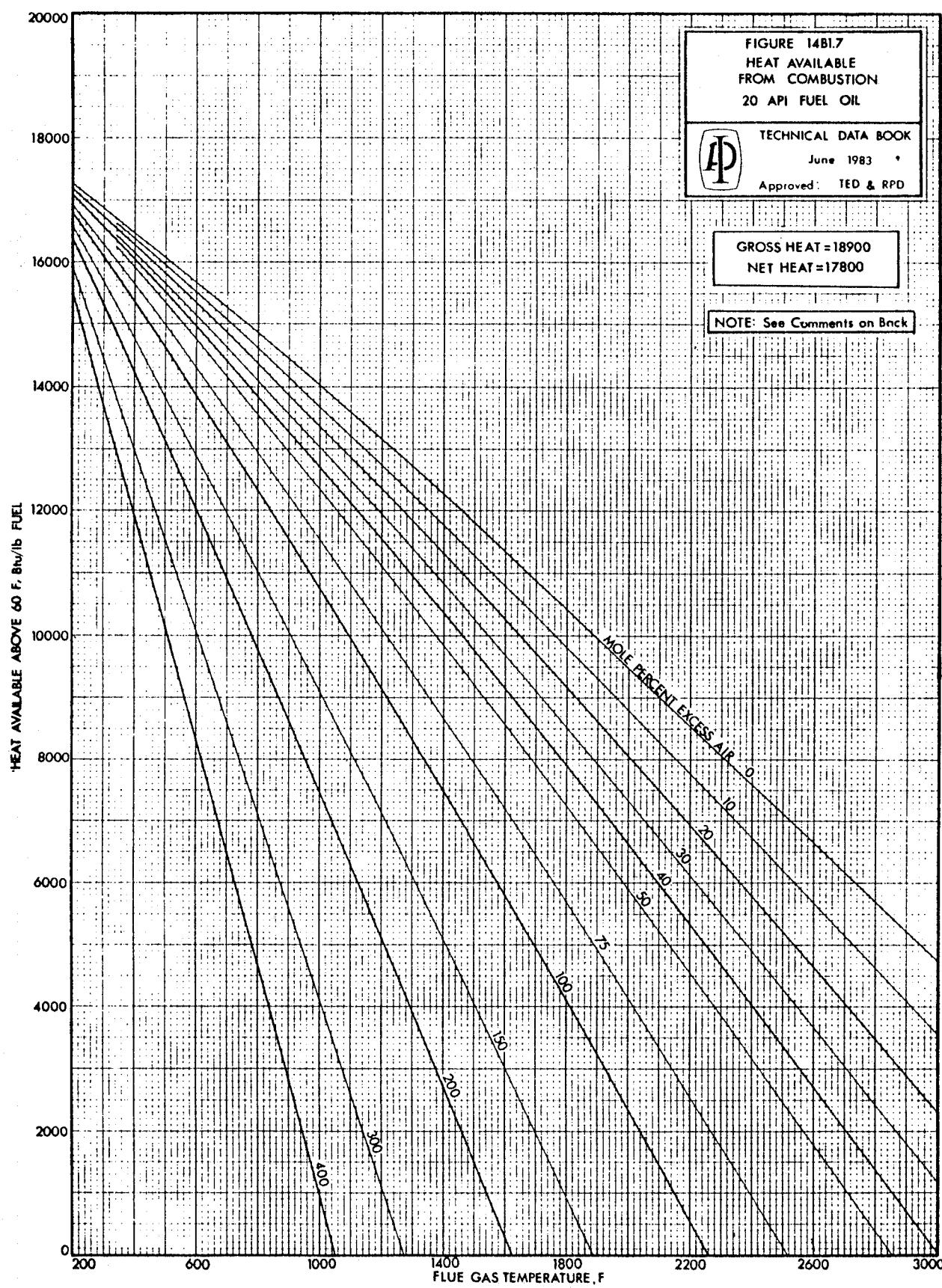
An experimental value is 18,088 British thermal units per pound of fuel.

From equations (14A1.3-3) and (14A1.3-4), the net heat of combustion is

$$-\Delta H_{c,60}^*(\text{net}) = 16,796 + 54.5(11.3) - 0.217(11.3)^2 - 0.0019(11.3)^3 \\ = 17,381$$

$$-\Delta H_{c,60}(\text{net}) = 17,381 - 0.01(17,381)(0.30 - 0.19 + 0.75) + 40.5(-0.19) - 10.53(0.30) \\ = 17,221 \text{ British thermal units per pound of fuel}$$

An experimental value is 17,128 British thermal units per pound of fuel.



COMMENTS ON FIGURES 14B1.1 THROUGH 14B1.7**Purpose**

The heat available from the combustion of refinery gases and fuel oils to gaseous products is given in Figures 14B1.1 through 14B1.7 as a function of temperature and percent excess air.

Limitations

An allowance was made for an average sulfur and inert content in the fuel, but not for the presence of water.

Reliability

The estimated average deviation of these figures is 1 percent for the fuels defined in the Introduction.

Special Comments

Figures 14B1.1 and 14B1.2 were derived using only mixtures of paraffin gases. The figure more nearly corresponding to the gross heat of combustion of the fuel gas can be used without interpolation with very little error. In correcting for the variation in impurities, however, the available heat must be adjusted in proportion to the weight percentage of the hydrocarbon present in the fuel gas. Consider half of the hydrogen sulfide a hydrocarbon (i.e., a source of heat) and half as an inert gas (see Example).

Figures 14B1.3 through 14B1.7 represent the heat available from fuel oils having API gravities of 0, 5, 10, 15, and 20 degrees. If the impurities are known to be appreciably different from the average values, the available heat may be corrected in direct proportion to the weight percentage of the hydrocarbon present in the fuel, with sulfur considered an inert material. The average impurities used to develop the figures are tabulated in the Introduction.

Interpolation between the figures is unnecessary; the available heat at any temperature and percent of excess air can be read from the chart which most nearly corresponds to the gravity of the fuel oil.

Literature Source

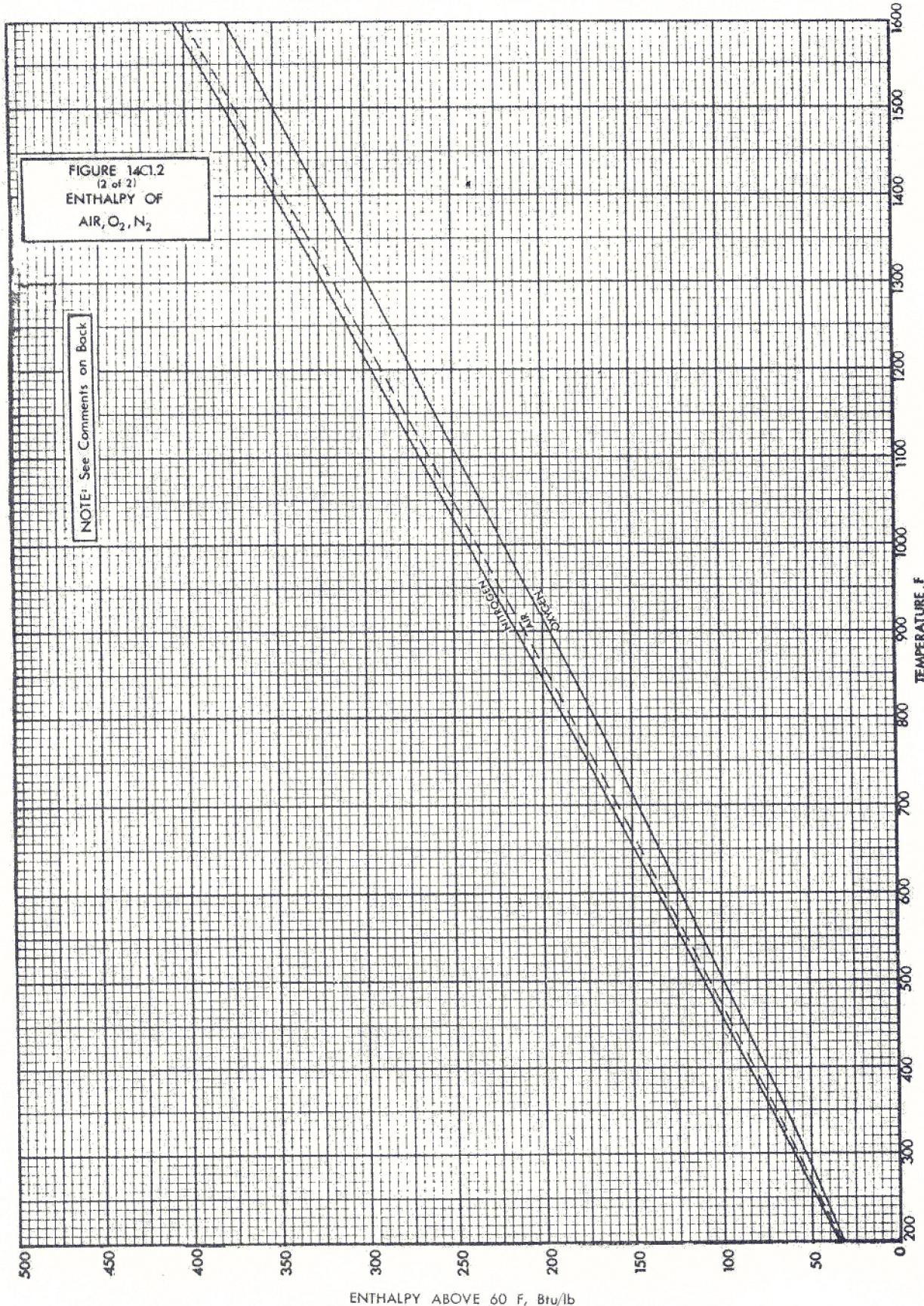
These charts were patterned after those of Maxwell, *Data Book on Hydrocarbons*, D. Van Nostrand Company, Inc., Princeton, N.J. (1950). The figures were replotted to be consistent with the more recent enthalpy data in Chapter 7.

Example

Estimate the heat available from the combustion of a refinery gas having a gross heat of combustion of 1200 British thermal units per cubic foot (60 F) with 100 percent excess air. The fuel contains the following impurities: 8.0 percent by weight hydrogen sulfide and 12.0 percent by weight inert gases. The flue gases exit at 2000 F.

Inasmuch as 1200 British thermal units per cubic foot (60 F) is closer to 1000 than 1600, Figure 14B1.1 should be used. Because the amount of impurities is significantly larger than the average values, the heat available must be corrected. From Figure 14B1.1, the uncorrected heat available is 1950 British thermal units per pound of fuel for the average fuel containing 8.3 percent inert gases from the table in the Introduction. Half the hydrogen sulfide, or 4 percent by weight, must be considered inert gases. Therefore, the total amount of impurities is $4 + 12 = 16$ percent by weight.

Total heat available = $(1950)(100 - 16)/(100 - 8.3) = 1786$ British thermal units per pound of fuel.



COMMENTS ON FIGURES 14C1.1 and 14C1.2**Purpose**

The enthalpy above 60 F for various flue gas components is plotted as a function of temperature. The enthalpy values are for low-pressure gases only (less than 50 pounds per square inch absolute).

Reliability

The estimated average deviation of these figures is 1 percent.

Special Comments

To prepare the figures, the ideal gas enthalpies given in Chapter 7 were converted to a basis of zero for the ideal gas at 60 F. This basis is preferable for combustion calculations inasmuch as standard heats of combustion are normally given at these conditions. The curve for air was obtained by assuming a composition of 21 percent by volume oxygen and 79 percent by volume nitrogen. No correction has been made for dissociation of the molecules at high temperatures.

Literature Source

The figures were plotted using the ideal gas enthalpy data given in Chapter 7.

PROCEDURE 14D1.1**GROSS/NET CALORIFIC VALUE OF COALS****Discussion**

The following equation is used to estimate the gross calorific value of coal:

$$Q_v = 146.58C + 568.78H + 29.4S - 6.58A - 51.53(O + N) \quad (14D1.1-1)$$

Where:

Q_v = gross calorific value at constant volume, British thermal units per pound, on a dry basis.

C = weight percent of carbon.

H = weight percent of hydrogen.

S = weight percent of total sulfur.

A = weight percent of ash.

(O + N) = weight percent of oxygen plus nitrogen by difference.

The weight percents are on a dry basis.

The gross calorific value at constant pressure is obtained from the equation (14D1.1-2).

$$Q_p = Q_v + 2.6H - 0.33O \quad (14D1.1-2)$$

Where:

Q_p = gross calorific value at constant pressure.

Equation (14D1.1-3) is used to calculate the net or low calorific value at constant pressure.

$$Q_p(\text{net}) = Q_v - 92.2H - (0.33)O - 10.50M \quad (14D1.1-3)$$

Where:

$Q_p(\text{net})$ = net calorific value at constant pressure.

M = percent moisture in the coal.

Q_v , H, O are on a moist basis.

Procedure

Step 1: Obtain the ultimate analysis and percent moisture of the coal.

Step 2: Use equation (14D1.1-1) or (14D1.1-2) to calculate the gross calorific value.

Step 3: Calculate the net calorific value from equations (14D1.1-1) and (14D1.1-3).

COMMENTS ON PROCEDURE 14D1.1**Purpose**

This procedure may be used to predict the gross and net calorific value of a coal given the ultimate analysis and percent moisture of the coal.

Reliability

Gross calorific values estimated by this procedure have an average error of 115 British thermal units per pound.

Literature Source

Equations (14D1.1-1) through (14D1.1-3) were given in *Coal Conversion Systems Technical Data Book*, U.S. Department of Energy (1978).

Example

Calculate the gross calorific value of an Illinois No. 6 coal with the following composition given on a dry basis:

Carbon	= 68.92%
Hydrogen	= 5.01%
Nitrogen	= 1.01%
Sulfur	= 6.66%
Ash	= 10.84%
Oxygen	= 7.57% (by difference)

From equation (14D1.1-1)

$$Q_v = 146.58(68.92) + 568.78(5.01) + 29.4(6.66) - 6.58(10.84) - 51.53(7.57 + 1.01) \\ = 12,634 \text{ British thermal units per pound}$$

$$Q_p = 12,634 + 2.6(5.01) - 0.33(7.57) \\ = 12,645 \text{ British thermal units per pound}$$

The experimental value is 12,773 British thermal units per pound.

CHAPTER 15

ADSORPTION EQUILIBRIA

Added Chapter 15 Revising the First Edition (1966),
Second Edition (1970), Third Edition(1976), and Fourth
Edition (1983)

PREFACE

This chapter on adsorption is the first completely new chapter added to the *Technical Data Book—Petroleum Refining* since its first edition. The Technical Data Committee felt that the use of physical adsorption for separations, the technical advances that have been made in the area of adsorption, and the lack of sources of practical design information on adsorption were justification for addition of this new chapter. During the past 2 years an extensive data bank on the physical adsorption equilibria of gases and liquids on solids has been collected, and potentially useful correlations have been evaluated with this data bank. Whenever possible, recommended procedures are given in the chapter for correlating or predicting equilibria data. In addition, bibliographies of available data and recommended references for studying the treatment of adsorption data are given. This chapter deals only with physical adsorption. Chemical adsorption is not considered.

Detailed results of the evaluations used in selecting the recommended procedures are given in Documentation Report No. 15-83, available from University Microfilms, Ann Arbor, Michigan.

Work on this chapter was done by S. D. Mehta and the project directors, Ronald P. Danner and Thomas E. Daubert. The chapter coordinator for the Technical Data Committee was G. E. Merritt, Arco Petroleum Products Company. Many other members of the committee contributed useful suggestions.

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August 1983

CHAPTER 15

ADSORPTION EQUILIBRIA

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CHAPTER 15

ADSORPTION EQUILIBRIA

15-0 INTRODUCTION

Gas Adsorption

Gas adsorption is commonly used to separate gas mixtures and to remove contaminants from gaseous products or discharge streams. The first two sections of this chapter present a summary of the available information on gas adsorption as applied to gas separation (physical adsorption) and recommend state-of-the-art procedures for treatment of pure-gas isotherm data and for predicting multicomponent adsorption equilibria. The area of chemical adsorption germane to catalytic systems is not discussed in this chapter.

Physical adsorption is characterized by relatively low heats of adsorption (of the order of magnitude of heats of vaporization) and by highly reversible adsorption and desorption with rising or falling pressure. Chemical adsorption, on the other hand, exhibits high heats of adsorption (of the order of magnitude of chemical reaction heats) and highly irreversible adsorption. In fact, the desorbed material may have a different chemical composition than the adsorbed material.

Modeling of physical adsorption of gases has been approached in several different ways, as described below.

Method 1: The adsorbed layer has been treated as a two-dimensional phase whose behavior can be described by a two-dimensional equation of state analogous to the ideal gas equation, the van der Waals equation, the virial equation, and the like. In such an equation the volume per mole of gas is replaced by area of the adsorbent covered per mole, and the normal three-dimensional pressure is replaced by a pressure exerted by the molecules moving in only two dimensions, called the spreading pressure. While this spreading pressure cannot be measured directly, it can be calculated from adsorption data as described in Procedure 15B1.7.

Method 2: The solid adsorbent has been considered as a source of a potential field that causes the gas around it to assume density gradients just as the earth causes density gradients in its surrounding atmosphere.

Method 3: The interaction between the solid surface and the gas molecules has been treated in terms of the kinetics of the molecules colliding with the surface,

sticking for some period of time, and then escaping from the surface. This type of modeling leads directly to the Langmuir and Brunauer-Emmett-Teller (BET) equations.

Method 4: For solids that have uniform, well-defined micropores, a simple statistical thermodynamic model has been developed. In this case, it is assumed that the adsorbed molecules are confined within the cavities of the solid rather than at localized sites and that the adsorbate-adsorbent interaction potential is independent of the number of sorbate molecules present within a cavity. The adsorbate-adsorbate interactions within a cavity are treated by an equation of state.

Method 5: The adsorbed phase is treated as an equilibrium phase analogous to the liquid phase in vapor-liquid equilibrium. The adsorbed phase is characterized by the two-dimensional spreading pressure instead of the normal three-dimensional pressure, and the volume per mole is replaced by the area covered per mole. This type of treatment is referred to as the thermodynamic solution theory of adsorption.

Although each of these methods of modeling adsorption has its advantages and disadvantages, the following generalizations can be made:

- a. For correlating the temperature effects on the adsorption of a pure gas on a particular solid or relating the adsorptivity of very similar components on a particular solid, the potential theory approach (method 2) is most useful.
- b. For characterizing surface areas of solids, the BET method based on method 3 has received universal acceptance.
- c. For correlating and predicting gas mixture adsorption equilibria, the thermodynamic solution theory (method 5) has been most successful.

The equilibrium between an adsorbed phase and a bulk gas phase involves an additional variable, the area of the solid, and one more degree of freedom than the case of vapor-liquid equilibrium. The nature of the solid surface is quite complex and difficult to characterize. Furthermore, the collection of data for the adsorption equilibria of gas mixtures on a solid adsorbent is a difficult experimental task. Thus it is not surprising that gas adsorption lags behind vapor-liquid equilibria in both theoretical developments and technology. Fortunately,

the experimental procedure required for the collection of pure-gas isothermal adsorption data is relatively simple, at least in moderate pressure and temperature ranges. The most useful methods of predicting gas-mixture adsorption equilibria use the pure-gas isotherms to characterize the interaction between the gas molecules (adsorbate) and the solid surface (adsorbent).

Frequently, little information is available to characterize the surface of a solid adsorbent. One parameter that is sometimes given, however, is the BET surface area. This surface area is calculated by estimating the number of nitrogen molecules it takes to completely cover the surface with a single layer of molecules at the normal boiling point of nitrogen, and multiplying that number by the area covered per molecule. The volume of nitrogen for the monolayer coverage is calculated from the BET equation [equation (15A1.13-1)]. While these surface areas are rather arbitrary, they do indicate relative adsorptivities for *similar* adsorbents. Ratios of the surface areas of two adsorbents of the same type can be used to predict the adsorption amount on one of them if the other is known. Surface area comparisons should be viewed with skepticism, however, if the adsorbents are quite different in polarity or pore structure.

Liquid Adsorption

The adsorption of liquid mixtures on solids is important in many industrial processes and in chromatographic separations. In spite of this fact, study of liquid adsorption has received serious attention only in the later part of this century. In the last section of this chapter, the available data and useful correlation methods for liquid-solid equilibrium are summarized. Here again, as in the sections on gas adsorption, consideration is given only to physical adsorption; chemisorption is excluded from the discussion.

There is a basic difference between the treatment of adsorption at the liquid-solid interface and adsorption at the gas-solid interface. This is because in the case of adsorption from liquid mixtures, the absolute amount adsorbed cannot be measured directly. Experimentally, one determines changes in bulk liquid concentration, which is then used to calculate the surface excess. The surface excess is defined as the amount of adsorbate found in the adsorption layer minus the amount that would be found there if the bulk concentration extended uniformly up to the solid surface. Thus, for liquid adsorption, the pertinent variable describing the equilibrium is the surface excess rather than the actual amount adsorbed.

Adsorption isotherms of binary liquid systems are relatively easy to determine since changes in concentration can be measured directly. Although there are methods available to qualitatively predict binary liquid adsorption isotherms by using the pure-vapor isotherms of each of the two components, one can seldom use these methods, because the vapor data are usually not available. Representation of the binary liquid data by an analytical expression facilitates interpolation or extrapolation of the data in the range of interest. There are two useful methods for doing this: a linear correlation for the surface excess, based on the assumption of monolayer adsorption from an ideal solution; and a more accurate nonlinear correlation for the adsorbed phase mole fraction, based on the assumption of regular bulk and adsorbed solutions. These correlations could presumably also be useful in methods to predict multi-component liquid adsorption equilibrium from binary liquid data.

Chapter Contents

A summary of some of the most useful sources of information on adsorption is given below. References for the correlation methods that have been judged to be of the most potential use are listed, and bibliographies of the available adsorption data for pure-gas systems, gas mixtures, and liquid mixtures are given in Tables 15-0.1, 15-0.2 and 15-0.3.

Figures 15A1.1 through 15A1.10 provide typical isothermal pure-gas adsorption data. Table 15A1.11 gives the adsorption capacities of various adsorbents for water. Table 15A1.12 provides estimates of the isosteric heat of adsorption in a number of temperature ranges. These tables can be helpful in preliminary comparisons and selection of systems for further study. Procedures 15A1.13 and 15A1.14 describe the use of the BET model and a solution thermodynamic model for correlation of pure-gas isotherm data.

The use of the potential theory for correlating the temperature effects on pure-gas adsorption is described in Procedure 15A2.1. Some typical examples and potentially useful data are given in Figures 15A2.2 through 15A2.6.

Section 15B treats gas-mixture adsorption. Some typical adsorption phase equilibrium diagrams are shown in Figures 15B1.1 through 15B1.6. Procedures 15B1.7 and 15B1.8 present two solution thermodynamic models that are useful for the prediction of gas-mixture equilibria from pure-gas isotherm data.

(text continued on page 15-9)

TABLE 15-0.1

LITERATURE SOURCES OF PURE-GAS ADSORPTION DATA

Component	Adsorbent	Temperature Range (F)	Pressure Range (psia)	Reference
Methane	Active carbon	-77 to 300	0 to 1000	21,38,39,72,97,98,100,120, 121,126
	Silica gel	75 to 300	15 to 2000	38, 72,77
	Molecular sieve 4A	-100 to 300	0 to 20	72
Ethane	Active carbon	-77 to 400	0 to 1000	21,38,62,66,72,97,98,120,121
	Silica gel	32 to 300	2 to 2000	38,52,72,77
	Zeolites (general)	77 to 200	0 to 15	12,13
	Molecular sieve 4A	32 to 600	0 to 20	72
	Molecular sieve 13X	32 to 212	0 to 20	22,50
Propane	Active carbon	32 to 450	0 to 1000	38,52,70,72,97,120,121
	Silica gel	-30 to 300	0 to 1000	38,52,67,70,72,76,77
	Molecular sieve 4A	77	3 to 20	72
	Molecular sieve 5A	77 to 185	0 to 15	47,72
	Molecular sieve 13X	77	0 to 15	72
<i>n</i> -Butane	Active carbon	68 to 400	0 to 1000	38,97,120
	Silica gel	75 to 300	10 to 1000	38
	Molecular sieve 13X	77	0 to 15	72
<i>i</i> -Butane	Active carbon	75 to 300	10 to 1000	38
	Silica gel	75 to 300	10 to 1000	38,77
	Molecular sieve 13X	77 to 212	0 to 20	50
<i>n</i> -Pentane	Active carbon	75 to 300	10 to 1000	38
	Silica gel	75 to 300	10 to 1000	38,77
	Molecular sieve 5A	32 to 660	0 to 4	72
<i>i</i> -Pentane	Active carbon	75 to 300	10 to 1000	38
	Silica gel	75 to 300	10 to 1000	38
<i>n</i> -Hexane	Molecular sieve 13X	77	0 to 15	72
<i>n</i> -Heptane	Active carbon	77	0 to 1	72
	Silica gel	77 to 300	0 to 1	72
	Molecular sieve 5A	77 to 300	0 to 1	72
	Molecular sieve 13X	77 to 300	0 to 1	72
Ethylene	Active carbon	-77 to 400	0 to 250	9,21,52,72,97,98,120,121
	Silica gel	32 to 104	0 to 15	52,67,71,72
	Zeolites (general)	77 to 200	0 to 15	13
	Molecular sieve 4A	32 to 300	0 to 20	72
	Molecular sieve 5A	-46 to 572	0 to 15	25,47,72
	Molecular sieve 13X	77 to 212	0 to 23	22,50
Propene	Active carbon	32 to 250	0 to 120	21,52,66,70,72,97,120,121
	Silica gel	-32 to 104	0 to 15	52,67,70,72,76
	Molecular sieve 4A	77 to 660	0 to 20	72
	Molecular sieve 5A	32 to 365	0 to 6	25
	Molecular sieve 13X	77 to 572	0 to 15	72
1-Butene	Active carbon	77	0 to 15	72
	Silica gel	77	0 to 15	72
	Molecular sieve 5A	77	0 to 15	72
Acetylene	Active carbon	68 to 250	0 to 20	66,71,72,97,120
	Silica gel	77	2 to 14	71
	Molecular sieve 4A	77	0 to 20	72
Benzene	Active carbon	77	0 to 1.4	72
	Silica gel	77	0 to 1.4	72
	Molecular sieve 5A	77	0 to 1.4	72
	Molecular sieve 13X	77 to 300	0 to 1.4	72

TABLE 15-0.1 (Continued)

Component	Adsorbent	Temperature Range (F)	Pressure Range (psia)	Reference
Oxygen	Silica gel	32 to 212	0 to 15	75
	Zeolites (general)	-320 to 0	0 to 15	2
	Molecular sieve 4A	-300 to 122	0 to 15	72
	Molecular sieve 5A	-200 to -97.6	0 to 31	23,102
	Molecular sieve 10X	-200 to 32	0 to 42	23,26,91
	Molecular sieve 13X	32 to 212	0 to 15	75
Nitrogen	Active carbon	-320 to 300	0 to 220	33,52,81,97,126
	Silica gel	-171	0 to 7	52
	Zeolites (general)	-145 to 0	0 to 15	2
	Molecular sieve 4A	-108 to 32	0 to 15	102
	Molecular sieve 5A	-320 to 32	0 to 31	23,72,102
	Molecular sieve 10X	-320 to 32	0 to 37	23,91
Carbon dioxide	Molecular sieve 13X	-320 to -297	0 to 15	72,123
	Active carbon	-77 to 300	0 to 1000	9,38,52,72,81,97,98,100,120, 121,126
	Silica gel	32 to 300	0 to 1000	38,52,72,75
	Zeolites (general)	-107 to 320	0 to 735	17
	Molecular sieve 4A	-100 to 660	0 to 20	72
	Molecular sieve 5A	32 to 575	0 to 20	72
Carbon monoxide	Active carbon	77 to 400	0 to 260	97,126
	Silica gel	32 to 212	0 to 15	75
	Molecular sieve 4A	-100 to 32	0 to 15	72
	Molecular sieve 5A	-320 to 32	0 to 20	23,34,72,102
	Molecular sieve 10X	-200 to 32	0 to 38	23,26,91
Hydrogen	Active carbon	32 to 200	0 to 260	31,97,126
Helium	Active carbon	-280 to -190	28 to 1632	33
Hydrogen sulfide	Active carbon	-6 to 212	0 to 20	40
	Silica gel	302	0 to 8	37
	Molecular sieve 4A	77 to 302	0 to 4	72
	Molecular sieve 5A	77 to 302	0 to 15	72
	Molecular sieve 13X	77 to 302	0 to 8	37

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TABLE 15-0.2

LITERATURE SOURCES OF GAS-MIXTURE ADSORPTION DATA

Gas-Mixture Components	Adsorbent	Temperature (F)	Pressure (psia)	Reference
Two-Component Systems				
CH ₄ –C ₂ H ₆	AC-40 active carbon Nuxit-AL active carbon Silica gel	68 68 77	1.5 14.7 0 to 1400	21 122 78
C ₃ H ₆	Columbia G active carbon	140	14.7	125
C ₂ H ₄	AC-40 active carbon Nuxit-AL active carbon	68 68	1.5 14.4	21 122
CO	BPL active carbon	77	50	126
CO ₂	BPL active carbon	77	50	126
C ₂ H ₆ –C ₃ H ₈	Molecular sieve MSC-5A Nuxit-AL active carbon	41, 86 68, 140	1.9, 5.8 14.7	89 122
i-C ₄ H ₁₀	Molecular sieve 13X	77, 122	20	50
C ₂ H ₄	AC-40 active carbon Molecular sieve 13X	68 77, 122	1.5 20	21 22
Nuxit-AL active carbon	68, 140	14.7	122	
C ₃ H ₆	AC-40 active carbon BPL active carbon	68 86, 104, 122	1.5 3.9, 5.8, 7.7	21 65
CO ₂	Columbia G active carbon Silica gel	32, 86 32, 77	14.7 14.7	52 52
C ₃ H ₈ –n-C ₄ H ₁₀	Columbia G active carbon Nuxit-AL active carbon	140 68	14.7 14.5	111 122
C ₂ H ₄	Silica gel	32, 77, 104	14.7	67
C ₃ H ₆	GLC active carbon Nuxit-AL active carbon	77 68	14.7 14.7	70 122
Silica gel	77	14.7	70	
CO ₂	Columbia G active carbon Silica gel	32, 86 32, 86	14.7 14.7	52 52
i-C ₄ H ₁₀ –C ₂ H ₄	Molecular sieve 13X	77, 122, 212	20	50
C ₂ H ₄ –C ₃ H ₆	AC-40 active carbon Nuxit-AL active carbon	68 68	1.45 14.7	21 122
Silica gel	32, 77, 104	14.7	67	
C ₂ H ₂	PCC active carbon Silica gel	77 77	14.7 14.7	71 71
CO ₂	Columbia G active carbon Molecular sieve 13X	32, 86 77, 122	14.7 20	52 50
Nuxit-AL active carbon	68	14.7	122	
Silica gel	32, 77	14.7	52	
C ₃ H ₆ –CO ₂	Columbia G active carbon Silica gel	32, 86 32, 77	14.7 14.7	52 52
Molecular sieve 5A	-200	14.7	23	
Molecular sieve 10X	-200	14.7	23	
CO	Molecular sieve 10X	-150, -50, 32	14.7	91
Molecular sieve 5A	-200	14.7	23	
Molecular sieve 10X	-200	14.7	23	
Molecular sieve 10X	-150, -50, 32	14.7	91	
Molecular sieve 10X	-150, -50, 32	14.7	91	
N ₂ –CO	Molecular sieve 5A	-200	14.7	23
Molecular sieve 10X	-200	14.7	23	

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TABLE 15-0.2 (Continued)

Gas-Mixture Components	Adsorbent	Temperature (F)	Pressure (psia)	Reference
Two-Component Systems				
CO ₂ -CO	BPL active carbon	77	50, 100	126
H ₂	Columbia G active carbon	32	14.7	52
Three-Component Systems				
CH ₄ -C ₂ H ₆ -C ₂ H ₄	AC-40 active carbon	68	1.5	21
CH ₄ -C ₂ H ₆ -H ₂	Nuxit-AL active carbon	68	14.7	122
CH ₄ -C ₃ H ₈ -n-C ₄ H ₁₀	Columbia G active carbon	140	14.7	125
CH ₄ -CO ₂ -CO	BPL active carbon	77	50	126
C ₂ H ₆ -C ₂ H ₄ -C ₃ H ₆	AC-40 active carbon	68	1.5	21
C ₂ H ₆ -C ₂ H ₄ -H ₂	Nuxit-AL active carbon	68	14.7	122
O ₂ -N ₂ -CO	Molecular sieve 10X	-200	14.7	26
Four-Component Systems				
CH ₄ -CO ₂ -CO-H ₂	BPL active carbon	77	50	126

TABLE 15-0.3
LITERATURE SOURCES OF LIQUID-MIXTURE ADSORPTION DATA

Liquid-Mixture Components	Adsorbent	Temperature (F)	Reference
Two-Component Systems			
Acetone-chloroform	Active carbon	77	61
Anthracene-cyclohexane	Chemviron type CAL	77	106
	Graphon, spheron 6	86	127
Benzene-			
Bromobenzene	Alumina	77	18
	Silica gel	77	41
Chlorobenzene	Alumina	77	18
	Silica gel	77	41
Chloroform	Boehmite	68	55,58
Cyclohexane	Active carbon, carbon black, graphite, alumina	77	88
	Boehmite	68	55,58
	BPL active carbon	86	84
	CabOSil, HiSil, graphon	86	79
	Graphon, spheron 6	86	127
Dioxane	Silica gel	32,68,77,86,140	73,109,113,117
Ethanol	Silica gel	68	117
	Active carbon, alumina	77	88
	Boehmite, γ -alumina, gibbsite, titania gel	77,140	55,56,58
	BPL active carbon	32,86,140	109
Ethyl acetate	CabOSil, HiSil, graphon	86	79
Ethylene dichloride	BPL active carbon	86	84
	Boehmite, γ -alumina, titania gel, silica gel	68	55,56,58
	BPL active carbon, silica gel	86	109
Methanol	Active carbon, alumina, silica gel	77	88
	Active carbon	77	88
	Boehmite, γ -alumina, gibbsite	77	55
Methyl acetate	CAL active carbon	77	108
	Active carbon	77	88
<i>n</i> -Butanol	Boehmite, silica gel	68,140	55,56,58
	Boehmite, γ -alumina, gibbsite, γ -Al(OH) ₃	68	55,56,58
<i>n</i> -Butylamine	Boehmite, silica gel, γ -alumina	68	57,58
<i>n</i> -Decane	CAL active carbon	77	108
<i>n</i> -Heptane	CAL active carbon	77	108
<i>n</i> -Hexane	Silica gel	77,86	35,109
Nitrobenzene	CAL active carbon	77	108
Nitromethane	Alumina, silica gel	86	116
<i>n</i> -Octane	Alumina, silica gel	86	116
2,2,4-Trimethylpentane	CAL active carbon	77	108
Benzoic acid-	CAL active carbon	77	108
Carbon tetrachloride	Graphon, spheron 6	86	128
Water	Nuxit LBS, Nuxit AL III active carbons	77	106
Benzyl alcohol-water	Molecular sieve 5A	77	51
Bromobenzene-toluene	Alumina	77	18
Carbon tetrachloride-	Silica gel	77	41
Chloroform	Active carbon	77	88
1-Naphthoic acid	Graphon, spheron 6	86	127
2-Naphthoic acid	Graphon, spheron 6	86	127

TABLE 15-0.3 (Continued)

Liquid-Mixture Components	Adsorbent	Temperature (F)	Reference
Two-Component Systems			
Chlorobenzene-toluene	Alumina	77	18
	Silica gel	77	41
Cyclohexane-			
Dioxane	Silica gel	68	117
Ethanol	BPL active carbon	86	109
	CabOSil, HiSil, graphon	86	79
Ethyl acetate	BPL active carbon	86	84
Naphthalene	Graphon, spheron 6	86	127
<i>n</i> -Heptane	Silica gel	86	109
Nitrobenzene	Alumina, silica gel	86	116
Piperidine	γ -Alumina, boehmite, silica gel	68	57
Pyridine	Boehmite, silica gel, γ -alumina	68,140	57,58
Stearic acid	Spheron 6, graphon	68	61
Dioxane-			
Nitrobenzene	Alumina, silica gel	86	116
Nitromethane	Alumina, silica gel	86	116
Water	Molecular sieve 5A	77	51
Ethanol-			
Pyridine	Active carbon	77	88
Water	Active carbon	77	88
Ethylenediamine-water	Molecular sieve 4A	77	51
Ethylene dichloride-			
methyl acetate	Boehmite	68	55,58
Furfuryl alcohol-water	Molecular sieve 5A	68	60
Methanol-			
<i>n</i> -Heptane	CAL active carbon	77	108
<i>n</i> -Octane	CAL active carbon	77	108
<i>n</i> -Nonane	CAL active carbon	77	108
<i>n</i> -Decane	CAL active carbon	77	108
<i>t</i> -Butanol	Molecular sieve 5A	86	4
Toluene	CAL active carbon	77	108
2,2,4-Trimethylpentane	CAL active carbon	77	108
Water	Molecular sieve 5A	86	4
<i>n</i> -Butanol-water	Nuxit A I, Nuxit A III active carbons	77	106
<i>n</i> -Decane-			
<i>n</i> -Heptane	Molecular sieve 5A	86,140,194	114
<i>n</i> -Octane	CAL active carbon	77	108
<i>n</i> -Dodecane	Molecular sieve 5A	86,140,194	114
<i>n</i> -Tetradecane	Molecular sieve 5A	86,140,194	114
2,2,4-Trimethylpentane	CAL active carbon	77	108
<i>n</i> -Dodecane-			
<i>n</i> -Heptane	Molecular sieve 5A	86,140,194	114
<i>n</i> -Tetradecane	Molecular sieve 5A	86,140,194	114
<i>n</i> -Heptane- <i>n</i> -Tetradecane	Molecular sieve 5A	86,140,194	114
<i>n</i> -Hexane-toluene	CAL active carbon	77	108
<i>n</i> -Octane-toluene	CAL active carbon	77	108
<i>t</i> -Butanol-water	Molecular sieve 5A	86	4
Three-Component Systems			
Benzene-cyclohexane-			
ethyl acetate	BPL active carbon	86	84
Methanol- <i>t</i> -butanol-			
water	Molecular sieve 5A	86	4

Adsorption from liquid mixtures is considered in Section 15C. Some representative isotherms for binary systems are given in Figures 15C1.1 through 15C1.10. Procedures 15C1.11 and 15C1.12 describe the use of the linear and nonlinear correlations for the treatment of the adsorption isotherms of binary liquid mixtures.

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These references are recommended for those interested in further study of the methods of treating adsorption equilibria.

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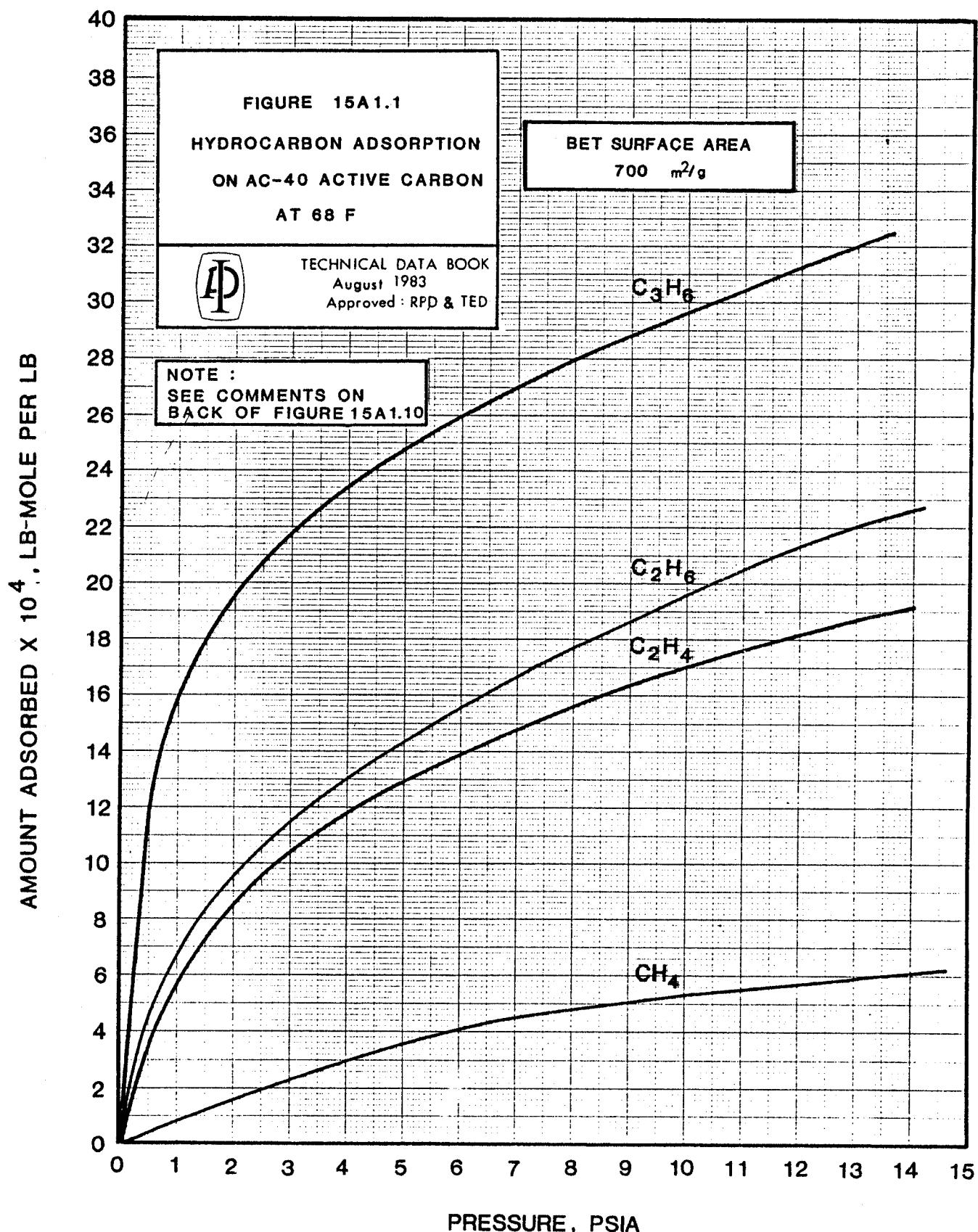
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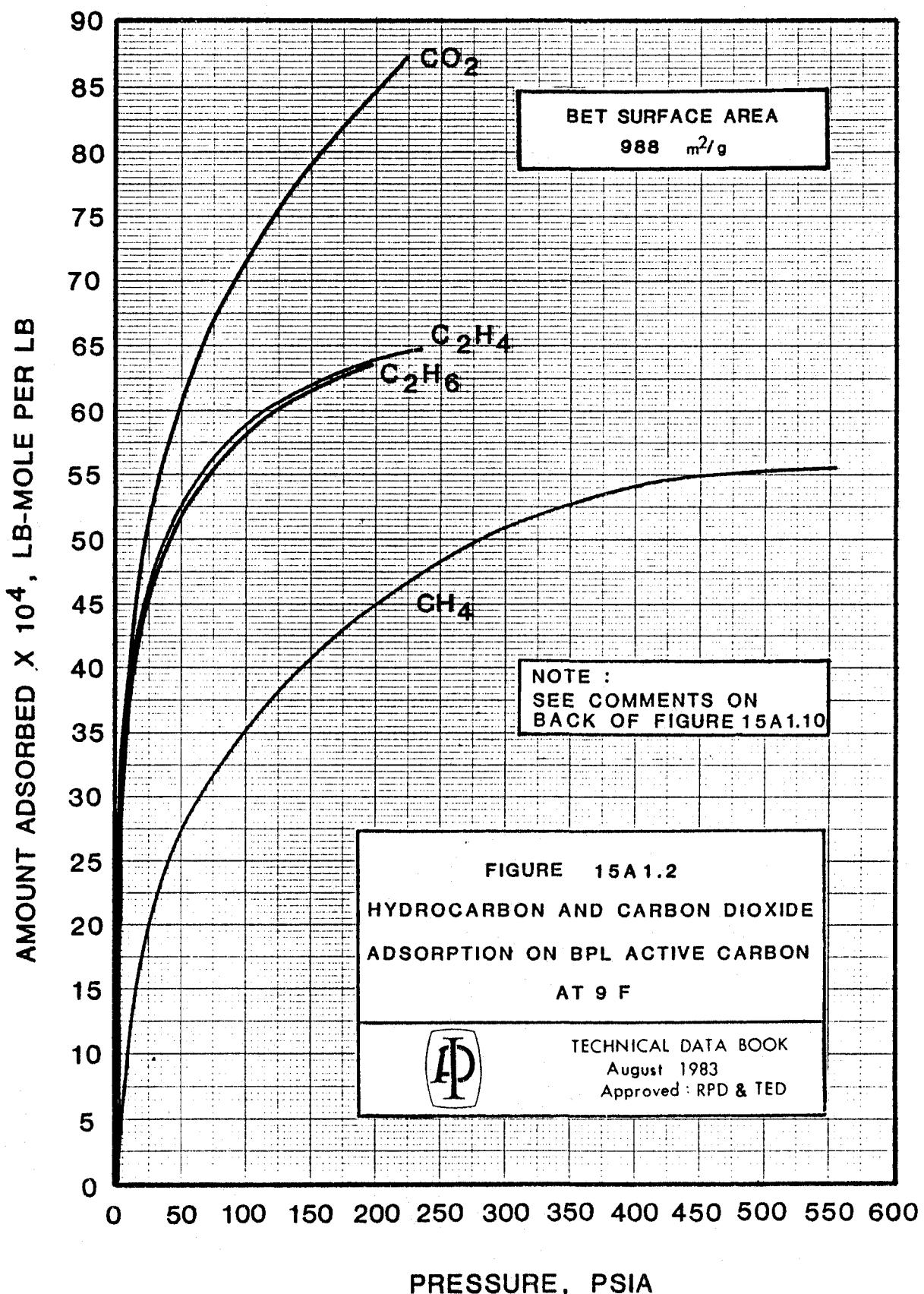
Statistical thermodynamic model:

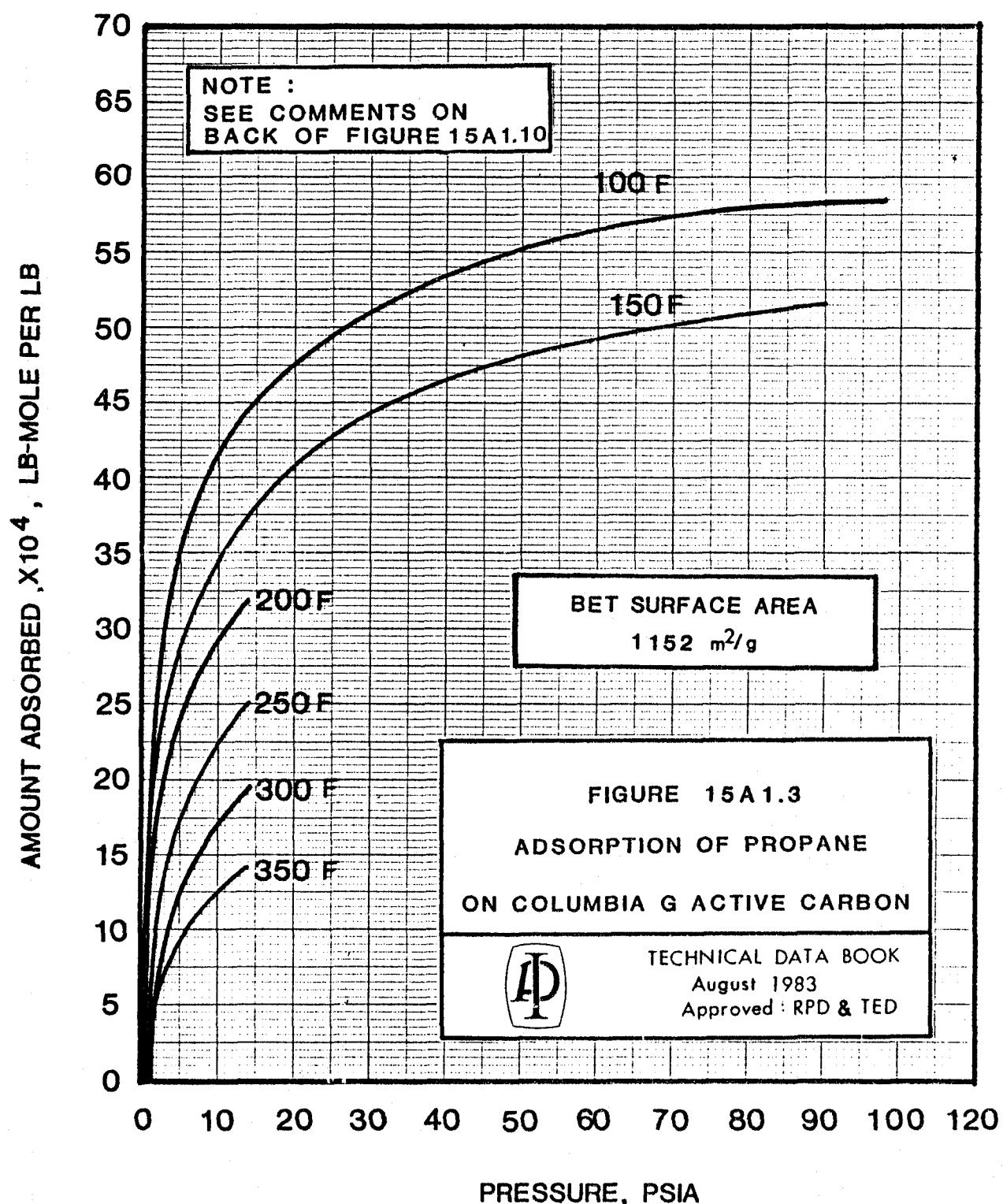
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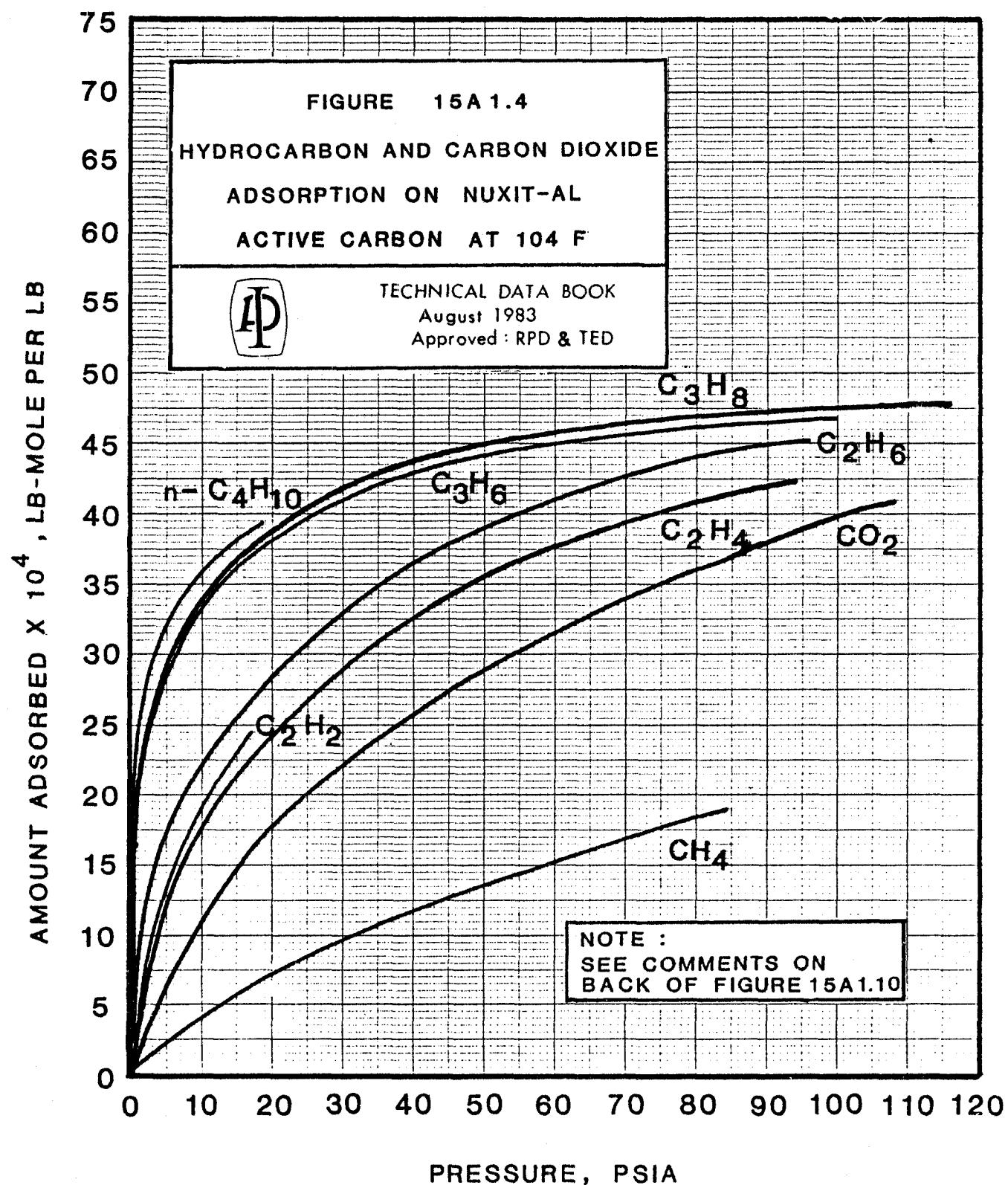
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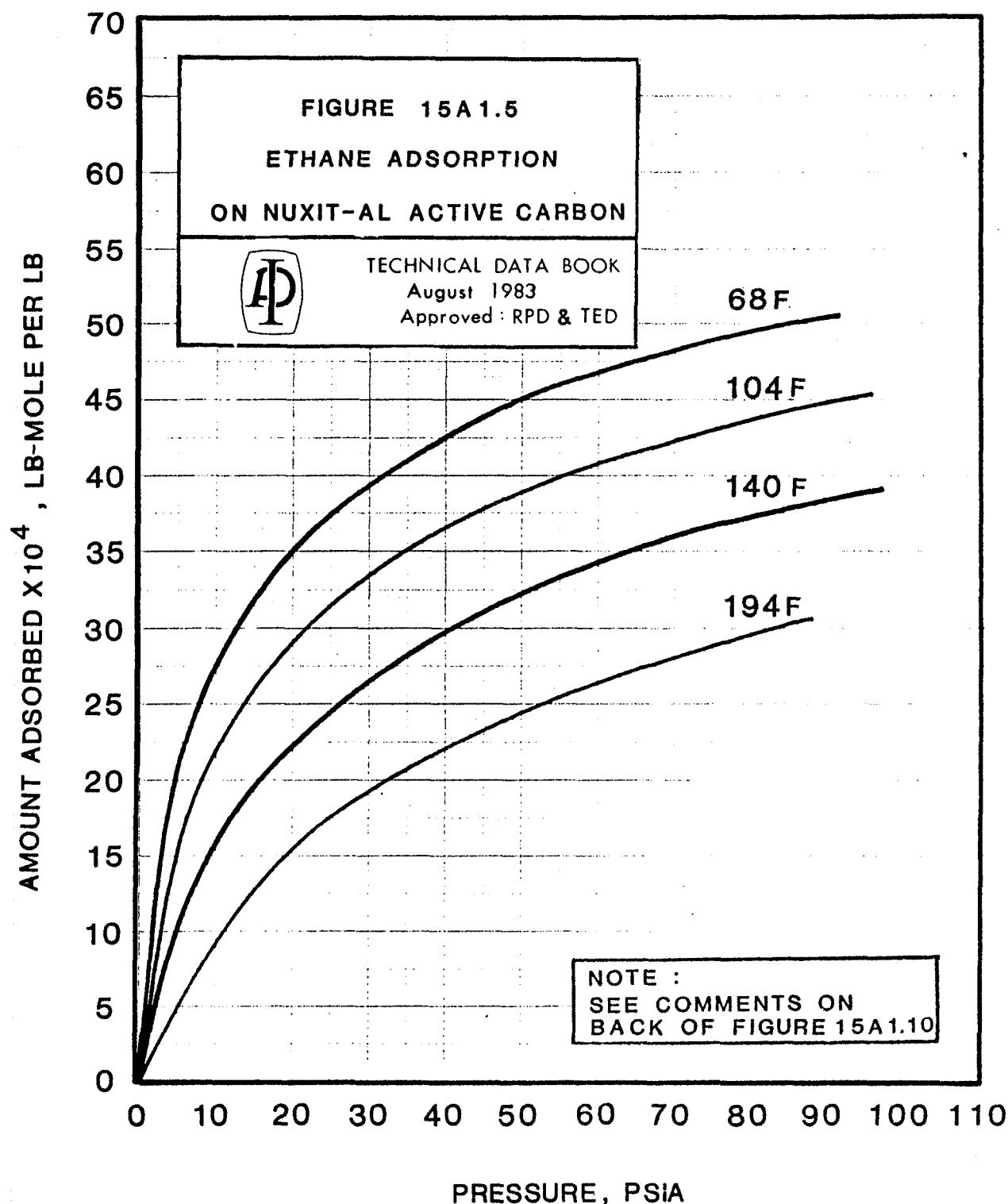
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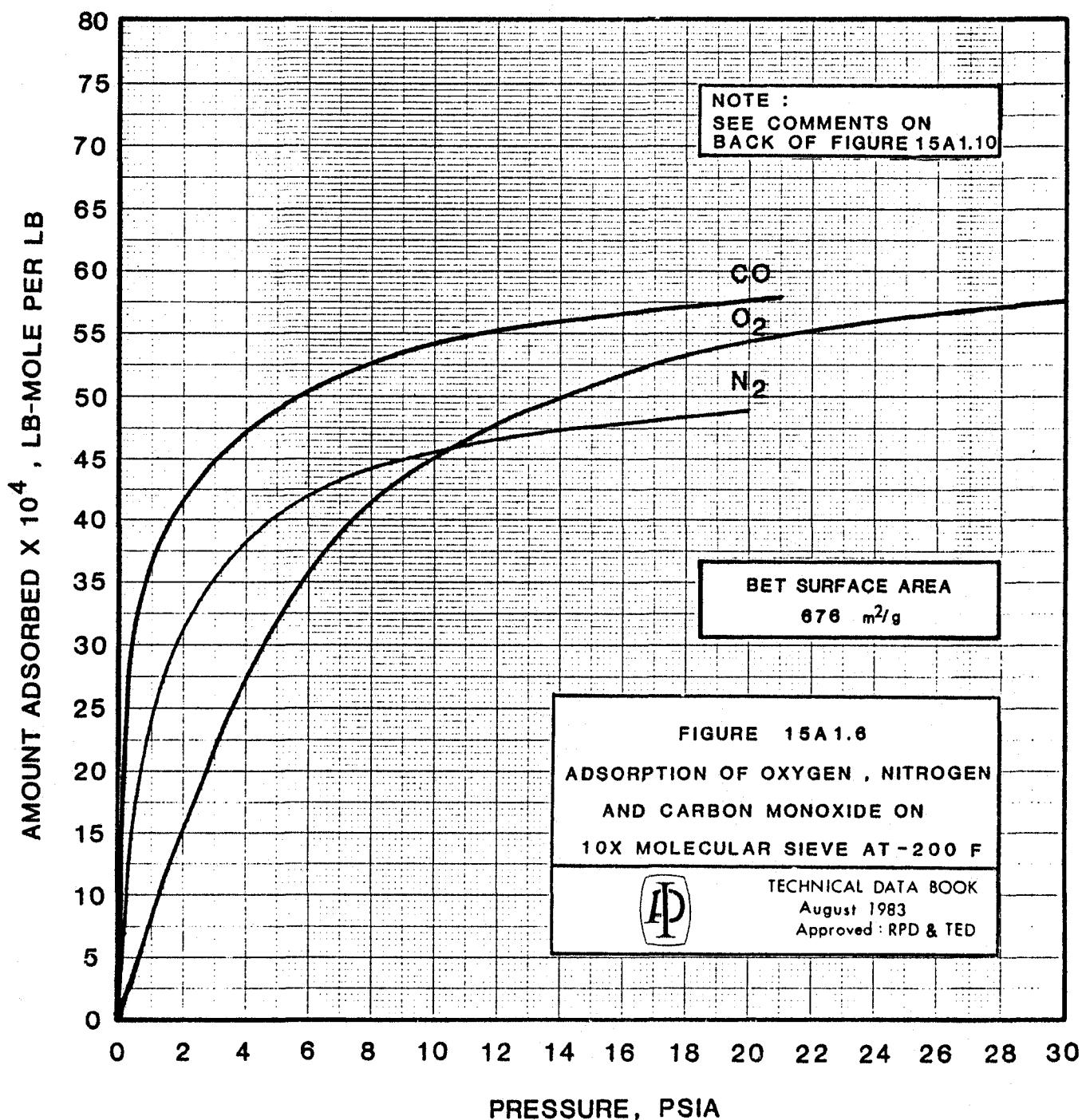


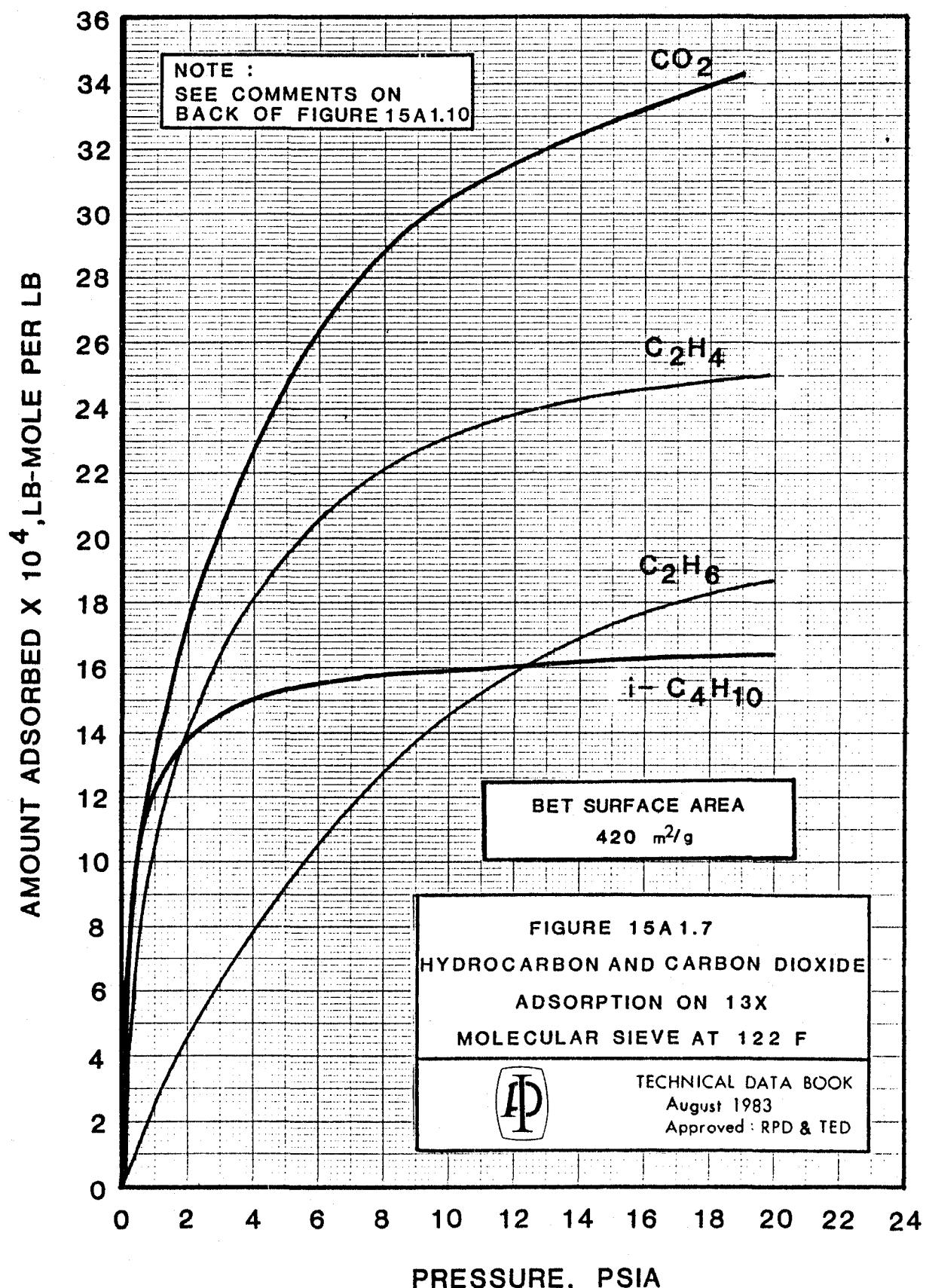


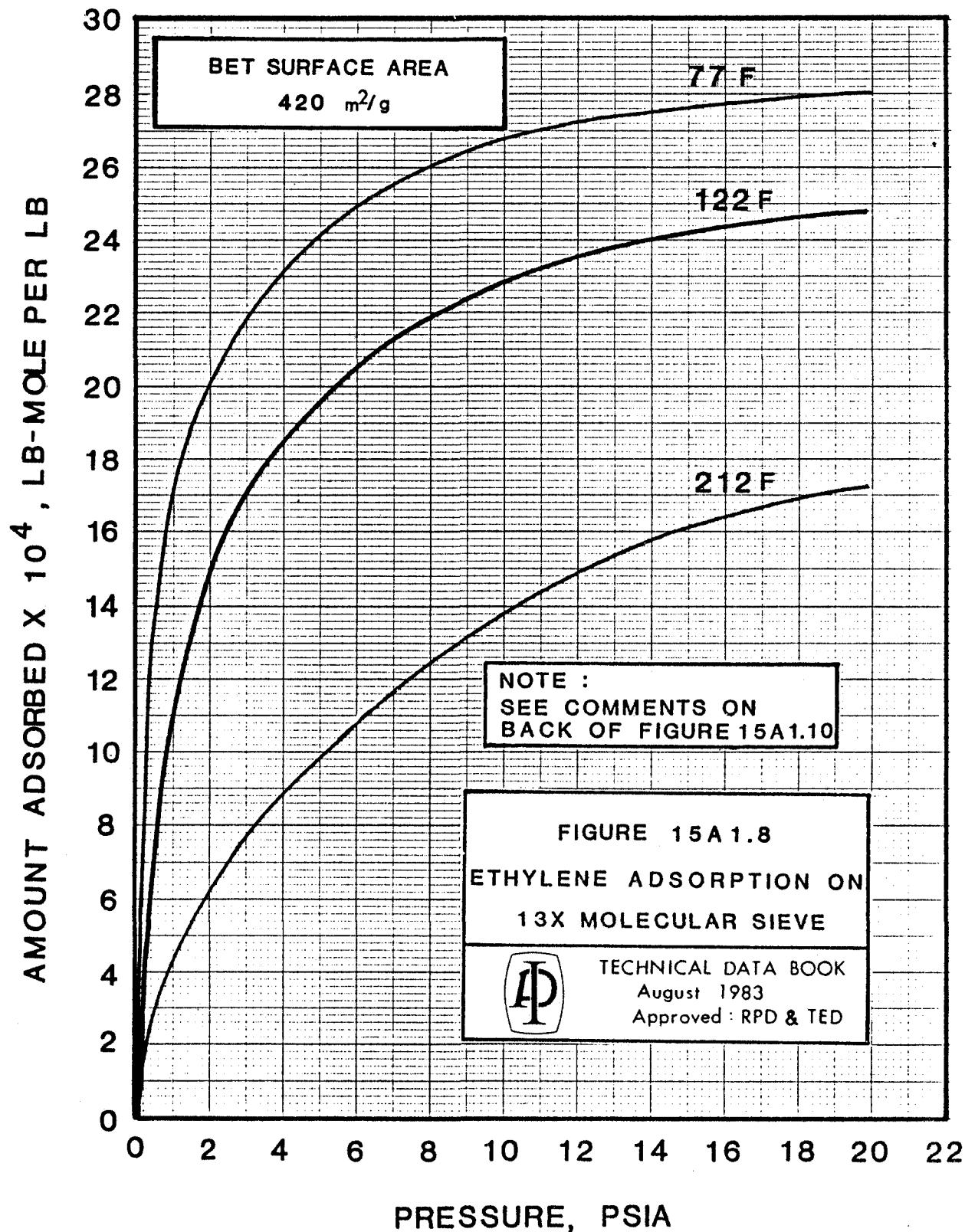


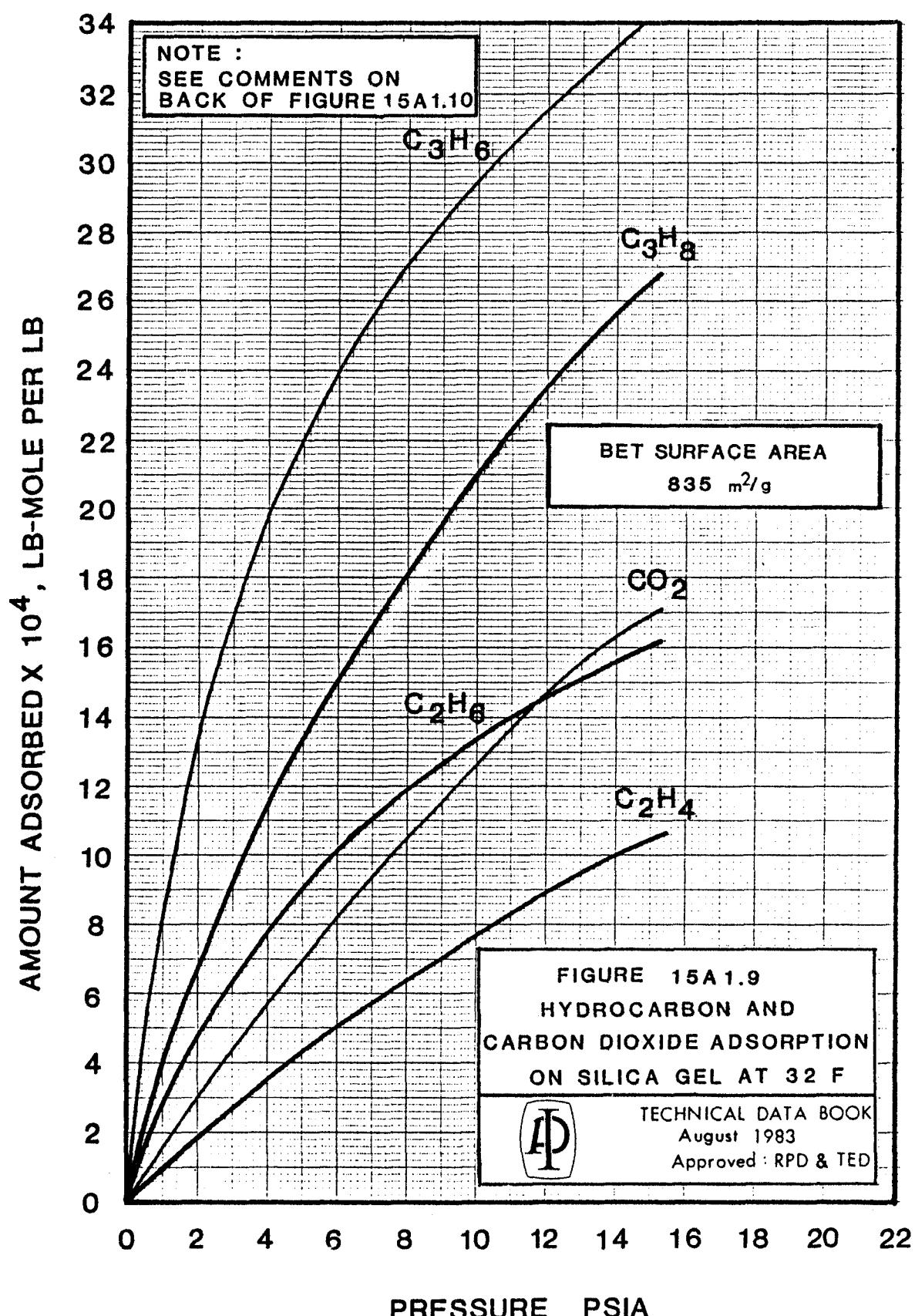


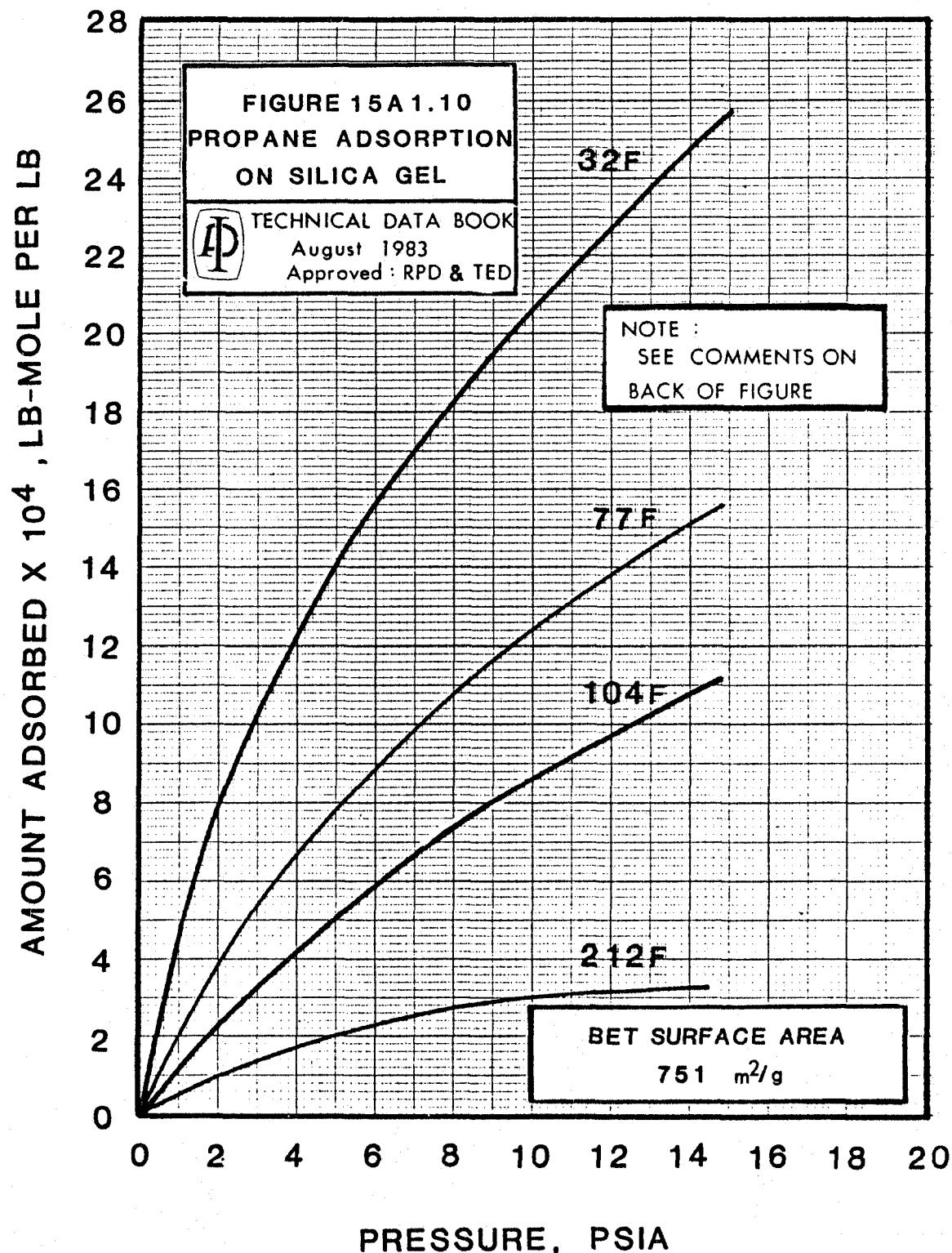












COMMENTS ON FIGURES 15A1.1 THROUGH 15A1.10**Purpose**

The pure-component isothermal adsorption capacities of various hydrocarbons and certain important nonhydrocarbons are shown as a function of pressure for several important adsorbents. These capacities are given in units of pound moles of adsorbate per pound of adsorbent.

Reliability

In addition to the usual reliability considerations in phase equilibria data, the extent of regeneration of the solid surface must be considered in adsorption equilibria. For physical adsorption on highly porous materials such as those represented in these figures, the results are not highly sensitive to the actual regeneration conditions as long as the solids are heated to a sufficiently high temperature in a moderate vacuum or while being purged with a dry, inert gas to drive off any adsorbed water. In general this requires temperatures above 400 F. Adjustments for different sources and batches of adsorbent and for variations in regeneration conditions can be made by multiplying the amount adsorbed by the ratio of the BET surface area of the actual sample to the BET surface area of the adsorbent given in the figure.

Literature Sources

- Figure 15A1.1 (21)
- Figure 15A1.2 (98)
- Figure 15A1.3 (97)
- Figure 15A1.4 (120, 121)
- Figure 15A1.5 (120, 121)
- Figure 15A1.6 (23)
- Figure 15A1.7 (22, 50)
- Figure 15A1.8 (22, 50)
- Figure 15A1.9 (52)
- Figure 15A1.10 (67, 70)

TABLE 15A1.11

ADSORPTION CAPACITIES OF VARIOUS ADSORBENTS FOR WATER VAPOR

Adsorbent ^a	BET Area (m ² /g)	Temperature (F)	Adsorption Capacity, (lb-mol/lb) × 10 ⁴						Reference
			0.1	0.2	0.3	0.4	0.5	0.6	
Active carbons									
Carbon 1	530	68	0.2	1.0	13.0	31.1	55.8	69.2	76.0
Charcoal S 600H [1112]	—	83	0.9	1.8	3.6	5.4	10.7	72.3	130
Charcoal S 600H [1112]	—	32	0.9	2.2	3.6	5.0	17.9	112	139
Deoxygenated coconut shell charcoal	1190	81	0.0	5.6	11.1	33.4	77.8	145	146
Deoxygenated Darco G60	—	83	—	0.0	2.2	4.5	9.8	26.8	189
Aluminas	7.5	77	6.6	9.3	11.0	23.9	29.3	40.1	58.0
Alumina DC-U [2192] 6	94	72	12.0	18.1	22.1	—	—	—	—
γ-Alumina Woelm W 200 18A	220	77	20.0	31.9	—	—	—	—	108
η-Alumina [77] 12	220	77	41.6	52.7	—	—	—	—	—
η-Alumina [1364] 12	220	77	42.2	53.0	—	—	—	—	—
Carbon blacks	767	77	—	—	0.0	4.5	13.4	29.0	64.7
Black Pearls I [2192]	1000	83	—	0.0	0.4	4.6	6.7	20.1	44.6
Carbolac I [2012]	83	64	0.01	0.02	0.03	0.03	0.05	0.05	80.4
Graphon L-2739 [752] 12	26	77	4.5	8.0	13.1	17.1	18.8	20.1	21.2
Lampblack T	167	77	—	—	0.0	4.5	7.6	12.1	22.3
Mogul carbon black [2192]	129	77	2.2	6.7	11.2	14.3	17.0	18.8	21.0
Spheron 4	107	77	—	—	0.0	1.1	4.9	8.3	10.5
Spheron 6 [1832]	114	86	4.3	4.5	14.1	17.5	18.3	19.2	20.9
Spheron 6 [572] 24	110	83	0.4	0.8	0.9	1.3	1.3	3.6	4.5
Spheron 6 (hydrogen-treated at 2012 F)	—	—	—	—	—	—	—	—	4.9
Oxides and oxide gels									
Alumina gel [1112] 4	189	68	29.5	36.3	42.2	47.3	—	—	—
Chromium oxide gel A [356] 2	133	77	27.9	35.5	42.6	—	—	—	—
Chromium oxide gel A [653] 0	57	77	16.7	20.6	23.7	—	—	—	—
Chromium oxide gel C1 [482] 0	218	77	23.3	33.4	46.5	—	—	—	—
Silica gel [1112] 4	640	68	8.6	20.1	40.3	65.7	101	—	—
Silica gel (treated at 77 F)	358	68	17.4	22.3	28.1	33.9	40.6	50.0	66.1
Silica gel Davidson-03 [248]	793	95	33.3	66.8	94.3	128	156	178	194
Silica gel Davidson-03 [752]	580	95	27.8	55.6	83.4	106	151	161	167
Silica gel Davidson-03 [1832]	14	95	—	—	—	—	0.02	5.6	5.7
Silica gel Davidson-59 [248]	273	95	11.1	27.8	33.3	38.9	44.4	55.6	66.8
Silica gel Davidson-59 [752]	299	95	11.1	11.2	13.9	16.7	22.1	27.8	33.3
Silica gel Davidson-59 [1832]	17	95	—	—	—	—	—	0.0	5.6
Silico-aluminum oxide gel SA-25 [1112] 4	423	68	28.3	35.9	43.4	54.8	68.0	—	—
Silico-aluminum oxide gel SA-50 [1112] 4	427	68	32.4	41.9	49.6	61.0	71.2	—	—
Silico-aluminum oxide gel SA-75 [1112] 4	317	68	35.4	43.8	50.9	59.4	70.8	—	—
Silico-aluminum oxide SIAI 20-80	100	77	36.1	43.3	46.1	47.2	48.3	50.1	—
Silico-aluminum oxide SIAI 50-50	50	77	30.5	38.9	44.4	46.1	47.2	49.4	—
Silico-aluminum oxide SIAI 90-10	420	77	55.5	73.8	86.1	91.6	103	108	—
Silico-ferric oxide SiFe 50-50	110	77	30.5	38.9	44.4	46.1	47.2	49.4	—

TABLE 15A1.11 (Continued)

Adsorbent ^a	BET Area (m ² /g)	Temperature (F)	Adsorption Capacity, (lb-mol/lb) × 10 ⁴							Reference
			0.1	0.2	0.3	0.4	0.5	0.6	0.7	
Silicas and silicates										
Aerosil [77]	163	77	6.5	9.1	11.4	14.5	19.2	—	—	24
Aerosil [842]	163	77	2.1	4.1	6.5	8.3	10.4	—	—	—
Aerosil [1922]	163	77	0.7	1.0	1.3	1.6	1.8	2.1	—	24
Aerosil 120 (rehydrated)	189	86	5.3	8.5	11.5	14.2	17.6	—	—	—
Aerosil 400	207	81	4.1	6.2	8.4	10.4	12.8	16.4	—	46
Aerosil 700	200	86	1.2	2.0	3.1	4.3	5.7	7.7	—	46
CabOSi [284] 11	67	75	4.2	7.8	10.3	12.9	16.2	20.5	35.7	58.9
CabOSi [1652] 8	162	75	0.7	1.4	2.1	2.9	4.4	7.8	13.2	57.9
CabOSi M-5	190	50	3.0	4.5	6.1	7.5	10.4	15.2	18.0	30.3
Fransil	39	77	1.4	2.1	2.5	—	—	—	—	—
HiSil 233 [77] 12	90	77	23.6	29.9	32.6	35.3	38.4	44.6	—	—
HiSil 233 [230] 12	70	77	23.2	29.0	31.3	33.4	35.7	39.2	—	8
HiSil 233 (HMDS-treated)	123	32	34.3	38.9	42.6	46.3	50.4	56.5	63.9	—
HiSil 233 (HMDS-treated)	123	77	22.2	25.0	27.3	28.7	29.6	30.6	31.0	—
HiSil 233-700 [338]	96	77	5.2	7.7	9.6	11.3	13.0	—	—	—
HiSil 233-800 [338]	104	77	7.4	9.7	11.7	13.8	15.8	18.9	22.7	—
HiSil 233	133	50	25.3	31.7	33.8	36.9	40.1	46.4	—	—
Manosil 400	205	81	13.8	19.0	22.8	26.7	31.5	36.6	40.8	—
NaHSiL 650	104	77	7.4	9.6	11.7	13.8	15.8	18.9	22.7	—
Porous silica glass (treated at 77 F)	150	68	13.4	17.4	20.5	23.7	29.0	34.8	45.1	68.3
Precipitated silica [77] 18	156	77	25.9	31.6	34.6	37.2	41.3	46.2	54.0	63.1
Silica A	420	77	8.9	16.1	19.6	25.0	35.7	50.0	67.9	92.9
SilicAR CC-7 [392] 24	307	43	11.1	27.8	38.6	55.6	83.2	100.1	133	250
Silicic acid AR 100 [392] 24	655	43	38.9	55.6	72.3	88.9	106	122	139	161
Silicic acid AR 100 (AW) [392] 24	312	65	33.3	55.4	72.2	88.7	106	122	139	206
Zeolites										
KNaX zeolite [752] 100	—	73	141	150	—	—	—	—	—	19
KNaX zeolite [752] 100	—	212	130	138	142	145	149	151	154	157
NaX zeolite [752] 100	—	73	158	173	—	—	—	—	—	19
NaX zeolite [752] 100	—	212	149	157	163	167	171	176	180	182
NaX zeolite [896] 5	—	72	145	157	162	166	170	175	177	183
Molecular sieve 13X [662]	—	100	122	129	134	141	144	145	146	149
Molecular sieve 5A [662]	—	100	97	100	104	106	110	111	112	151
Molecular sieve 4A [662]	—	400	88	95	100	104	106	111	112	112
Molecular sieve 4A [662]	—	100	111	116	118	121	122	123	126	129
Molecular sieve 4A [662]	—	400	99	107	112	117	119	122	123	128

^aThe adsorbent specification includes, if available, the degassing temperature and the time for which the adsorbent was degassed, as follows: Adsorbent name, [degassing temperature (F)], time of degasification (hours).

COMMENTS ON TABLE 15A1.11**Purpose**

These water adsorption capacities were extracted from the literature in order to provide a means of getting an approximate adsorption capacity for water vapor on commonly encountered adsorbents. The capacities are based on adsorption from air or another carrier gas that is essentially not adsorbed compared to water.

Reliability

In addition to the usual reliability considerations in phase equilibria data, the extent of regeneration of the solid must be considered in adsorption equilibria. Because of this, the degassing temperature and time have been included in the adsorbent specification whenever possible.

Special Comments

The pressures in Table 15A1.11 are not absolute pressures, but rather relative pressures p/p^* , where p is the partial pressure of water and p^* is the vapor pressure of water at the temperature of adsorption. The vapor pressure of water between 32 F and 420 F can be calculated with less than 0.15 percent error from the following equation:

$$\ln p^* = 66.893 - \frac{1.2928 \times 10^4}{T} - 6.9875 \ln T + 1.1714 \times 10^{-6} T^2 \quad (15A1.11-1)$$

where p^* is in pounds per square inch absolute and T is in degrees Rankine.

TABLE 15A1.12
ISOSTERIC HEATS OF ADSORPTION OF VARIOUS GASES

Adsorbate	Temperature Range (F)	Amount Adsorbed (lb-mol/lb) × 10 ⁴	Isosteric Heat of Adsorption, Btu/lb-mol						
			Active Carbon				Molecular Sieves ^a		
			ASC	BPL	Columbia G	Nuxit-AL	Silica Gel	10X	13X
Methane	8-104	10	—	7,810	—	7,340	—	—	—
		15	—	7,230	—	6,820	—	—	—
		20	—	7,000	—	—	—	—	—
	100-150	10	—	—	8,390	—	—	—	—
		15	—	—	7,720	—	—	—	—
		20	—	—	7,320	—	—	—	—
Ethane	8-104	5	—	—	—	—	8,840	—	8,290
		10	—	—	—	9,190	—	—	12,500
		20	—	9,960	—	11,960	—	—	13,420
	77-150	30	—	12,100	—	10,530	—	—	—
		10	—	19,740	—	12,930	—	—	11,450
		20	—	13,280	8,810	12,340	—	—	12,130
Propane	32-104	10	—	—	—	—	11,330	—	—
		14	—	—	—	26,420	—	—	—
		40	—	—	12,170	14,560	—	—	—
	100-150	20	—	—	8,620	11,980	—	—	—
		30	—	—	12,800	13,180	—	—	—
		40	—	—	13,110	13,390	—	—	—
<i>n</i> -Butane	100-150	20	—	—	—	12,930	—	—	—
		30	—	—	—	13,670	—	—	—
		35	—	—	17,080	16,790	—	—	—
<i>i</i> -Butane	77-122	10	—	—	—	—	—	—	19,590
		12	—	—	—	—	—	—	14,920
		15	—	—	—	—	—	—	20,100
Ethylene	8-104	0.5	—	—	—	—	10,600	—	—
		5	—	—	—	—	11,430	—	—
		10	—	—	—	—	9,120	—	—
		20	—	10,0990	8,460	—	—	—	—
		30	—	9,930	8,940	—	—	—	—
	77-122	10	—	—	—	—	—	—	16,460
		15	—	—	—	—	—	—	16,870
		20	—	—	—	—	—	—	13,790
	100-150	10	—	—	5,840	11,620	—	—	—
		20	—	—	6,550	10,800	—	—	—
		30	—	—	10,120	10,640	—	—	—
Propylene	32-104	15	—	—	—	—	12,900	—	—
		21	—	—	—	—	11,200	—	—
		40	—	—	11,120	—	—	—	—
	100-150	45	—	—	10,350	—	—	—	—
		25	—	9,930	15,040	9,900	—	—	—
		30	—	8,780	14,160	12,750	—	—	—
Acetylene	100-150	40	—	11,020	13,650	—	—	—	—
		10	—	9,590	—	15,810	—	—	—
		20	—	8,190	—	—	—	—	—
Carbon dioxide	8-86	40	—	—	12,820	—	—	—	—
		8	—	—	10,010	—	8,860	—	—
		20	—	12,560	8,190	—	—	—	—
		30	—	9,500	—	—	—	—	—
		40	—	9,590	—	—	—	—	—

TABLE 15A1.12 (Continued)

Adsorbate	Temperature Range (F)	Amount Adsorbed (lb-mol/lb) × 10 ⁴	Isosteric Heat of Adsorption, Btu/lb-mol						
			Active Carbon				Molecular Sieves*		
			ASC	BPL	Columbia G	Nuxit-AL	Silica Gel	10X	13X
Carbon dioxide	77-150	5	12,180	7,130	—	8,950	—	—	—
		10	11,030	5,560	—	10,720	—	—	18,400
		20	—	—	19,310	9,620	—	—	18,760
Carbon monoxide	-50-32	5	—	—	—	—	—	10,830	—
		10	—	—	—	—	—	8,960	—
		12	—	—	—	—	—	8,940	—
	100-200	5	—	—	7,220	—	—	—	—
		10	—	—	5,280	—	—	—	—
		12	—	—	5,240	—	—	—	—
Oxygen	-50-32	1	—	—	—	—	—	5,220	—
		2	—	—	—	—	—	5,250	—
		3	—	—	—	—	—	5,250	—
Nitrogen	-50-32	1	—	—	—	—	—	4,850	—
		6	—	—	—	—	—	8,340	—
	86-150	1	12,030	13,770	—	—	—	—	—
		6	—	—	6,490	—	—	—	—
		15	—	—	5,970	—	—	—	—
Hydrogen	150-200	1	—	—	5,130	—	—	—	—
		2	—	—	4,870	—	—	—	—
		2.5	—	—	4,800	—	—	—	—

* Pellet form containing 20 percent binder.

COMMENTS ON TABLE 15A1.12**Purpose**

The values of the isosteric heats of adsorption in Table 15A1.12 were calculated from data in the literature and are provided as a means of comparing the thermal effects associated with the adsorption of different gases on the most frequently encountered adsorbents.

Special Comments

The isosteric heats of adsorption (heats of adsorption at constant amount adsorbed) were calculated from adsorption isotherm data using a form of the Clausius-Clapeyron equation:

$$q_{st} = \left[\frac{-RT_1T_2}{(T_1 - T_2)} \ln \frac{p_1}{p_2} \right] N^s \quad (15A1.12-1)$$

Where:

q_{st} = isosteric heat of adsorption, in British thermal units per pound-mole.

R = gas constant, 1.986 British thermal units per (pound-mole) (degree R).

T = temperature, in degrees Rankine.

p = pressure, in pounds per square inch.

N^s = amount adsorbed, in pound-moles per pound of adsorbent.

Equation (15A1.12-1) is theoretically correct only in the case where the heat of adsorption is independent of temperature. The closer the temperatures T_1 and T_2 , the more closely this requirement is met. The equation can be used, however, as an approximation for the isosteric heat of adsorption when the isotherm temperatures are separated by a reasonable amount.

Reliability

The values of the isosteric heat of adsorption given in the table are not very accurate, and should be used with caution. The usefulness of the table lies in its ability to indicate trends in the heat of adsorption as certain variables or parameters are changed. The values given in the table, though not quantitatively accurate, may also be useful in design calculations.

Literature Sources

The isotherm data used to calculate the isosteric heats of adsorption were extracted from the following sources:

ASC active carbon (81)

BPL active carbon (33, 39, 66, 81, 98, 100)

Columbia G active carbon (52, 97)

Nuxit-AL active carbon (120, 121)

Silica gel (52, 67, 70, 71)

Molecular sieve 10X (91)

Molecular sieve 13X (22, 50)

PROCEDURE 15A1.13

CORRELATION OF PURE-COMPONENT ISOTHERMAL ADSORPTION DATA

Discussion

If three or more values are known for the total amount of a pure gas adsorbed at varying pressure and constant temperature, the following equation, known as the BET equation, can be used to interpolate the data or extrapolate it over a limited range:

$$\frac{p}{N^s(p^\circ - p)} = \frac{1}{N^{s,m}C} + \frac{C-1}{N^{s,m}C} \cdot \frac{p}{p^\circ} \quad (15A1.13-1)$$

Where:

p = adsorption equilibrium pressure, in pounds per square inch absolute.

p° = vapor pressure of adsorbate at the adsorption temperature, in pounds per square inch absolute.

N^s = number of moles of gas adsorbed at any pressure, in pound-moles adsorbed per pound of adsorbent.

$N^{s,m}$ = regression constant that represents the total amount adsorbed if the entire surface is covered with one layer of adsorbed molecules, in pound-moles adsorbed per pound of adsorbent.

C = regression constant, unitless.

The isothermal data may be plotted as $p/[N^s(p^\circ - p)]$ versus the relative pressure, p/p° . In the relative pressure range of 0.05 to 0.40 the plot will usually be linear. Serious deviations may occur outside this range. The constants $N^{s,m}$ and C can be determined from the slope and ordinate intercept of the straight-line portion.

$$\text{slope} + \text{intercept} = \frac{C-1}{N^{s,m}C} + \frac{1}{N^{s,m}C} = \frac{1}{N^{s,m}} \quad (15A1.13-2)$$

$$C = \frac{1}{1 - (\text{slope})N^{s,m}} \quad (15A1.13-3)$$

Procedure

Step 1: Plot the data in the form of $p/[N^s(p^\circ - p)]$ versus p/p° .

Step 2: In the relative pressure (p/p°) region from 0.05 to 0.40, construct a straight line representing the data as closely as possible, and determine the slope and intercept. Alternatively the slope and intercept can be obtained from a simple regression analysis of the data in the appropriate form.

Step 3: Calculate $N^{s,m}$ and C from equations (15A1.13-2) and (15A1.13-3).

Step 4: Equation (15A1.13-1) may now be used to interpolate or extrapolate the data in the relative pressure range between 0.05 and 0.40.

COMMENTS ON PROCEDURE 15A1.13

Purpose

Procedure 15A1.13 is given as a method of interpolating or extrapolating pure-gas adsorption data at constant temperature over the relative pressure (p/p°) range of 0.05 to 0.40. If a better representation is required over a larger pressure range, Procedure 15A1.14 is recommended. The value of $N^{s,m}$ calculated by this procedure can also be used to calculate the surface area of the adsorbent. The surface area calculated from the $N^{s,m}$ value for the adsorption of nitrogen at its normal boiling point has become the accepted characterization surface area (BET area) for industrial adsorbents. In this calculation, 1 cubic centimeter of nitrogen at 77 F and 1 atmosphere is assumed to cover 4.37 square meters of surface.

Limitations

For most adsorption systems, reasonable linearity has been observed when the data are plotted as indicated by equation (15A1.13-1) in the relative pressure range of 0.05 to 0.40. Outside this range large deviations are often encountered.

Reliability

Within the recommended range of application, equation (15A1.13-1) will usually represent the data within 5 percent.

Literature Source

Equation (15A1.13-1) was originally developed by Brunauer, S., Emmett, P. H., and Teller, E., *J. Am. Chem. Soc.* **60** 309 (1938).

Example

Find the value of $N^{s,m}$ and C for adsorption of propylene on Columbia G active carbon at 86 F.

The isotherm data of Jelinek (52) are given in the table below along with the appropriate form of the data for the procedure. (From Chapter 5, the vapor pressure of propylene at 86 F is 185 pounds per square inch absolute.)

p (psia)	$N_s \times 10^3$ (lb-mol per lb)	p per p°	$p/[N_s(p^\circ - p)]$ (lb per lb-mol)
6.38	4.304	0.0345	—
10.01	4.661	0.0541	12.27
15.31	5.115	0.0828	17.65
14.60	5.003	0.0789	17.12
3.06	3.570	0.0165	—
5.59	4.127	0.0302	—
9.33	4.640	0.0504	11.44
12.37	4.890	0.0669	14.66
14.74	5.084	0.0797	17.04

A linear regression for the six points for which $0.05 < p/p^\circ < 0.4$ yields a slope of 191.8 pounds per pound-mole and an intercept of 1.830 pounds per pound-mole.

Therefore,

$$N^{s,m} = \frac{1}{\text{slope} + \text{intercept}} = \frac{1}{191.8 + 1.83} = 5.164 \times 10^{-3} \text{ pound-moles per pound}$$

and

$$C = \frac{1}{1 - (\text{slope})N^{s,m}} = \frac{1}{1 - (191.8)(5.164 \times 10^{-3})} = 104.8$$

PROCEDURE 15A1.14

ALTERNATE COMPUTER PROCEDURE FOR CORRELATION OF
PURE-COMPONENT ISOTHERMAL ADSORPTION DATA**Discussion**

If numerous values are known for the total amount of a pure gas adsorbed at varying pressure and constant temperature, the following equation, based on the vacancy solution model of adsorption, can be used to interpolate or extrapolate the data over wide ranges of pressure:

$$p = \left[\frac{N_1^{s,\infty}}{b_1} \frac{\theta}{1-\theta} \right] \exp \left[\frac{\alpha_{1v}\theta}{1+\alpha_{1v}\theta} \right] \quad (15A1.14-1)$$

$$N_1^{s,\infty} = N_{o1}^{s,\infty} \exp \left[\frac{r_1}{T} \right] \quad (15A1.14-2)$$

$$b_1 = b_{o1} \exp \left[\frac{-q_1}{RT} \right] \quad (15A1.14-3)$$

$$\alpha_{1v} = m_1 N_1^{s,\infty} - 1 \quad (15A1.14-4)$$

Where:

p = adsorption equilibrium pressure, in pounds per square inch absolute.

$N_1^{s,\infty}$ = regression constant representing maximum amount of adsorption of gas 1, in pound-moles adsorbed per pound of adsorbent.

b_1 = regression constant representing slope of the isotherm at infinite dilution of gas 1 (Henry's law constant), in pound-moles adsorbed per (pound of adsorbent) (pound per square inch).

θ = fraction of surface covered, $N_1^s/N_1^{s,\infty}$.

N_1^s = amount of gas 1 adsorbed at any pressure, in pound-moles adsorbed per pound of adsorbent.

α_{1v} = a regression parameter (> -1) representing interactions between the gas molecules and the solid surface, unitless.

$N_{o1}^{s,\infty}$ = temperature-independent constant characterizing each adsorbate-adsorbent system, in pound-moles per pound of adsorbent.

r_1 = temperature-independent constant characterizing each adsorbate-adsorbent system, in degrees Rankine.

T = adsorption equilibrium temperature, in degrees Rankine.

b_{o1} = temperature-independent constant characterizing each adsorbate-adsorbent system, in pound-moles adsorbed per (pound of adsorbent) (pounds per square inch).

q_1 = temperature-independent constant characterizing each adsorbate-adsorbent system, in British thermal units per pound-mole.

R = gas constant, 1.986 British thermal units per (pound-mole) (degree Rankine).

m_1 = temperature-independent constant of proportionality, in pounds of adsorbent per pound-mole adsorbed.

Procedure

Step 1: Collect all data for the system of interest in terms of p , N_1^s , and T . For a non-isothermal data set, use equations (15A1.14-1) through (15A1.14-4) to regress $N_1^{s,\infty}$, r_1 , b_{o1} , q_1 , and m_1 . For an isothermal data set, equation (15A1.14-1) should be used to regress $N_{o1}^{s,\infty}$, b_1 , and α_{1v} . The nonlinear regression algorithm in the International Mathematical and Statistical Library, which uses a Marquardt-Levenberg optimization algorithm, has been found to be quite useful for these regressions. Other nonlinear regression methods, however, can also be used.

Step 2: The data for a nonisothermal system can be interpolated or extrapolated by use of equations (15A1.14-1) through (15A1.14-4). For isothermal systems use (15A1.14-1).

COMMENTS ON PROCEDURE 15A1.14

Purpose

Procedure 15A1.14 is given as a method of interpolating or extrapolating pure-gas adsorption data for isothermal or nonisothermal systems over a wide pressure range. This procedure can be applied over a much wider pressure range than Procedure 15A1.13. Also, this procedure may be used to interpolate or extrapolate nonisothermal data; Procedure 15B1.8 can be used only with isothermal data.

Reliability

The reliability of the extrapolations obtained with this method depends upon the accuracy and range of the data that were regressed. More meaningful values for the regression constants are obtained if the data include very low pressure values as well as pressure approaching that which saturates the surface. In general, equation (15A1.14-1) will represent pure-gas isotherm data to within 2 percent.

Literature Source

Equation (15A1.14-1) was taken from Cochran, T. W., Kabel, R. L., Danner, R. P., "Vacancy Solution Theory of Adsorption Using Flory-Huggins Activity Coefficient Equations," *AIChE Journal* 31 268 (1985).

Example

The data sets and listing of regression constants below are provided as a means of checking the reliability of any nonlinear regression algorithm. The objective function used to obtain the constants was $\sum[\ln p_{\text{exp}} - \ln p_{\text{pred}}]^2$ where p_{exp} is the experimental adsorption pressure, and p_{pred} is the predicted value, and the sigma sign denotes summation over all data points. This example uses isothermal data; therefore, only $N_1^{s,\infty}$, b_1 , and α_{lv} , are regressed.

The following data are for oxygen adsorption on 10X molecular sieve at -50 F (91):

p (psia)	$N_a \times 10^4$ (lb-mol per lb)	p (psia)	$N_a \times 10^4$ (lb-mol per lb)
0.32	0.098	13.45	3.922
0.83	0.268	15.40	4.435
1.61	0.518	17.35	4.908
2.10	0.687	19.25	5.367
2.93	0.941	21.20	5.849
3.61	1.160	23.13	6.300
5.80	1.811	25.05	6.732
7.71	2.342	27.01	7.183
9.64	2.869	28.90	7.593
11.58	3.400	30.80	8.008

$$N_1^{s,\infty} = 4.00 \times 10^{-3} \text{ pound-moles per pound}$$

$$b_1 = 3.24 \times 10^{-5} \text{ pound-moles per (pound) (pound per square inch)}$$

$$\alpha_{lv} = 4.2 \times 10^{-5}$$

The following data are for nitrogen adsorption on 10X molecular sieve at -50 F (91):

p (psia)	$N_a \times 10^4$ (lb-mol per lb)	p (psia)	$N_a \times 10^4$ (lb-mol per lb)
0.42	1.521	10.62	9.579
0.79	2.289	12.54	10.440
1.24	3.003	14.46	11.261
1.77	3.672	18.34	12.688
2.35	4.305	20.26	13.322
2.89	4.792	22.19	13.857
3.84	5.599	24.09	14.397
4.77	6.291	27.97	15.459
6.69	7.509	29.85	15.940
8.67	8.606	30.80	16.204

$$N_1^{s,\infty} = 5.34 \times 10^{-3} \text{ pound-moles per pound}$$

$$b_1 = 4.619 \times 10^{-4} \text{ pound-moles per (pound)(pound per square inch)}$$

$$\alpha_{lv} = 3.580$$

**PROCEDURE 15A2.1
CORRELATION OF ADSORPTION CAPACITIES**

Discussion

This procedure, based on the potential theory, provides a method that may be useful in correlating and predicting pure-component adsorption data. In many cases this method can correlate the temperature dependence for the adsorption of a single adsorbate on a specific adsorbent. It can also correlate data for a number of different adsorbates (at least for homologous series) on the same solid.

The data must be put into the following functional form and plotted accordingly:

$$\frac{RT}{V^s} \ln \frac{f^s}{f} = f(N_a V^s) \quad (15A2.1-1)$$

Where:

R = universal gas constant, 10.731 (pounds per square inch absolute)(cubic feet) per (pound-mole)(degree Rankine).

T = temperature, in degrees Rankine.

V^s = saturated liquid volume of the adsorbate at the temperature where the vapor pressure is equal to the adsorption pressure, in cubic feet per pound-mole.

f^s = fugacity of the vapor at the temperature of adsorption and the equilibrium vapor pressure, in pounds per square inch.

f = fugacity of the vapor at the temperature and pressure of adsorption, in pounds per square inch.

N_a = amount of gas adsorbed per unit mass of adsorbent, in pound-moles of gas per pound of solid.

This relationship simply says that there should be a correlation among adsorption data if they are plotted according to the indicated form. The functional relationship is not defined by an analytical equation.

Procedure

Step 1: For each adsorption pressure of interest, find the temperature for each adsorbate at which it would have a vapor pressure equivalent to the adsorption pressure. Equations containing specific constants like the Antoine equation, available vapor pressure plots, or generalized vapor pressure methods can be used (see Chapter 5).

Step 2: Using the graphs or procedures given in Chapter 6, find the saturated liquid volume, V^s , for each adsorbate at the appropriate temperature determined in Step 1. If this temperature is higher than the critical temperature of the adsorbate, an extrapolation of the saturated liquid volume data is required.

Step 3: Using the vapor pressure relations again, find the vapor pressure of all adsorbates corresponding to each adsorption temperature of interest.

Step 4: Calculate the fugacity of each adsorbate at the temperatures of interest and the corresponding vapor pressure (f^s) using the methods given in Chapter 7. If the temperature is above the critical temperature of a gas, an extrapolation of the vapor pressure data is required. If a more approximate procedure is acceptable or if the vapor pressures are not too high, the vapor pressure may be substituted for the fugacity.

Step 5: Calculate the fugacity of each adsorbate at the temperature and pressure of the adsorption system (f) using the same procedure or approximation as in Step 4.

Step 6: Using the experimental data (moles adsorbed as a function of pressure), calculate

$$X = \frac{RT}{V^s} \ln \frac{f^s}{f} \quad (15A2.1-2)$$

$$Y = N_a V^s \quad (15A2.1-3)$$

Step 7: Plot Y versus X . Generally a more linear relation is obtained if semilog paper is used to plot $\log Y$ as a function of X .

COMMENTS ON PROCEDURE 15A2.1**Purpose**

This procedure is intended to provide a technique for correlating pure-gas adsorption data as a function of temperature or data for a number of different gases on the same solid. If a successful correlation is achieved, the method can be used to interpolate or extrapolate the data as a function of temperature or to predict the adsorptivity of some other similar gas on the same solid.

Reliability

This method must be evaluated on a case-by-case basis. No reliable guidelines for determining when this procedure will be successful have been found. Using all the available data, one should attempt to correlate them according to this procedure. The extent to which it can be used for further extrapolation or prediction then depends on the judgements of the correlator and the extent of approximation that can be accepted.

Special Comments

This potential-theory procedure is generally most successful for coalescing data at various temperatures for a single gas adsorbed on a single adsorbent. It has also been found in a number of cases to correlate data for a number of adsorbates on the same solid, particularly if the adsorbates are all in a homologous series. Potential-theory plots also appear to be more successful for nonpolar adsorbents, such as activated carbon, than for more polar solids, such as silica gel and molecular sieves. Figures 15A2.2 through 15A2.6 are typical potential-theory plots. See the comments regarding these figures for further guidelines on the applicability of the potential theory.

Literature Source

This procedure was recommended by Lewis, W. K., Gilliland, E. R., Chertow, B., and Cadogan, W. P., *Ind. Eng. Chem.* **42** 1326 (1950).

Example

Find the point on the potential-theory plot corresponding to the following data point of Szepesy and Illés (121) for the adsorption of ethylene on active carbon type Nuxit-AL: $T = 104$ F, $p = 18.19$ pounds per square inch absolute, and $N_a = 2.426 \times 10^{-3}$ pound-moles per pound.

With constants for the Antoine equation obtained from Reid, Prausnitz, and Sherwood (99), the vapor pressure is given as:

$$\ln p^s(\text{mm Hg}) = 15.5368 - \frac{1347.01}{T(\text{K}) - 18.15}$$

The temperature at which ethylene would have a vapor pressure equal to the adsorption pressure (940.5 millimeters of mercury) is 173.15 K or -148.0 F.

From Chapter 1, the critical pressure and critical temperature (p_c and T_c) of ethylene are 729.8 pounds per square inch absolute and 48.58 F.

Using the saturated liquid volume calculation given in Chapter 6,

$$T_r = \frac{-148.0 + 459.7}{48.58 + 459.7} = 0.613$$

$$V^s = \left[\frac{P_l T_c}{p_c} \right] Z_{\text{RA}}^{[1.0 + (1.0 - T_r)^{2/7}]} = \left[\frac{(10.732)(48.58 + 459.7)}{729.8} \right] (0.2813)^{[1.0 + (1.0 - 0.613)^2]} \\ = 0.799 \text{ cubic foot per pound-mole}$$

From the Antoine equation, the extrapolated vapor pressure at the temperature of interest (104 F) is found to be 58,143 millimeters of mercury or 1125 pounds per square inch absolute. From the procedure in Chapter 7, the fugacities f^* and f are obtained.

$$T_r^* = \frac{104 + 459.7}{48.58 + 459.7} = 1.109$$

$$p_r^* = \frac{1125}{729.8} = 1.54$$

$$\log(f^*/p^*) = -0.192$$

$$f^* = 723 \text{ pounds per square inch absolute}$$

$$T_r = 1.109$$

$$p_r = \frac{18.19}{729.8} = 0.0249$$

$$f/p \approx 1.0$$

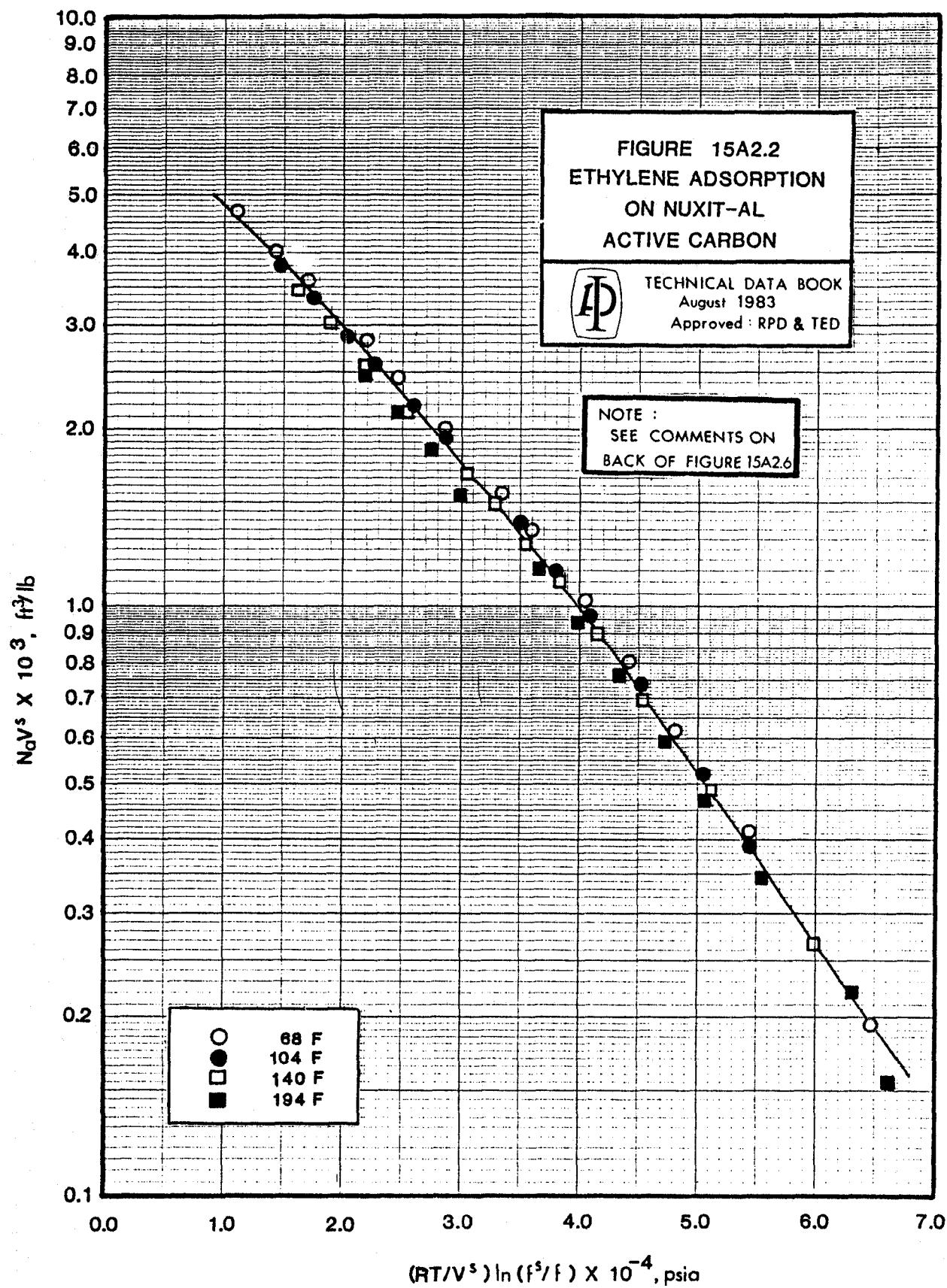
$$f = 18.19 \text{ pounds per square inch absolute}$$

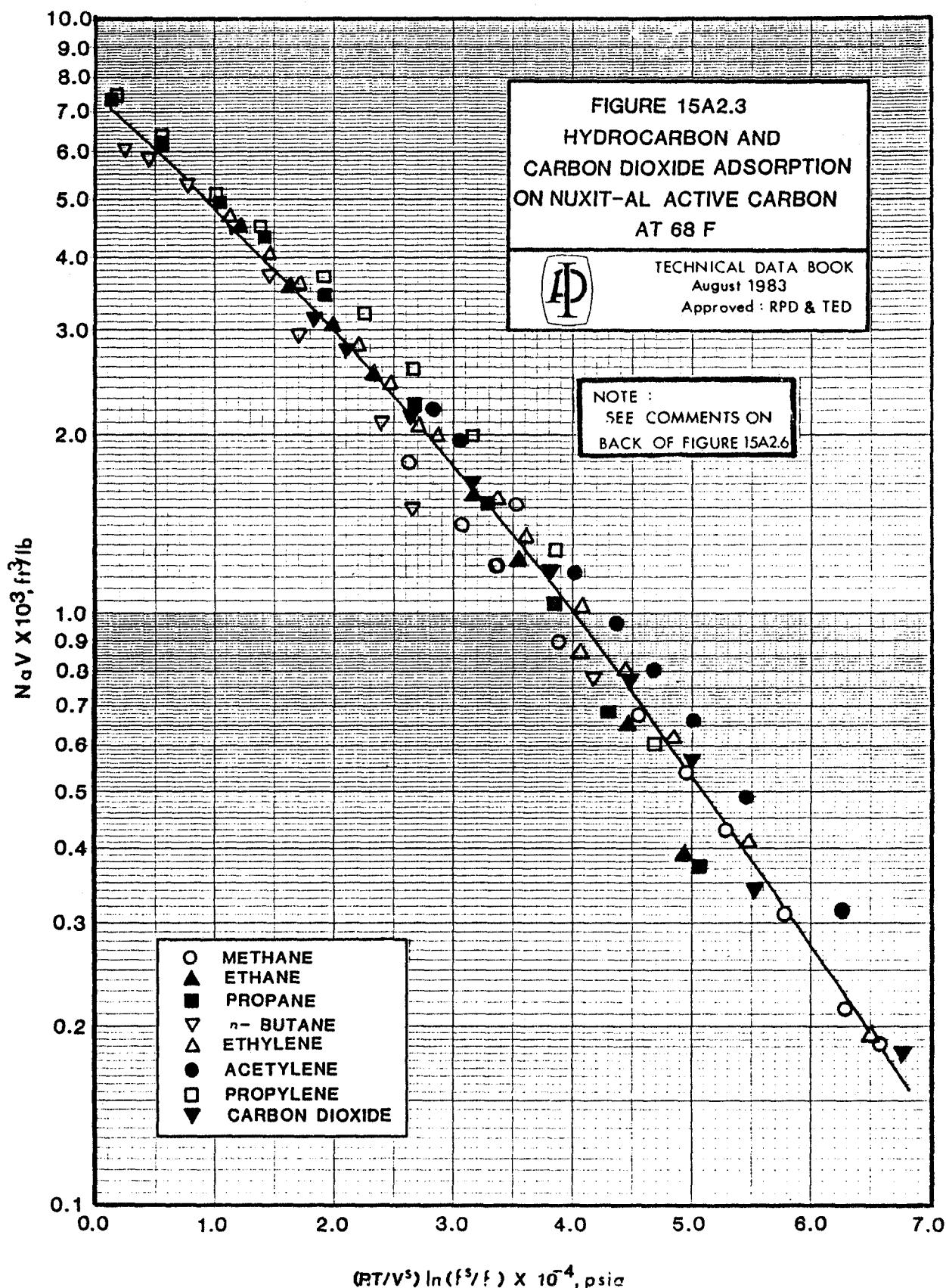
The abscissa and ordinate values are now computed as:

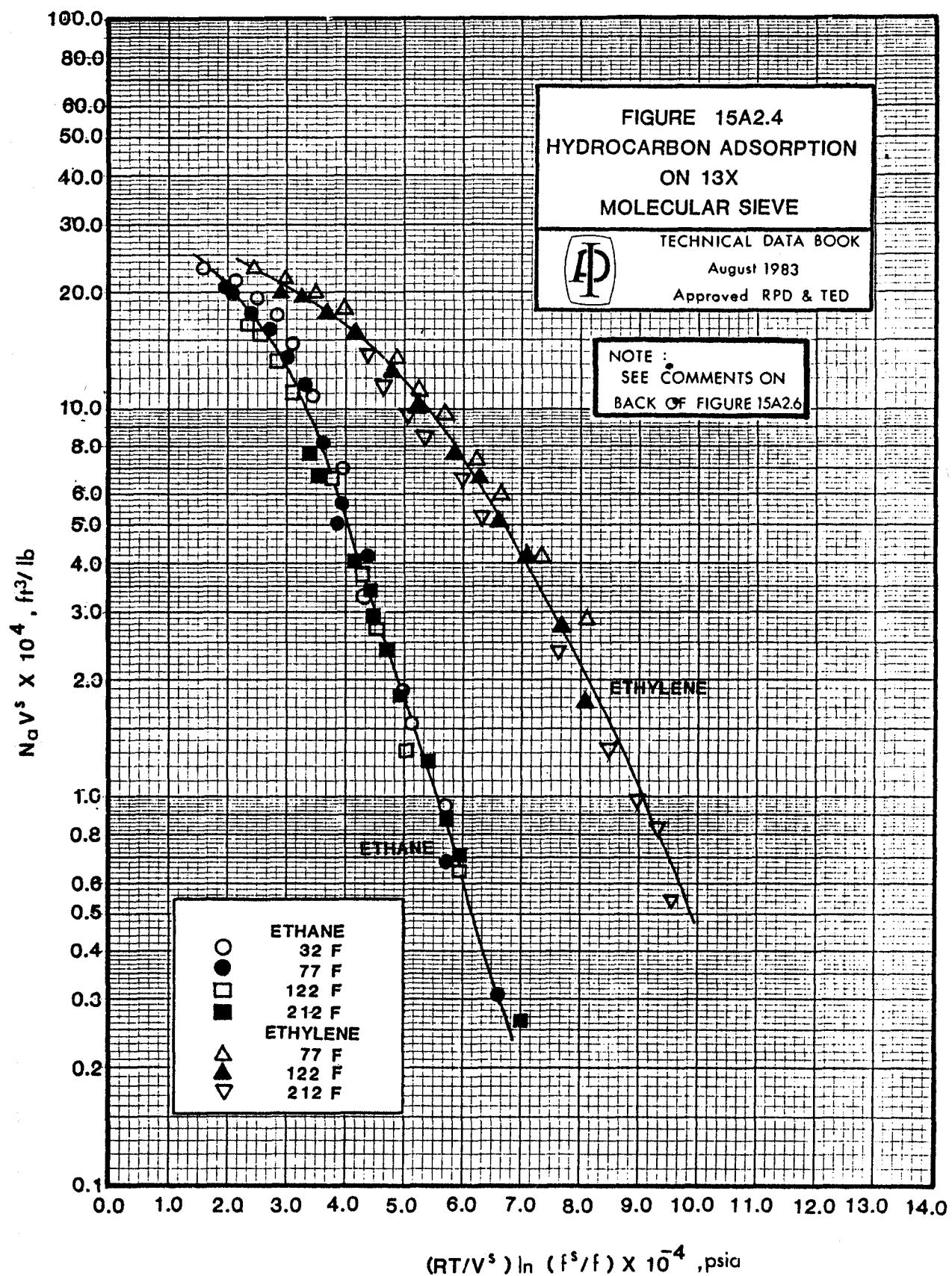
$$X = \frac{(10.731)(104 + 459.7)}{0.798} \ln \frac{723}{18.19} = 27,900 \text{ pounds per square inch absolute}$$

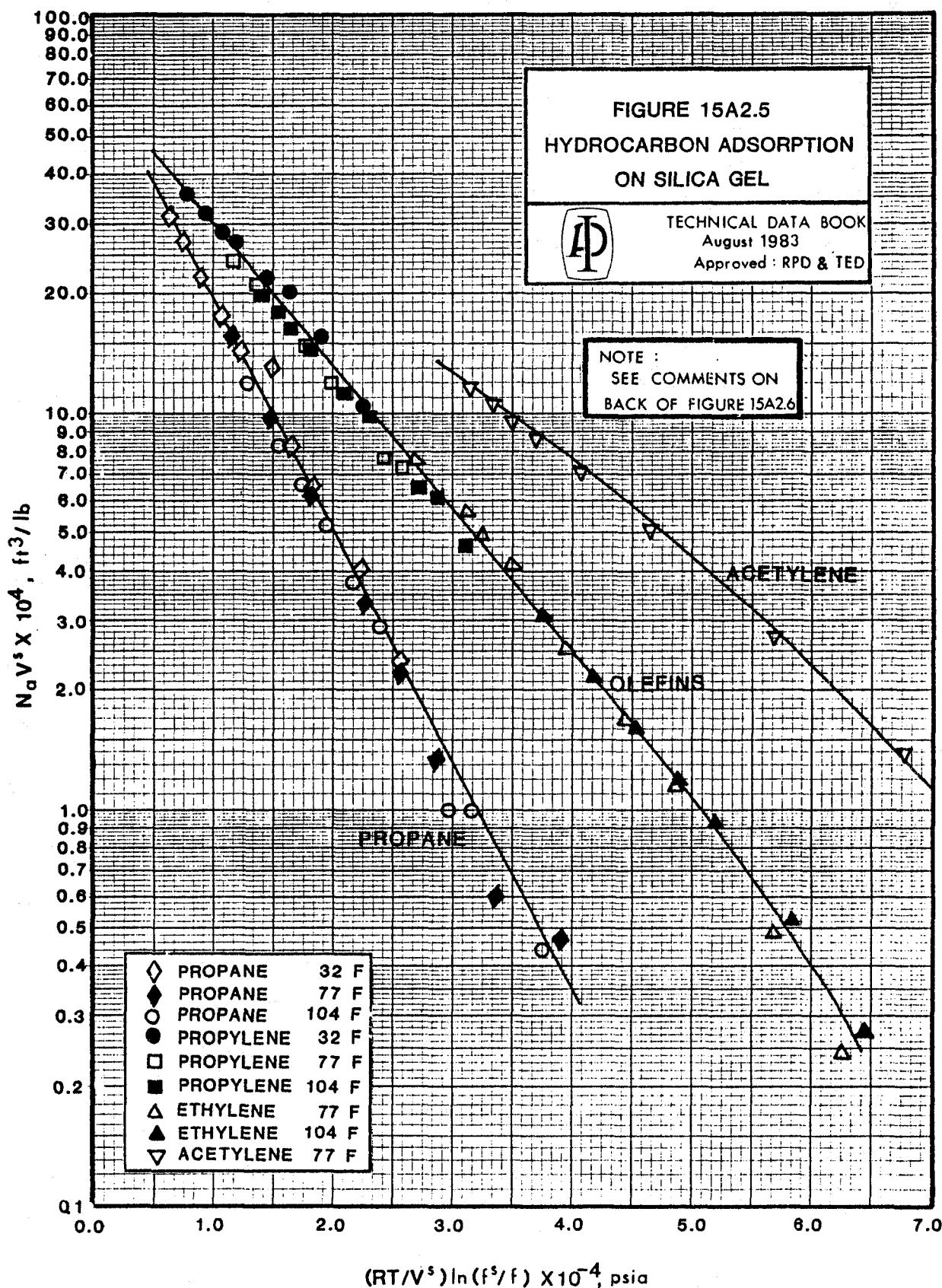
$$Y = (2.426 \times 10^{-3})(0.799) = 1.94 \times 10^{-3} \text{ cubic foot per pound}$$

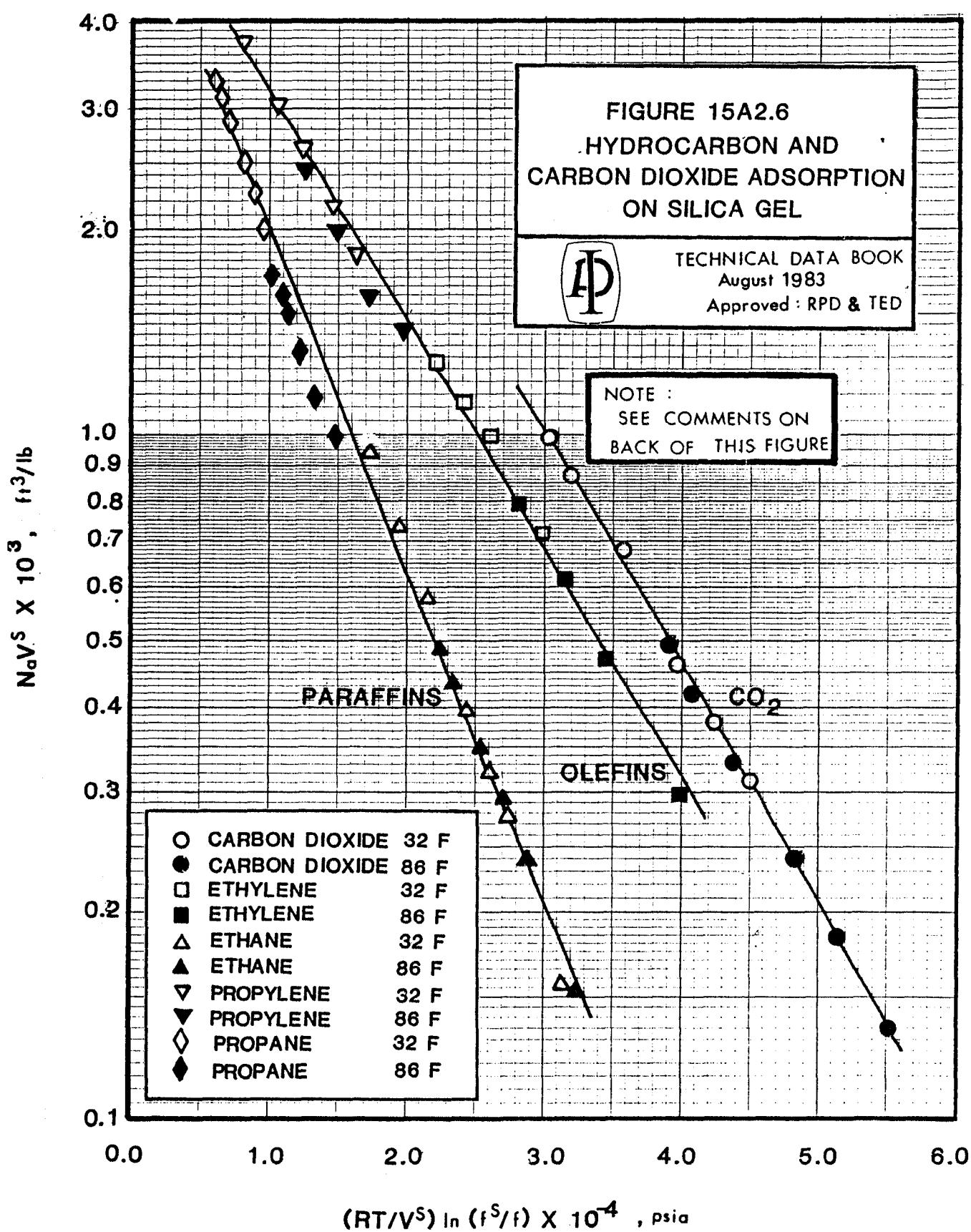
This value agrees well with the entire data set shown in Figure 15A2.2.











COMMENTS ON FIGURES 15A2.2 THROUGH 15A2.6**Purpose**

These figures are representative of potential-theory plots for pure-component adsorption data. They have been prepared according to Procedure 15A2.1. These figures should be useful for reading specific data and as guidelines for the preparation of other potential-theory plots.

Special Comments

Figure 15A2.2 is an example of the ability of a potential-theory plot to correlate temperature dependency. In this case an excellent relationship is found for the adsorption of ethylene on activated carbon (Nuxit-AL) over the temperature range of 68 to 194 F.

The behavior of a number of different kinds of adsorbates on a single solid at a constant temperature is depicted in Figure 15A2.3. On this relatively nonpolar active carbon, data for eight adsorbates have been correlated reasonably well. The scatter becomes more pronounced at lower pressures (higher abscissa values).

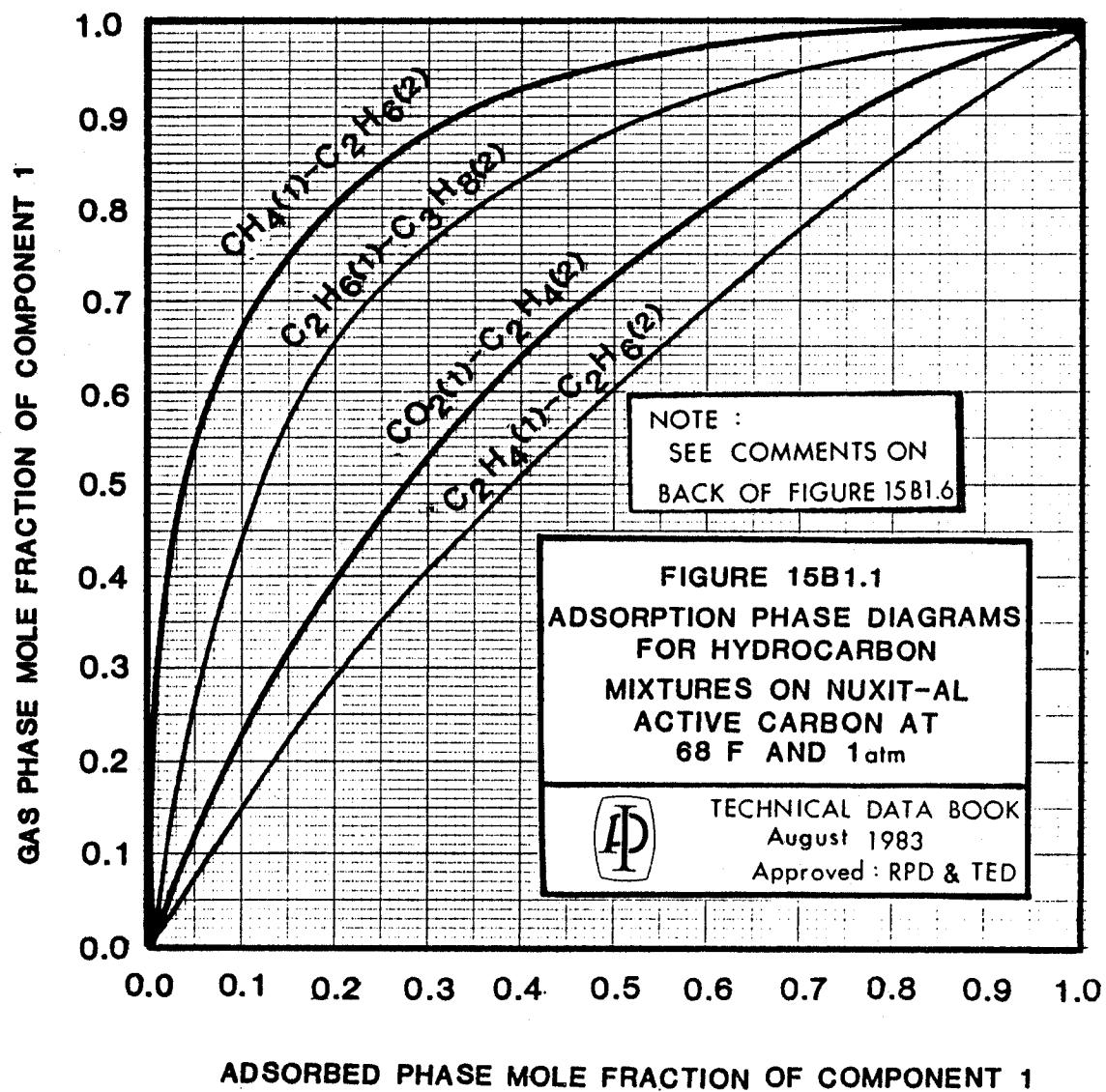
The type of behavior often observed on the more polar adsorbents, silica gel and molecular sieves, is shown in Figures 15A2.4 through 15A2.6. The different classes of compounds fall into separate correlations. Furthermore, there seems to be more scatter with temperature for the more highly adsorbed gases.

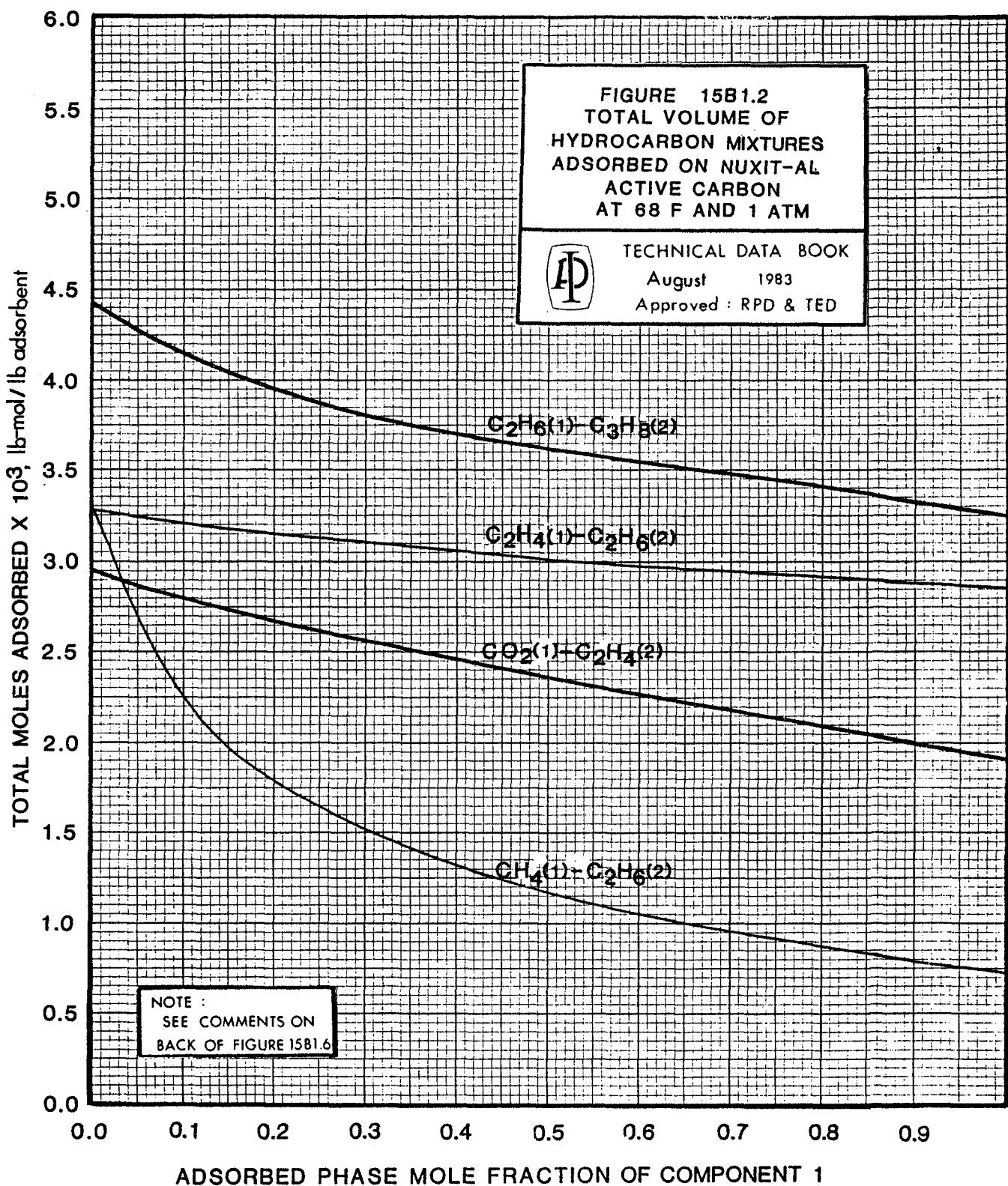
Reliability

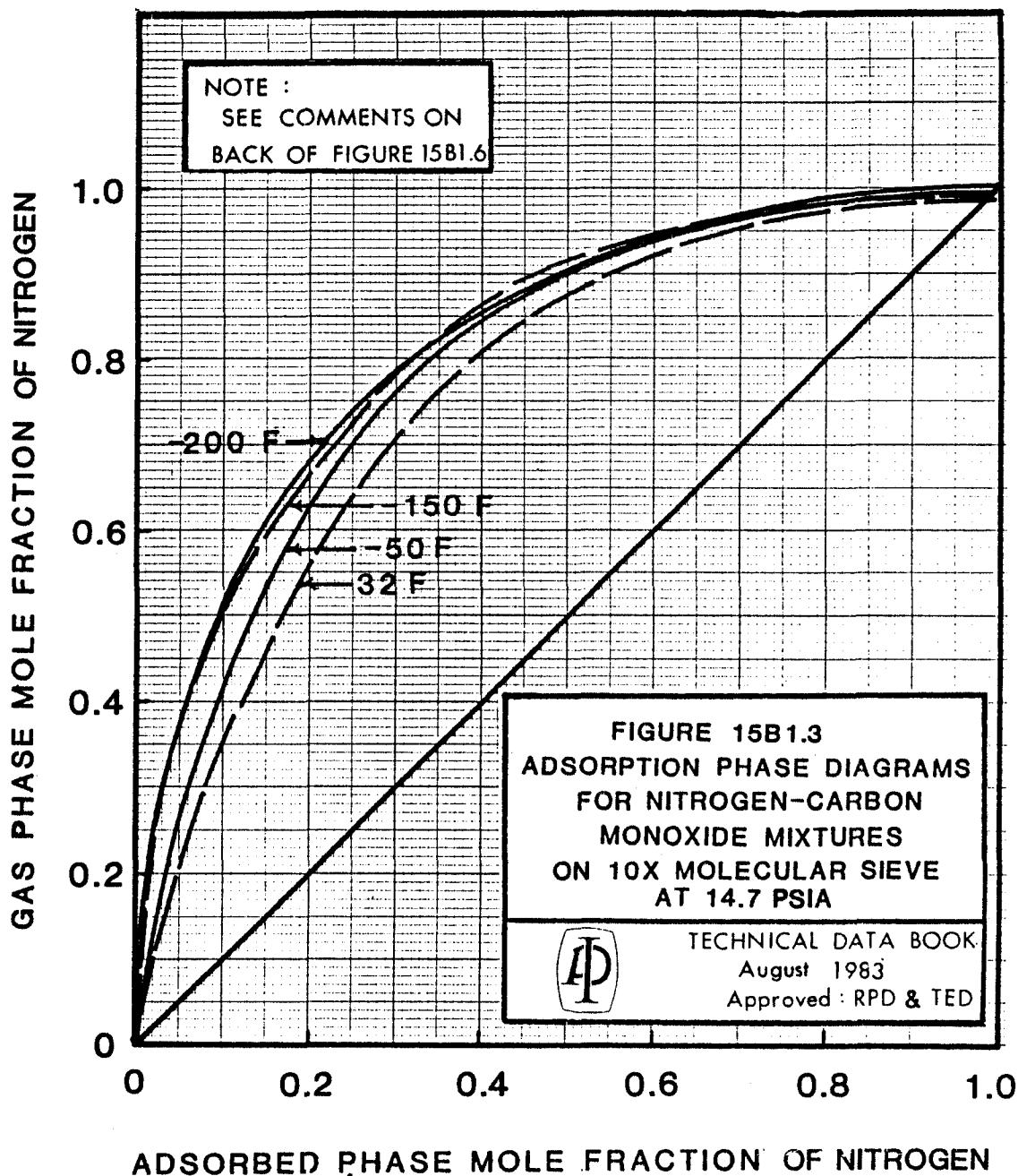
In addition to the usual reliability considerations in phase equilibria data, the extent of regeneration of the solid surface must be considered in adsorption equilibria. For physical adsorption on highly porous materials such as those represented in these figures, the results are not highly sensitive to the actual regeneration conditions as long as the solids are heated to a sufficiently high temperature in a moderate vacuum or while being purged with a dry inert gas to drive off any adsorbed water. In general this requires temperatures above 400 F in a vacuum less than 0.02 millimeters of mercury. Adjustment for different sources and batches of adsorbent and for variations in regeneration conditions can be made by multiplying the amount adsorbed by the ratio of the BET surface area of the actual sample to the BET surface area of the adsorbent given in the figure.

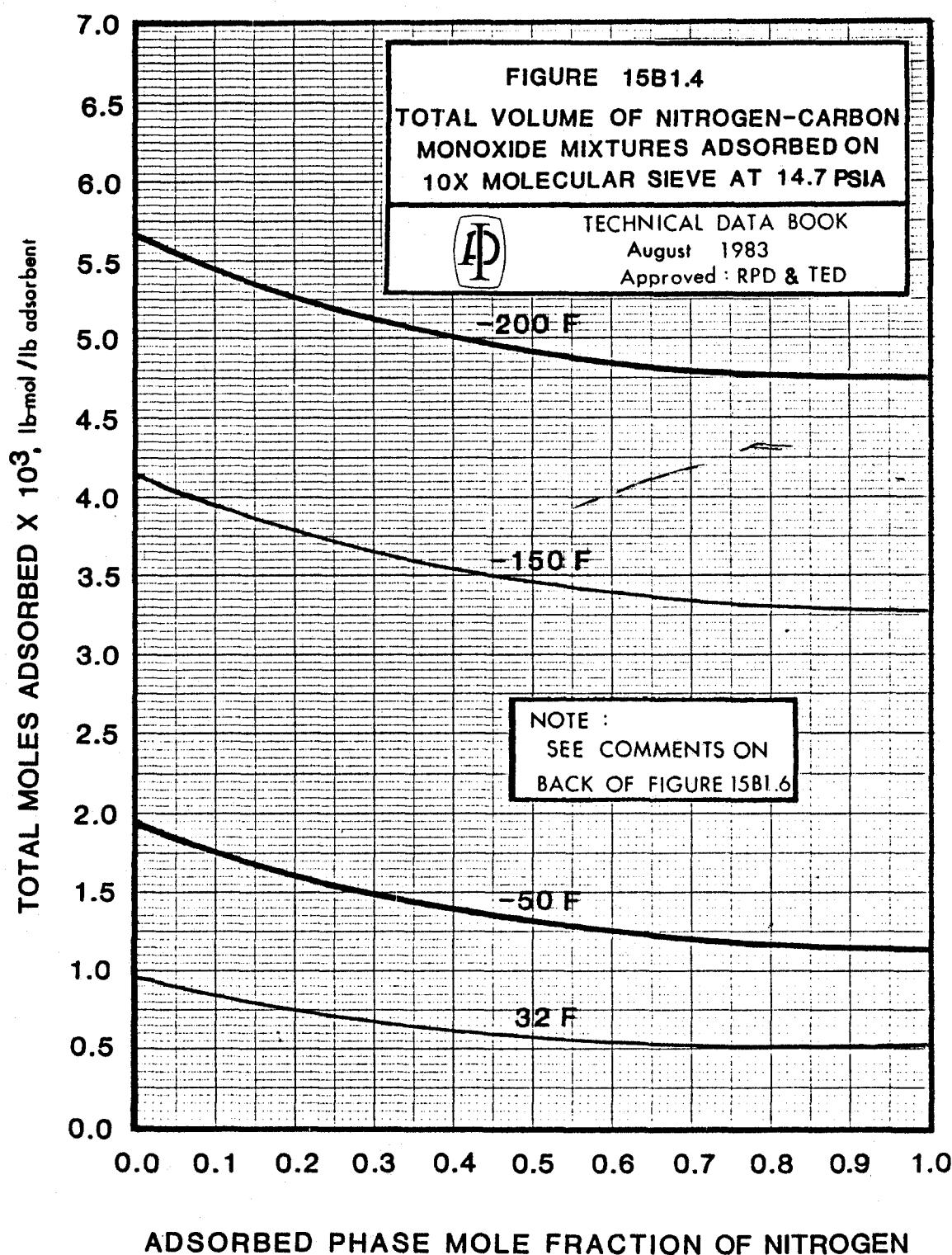
Literature Sources

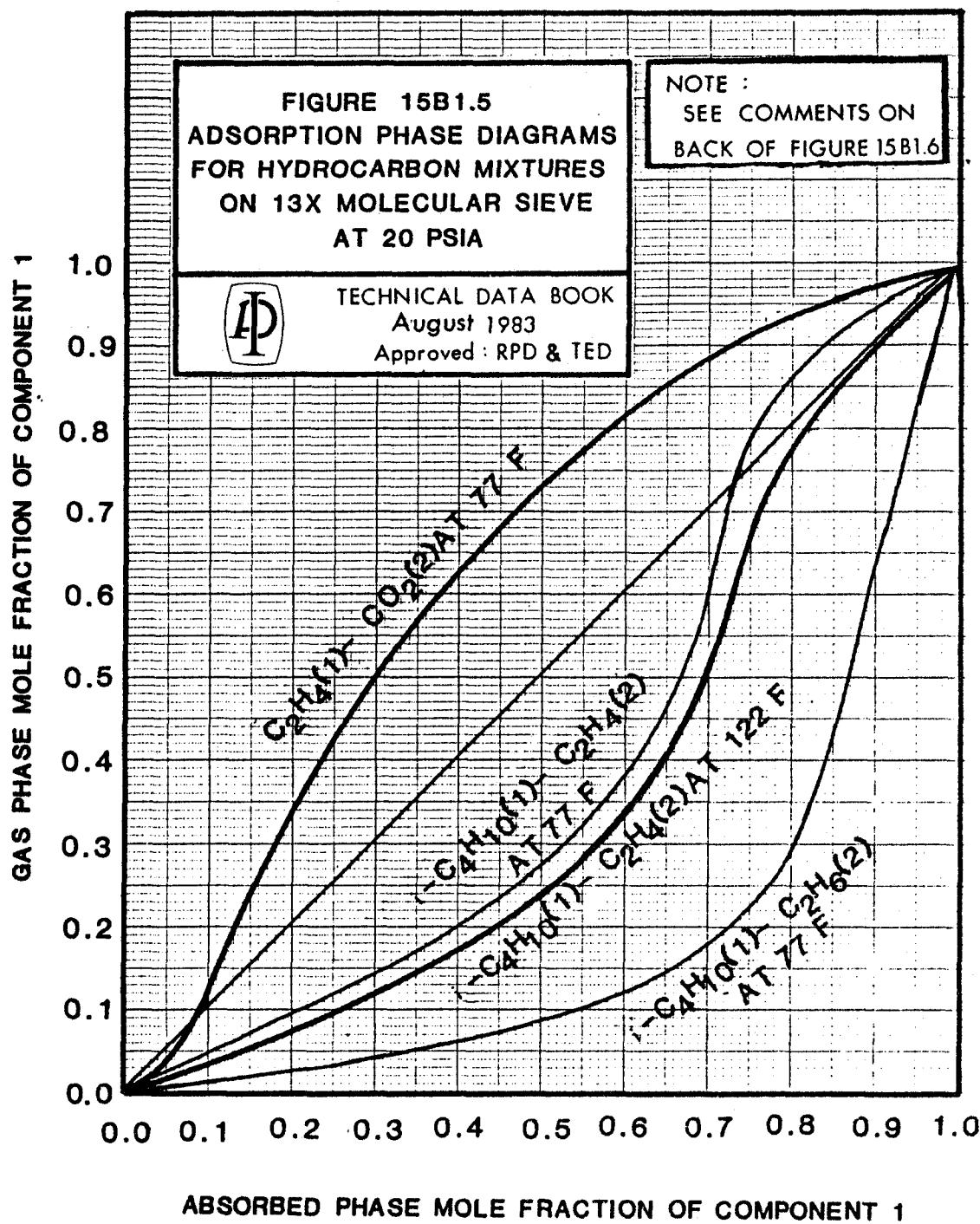
- Figure 15A2.2 (120, 121)
- Figure 15A2.3 (120, 121)
- Figure 15A2.4 (50)
- Figure 15A2.5 (67, 70, 71)
- Figure 15A2.6 (52).

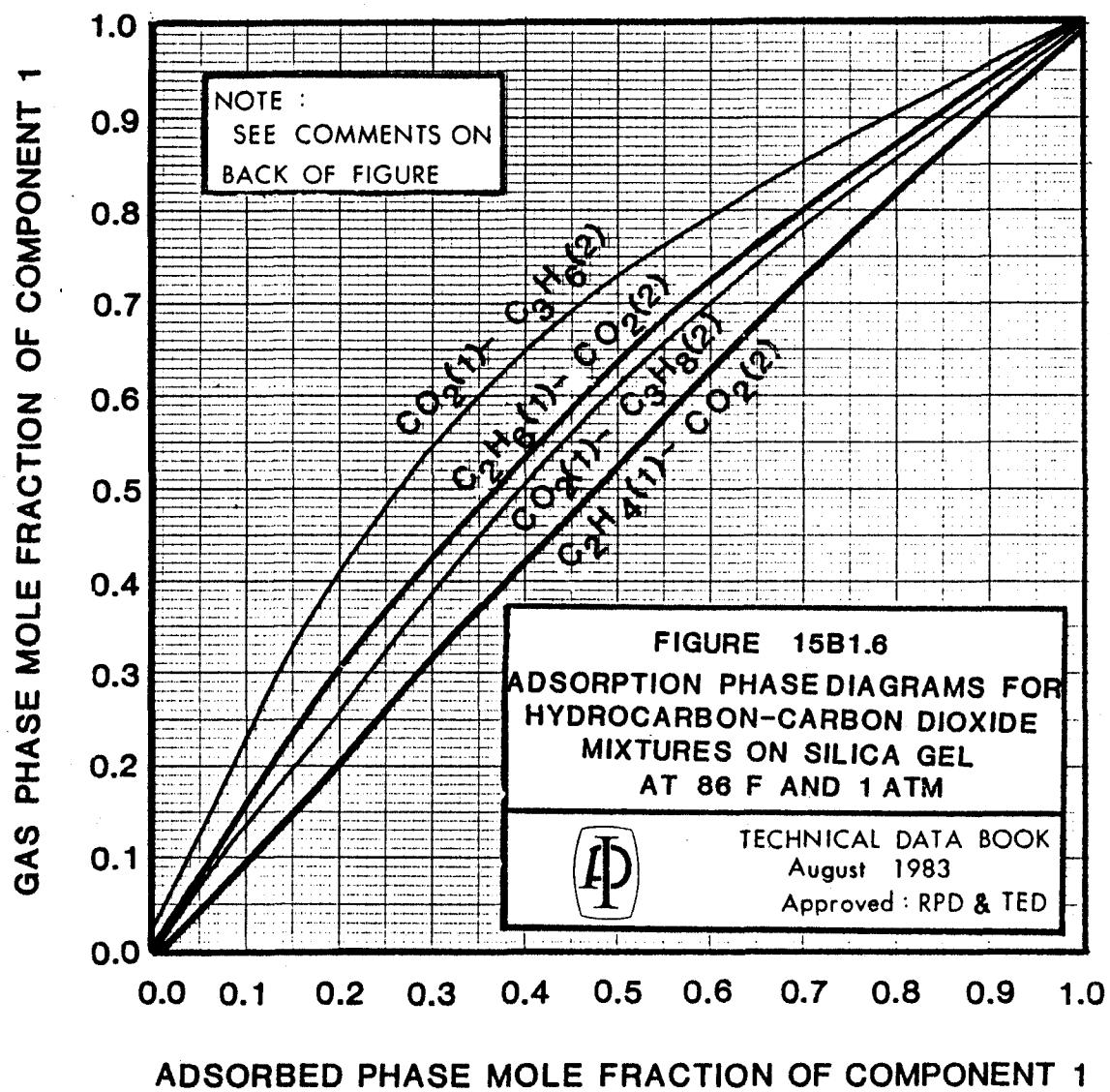












COMMENTS ON FIGURES 15B1.1 THROUGH 15B1.6

Purpose

These figures are representative of binary adsorption phase equilibrium diagrams and of the variation of the total volume adsorbed with composition for several important adsorbents.

Reliability

The cautions given for Figures 15A1.1 through 15A1.10 regarding the extent of regeneration of the solid surface also apply to gas mixtures, especially to the total amount adsorbed. The phase compositions, however, are much less sensitive to variations in the regeneration conditions.

Literature Sources

- Figure 15B1.1 (122)
- Figure 15B1.2 (122)
- Figure 15B1.3 (91)
- Figure 15B1.4 (91)
- Figure 15B1.5 (50)
- Figure 15B1.6 (52).

PROCEDURE 15B1.7**PREDICTION OF GAS-MIXTURE ADSORPTION EQUILIBRIUM FROM PURE-GAS ISOTHERMAL DATA****Discussion**

If the pure-component adsorption data are available for all components of a gas mixture, this method can be used to predict the mixed-gas adsorption equilibria. This method is based on ideal adsorbed solution assumptions and cannot predict highly nonideal behavior; an alternate method that can do so is given as Procedure 15B1.8. The following equations describe the equilibrium relationships that must be simultaneously satisfied.

$$\pi_i A / RT = \int_0^{p_i^\circ} N_{a,i} d \ln p_i = \int_0^{p_i^\circ} \frac{N_{a,i}}{p_i} d p_i \quad (15B1.7-1)$$

$$\sum x_i = 1 \quad (15B1.7-2)$$

$$\sum y_i = 1 \quad (15B1.7-3)$$

$$\pi_1 = \pi_2 = \dots = \pi_n \quad (15B1.7-4)$$

$$p_T y_i = p_i^\circ x_i \quad (15B1.7-5)$$

Where:

π_i = spreading pressure of component i , in pounds per foot.

A = surface area of the adsorbent, in square feet per pound.

R = universal gas constant, 1545.4 foot-pounds per (pound-mole) (degree Rankine).

T = temperature, in degrees Rankine.

$N_{a,i}$ = amount of component i adsorbed, in pound-moles of gas per pound of adsorbent.

p_i = equilibrium adsorption pressure, in pounds per square inch absolute.

x_i = mole fraction of component i in the adsorbed phase.

y_i = mole fraction of component i in the vapor phase.

p_T = total pressure of the adsorption system, in pounds per square inch absolute.

p_i° = pressure at which pure component i has a spreading pressure equal to the spreading pressure of the mixture, in pounds per square inch absolute.

NOTE: The term $(\pi_i A / RT)$ is usually treated as a single quantity having the units of poundmoles of gas adsorbed per pound of solid.

Equation (15B1.7-5) is the equivalent of Raoult's Law in vapor-liquid equilibria except that in place of the vapor pressure at the temperature of interest, the pressure of the pure gas that gives the same spreading pressure as found in the mixture is used. The spreading pressure (or $\pi A / RT$) is not a measured quantity; it is calculated from the isotherm data according to equation (15B1.7-1).

For each component, equations of the form of equation (15B1.7-1) and of equation (15B1.7-5) can be written. The entire set of equations is then solved simultaneously.

The total amount adsorbed is calculated from the following equation:

$$\frac{1}{N_{a,m}} = \sum_{i=1}^n \frac{x_i}{N_{a,i}^\circ} \quad (15B1.7-6)$$

Where:

$N_{a,m}$ = amount of gas mixture adsorbed, in pound-moles per pound of solid.

x_i = mole fraction of component i in the adsorbed phase.

$N_{a,i}^\circ$ = amount of pure component i adsorbed at the same temperature and spreading pressure as the mixture, in pound-moles per pound of solid.

n = number of components in the gas mixture.

Procedure**A. Binary Systems**

Step 1: Using the pure-component isotherm data (*all* at the *same* temperature), calculate $\pi A / RT$ for each adsorbate according to equation (15B1.7-1). For hand calculations, the data can be plotted as $N_{a,i}/p_i$ versus p_i and the areas can be determined graphically to yield $\pi A / RT$ as a function of pressure. Note that $N_{a,i}/p_i$ is determinant at zero pressure and, if the data are of sufficient accuracy and at low enough pressures, a reasonable extrapolation can be made.

15B1.7

If the calculations are being done using a computer, and Procedure 15A1.14 has been used to correlate the pure-component data, the spreading pressure is given directly by

$$\frac{\pi A}{RT} = N_1^{s,\infty} \ln(\gamma_v x_v^s) \quad (15B1.7-7)$$

$$\ln \gamma_v^s = \frac{\alpha_{1v} x_1^s}{1 + \alpha_{1v} x_1^s} - \ln(1 + \alpha_{1v} x_1^s) \quad (15B1.7-8)$$

$$x_1^s = \frac{N_1^s}{N_1^{s,\infty}} \quad (15B1.7-9)$$

$$x_v^s = 1 - x_1^s \quad (15B1.7-10)$$

Where:

$(\pi A/RT)$ = spreading pressure function, in pound-moles of gas adsorbed per pound of solid.

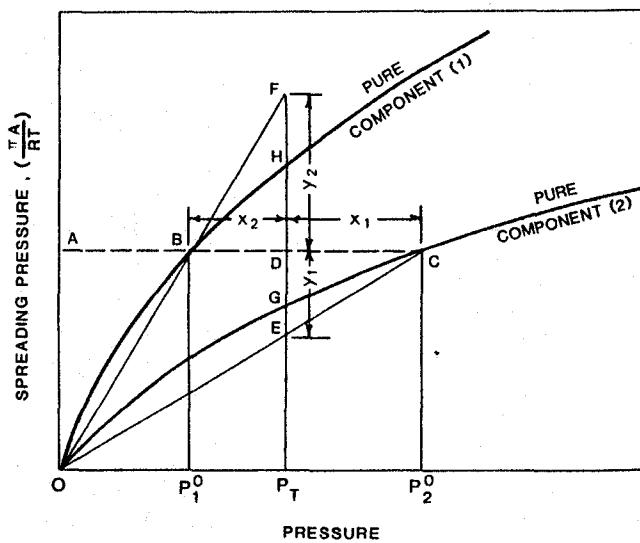
$N_1^{s,\infty}$ = constant obtained from pure-component regression representing maximum amount of adsorption of gas 1, in pound-moles of gas adsorbed per pound of solid.

N_1^s = amount of gas 1 adsorbed, in pound-moles of gas adsorbed per pound of solid.

α_{1v} = constant obtained from pure-component regression for component i representing the interactions between the gas molecules and the solid surface, unitless.

Step 2: Prepare a graph containing a curve for each component in the form of $\pi A/RT$ versus p_i .

Step 3: There are now nine unknowns, π_1 , π_2 , p_1^0 , p_2^0 , p_T , x_1 , x_2 , y_1 , and y_2 . There are five equations [equations (15B1.7-2) through (15B1.7-4) and two equations of the form of equation (15B1.7-5)] and two curves giving the $\pi A/RT$ relationships. By specifying p_T and y_1 , these equations may now be solved for the other five unknowns. A graphical procedure may be employed as shown in the accompanying figure.



The total pressure, p_T , is selected and then some point A between points G and H. Then

$$y_1 = \frac{DE}{FE} \quad \text{and} \quad x_1 = \frac{DC}{BC}$$

The entire calculation may be done analytically if the isotherm data have been regressed as described in Step 1. That is, if one has $N_{i,0}/p_i = f_i(p_i)$, then the two components have equal spreading pressures according to equation (15B1.7-1) when

$$\int_0^{p_1^0} f_1(p_1) d \ln p_1 = \int_0^{p_2^0} f_2(p_2) d \ln p_2 \quad (15B1.7-11)$$

Here $p_1^0 = p_T y_1/x_1$ and $p_2^0 = p_T(1 - y_1)/(1 - x_1)$. If an x_1 and p_T are selected, one can determine at what y_1 value equation (15B1.7-11) is satisfied.

Step 4: Calculate the total amount adsorbed from equation (15B1.7-6). To find $N_{a,i}^o$ use the selected mixture spreading pressure (point A) to obtain p_1^o and p_2^o . $N_{a,i}^o$ is the amount of each pure gas adsorbed corresponding to these pressures.

B. Multicomponent Systems

Step 1: Calculate the $\pi A/RT$ relationship for each pure component using the isotherm data just as in the binary case.

Step 2: Prepare a graph containing a curve for each component in the form of $\pi A/RT$ versus p_i .

Step 3: Select a p_T , vapor phase composition of interest, and $(n - 2)$ values of the adsorbed phase composition. Because of the increased number of degrees of freedom, there are an infinite number of adsorbed phase compositions corresponding to any vapor phase composition and total pressure. Thus the adsorbed phase compositions of all components save two must be specified. The remaining two compositions are then calculated from the following equation:

$$x_1 = \frac{p_T(1 - \sum_{i=3}^n y_i) - p_2^o(1 - \sum_{i=3}^n x_i)}{p_1^o - p_2^o} \quad (15B1.7-12)$$

$$\sum_{i=1}^n x_i = 1 \quad (15B1.7-13)$$

The summations in equation (15B1.7-12) are over all components whose phase compositions have been specified, and components 1 and 2 are those with unknown adsorbed phase compositions.

COMMENTS ON PROCEDURE 15B1.7

Purpose

This procedure is given as a method of predicting multicomponent gas adsorption equilibria using only the pure-gas isotherm data. Both the equilibria phase compositions and the total volume adsorbed are predicted. A relatively simple graphical method is described for binary systems. This method assumes ideal adsorbed solution behavior and cannot predict highly nonideal behavior such as adsorption azeotropes. Unfortunately there are no clear guidelines to determine when a system is going to be nonideal. However, if the pure-component isotherms intersect at a pressure below the total system pressure, a nonideal adsorption system should be suspected. Also at high surface coverages this procedure tends to give less satisfactory predictions. Better results for nonideal systems may be obtained using Procedure 15B1.8.

Reliability

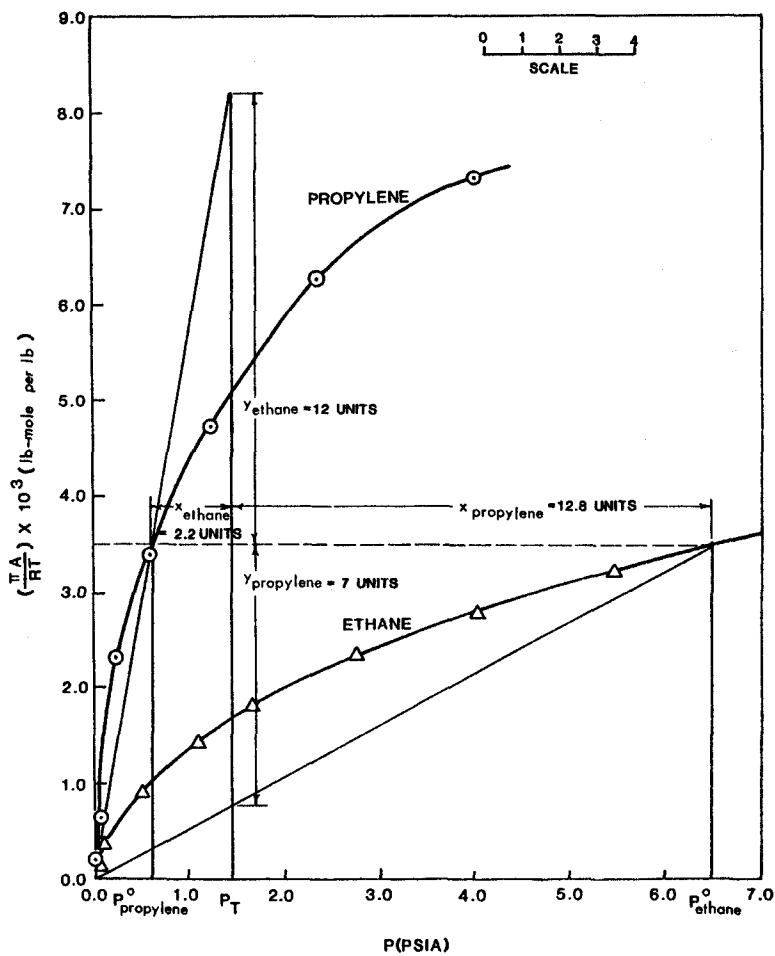
For systems where the surface coverage is less than 50 percent and where the pure-component isotherms do not intersect at a pressure below the total system pressure, this procedure generally gives reasonable predictions. Most of the evaluations of this method have been for binary systems, although a few ternary and quaternary systems have been studied.

Literature Sources

This procedure, with the exception of the vacancy solution equations in Step 1, came from Myers, A. L., and Prausnitz, J. M., *AIChE Journal* 11 121 (1965). The equations in Step 1c are from Cochran, T. W., Kabel, R. L., and Danner, R. P., "Vacancy Solution Theory of Adsorption Using the Flory-Huggins Activity Coefficient Equations," *AIChE Journal* 31 268 (1985).

Example

The graphical techniques involved in the procedure are illustrated for the adsorption of ethane-propylene on active carbon AC-40 at 68 F and 1.45 pounds per square inch absolute. The pure-component data of Costa et al. (21) are expressed in the form ($\pi A/RT$) versus p



in the adjoining figure. A value of 0.0035 pound-mole per pound is selected for the spreading pressure and the phase compositions are calculated.

$$y_{\text{ethane}} = \frac{12}{12+7} = 0.63$$

$$x_{\text{ethane}} = \frac{2.2}{2.2+12.8} = 0.15$$

At $y_{\text{ethane}} = 0.63$, the experimental (interpolated) value of x_{ethane} is 0.17 (21).

The values of $p_{\text{ethane}}^{\circ}$ and $p_{\text{propylene}}^{\circ}$ are found from the figure to be 6.5 and 0.6 pounds per square inch absolute respectively. At these values of the adsorption pressure, the amount adsorbed interpolated from the pure-component data of Costa et al. (21) is 0.000165 pound-mole per pound for ethane and 0.000145 pound-mole per pound for propylene. The total amount adsorbed is calculated from equation (15B1.7-6):

$$N_{a,m} = \left[\sum \frac{x_i}{N_{a,i}} \right]^{-1} = \left[\frac{0.15}{0.000165} + \frac{(1-0.15)}{0.000145} \right]^{-1} = 1.48 \times 10^{-4} \text{ pound-mole per pound}$$

No experimental value is available.

PROCEDURE 15B1.8

ALTERNATE COMPUTER METHOD FOR PREDICTION OF GAS-MIXTURE
ADSORPTION EQUILIBRIUM FROM PURE-GAS ISOTHERMAL DATA

Discussion

If the pure-component isotherm data have been regressed according to Procedure 15A1.14, the prediction of multicomponent equilibrium can be made using the following equations:

$$\phi_i y_i p_T = \gamma_i^s x_i \frac{N_m^s N_i^{s,\infty}}{N_m^{s,\infty} b_i} \left[\frac{\exp \alpha_{iv}}{1 + \alpha_{iv}} \right] \exp \hat{\pi}_i \quad (15B1.8-1)$$

$$\ln \gamma_i^s = -\ln \left[\sum_{j=1}^n \frac{x_j^s}{1 + \alpha_{ij}} \right] + \left[1 - \left(\sum_{j=1}^n \frac{x_j^s}{1 + \alpha_{ij}} \right)^{-1} \right] \quad (15B1.8-2)$$

$$\alpha_{ij} = \frac{\alpha_{iv} + 1}{\alpha_{ji} + 1} - 1 \quad (15B1.8-3)$$

$$N_m^{s,\infty} = \sum_{i=1}^n x_i N_i^{s,\infty} \quad (15B1.8-4)$$

$$\hat{\pi}_i = \left[\frac{N_i^{s,\infty} - N_m^{s,\infty}}{N_m^s} - 1 \right] \ln (\gamma_v^s x_v^s) \quad (15B1.8-5)$$

$$x_i^s = \frac{x_i N_m^s}{N_m^{s,\infty}} \quad (15B1.8-6)$$

$$x_v^s = 1 - \sum_{j=1}^n x_j^s \quad (15B1.8-7)$$

$$N_i^{s,\infty} = N_{oi}^{s,\infty} \exp \left[\frac{r_i}{T} \right] \quad (15B1.8-8)$$

$$b_i = b_{oi} \exp \left[\frac{-q_i}{RT} \right] \quad (15B1.8-9)$$

$$\alpha_{iv} = m_i N_i^{s,\infty} - 1 \quad (15B1.8-10)$$

Where:

ϕ_i = fugacity coefficient of component i at the temperature and pressure of the adsorption system, unitless.

y_i = mole fraction of component i in the vapor phase.

p_T = total pressure of adsorption system, in pounds per square inch absolute.

x_i = mole fraction of component i in the adsorbed phase.

N_m^s = amount of gas mixture adsorbed, in pound-moles per pound of adsorbent.

$N_i^{s,\infty}$ = constant obtained from pure-component regression representing the maximum amount of adsorption of component i , in pound-moles per pound of adsorbent.

α_{iv} = constant obtained from pure-component regression for component i representing the interactions between gas molecules and the solid surface, unitless.

b_i = constant obtained from pure-component regression representing the slope of the isotherm of component i at infinite dilution, in pound-moles per (pound of adsorbent)(pound per square inch).

$N_{oi}^{s,\infty}$ = temperature-independent constant characterizing each adsorbate-adsorbent system, in pound-moles per pound of adsorbent.

r_i = temperature-independent constant characterizing each adsorbate-adsorbent system, in degrees Rankine.

T = adsorption equilibrium temperature, in degrees Rankine.

b_{oi} = temperature-independent constant characterizing each adsorbate-adsorbent system, in pound-moles adsorbed per (pound of adsorbent) (pound per square inch).

q_i = temperature-independent constant characterizing each adsorbate-adsorbent system, in British thermal units per pound-mole.

R = gas constant, 1.986 British thermal units per (pound-mole) (degree Rankine).

m_i = temperature-independent constant of proportionality, in pounds of adsorbent per pound-mole adsorbed.

NOTE: In equation (15B1.8-2) the summations are to be taken over all components and the vacancies, v. Equation (15B1.8-3) also implies that $\alpha_{ii} = 0$ and $(1 + \alpha_{ij}) = 1/(1 + \alpha_{ji})$.

Procedure**A. Binary Systems**

Step 1: Obtain the pure-component parameters as described in Procedure 15A1.14.

Step 2: Select an arbitrary value of x_1 . ($x_2 = 1 - x_1$)

Step 3: The operative equations for the binary case are as follows:

$$\phi_1 y_1 p_T = \gamma_1^s x_1 \frac{N_m^s N_1^{s,\infty}}{N_m^{s,\infty} b_1} \left[\frac{\exp \alpha_{1v}}{1 + \alpha_{1v}} \right] \exp \hat{\pi}_1 \quad (15B1.8-11)$$

$$\phi_2 y_2 p_T = \gamma_2^s x_2 \frac{N_m^s N_2^{s,\infty}}{N_m^{s,\infty} b_2} \left[\frac{\exp \alpha_{2v}}{1 + \alpha_{2v}} \right] \exp \hat{\pi}_2 \quad (15B1.8-12)$$

$$\ln \gamma_1^s = -\ln \left[x_1^s + \frac{x_2^s}{1 + \alpha_{12}} + \frac{x_v^s}{1 + \alpha_{1v}} \right] + \left[1 - \left(x_1^s + \frac{x_2^s}{1 + \alpha_{12}} + \frac{x_v^s}{1 + \alpha_{1v}} \right)^{-1} \right] \quad (15B1.8-13)$$

$$\begin{aligned} \ln \gamma_2^s = & -\ln \left[(1 + \alpha_{12}) x_1^s + x_2^s + \frac{x_v^s}{1 + \alpha_{2v}} \right] \\ & + \left[1 - \left((1 + \alpha_{12}) x_1^s + x_2^s + \frac{x_v^s}{1 + \alpha_{2v}} \right)^{-1} \right] \end{aligned} \quad (15B1.8-14)$$

$$\begin{aligned} \ln \gamma_v^s = & -\ln \left[(1 + \alpha_{1v}) x_1^s + (1 + \alpha_{2v}) x_2^s + x_v^s \right] \\ & + \left[1 - \left[(1 + \alpha_{1v}) x_1^s + (1 + \alpha_{2v}) x_2^s + x_v^s \right]^{-1} \right] \end{aligned} \quad (15B1.8-15)$$

$$N_m^{s,\infty} = x_1 N_1^{s,\infty} + x_2 N_2^{s,\infty} \quad (15B1.8-16)$$

$$x_i^s = \frac{x_i N_m^s}{N_m^{s,\infty}} \quad \text{for } i = 1 \text{ or } 2 \quad (15B1.8-17)$$

$$x_v^s = 1 - x_1^s - x_2^s \quad (15B1.8-18)$$

$$\hat{\pi}_i = \left[\frac{N_i^{s,\infty} - N_m^{s,\infty}}{N_m^s} - 1 \right] \ln (\gamma_v^s x_v^s) \quad \text{for } i = 1 \text{ or } 2 \quad (15B1.8-19)$$

$$N_1^{s,\infty} = N_{o1}^{s,\infty} \exp \left[\frac{r_1}{T} \right] \quad (15B1.8-20)$$

$$N_2^{s,\infty} = N_{o2}^{s,\infty} \exp \left[\frac{r_2}{T} \right] \quad (15B1.8-21)$$

$$b_1 = b_{o1} \exp \left[\frac{-q_1}{RT} \right] \quad (15B1.8-22)$$

$$b_2 = b_{o2} \exp \left[\frac{-q_2}{RT} \right] \quad (15B1.8-23)$$

$$\alpha_{1v} = m_1 N_{o1}^{s,\infty} - 1 \quad (15B1.8-24)$$

$$\alpha_{2v} = m_2 N_{o2}^{s,\infty} - 1 \quad (15B1.8-25)$$

Step 4: Solve the two equilibrium equations (15B1.8-11 and 15B1.8-12) simultaneously for y_1 ($y_2 = 1 - y_1$) and N_m^s by trial and error. At moderate pressures the fugacity coefficients, ϕ_i , can be set equal to 1, and the two independent equations can be summed to eliminate y_i . This permits a simpler solution for N_m^s , and then y_i values can be calculated directly from the appropriate equilibrium equation.

B. Multicomponent Systems

The above binary procedure can be extended to multicomponent systems. An equilibrium equation of the form of equation (15B1.8-1) must be written for each component. The activity coefficient equations become more complex, but the form of equation (15B1.8-2) is readily programmed on a digital computer.

COMMENTS ON PROCEDURE 15B1.8

Purpose

Procedure 15B1.8 is given as a method of predicting adsorption equilibrium for a multi-component system when the pure-component data have been regressed using Procedure 15A1.14 (the vacancy solution theory).

Reliability

This procedure usually gives predictions that are within 5 percent in the adsorbed phase mole fraction. For highly nonideal systems such as those that form adsorption azeotropes, larger errors (10–15 percent in the adsorbed phase mole fraction) have been observed. The total amount adsorbed is almost always predicted to within 5 percent.

Literature Source

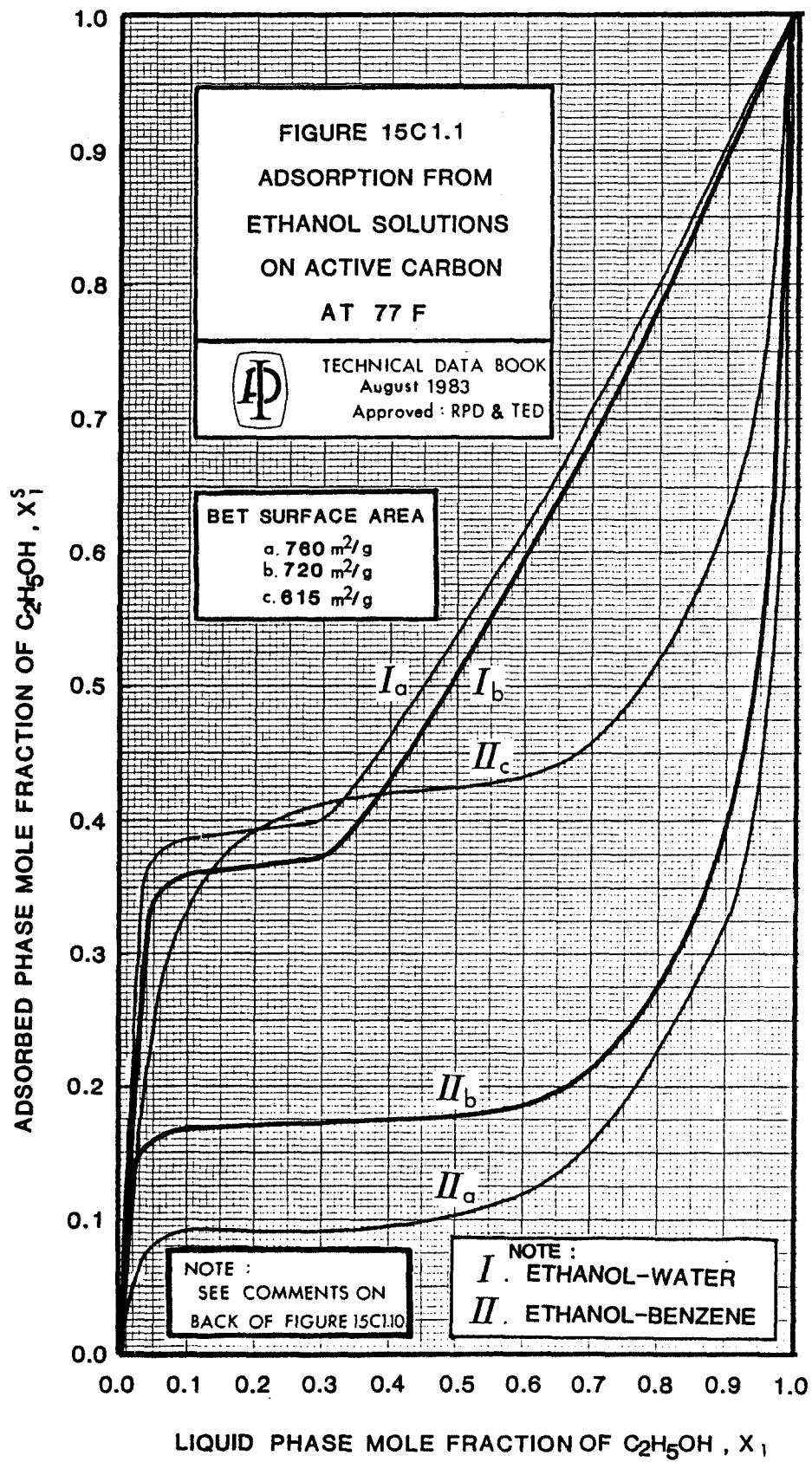
This procedure was taken from Cochran, T. W., Kabel, R. L., and Danner, R. P., "Vacancy Solution Theory of Adsorption Using Flory-Huggins Activity Coefficient Equations," *AIChE Journal* 31 268 (1985).

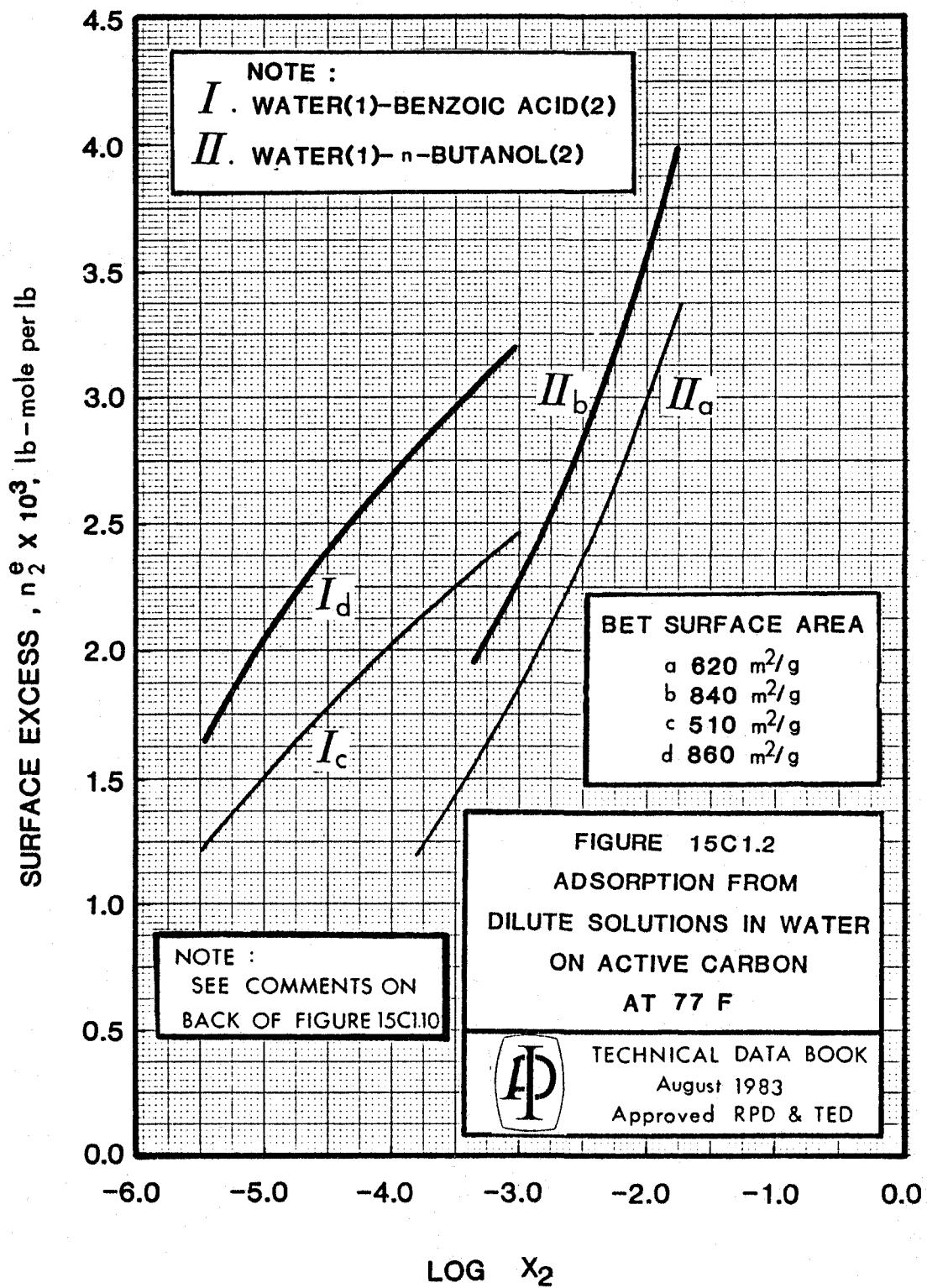
Example

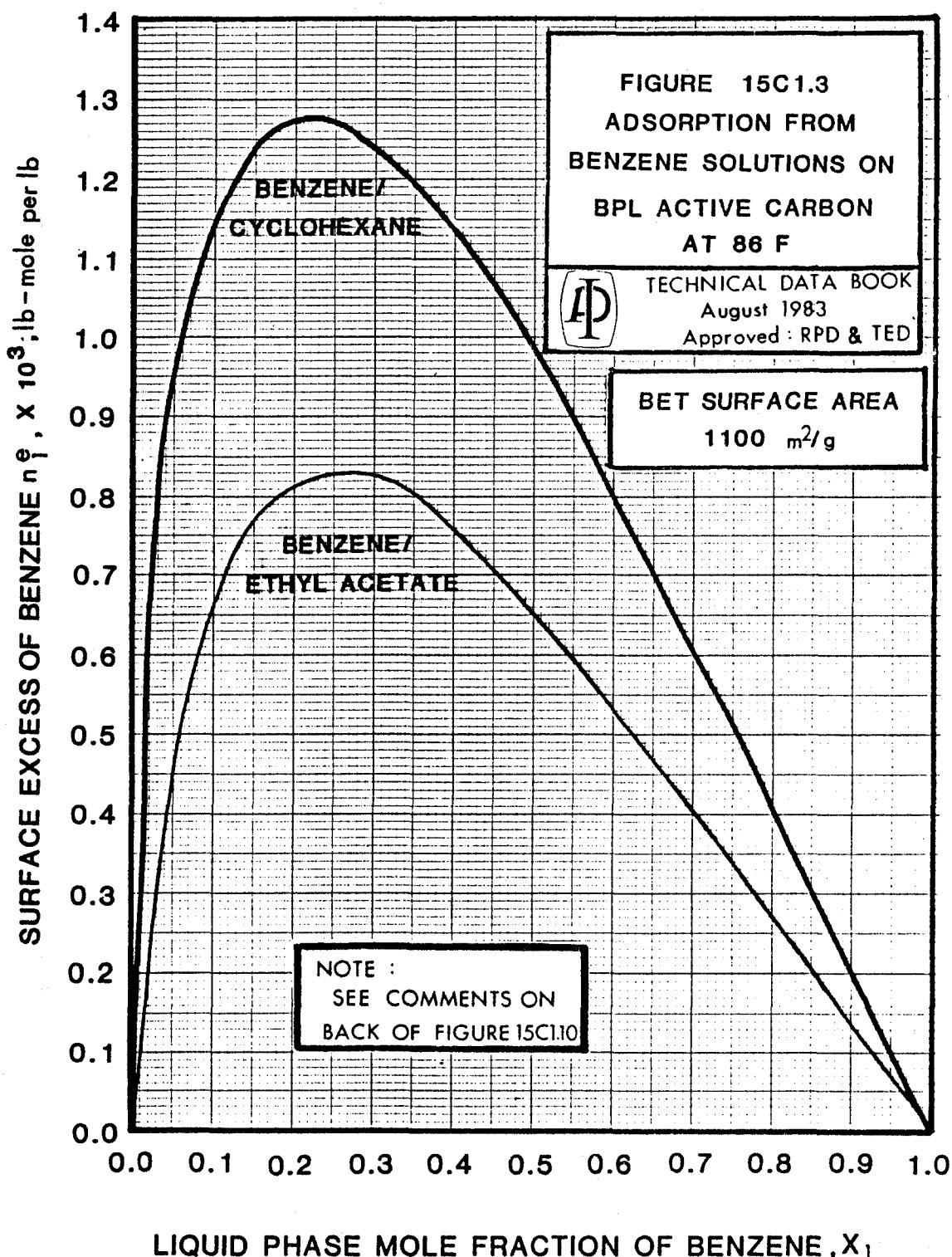
Using the regression constants obtained in the example of Procedure 15A1.14, the binary adsorption equilibria of nitrogen-oxygen on 10X molecular sieve at –50 F and 14.7 pounds per square inch absolute can be predicted. The results are given here as a means of checking a computer program.

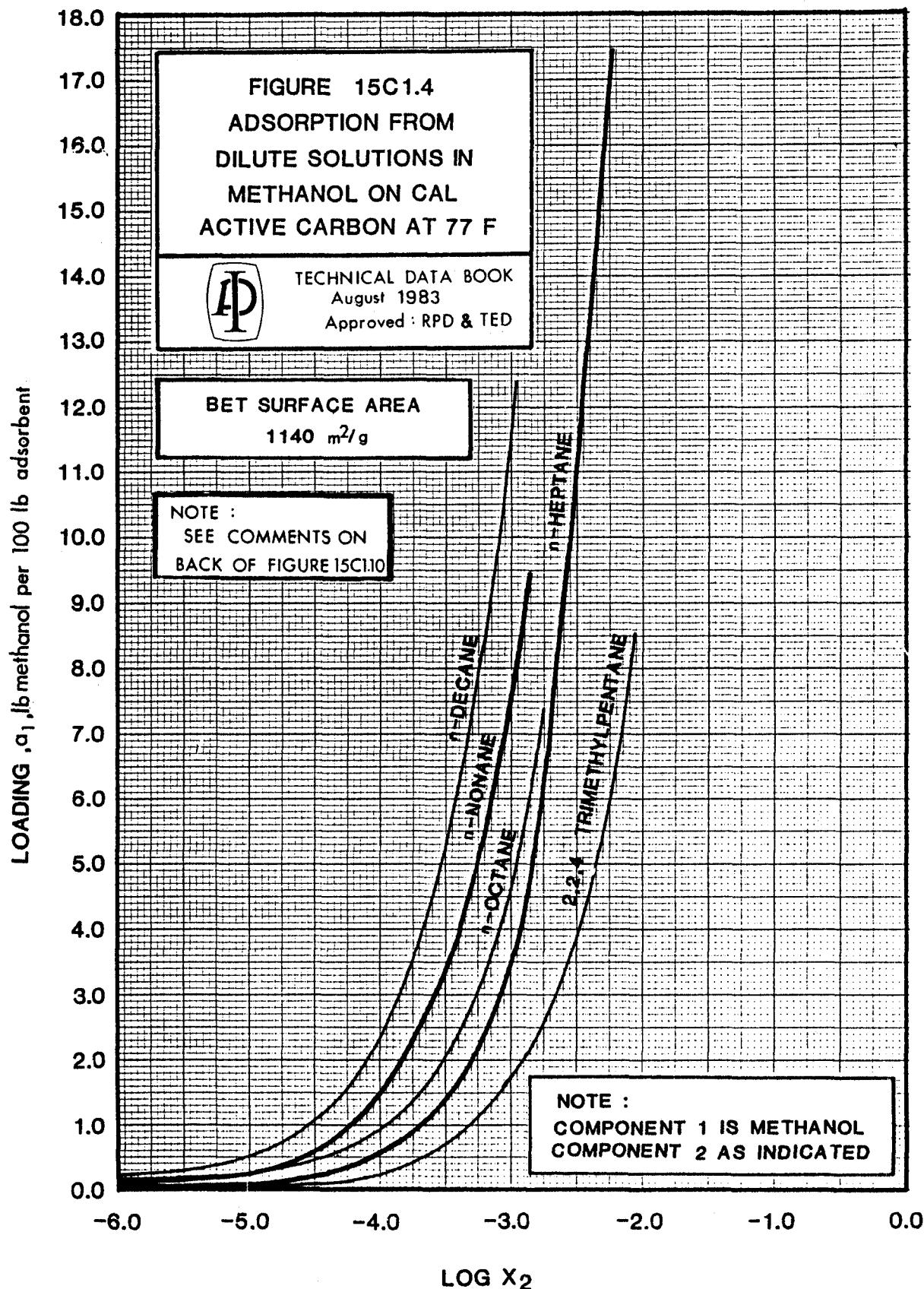
Regression Constant	Oxygen	Nitrogen
$N_i^{s,\infty}$, lb-mol per lb	4.00×10^{-3}	5.34×10^{-3}
b_i , lb-mol per (lb)(psia)	3.234×10^{-5}	4.619×10^{-4}
α_{iv}	4.2×10^{-5}	3.580
<hr/>		
x_{oxygen}	y_{oxygen}	$N_m^s \times 10^4$ (lb-mol per lb)
	Observed ^a	Calculated
0.0103	0.0466	0.0359
0.1065	0.3905	0.3255
0.3133	0.7801	0.7129
0.5745	0.9144	0.9163
0.7766	0.9669	0.9745
0.9161	0.9867	0.9933

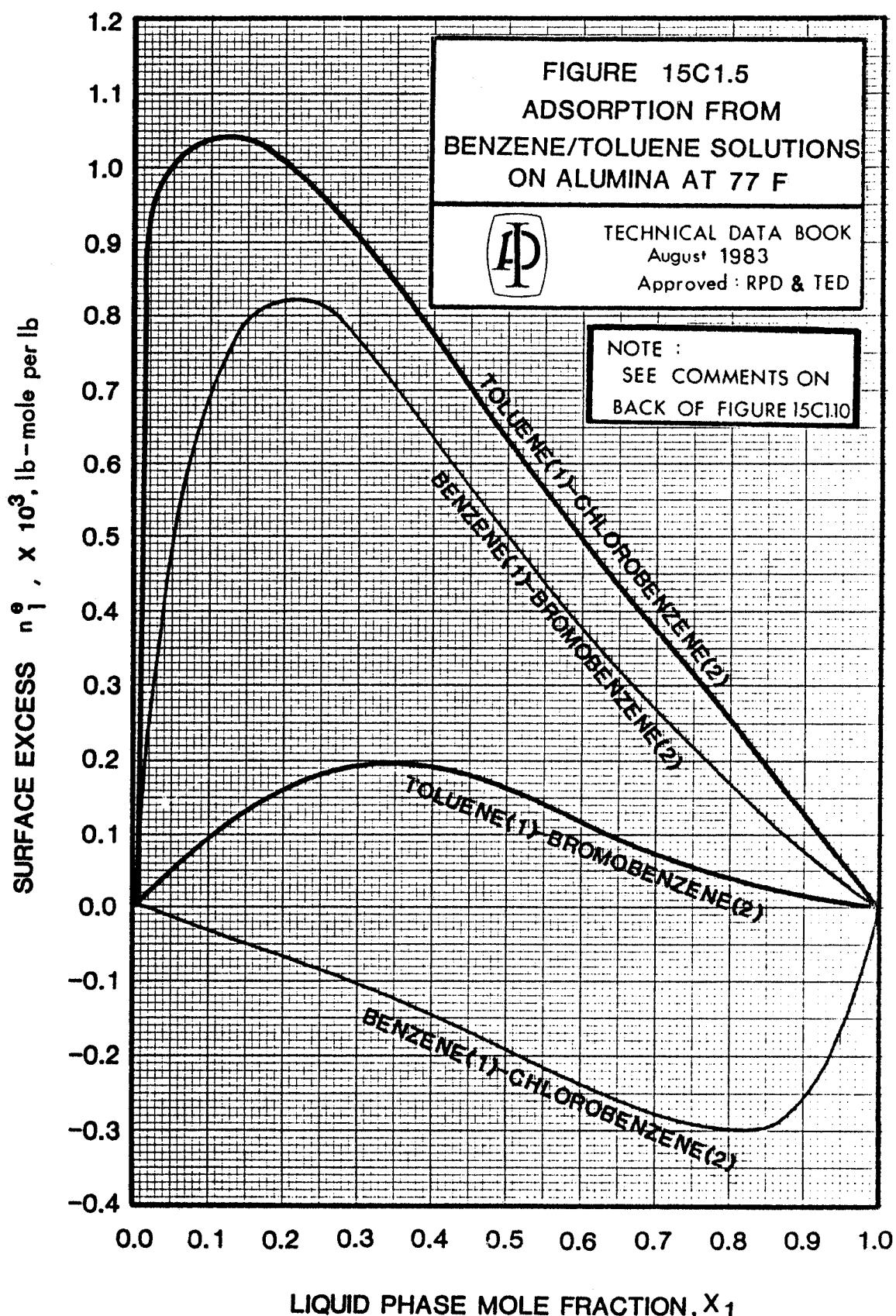
^aFrom Nolan et al. (91).

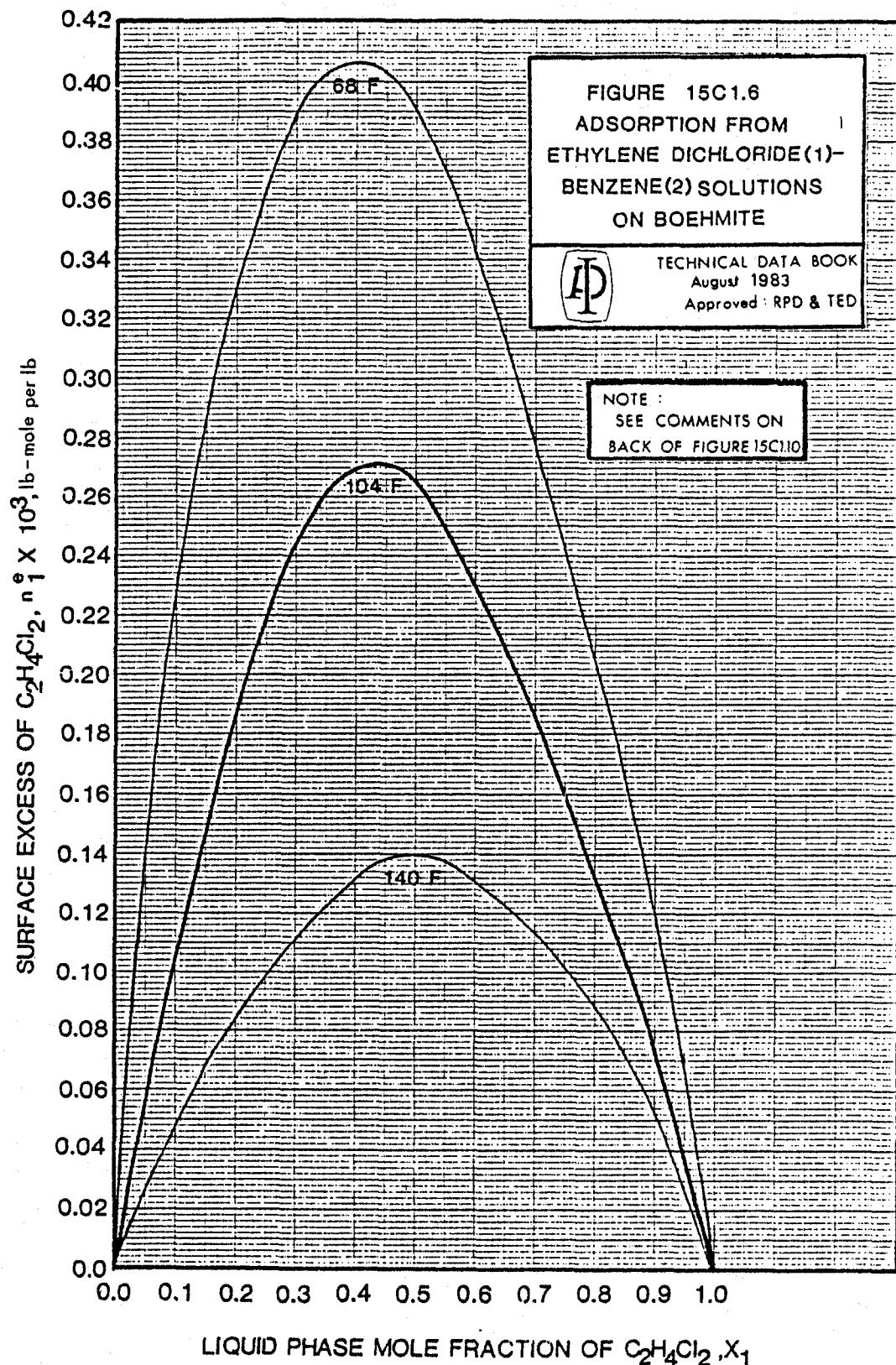


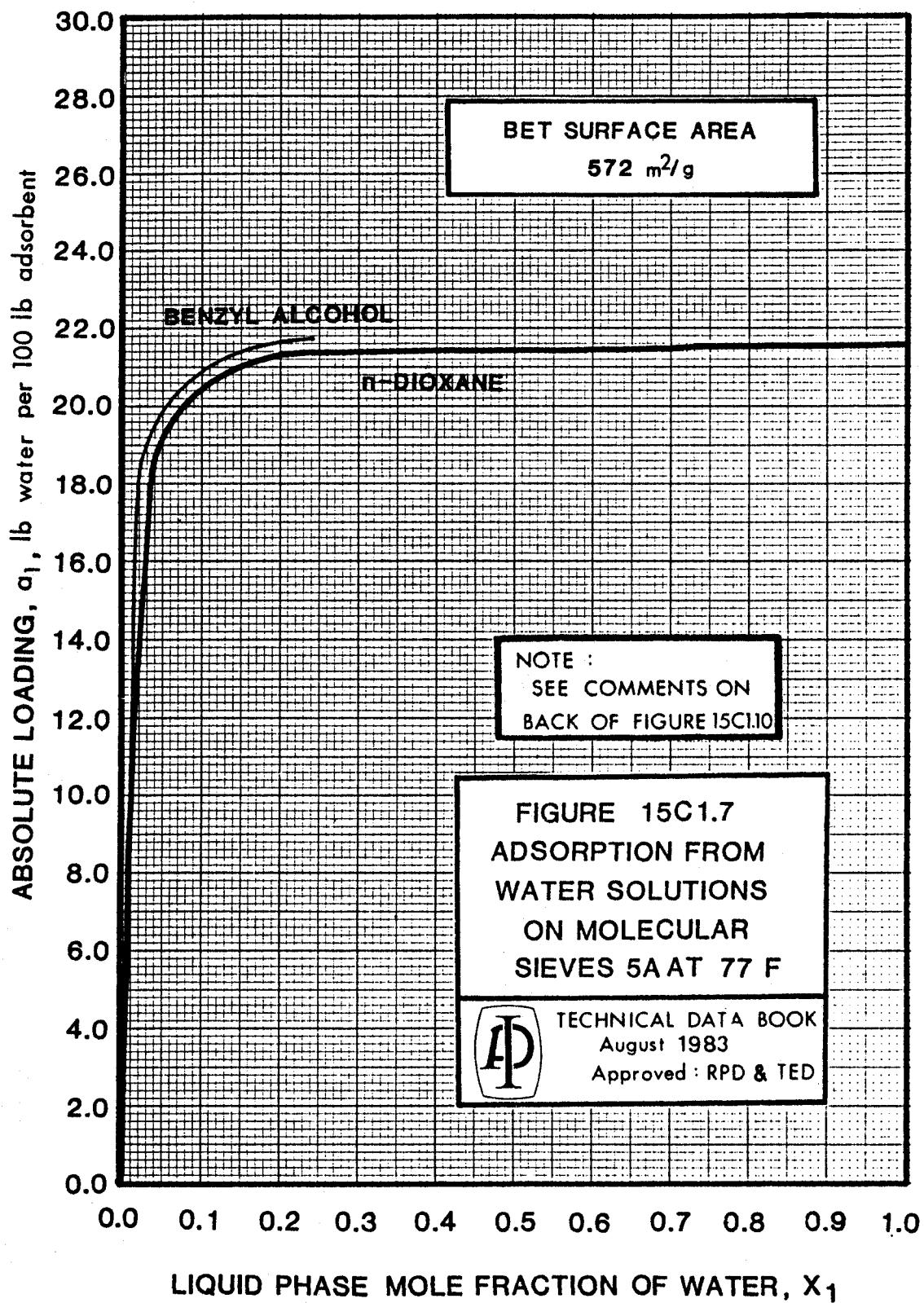


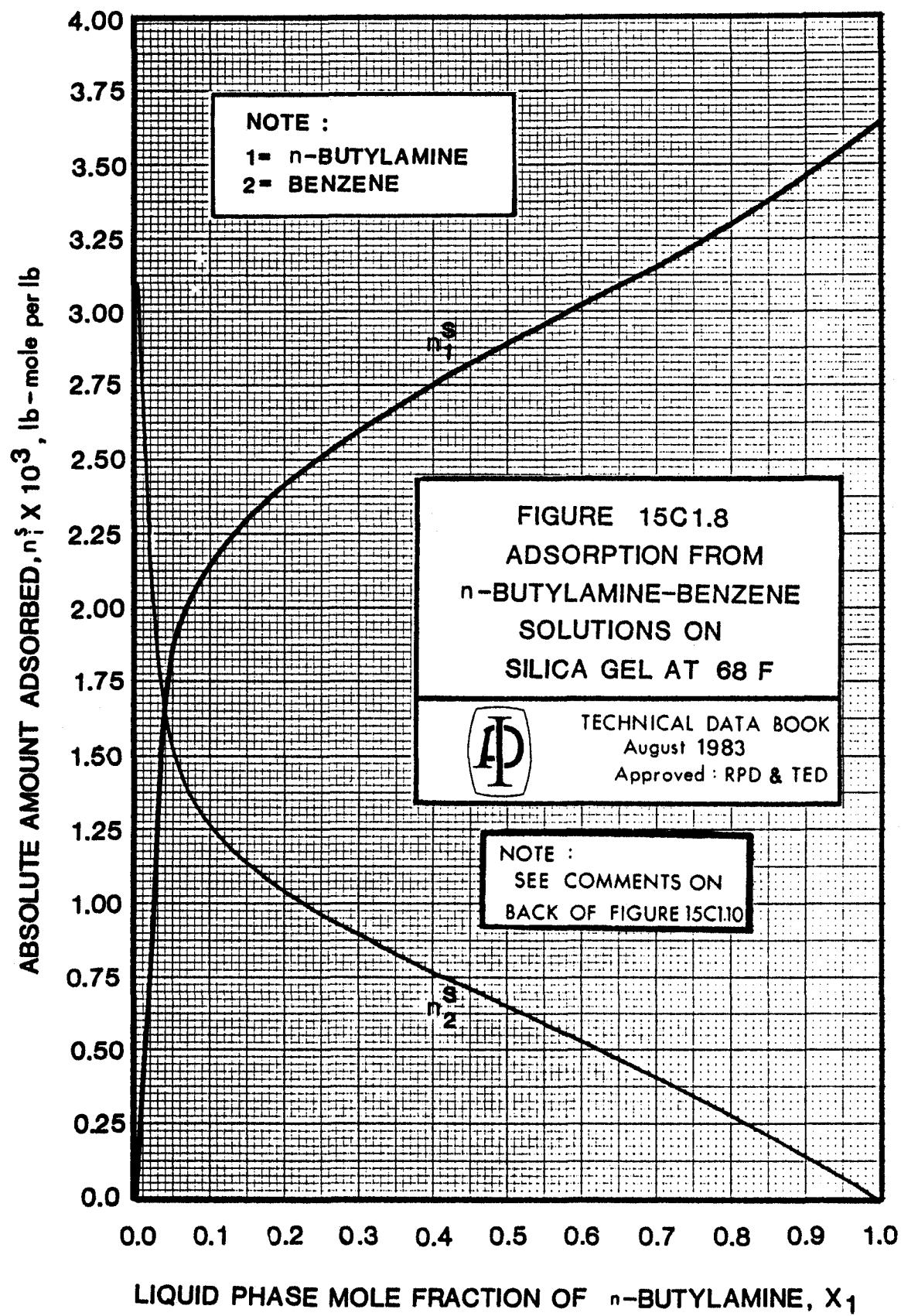


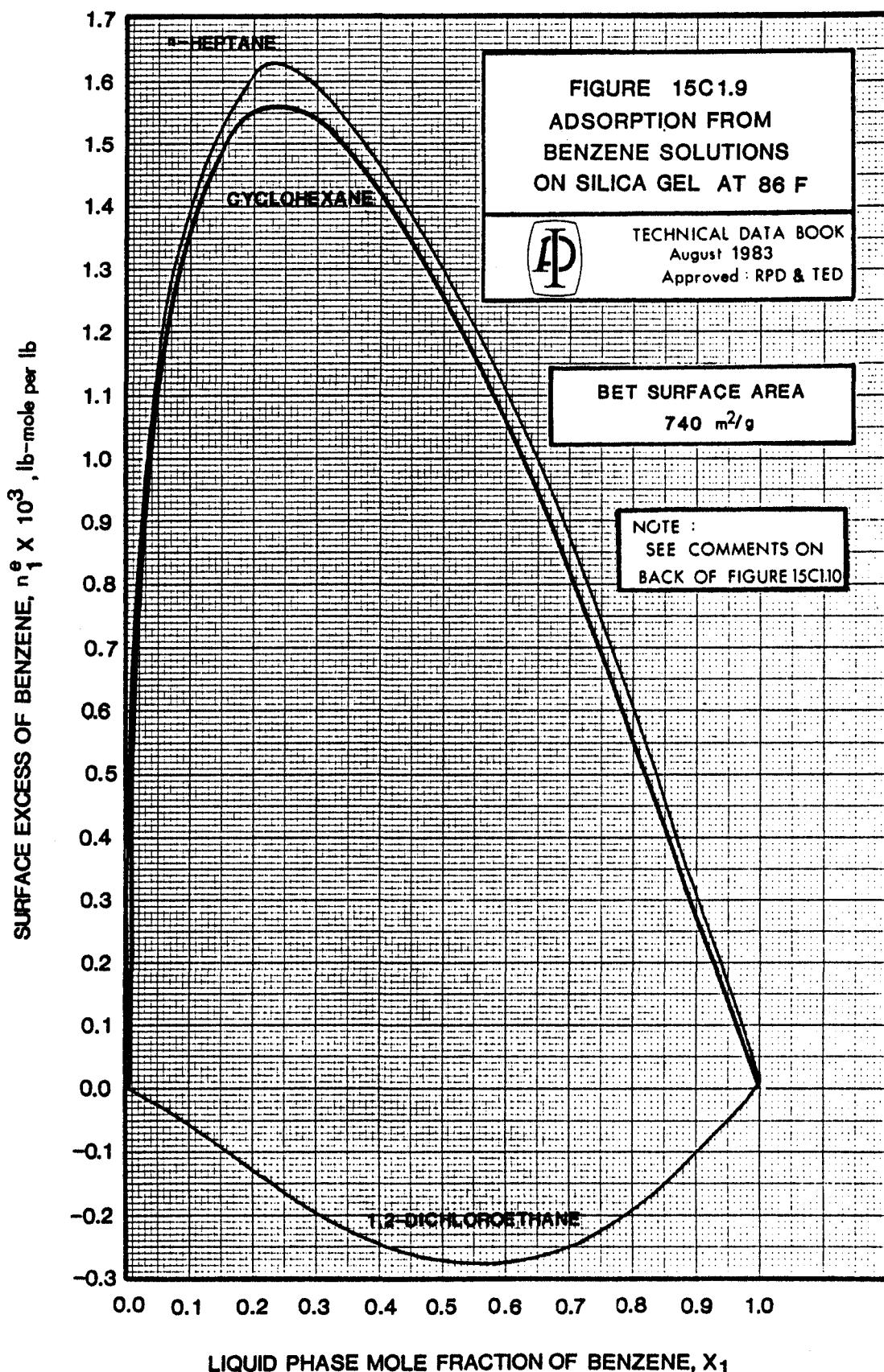


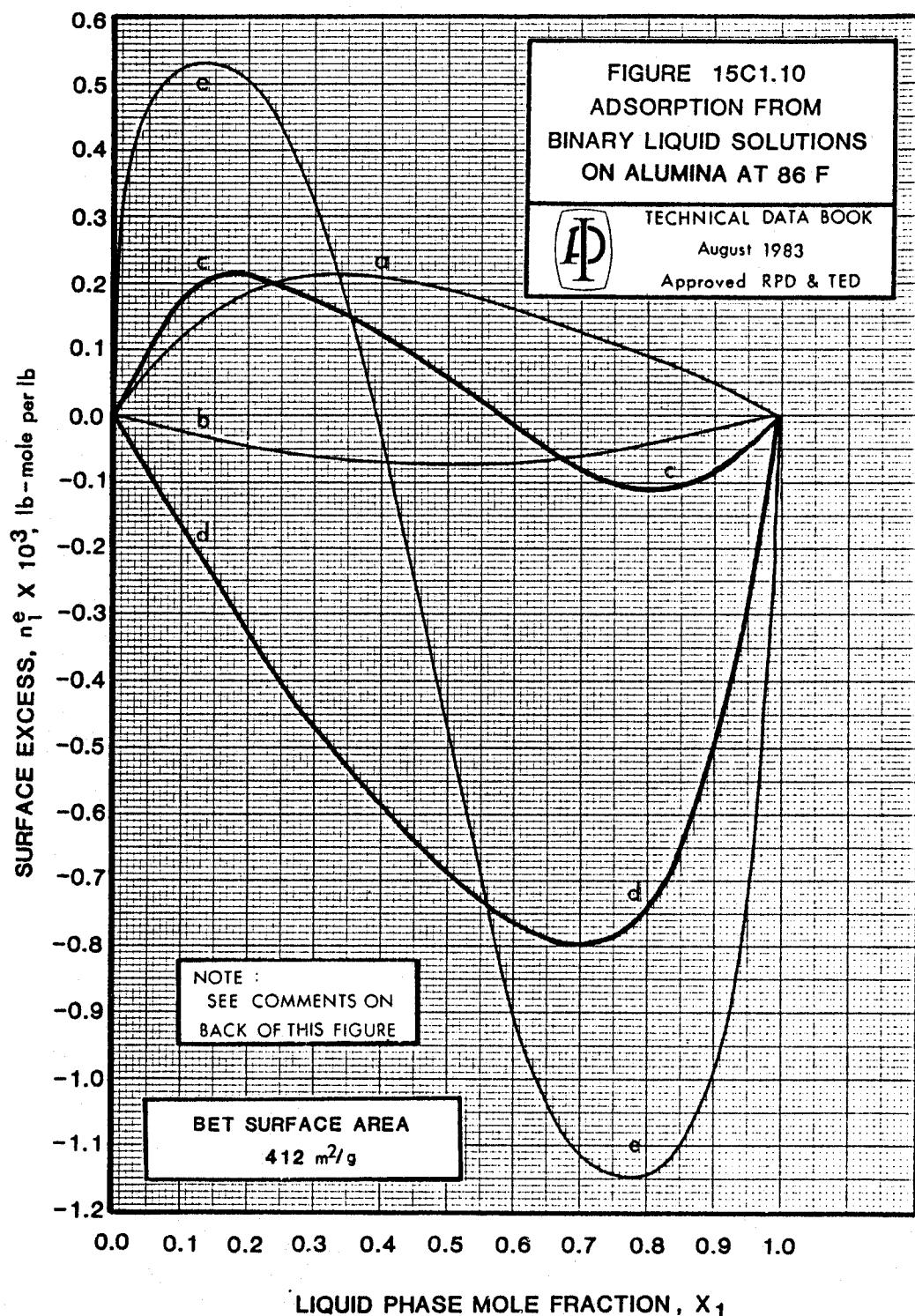












CURVE	COMPONENT 1	COMPONENT 2
a	DIOXANE	NITROBENZENE
b	DIOXANE	NITROMETHANE
c	BENZENE	NITROBENZENE
d	BENZENE	NITROMETHANE
e	CYCLOHEXANE	NITROBENZENE

COMMENTS ON FIGURES 15C1.1 THROUGH 15C1.10**Purpose**

Adsorption isotherms for some representative binary liquid systems are shown as a function of the bulk-phase mole fraction for several important adsorbents.

Reliability

The reliability considerations for liquid adsorption data are similar to those for gas adsorption data (Figures 15A1.1 through 15A1.10). The adsorbents used should be degassed for a sufficiently long time before use, though the results are not very sensitive to the regeneration conditions. One should exercise caution in using liquid adsorption data directly from the literature, since some data sources give the total adsorption data while others provide just the amount of physical adsorption by subtracting the slight effect of chemisorption from the total adsorption isotherm.

Special Comments

Figures 15C1.1 through 15C1.10 illustrate the different ways in which liquid-solid adsorption isotherms are expressed. For the purpose of processing these data by means of Procedures 15C1.11 and 15C1.12, they must first be converted into the format appropriate to the procedure being used.

Literature Sources

- Figure 15C1.1 (88)
- Figure 15C1.2 (106)
- Figure 15C1.3 (84)
- Figure 15C1.4 (108)
- Figure 15C1.5 (18)
- Figure 15C1.6 (55)
- Figure 15C1.7 (51)
- Figure 15C1.8 (57)
- Figure 15C1.9 (109)
- Figure 15C1.10 (116)

PROCEDURE 15C1.11

CORRELATION OF BINARY-LIQUID-MIXTURE
ISOTHERMAL ADSORPTION DATA**Discussion**

Binary-liquid-mixture adsorption isotherms are usually given in terms of the surface excess of one of the components as a function of its mole fraction in the liquid phase. The relation between the surface excess and the absolute amounts adsorbed is given by the following equation:

$$n_i^e = \frac{n_o(x_{i,o} - x_i)}{m} = n_i^s x_2 - n_i^s x_1 \quad (15C1.11-1)$$

Where:

n_i^e = surface excess of component i , in pound-moles per pound.

n_o = total number of moles of liquid before adsorption, in pound-moles.

$x_{i,o}$ = mole fraction of component i in bulk solution before adsorption.

x_i = mole fraction of component i in bulk solution after adsorption.

m = mass of adsorbent, in pounds.

n_i^s = number of moles of component i adsorbed on the surface per unit mass of solid, in pound-moles per pound.

If there are three or more surface excess points available, the following equation can be used to interpolate or extrapolate the data:

$$\frac{x_1 x_2}{n_i^e} = \frac{1}{M} \left[x_1 + \frac{1}{(K-1)} \right] \quad (15C1.11-2)$$

Where:

M = regression constant representing the total number of moles that can be accommodated in the adsorbed phase per unit mass of adsorbent, in pound-moles per pound.

K = regression constant representing the coefficient of separation achieved by adsorption, unitless.

Thus the isothermal data may be plotted as $x_1 x_2 / n_i^e$ versus x_1 . Although equation (15C1.11-2) was derived for the case of *ideal* solutions, the linear relation is usually found to hold, at least for a limited range of x_1 . In most cases, a reasonably linear plot will be obtained up to a liquid-phase mole fraction of 0.8 of the preferentially adsorbed component. The constants M and K can be determined from the slope and ordinate intercept of the straight-line portion:

$$\frac{1}{\text{slope}} = M \quad (15C1.11-3)$$

and

$$\frac{\text{slope}}{\text{intercept}} + 1 = K \quad (15C1.11-4)$$

Frequently, the isothermal data appearing in the literature are expressed in terms of variables other than the surface excess. For instance, the absolute amounts adsorbed of the two components may be given as a function of the bulk phase composition. Then equation (15C1.11-1) must be used to convert the data to the standard format. In other cases, the adsorbent loading may be given. The following equation must be used to calculate the surface excess from the loading:

$$n_i^e = \frac{a_1 (1 - x_1)}{100 M_1} \quad (15C1.11-5)$$

Where:

a_1 = loading of component 1, in pounds per 100 pounds of adsorbent.

M_1 = molecular weight of component 1, in pounds per pound-mole.

The computed surface excess can then be used to apply the linear correlation discussed above.

15C1.11

Procedure

Step 1: Plot the data in the form x_1x_2/n_i^e versus x_1 .

Step 2: Determine from the signs of the n_i^e values which is the more strongly adsorbed component. If the n_i^e values are mostly positive, component 1 is preferentially adsorbed; if they are mostly negative, component 2 is preferentially adsorbed.

Step 3: Construct a straight line representing the data as closely as possible for the range $x_i = 0$ to $x_i = 0.8$, where x_i is the mole fraction of the preferentially adsorbed component. Determine the slope and intercept. Alternatively, the data can be regressed to yield the value of the slope and intercept.

Step 4: Calculate M and K from equations (15C1.11-3) and (15C1.11-4).

Step 5: Equation (15C1.11-2) may now be used to interpolate or extrapolate the data in the range $x_i = 0$ to $x_i = 0.8$.

COMMENTS ON PROCEDURE 15C1.11**Purpose**

This procedure is given as a method of interpolating or extrapolating binary-liquid-mixture adsorption isotherm data up to a mole fraction of 0.8 for the preferentially adsorbed component.

Special Comments

In most cases, liquid-mixture adsorption equilibria are expressed as isotherms where values for the surface excess of one component are given at varying compositions of the bulk liquid. A number of sources, however, give the equilibrium data in other formats. One frequently-occurring format is the mole fraction in the adsorbed phase x_1^s versus the bulk phase mole fraction x_1 . If the data are in this form, or if the data can be converted to this form, Procedure 15C1.12 should be used. If the data are in such a form that one can calculate either n_1^e or x_1^s , then Procedure 15C1.12 should be used instead, since it has been found to give a better representation of the data and it works over the entire composition range of the bulk liquid.

Limitations

For most liquid-mixture adsorption systems, reasonable linearity has been observed when the data are plotted as indicated by equation (15C1.11-2) in the mole fraction range of 0 to 0.8. Outside this range, large deviations may be expected.

Reliability

Within the recommended range of application, equation (15C1.11-2) will usually represent the data within 5 percent. For systems that are highly nonideal, the deviations may be higher.

Literature Source

Equation (15C1.11-2) was originally developed by Everett, D. H., *Trans. Faraday Soc.* **60** 1803 (1964).

Example

Find the values of M and K for the adsorption of benzene (component 1) and cyclohexane (component 2) on silica gel at 86 F.

The data of Sircar et al. (113), expressed in the appropriate form for the procedure, are given below.

x_1	$n_1^e \times 10^3$ (lb-mol per lb)	$x_1 x_2 / n_1^e$ (lb per lb-mol)
0.051	1.05	46.09
0.117	1.47	70.28
0.187	1.61	94.43
0.268	1.59	123.38
0.357	1.50	153.03
0.395	1.41	169.49
0.544	1.20	206.72
0.794	0.59	277.23
0.900	0.30	—

A linear regression using the eight values for which $x_1 < 0.8$ yields a slope of 311.7 pounds per pound-mole and an intercept of 36.92 pounds per pound-mole.

The values of M and K can now be calculated from equations (15C1.11-3) and (15C1.11-4).

$$M = \frac{1}{311.7} = 3.21 \times 10^{-3} \text{ pound-mole per pound}$$

$$K = \frac{311.7}{36.92} + 1 = 9.44$$

PROCEDURE 15C1.12

ALTERNATE COMPUTER PROCEDURE FOR CORRELATION OF BINARY-LIQUID-MIXTURE ISOTHERMAL ADSORPTION DATA

Discussion

If three or more values for the adsorbed phase mole fraction at varying liquid-phase mole fractions are known, the following equation can be used to interpolate or extrapolate the data over the entire composition range:

$$x_1^s = \frac{x_1}{k(1-x_1)\exp[q(2x_1-1)]+x_1} \quad (15C1.12-1)$$

Where:

x_1^s = adsorbed-phase mole fraction of component 1.

x_1 = liquid-phase mole fraction of component 1.

k = regression constant representing the coefficient of separation achieved by adsorption, unitless.

q = regression constant representing the interaction between components 1 and 2 at the given temperature, unitless.

Equation (15C1.12-1) has been found to be valid for most of the systems investigated. Its use is recommended when one has the proper number of data points available for regression.

In cases where the data are given in terms of absolute adsorption, the following equation should be used to convert the data to the format necessary for applying the nonlinear correlation:

$$x_1^s = \frac{n_1^s}{n_1^s + n_2^s} \quad (15C1.12-2)$$

Where:

n_i^s = absolute amount of component i adsorbed per unit mass of adsorbent, in pound-moles per pound.

The data can then be regressed according to equation (15C1.12-1) to yield the values of k and q .

Procedure

Step 1: Collect all the isotherm data for the system of interest in terms of x_1^s versus x_1 . These data must then be regressed in the form of equation (15C1.12-1) using a nonlinear algorithm.

Step 2: The data can now be interpolated or extrapolated by use of equation (15C1.12-1).

COMMENTS ON PROCEDURE 15C1.12

Purpose

This procedure is given as a method of interpolating or extrapolating binary-liquid-mixture isothermal adsorption data over the entire composition range of the liquid.

Reliability

The reliability of the interpolations and extrapolations obtained with this method depends upon the accuracy and range of the data that were regressed. More meaningful values for the regression constants are obtained if the data straddle the entire liquid composition range. In general, equation (15C1.12-1) will represent the data to within 2 percent. For systems with strong deviations from ideal behavior or those with a high scatter in the data points, the deviation will be higher.

Literature Source

Equation (15C1.12-1) was taken from Nagy, L. G., and Schay, G., *Acta Chim. Acad. Sci. Hung.* **39** 365 (1963).

Example

The data sets and listing of regression constants below are provided as a means of checking the reliability of any nonlinear regression algorithm. The objective function used to obtain the constants was

$$\sum \left[x_{1,\text{exp}}^s - x_{1,\text{pred}}^s \right]^2$$

Where:

$x_{1,\text{exp}}^s$ = experimental value of the adsorbed phase mole fraction.

$x_{1,\text{pred}}^s$ = predicted value of the adsorbed phase mole fraction.

Sigma denotes summation over all data points.

The following data are for *n*-butylamine (component 1) and benzene (component 2) on boehmite at 68 F (58):

x_1	x_1^s	x_1	x_1^s	x_1	x_1^s
0.10	0.536	0.40	0.740	0.70	0.827
0.20	0.636	0.50	0.776	0.80	0.843
0.30	0.694	0.60	0.810	0.90	0.868

$k = 0.308$

$q = 1.399$

The following data are for ethylene dichloride (component 1) and benzene (component 2) on silica gel at 68 F (58):

x_1	x_1^s	x_1	x_1^s	x_1	x_1^s
0.10	0.158	0.40	0.524	0.70	0.786
0.20	0.295	0.50	0.621	0.80	0.861
0.30	0.417	0.60	0.707	0.90	0.934

$k = 0.615$

$q = 0.058$

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