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Basic Principles and Calculations

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Introduction to Engineering Calculations

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The allocation of resources in the United States and elsewhere is beginning a period of transition. Air and water, for example, at one time were the economist's favorite examples of "free goods." However, people are accepting the fact that air and water indeed are natural resources of ever-increasing value and are not simply infinite sources and sinks for man's uses in production and consumption. For you to learn how to appreciate and treat the problems that will arise in our modern technology, and especially in the technology of the future, it is necessary to learn certain basic principles and practice their application. This text describes the principles of making material and energy balances and illustrates their application in a wide variety of ways.

We begin in this chapter with a review of certain background information. You have already encountered most of the concepts to be presented in basic chemistry and physics courses. Why, then, the need for a review? First, from experience we have found it necessary to restate these familiar basic concepts in a somewhat more general and clearer fashion; second, you will need practice to develop your ability to analyze and work engineering problems. To read and understand the principles discussed in this chapter is relatively easy; to apply them to different unfamiliar situations is not. An engineer becomes competent in his profession by mastering the techniques developed by his predecessors—then, perhaps, he can pioneer new ones.

This chapter begins with a discussion of units, dimensions, and conversion factors, and then goes on to review some terms you should already be acquainted with, such as

- (a) Mole and mole fraction.
- (b) Density and specific gravity.
- (c) Measures of concentration.
- (d) Temperature.
- (e) Pressure.

It then provides some clues as to "how to solve problems" which should be of material aid in all the remaining portions of your work. Finally, the principles of stoichiometry are reviewed, and the technique of handling incomplete reactions is illustrated. Figure 1.0 shows the relation of the topics to be discussed to

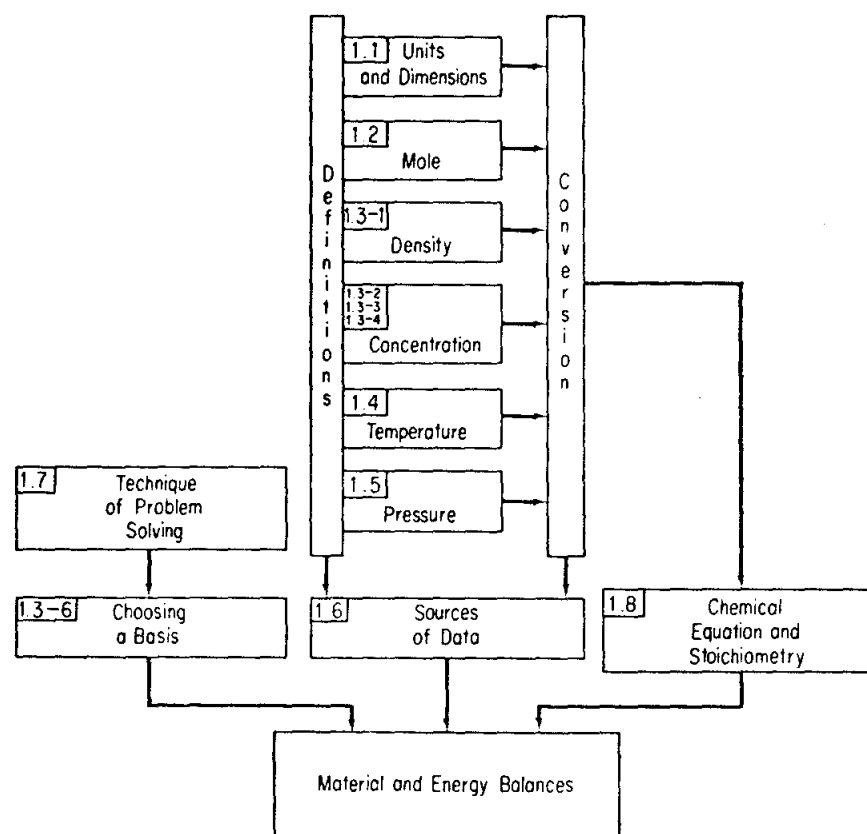


Fig. 1.0. Hierarchy of topics to be studied in this chapter (section numbers are in the upper left-hand corner of the boxes).

ension, and conversion should already be ac-

ts" which should be of. Finally, the principles dealing incomplete reactions to be discussed to

each other and to the ultimate goal of being able to solve problems involving both material and energy balances. At the end of the chapter you will find a check list of levels of skill you should possess after completing the chapter.

1.1 Units and dimensions

At some time in every student's life comes the exasperating sensation of frustration in problem solving. Somehow, the answers or the calculations do not come out as expected. Often this outcome arises because of inexperience in the handling of units. The use of units or dimensions along with the numbers in your calculations requires more attention than you probably have been giving to your computations in the past, but it will help avoid such annoying experiences. The proper use of dimensions in problem solving is not only sound from a logical viewpoint—it will also be helpful in guiding you along an appropriate path of analysis from what is at hand through what has to be done to the final solution.

Dimensions are our basic concepts of measurement such as *length, time, mass, temperature, etc.*; units are the means of expressing the dimensions, as *feet or centimeters* for length, or *hours or seconds* for time. Units are associated with some quantities you may have previously considered to be dimensionless. A good example is *molecular weight*, which is really the mass of one substance per mole of that substance. This method of attaching units to all numbers which are not fundamentally dimensionless has the following very practical benefits:

- (a) It diminishes the possibility of inadvertent inversion of any portion of the calculation.
- (b) It reduces the calculation in many cases to simple ratios, which can be easily manipulated on the slide rule.
- (c) It reduces the intermediate calculations and eliminates considerable time in problem solving.
- (d) It enables you to approach the problem logically rather than by remembering a formula and plugging numbers into the formula.
- (e) It demonstrates the physical meaning of the numbers you use.

The rule for handling units is essentially quite simple: treat the units as you would algebraic symbols. For example, you cannot add, subtract, multiply, or divide different units into each other and thus cancel them out—this may be done only for like units. You may be able to add pounds to pounds and calories to calories—subtract them, multiply them, or divide them—but you cannot divide 10 pounds by 5 calories and get 2 any more than you can change 2 apples into 2 bananas. The units contain a significant amount of information content that cannot be ignored.

EXAMPLE 1.1 Dimensions and units

Add the following:

- | | |
|-----|--------------------------|
| (a) | 1 foot + 3 seconds |
| (b) | 1 horsepower + 300 watts |

Solution:

The operation indicated by

$$1 \text{ ft} + 3 \text{ sec}$$

has no meaning since the dimensions of the two terms are not the same. One foot has the dimensions of length, whereas 3 sec has the dimensions of time. In the case of

$$1 \text{ hp} + 300 \text{ watts}$$

the dimensions are the same (energy per unit time) but the units are different. You must transform the two quantities into like units, such as horsepower, watts, or something else, before the addition can be carried out. Since $1 \text{ hp} = 746 \text{ watts}$,

$$746 \text{ watts} + 300 \text{ watts} = 1046 \text{ watts}$$

EXAMPLE 1.2 Conversion of units

If a plane travels at twice the speed of sound (assume that the speed of sound is 1100 ft/sec), how fast is it going in miles per hour?

Solution:

$$\frac{2}{\cancel{\text{sec}}} \left| \begin{array}{c} 1100 \text{ ft} \\ \hline \end{array} \right| \frac{1 \text{ mi}}{5280 \text{ ft}} \left| \begin{array}{c} 60 \text{ sec} \\ \hline \end{array} \right| \frac{60 \text{ min}}{1 \text{ min}} \left| \begin{array}{c} 60 \text{ mi} \\ \hline \end{array} \right| \frac{1 \text{ hr}}{1 \text{ hr}} = 1500 \frac{\text{mi}}{\text{hr}}$$

or

$$\frac{2}{\cancel{\text{sec}}} \left| \begin{array}{c} 1100 \text{ ft} \\ \hline \end{array} \right| \frac{60 \frac{\text{mi}}{\text{hr}}}{88 \frac{\text{ft}}{\text{sec}}} = 1500 \frac{\text{mi}}{\text{hr}}$$

You will note in Example 1.2 the use of what is called the *dimensional equation*. It contains both units and numbers. The initial speed, 2200 ft/sec, is multiplied by a number of ratios (termed *conversion factors*) of equivalent values of combinations of time, distance, etc., to arrive at the final desired answer. The ratios used are simple well-known values and thus the conversion itself should present no great problem. Of course, it is possible to look up conversion ratios, which will enable the length of the calculation to be reduced; for instance, in Example 1.2 we could have used the conversion factor of 60 mi/hr equals 88 ft/sec. However, it usually takes less time to use values you know than to look up shortcut conversion factors in a handbook. Common conversion ratios are listed in Appendix A.

The dimensional equation has vertical lines set up to separate each ratio, and these lines retain the same meaning as an \times or multiplication sign placed between each ratio. The dimensional equation will be retained in this form throughout most of this text to enable you to keep clearly in mind the significance of units in problem solving. It is recommended that units always be written down next to the associated numerical value (unless the calculation is very simple) until you become quite familiar with the use of units and dimensions and can carry them in your head.

At any point in the dimensional equation you can determine the consolidated net units and see what conversions are still required. This may be carried out formally, as shown below by drawing slanted lines below the dimensional equation and writing the consolidated units on these lines, or it may be done by eye, mentally canceling and accumulating the units.

$$\frac{2 \times 1100 \text{ ft}}{\text{sec}} \left| \begin{array}{c} 1 \text{ mi} \\ 5280 \text{ ft} \end{array} \right| \frac{60 \text{ sec}}{1 \text{ min}} \left| \begin{array}{c} 60 \text{ min} \\ 1 \text{ hr} \end{array} \right|$$

$\frac{\text{ft}}{\text{sec}}$ $\frac{\text{mi}}{\text{sec}}$ $\frac{\text{mi}}{\text{min}}$

EXAMPLE 1.3 Use of units

Change 400 in.³/day to cm³/min.

Solution:

$$\frac{400 \text{ in.}^3}{\text{day}} \left| \begin{array}{c} (2.54 \text{ cm})^3 \\ 1 \text{ in.} \end{array} \right| \frac{1 \text{ day}}{24 \text{ hr}} \left| \begin{array}{c} 1 \text{ hr} \\ 60 \text{ min} \end{array} \right| = 4.56 \frac{\text{cm}^3}{\text{min}}$$

In this example note that not only are the numbers raised to a power, but the units also are raised to the same power.

There shall be one measure of wine throughout our kingdom, and one measure of ale, and one measure of grain . . . and one breadth of cloth. . . . And of weights it shall be as of measures.

So reads the standard measures clause of the *Magna Carta* (June 1215). The standards mentioned were not substantially revised until the nineteenth century. When the American Colonies separated from England, they retained, among other things, the weights and measures then in use. It is probable that at that time these were the most firmly established and widely used weights and measures in the world.

No such uniformity of weights and measures existed on the European continent. Weights and measures differed not only from country to country but even from town to town and from one trade to another. This lack of uniformity led the National Assembly of France during the French Revolution to enact a decree (May 8, 1790) that called upon the French Academy of Sciences to act in concert with the Royal Society of London to "deduce an invariable standard

for all of the measures and all weights." Having already an adequate system of weights and measures, the English did not participate in the French undertaking. The result of the French endeavor has evolved into what is known as the metric system.

The metric system became preferred by scientists of the nineteenth century, partly because it was intended to be an international system of measurement, partly because the units of measurement were theoretically supposed to be independently reproducible, and partly because of the simplicity of its decimal nature. These scientists proceeded to derive new units for newly observed physical phenomena, basing the new units on elementary laws of physics and relating them to the units of mass and length of the metric system. The Americans and the British adapted their system of measurements to the requirements of new technology as time went on for both business and commerce as well as scientific uses despite the fact that the other countries, one after another, turned toward the metric system.

Problems in the specification of the units for electricity and magnetism led to numerous international conferences to rectify inconsistencies and culminated in 1960 in the eleventh General Conference on Weights and Measures adopting the SI (Système International) system of units. As of this date (1973) the United States is the last large country not employing or engaged in transforming to some form of the SI units.

Table 1.1 shows the most common systems of units used by engineers in the last few decades. Note that the SI, the cgs, the fps (English absolute), and the British engineering systems all have three basically defined units and that the fourth unit is derived from these three defined units. Only the American engineering system has four basically defined units. Consequently, in the American engineering system you have to use a conversion factor, g_c , a constant whose numerical value is not unity, to make the units come out properly. We can use Newton's law to see what the situation is with regard to conversion of units:

$$F = Cma \quad (1.1)$$

where¹ F = force

m = mass

a = acceleration

C = a constant whose numerical value and units depend on those selected for F , m , and a

In the cgs system the unit of force is defined as the dyne; hence if C is selected to be $C = 1 \text{ dyne}/(\text{g})(\text{cm})/\text{sec}^2$, then when 1 g is accelerated at 1 cm/sec²

$$F = \frac{1 \text{ dyne}}{(\text{g})(\text{cm})} \left| \frac{1 \text{ g}}{\text{sec}^2} \right| 1 \text{ cm} = 1 \text{ dyne}$$

¹A list of the nomenclature is included at the end of the book.

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TABLE 1.1 COMMON SYSTEMS OF UNITS

	Length	Time	Mass	Force	Energy	Temperature	Remarks
<i>Absolute (Dynamic) Systems</i>							
Cgs	cm	sec	gram	dyne*	erg, joule, or calorie	°K, °C	Formerly common scientific
Fps (foot-lb-sec or English absolute)	ft	sec	lb	poundal*	ft poundal	°R, °F	
SI (also MKS)	meter	sec	kilogram	newton (N)*	joule (J)	K, °C	Internationally adopted units for ordinary and scientific use
<i>Gravitational Systems</i>							
British engineering	ft	sec	slug*	pound weight	Btu (ft)(lb) (ft)(lb _r)	°R, °F	
American engineering	ft	sec	pound mass (lb _m)	pound force (lb _f)	Btu or (hp)(hr)	°R, °F	Used by chemical and petroleum engineers in the U.S.

*Unit derived from basic units; all energy units are derived.

Similarly, in the SI system in which the unit of force is defined to be the newton (N), if $C = 1 \text{ N}/(\text{kg})(\text{m})/\text{sec}^2$, then when 1 kg is accelerated at 1 m/sec²,

$$F = \frac{1 \text{ N}}{(\text{kg})(\text{m})} \left| \frac{1 \text{ kg}}{\text{sec}^2} \right| 1 \text{ m} = 1 \text{ N}$$

However, in the American engineering system we ask that the numerical value of the force and the mass be essentially the same at the earth's surface. Hence, if a mass of 1 lb_m is accelerated at g ft/sec², where g is the acceleration of gravity (about 32.2 ft/sec² depending on the location of the mass), we can make the force be 1 lb_f by choosing the proper numerical value and units for C :

$$F = C \frac{1 \text{ lb}_m}{\text{sec}^2} \left| \frac{g \text{ ft}}{\text{lb}_m} \right| = 1 \text{ lb}_f \quad (1.2)$$

Observe that for Eq. (1.2) to hold, the units of C have to be

$$C \leftrightarrow \frac{\text{lb}_f}{\text{lb}_m \left(\frac{\text{ft}}{\text{sec}^2} \right)}$$

A numerical value of 1/32.174 has been chosen for the constant because g equals the numerical value of the average acceleration of gravity at sea level at 45° latitude when the latter is expressed in ft/sec². The acceleration of gravity, you may recall, varies a few tenths of 1 percent from place to place on the surface of the earth and changes considerably as you rise up from the surface as in a rocket. With this selection of units and with the number 32.174 employed in the denominator of the conversion factor, the inverse of C is given the special symbol g_c :

$$g_c = 32.174 \frac{(\text{ft})(\text{lb}_m)}{(\text{sec}^2)(\text{lb}_f)} \quad (1.3)$$

Division by g_c achieves exactly the same result as multiplication by C . You can see, therefore, that in the American engineering system we have the convenience that the numerical value of a pound mass is also that of a pound force if the numerical value of the ratio g/g_c is equal to 1, as it is approximately in most cases. Similarly, a 1-lb mass also usually weighs 1 lb (weight is the force required to support the mass at rest). However, you should be aware that these two quantities g and g_c are not the same. Note also that the pound (mass) and the pound (force) are not same units in the American engineering system even though we speak of *pounds* to express force, weight, or mass. Furthermore, if a satellite with a mass of 1 lb (mass) "weighing" 1 lb (force) on the earth's surface is shot up to a height of 50 mi, it will no longer "weigh" 1 lb (force), although its mass will still be 1 lb (mass).

In ordinary language most people, including scientists and engineers, omit the designation of "force" or "mass" associated with the pound or kilogram but pick up the meaning from the context of the statement. No one gets confused by the fact that a man is six feet tall but has only two feet. Similarly, one should

defined to be the newton
exerted at 1 m/sec²,

we ask that the numerical
value at the earth's surface.
where g is the acceleration of
of the mass), we can make
value and units for C :

(1.2)

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a constant because g equals
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entists and engineers, omit
the pound or kilogram but
ent. No one gets confused
feet. Similarly, one should

interpret the statement that a bottle "weighs" 5 kg as meaning the bottle has a mass of 5 kg and is attracted to the earth's surface with a force equal to a weight of 5 kg. Additional details concerning units and dimensions can be found in the articles by Silberberg and McKetta,² and by Whitney,³ in various books,^{4,5,6} and in the references at the end of this chapter. For systems used in the U. S. S. R., consult *Meas. Tech. (USSR) (English Trans.)*, no. 10 (April), 1964.

EXAMPLE 1.4 Use of g_c

One hundred pounds of water are flowing through a pipe at the rate of 10.0 ft/sec. What is the kinetic energy of this water in (ft)(lb_f)?

Solution:

$$\text{kinetic energy} = K = \frac{1}{2}mv^2$$

Assume the 100 lb of water means the mass of the water. (This would be numerically identical to the weight of the water if $g = g_c$)

$$K = \frac{1}{2} \left| \begin{array}{c} 100 \text{ lb}_m \\ \text{sec} \end{array} \right| \left| \begin{array}{c} (10.0 \text{ ft})^2 \\ \text{sec} \end{array} \right| \left| \begin{array}{c} 32.174 \frac{(\text{ft})(\text{lb}_m)}{(\text{sec}^2)(\text{lb}_f)} \end{array} \right| = 155 (\text{ft})(\text{lb}_f)$$

EXAMPLE 1.5 Use of g_c

What is the potential energy in (ft)(lb_f) of a 100-lb drum hanging 10 ft above the surface of the earth with reference to the surface of the earth?

Solution:

$$\text{potential energy} = P = mgh$$

Assume the 100 lb means 100 lb mass; $g = \text{acceleration of gravity} = 32.2 \text{ ft/sec}^2$.

$$P = \frac{100 \text{ lb}_m}{\text{sec}^2} \left| \begin{array}{c} 32.2 \text{ ft} \\ \text{sec}^2 \end{array} \right| \left| \begin{array}{c} 10 \text{ ft} \\ \text{sec}^2 \end{array} \right| \left| \begin{array}{c} 32.174 \frac{(\text{ft})(\text{lb}_m)}{(\text{sec}^2)(\text{lb}_f)} \end{array} \right| = 1000 (\text{ft})(\text{lb}_f)$$

Notice that in the ratio of g/g_c , or 32.2 ft/sec^2 divided by $32.174 \frac{(\text{ft})(\text{lb}_m)}{(\text{sec}^2)(\text{lb}_f)}$, the numerical values are almost equal. A good many people would solve the problem by saying $100 \text{ lb} \times 10 \text{ ft} = 1000 (\text{ft})(\text{lb})$ without realizing that in effect they are canceling out the numbers in the g/g_c ratio.

²J. H. Silberberg and J. J. McKetta, Jr., *Petroleum Refiner*, v. 32, 179-183 (April 1953), 147-150 (May 1953).

³H. Whitney, "The Mathematics of Physical Quantities," *American Math. Monthly*, v. 75, 115, 227 (1968).

⁴D. C. Ipsen, *Units, Dimensions, and Dimensionless Numbers*, McGraw-Hill, New York, 1960.

⁵S. J. Kline, *Similitude and Approximation Theory*, McGraw-Hill, New York, 1965.

⁶E. F. O'Day, *Physical Quantities and Units (A Self-Instructional Programmed Manual)*, Prentice-Hall, Englewood Cliffs, N. J., 1967.

EXAMPLE 1.6 Weight

What is the difference in the weight in Newtons of a 100-kg rocket at height of 10 km above the surface of the earth, where $g = 9.76 \text{ m/sec}^2$, as opposed to its weight on the surface of the earth, where $g = 9.80 \text{ m/sec}^2$?

Solution:

The weight in Newtons can be computed in each case from Eq. (1.1) with $a = g$ if we ignore the tiny effect of centripetal acceleration resulting from the rotation of the earth (less than 0.3 percent):

$$\text{weight difference} = \frac{100 \text{ kg}}{\text{sec}^2} \left| \frac{(9.80 - 9.76) \text{ m}}{\text{kg}(\text{m})} \right| \frac{1 \text{ N}}{\text{sec}^2} = 4.00 \text{ N}$$

Note that the concept of weight is not particularly useful in treating the dynamics of long-range ballistic missiles or of earth satellites because the earth is both round and rotating.

You should develop some facility in converting units from the SI and cgs systems into the American engineering system and vice versa, since these are the three sets of units in this text. Certainly you are familiar with the common conversions in the American engineering system from elementary and high school work. Similarly, you have used the SI and cgs system in physics, chemistry, and mathematics. If you have forgotten, Table 1.2 lists a short selection of essential conversion factors from Appendix A. Memorize them. Common abbreviations also appear in this table. Unit abbreviations are written in lowercase letters, except for the first letter when the name of the unit is derived from a proper name. The distinction between uppercase and lowercase letters should be followed, even if the symbol appears in applications where the other lettering is in uppercase style. Unit abbreviations have the same form for both singular and plural, and they are not followed by a period (except in the case of inches).

Other useful conversion factors will be discussed in subsequent sections of this book.

One of the best features of the SI system is that units and their multiples and submultiples are related by standard factors designated by the prefixes indicated in Table 1.3. Prefixes are not preferred for use in denominators (except for kg). The strict use of these prefixes leads to some amusing combinations of noneuphonious sounds, such as nanonewton, nembjoule, and so forth. Also, some confusion is certain to arise because the prefix M can be confused with m as well as with M ≈ 1000 derived from the Roman numerical. When a compound unit is formed by multiplication of two or more other units, its symbol consists of the symbols for the separate units joined by a centered dot (for example, N · m for newton meter). The dot may be omitted in the case of familiar units such as watthour (symbol Wh) if no confusion will result, or if the symbols are separated by exponents as in $N \cdot m^2 kg^{-2}$. Hyphens should not be used in symbols

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a 100-kg rocket at height of $\frac{1}{\text{sec}^2}$, as opposed to its weight

use from Eq. (1.1) with $a = g$ resulting from the rotation of

$$\frac{1 \text{ N}}{\frac{(\text{kg})(\text{m})}{\text{sec}^2}} = 4.00 \text{ N}$$

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TABLE 1.2 BASIC CONVERSION FACTORS

Dimension	American Engineering	Conversion: American Engineering to cgs	SI and cgs	Conversion: American Engineering to SI
Length	12 in. = 1 ft 3 ft = 1 yd 5280 ft = 1 mi	2.54 cm = 1 in. (2.54 cm) ³ = (1 in.) ³	10 mm* = 1 cm* 100 cm* = 1 m	3.28 ft = 1 m 35.31 ft ³ = 1.00 m ³
Volume	1 ft ³ = 7.48 gal	—	1 cm ³ * H ₂ O = 1 g 1 m ³ H ₂ O = 1000 kg	—
Density	1 ft ³ H ₂ O = 62.4 lb _m	—	—	—
Mass	1 ton _m = 2000 lb _m	1 lb = 454 g	1000 g = 1 kg	1 lb = 0.454 kg
Time	1 min = 60 sec 1 hr = 60 min	—	1 min* = 60 sec 1 hr* = 60 min*	—

*An acceptable but not preferred unit in the SI system.

TABLE 1.3 SI PREFIXES

Factor	Prefix	Symbol	Factor	Prefix	Symbol
10^{12}	Tera	T	10^{-1}	Deci*	d
10^9	Giga	G	10^{-2}	Centi*	c
10^6	Mega	M	10^{-3}	Milli	m
10^3	Kilo	k	10^{-6}	Micro	μ
10^2	Hecto*	h	10^{-9}	Nano	n
10^1	Deka*	da	10^{-12}	Pico	p
			10^{-15}	Femto	f
			10^{-18}	Atto	a

*Avoid except for areas and volumes.

for compound units. Positive and negative exponents may be used with the symbols for units. If a compound unit is formed by division of one unit by another, its symbol consists of the symbols for the separate units either separated by a solidus or multiplied by using negative powers (for example, m/s or $m \cdot s^{-1}$ for meters per second). We shall not use the center dot for multiplication in this text but shall use parentheses around the unit instead, a procedure less subject to misinterpretation in handwritten material.

EXAMPLE 1.7 Application of dimensions

A simplified equation for heat transfer from a pipe to air is

$$h = 0.026G^{0.6}/D^{0.4}$$

where h = the heat transfer coefficient in $\text{Btu}/(\text{hr})(\text{ft}^2)(^\circ\text{F})$

G = mass rate of flow in $\text{lb}_m/(\text{hr})(\text{ft}^2)$

D = outside diameter of the pipe in ft

If h is to be expressed in $\text{cal}/(\text{min})(\text{cm}^2)(^\circ\text{C})$, what should the new constant in the equation be in place of 0.026?

Solution:

To convert to $\text{cal}/(\text{min})(\text{cm}^2)(^\circ\text{C})$ we set up the dimensional equation as follows:

$$h = \frac{0.026G^{0.6}\text{Btu}}{D^{0.4}(\text{hr})(\text{ft}^2)(^\circ\text{F})} \left| \frac{252 \text{ cal}}{1 \text{ Btu}} \right| \left| \frac{1 \text{ hr}}{60 \text{ min}} \right| \left| \frac{(1 \text{ ft})^2}{(12 \text{ in.})^2} \right| \left| \frac{(1 \text{ in.})^2}{(2.54 \text{ cm})^2} \right| \left| \frac{1.8^\circ\text{F}}{1^\circ\text{C}} \right| = 2.11 \times 10^{-4} \frac{G^{0.6} \text{ cal}}{D^{0.4}(\text{min})(\text{cm}^2)(^\circ\text{C})}$$

(Note: See Sec. 1.4 for a detailed discussion of temperature conversion factors.) If G and D are to be used in units of

$$G': \frac{\text{g}}{(\text{min})(\text{cm}^2)}$$

$$D': \text{cm}$$

When an additional conversion is required:

$$\frac{2.11 \times 10^{-4}}{\text{Prefix}} \left| \begin{array}{c} G'(\text{g}) \\ (\text{min})(\text{cm}^2) \end{array} \right| \left| \begin{array}{c} 1 \text{ lb}_m \\ 454 \text{ g} \end{array} \right| \left| \begin{array}{c} 60 \text{ min} \\ 1 \text{ hr} \end{array} \right| \left| \begin{array}{c} (2.54 \text{ cm})^2 \\ 1 \text{ in.} \end{array} \right| \left| \begin{array}{c} (12 \text{ in.})^{2-0.6} \\ 1 \text{ ft} \end{array} \right|$$

$$\frac{1}{D'(\text{cm})} \left| \begin{array}{c} (1 \text{ in.})^{-0.4} \\ (2.54 \text{ cm}) \end{array} \right| \left| \begin{array}{c} (1 \text{ ft})^{-0.4} \\ (12 \text{ in.}) \end{array} \right| = 1.48 \times 10^{-2} \frac{(G')^{0.6} \text{ cal}}{(D')^{0.4}(\text{min})(\text{cm}^2)(^\circ\text{C})}$$

Dimensional considerations can also be used to help identify the dimensions of terms or quantities in terms in an equation. Equations must be dimensionally consistent; i.e., each term in an equation must have the same net dimensions and units as every other term to which it is added or subtracted. The use of dimensional consistency can be illustrated by an equation which represents gas behavior and is known as van der Waals' equation, an equation which will be discussed in more detail in Chap. 3:

$$(p + \frac{a}{V^2})(V - b) = RT$$

Inspection of the equation shows that the constant a must have the dimensions of [(pressure)(volume)²] in order for the expression in the first set of parentheses to be consistent throughout. If the units of pressure are atm and those of volume are cm^3 , then a will have the units specifically of [(atm)(cm)⁶]. Similarly, b must have the same units as V , or in this particular case the units of cm^3 .

1.2 The mole unit

What is a mole? The best answer is that a *mole* is a certain number of molecules atoms, electrons, or other specified types of particles.⁷ In particular, the 1969 International Committee on Weights and Measures approved the mole (sometimes abbreviated as mol) in the SI system as being "the amount of a substance that contains as many elementary entities as there are atoms in 0.012 kg of carbon 12." Thus in the SI and cgs systems the mole contains a different number of molecules than it does in the American engineering system. In the SI and cgs systems a mole has about 6.02×10^{23} molecules; we shall call this a *gram mole* (abbreviated *g mole*). In the American engineering system a *pound mole* (abbreviated *lb mole*) has $6.02 \times 10^{23} \times 454$ molecules. Thus the pound mole and the gram mole represent two different quantities. Here is another way to look at

⁷For a discussion of the requirements of the mole concept, refer to the series of articles in *J. Chem. Educ.*, v. 38, 549-556 (1961).

the mole unit:

$$\text{the g mole} = \frac{\text{mass in g}}{\text{molecular weight}} \quad (1.4)$$

$$\text{the lb mole} = \frac{\text{mass in lb}}{\text{molecular weight}} \quad (1.5)$$

or

$$\text{mass in g} = (\text{mol. wt})(\text{g mole}) \quad (1.6)$$

$$\text{mass in lb} = (\text{mol. wt})(\text{lb mole}) \quad (1.7)$$

The values of the molecular weights (relative molar masses) are built up from the tables of atomic weights based on an arbitrary scale of the relative masses of the elements. The terms atomic "weight" and molecular "weight" are universally used by chemists and engineers instead of the more accurate terms atomic "mass" or molecular "mass." Since weighing was the original method for determining the comparative atomic masses, as long as they were calculated in a common gravitational field, the relative values obtained for the atomic "weights" were identical with those of the atomic "masses." There have always been and are today some questions in issue about the standard reference element and its atomic weight. Many of the old standards such as H (atomic hydrogen) = 1, O (atomic oxygen) = 100, O = 1 and O = 16 have been discarded, and now ^{12}C = 12 exactly is used as the reference point on the chemist's scale, i.e., 12.000 g of carbon 12 contain 1 g mole or 6.023×10^{23} atoms (or 0.012 kg in the SI system).

On this scale of atomic weights, hydrogen is 1.008, carbon is 12.01, etc. (In most of our calculations we shall round these off to 1 and 12, respectively.) In your calculations you may attach any unit of mass you desire to these atomic weights, as, for example, a gram atom, a pound atom, a ton atom, etc. Thus a gram atom of oxygen is 16.00 g, a pound atom of oxygen is 16.00 lb, and a kilogram atom of hydrogen is 1.008 kg.

A compound is composed of more than one atom, and the molecular weight of the compound is nothing more than the sum of the weights of the atoms of which it is composed. Thus H_2O consists of 2 hydrogen atoms and 1 oxygen atom, and the molecular weight of water is $(2)(1.008) + 16.000 = 18.02$. These weights are all relative to the ^{12}C atom as 12.0000, and again, any mass unit can be attached to the molecular weight of water, such as 18.02 g/g mole, 18.02 lb/lb mole, etc.

You can compute average molecular weights for mixtures of constant composition even though they are not chemically bonded if their compositions are known accurately. Thus later on in Example 1.12 we shall show how to calculate the average molecular weight of air. Of course, for a material such as fuel oil or coal whose composition may not be exactly known, you cannot determine an exact molecular weight, although you might estimate an approximate average molecular weight good enough for engineering calculations.

EXAMPLE 1.8 Molecular weights

(1.4) If a bucket holds 2.00 lb of NaOH (mol. wt = 40.0), how many

(1.5) (a) Pound moles of NaOH does it contain?

(b) Gram moles of NaOH does it contain?

Solution:

(1.6) Basis: 2.00 lb NaOH

$$\frac{2.00 \text{ lb NaOH}}{40.0 \text{ lb NaOH}} \mid \frac{1 \text{ lb mole NaOH}}{1 \text{ lb mole NaOH}} = 0.050 \text{ lb mole NaOH}$$

$$\frac{2.00 \text{ lb NaOH}}{40.0 \text{ lb NaOH}} \mid \frac{1 \text{ lb mole NaOH}}{1 \text{ lb mole NaOH}} \mid \frac{454 \text{ g mole}}{1 \text{ lb mole}} = 22.7 \text{ g mole}$$

$$\frac{2.00 \text{ lb NaOH}}{40.0 \text{ lb NaOH}} \mid \frac{454 \text{ g}}{1 \text{ lb}} \mid \frac{1 \text{ g mole NaOH}}{40.0 \text{ g NaOH}} = 22.7 \text{ g mole}$$

EXAMPLE 1.9 Molecular weights

How many lb of NaOH are in 7.50 g mole of NaOH?

Solution:

Basis: 7.50 g mole NaOH

$$\frac{7.50 \text{ g moles NaOH}}{454 \text{ g moles}} \mid \frac{1 \text{ lb mole}}{1 \text{ lb mole NaOH}} \mid \frac{40 \text{ lb NaOH}}{1 \text{ lb mole NaOH}} = 0.66 \text{ lb NaOH}$$

1.3 Conventions in methods of analysis and measurement

There are certain definitions and conventions which we should mention at this time since they will be constantly used throughout this book. If you memorize them now, you will immediately have a clearer perspective and save considerable trouble later on.

1.3.1 Density. Density is the ratio of mass per unit volume, as, for example, gram/cm³ or lb/ft³. It has both a numerical value and units. To determine the density of a substance, you must find both its volume and its mass or weight. If the substance is a solid, a common method to determine its volume is to displace a measured quantity of inert liquid. For example, a known weight of a material can be placed into a container of liquid of known weight and volume, and the final weight and volume of the combination measured. The density (or specific gravity) of a liquid is commonly measured with a hydrometer. A known weight and volume is dropped into the liquid and the depth to which it

penetrates into the liquid is noted) or a Westphal balance (the weight of a known slug is compared in the unknown liquid with that in water). Gas densities are quite difficult to measure; one device used is the Edwards balance, which compares the weight of a bulb filled with air to the same bulb when filled with the unknown gas.

In most of your work using liquids and solids, density will not change very much with temperature or pressure, but for precise measurements for common substances you can always look up in handbook the variation of density with temperature. The change in density with temperature is illustrated in Fig. 1.1

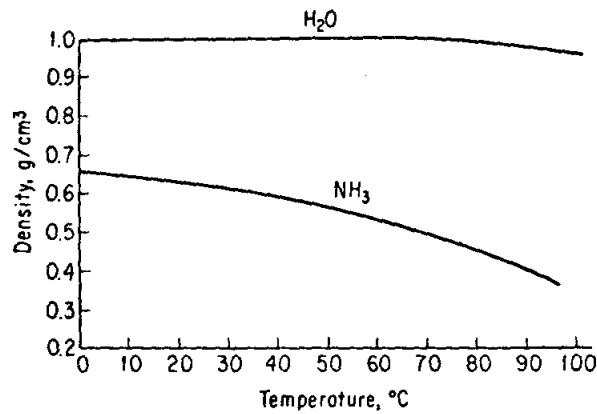


Fig. 1.1. Densities of liquid H₂O and NH₃ as a function of temperature.

for liquid water and liquid ammonia. Figure 1.2 illustrates how density also varies with composition. In the winter you may put antifreeze in your car radiator. The service station attendant checks the concentration of antifreeze by measuring the specific gravity and, in effect, the density of the radiator solution after it is mixed thoroughly. He has a little thermometer in his hydrometer kit in order to be able to read the density at the proper temperature.

1.3.2 Specific Gravity. Specific gravity is commonly thought of as a dimensionless ratio. Actually, it should be considered as the ratio of two densities—that of the substance of interest, *A*, to that of a reference substance. In symbols:

$$\text{sp gr} = \text{specific gravity} = \frac{(\text{lb}/\text{ft}^3)_A}{(\text{lb}/\text{ft}^3)_{\text{ref}}} = \frac{(\text{g}/\text{cm}^3)_A}{(\text{g}/\text{cm}^3)_{\text{ref}}} = \frac{(\text{kg}/\text{m}^3)_A}{(\text{kg}/\text{m}^3)_{\text{ref}}} \quad (1.8)$$

The reference substance for liquids and solids is normally water. Thus the specific gravity is the ratio of the density of the substance in question to the density of water. The specific gravity of gases frequently is referred to air, but may be referred to other gases, as will be discussed in more detail in Chap. 3.

balance (the weight of a known mass in water). Gas densities are measured towards balance, which comes when the bulb when filled with the

density will not change very much. Measurements for common liquids show the variation of density with temperature is illustrated in Fig. 1.1.

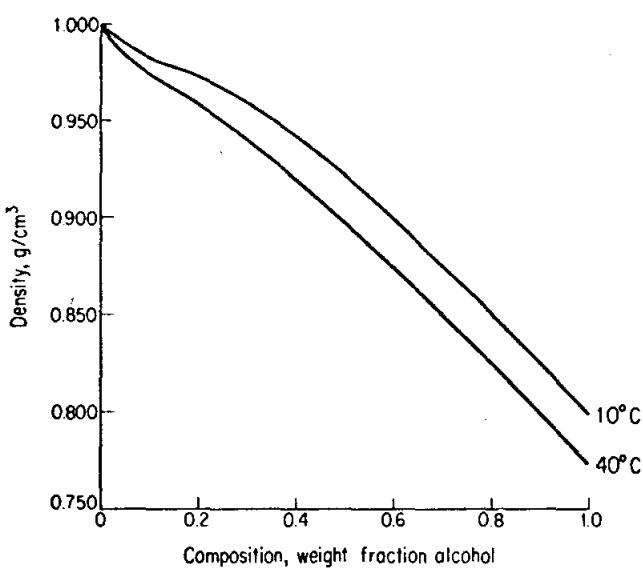


Fig. 1.2. Density of a mixture of ethyl alcohol and water as a function of composition.

Liquid density can be considered to be nearly independent of pressure for most common calculations, but, as just mentioned, it varies somewhat with temperature; therefore, to be very precise when referring to specific gravity, state the temperature at which each density is chosen. Thus

$$\text{sp gr} = 0.73 \frac{20^\circ}{4^\circ}$$

can be interpreted as follows: the specific gravity at 20°C referred to that of water at 4°C is 0.73. Since the density of water at 4°C is very close to 1.0000 in the cgs system, the numerical values of the specific gravity and density in this system are essentially equal. Since densities in the American engineering system are expressed in lb/ft³ and the density of water is about 62.4 lb/ft³, it can be seen that the specific gravity and density values are not numerically equal in the American engineering system.

In the petroleum industry the specific gravity of petroleum products is usually reported in terms of a hydrometer scale called °API. The equation for the API scale is

$${}^{\circ}\text{API} = \frac{141.5}{\text{sp gr } \frac{60^\circ}{60^\circ}} - 131.5 \quad (1.9)$$

or

$$\text{sp gr } \frac{60^\circ}{60^\circ} = \frac{141.5}{{}^{\circ}\text{API} + 131.5} \quad (1.10)$$

The volume and therefore the density of petroleum products vary with temperature, and the petroleum industry has established 60°F as the standard temperature for volume and API gravity. The National Bureau of Standards has published the National Standard Petroleum Oil Tables, NBS Circular C41 (1936), which relates API, density, specific gravity, and temperature for all petroleum oils. Thus you may convert any of the above properties at any temperature to any other temperature.

There are many other systems of measuring density and specific gravity which are somewhat specialized as, for example, the Baume ($^{\circ}\text{Be}$) and the Twaddell ($^{\circ}\text{Tw}$) systems. Relationships among the various systems of density may be found in standard reference books.

1.3-3 Specific Volume. The specific volume of any compound is the inverse of the density, that is, the volume per unit mass or unit amount of material. Units of specific volume might be ft^3/lb_m , ft^3/lb mole, cm^3/g , bbl/lb_m , or similar ratios.

1.3-4 Mole Fraction and Weight Fraction. Mole fraction is simply the moles of a particular substance divided by the total number of moles present. This definition holds for gases, liquids, and solids. Similarly, the weight fraction is nothing more than the weight of the substance divided by the total weight of all substances present. Mathematically these ideas can be expressed as

$$\text{mole fraction} = \frac{\text{moles of } A}{\text{total moles}} \quad (1.11)$$

$$\text{weight fraction} = \frac{\text{weight of } A}{\text{total weight}} \quad (1.12)$$

Mole percent and weight percent are the respective fractions times 100.

1.3-5 Analyses. The analyses of gases such as air, combustion products, and the like are usually on a dry basis—i.e., water vapor is excluded from the analysis. Such an analysis is called an *Orsat* analysis. In practically all cases the analysis of the gas is on a volume basis, which for the ideal gas is the same as a mole basis. Consider a typical gas analysis, that of air, which is approximately

$$\begin{array}{r} 21\% \text{ oxygen} \\ 79\% \text{ nitrogen} \\ \hline 100\% \text{ total} \end{array}$$

This means that any sample of air will contain 21 percent oxygen by volume and also 21 mole percent oxygen. Percent, you should remember, is nothing more than the fraction times 100; consequently the mole fraction of oxygen is 0.21.

Analyses of liquids and solids are usually given by weight percent, but occa-

vary with temperature. The standard temperature of Standards has NBS Circular C410 temperature for all properties at any temperature and specific gravity (volume ($^{\circ}\text{Be}$) and the systems of density

any compound is the or unit amount of mole, cm^3/g , bbl/lb_m ,

mole fraction is simply the number of moles present. The weight fraction is the total weight of expressed as

(1.11)

(1.12)

ons times 100.

combustion products, water is excluded from the practically all cases the usual gas is the same as air which is approximately

ent oxygen by volume remember, is nothing the fraction of oxygen is

eight percent, but occa-

sually by mole percent. In this text analyses of liquids and solids will always be assumed to be weight percent unless otherwise stated.

EXAMPLE 1.10 Mole fraction and weight fraction

An industrial-strength drain cleaner contains 5.00 lb of water and 5.00 lb of NaOH. What is the weight fraction and mole fraction of each component in the bottle of cleaner?

Solution:

Basis: 10.0 lb of total solution

component	lb	weight fraction	wt lb	lb moles	mole fraction
H ₂ O	5.00	$\frac{5.00}{10.0} = 0.500$	18.0	0.278	$\frac{0.278}{0.403} = 0.699$
NaOH	5.00	$\frac{5.00}{10.0} = 0.500$	40.0	0.125	$\frac{0.125}{0.403} = 0.311$
Total	10.00	1.000		0.403	1.00

The lb moles are calculated as follows:

$$\frac{5.00 \text{ lb H}_2\text{O}}{18.0 \text{ lb H}_2\text{O}} \mid \frac{1 \text{ lb mole H}_2\text{O}}{1 \text{ lb mole H}_2\text{O}} = 0.278 \text{ lb mole H}_2\text{O}$$

$$\frac{5.00 \text{ lb NaOH}}{40.0 \text{ lb NaOH}} \mid \frac{1 \text{ lb mole NaOH}}{1 \text{ lb mole NaOH}} = 0.125 \text{ lb mole NaOH}$$

Adding these quantities together gives the total lb moles.

EXAMPLE 1.11 Density and specific gravity

If dibromopentane has a specific gravity of 1.57, what is its density in lb_m/ft^3 , in g/cm^3 , and in kg/m^3 ?

Solution:

Our reference substance is water.

$$(a) \quad \frac{1.57 \text{ g DBP}}{1.00 \text{ g H}_2\text{O}} \mid \frac{1.00 \text{ g H}_2\text{O}}{\text{cm}^3} = 1.57 \frac{\text{g DBP}}{\text{cm}^3}$$

$$(b) \quad \frac{1.57 \frac{\text{lb}_m \text{DBP}}{\text{ft}^3}}{1.00 \frac{\text{lb}_m \text{H}_2\text{O}}{\text{ft}^3}} \mid \frac{62.4 \frac{\text{lb}_m \text{H}_2\text{O}}{\text{ft}^3}}{} = 97.9 \frac{\text{lb}_m \text{DBP}}{\text{ft}^3}$$

$$(c) \quad \frac{1.57 \text{ g DBP}}{\text{cm}^3} \mid \frac{(100 \text{ cm})^3}{1 \text{ m}} \mid \frac{1 \text{ kg}}{1000 \text{ g}} = 1.57 \times 10^3 \frac{\text{kg DBP}}{\text{m}^3}$$

Note how the units of specific gravity as used here clarify the calculation.

EXAMPLE 1.12 Compute the average molecular weight of air

Basis: 100 lb mole of air

component	moles = %	mol. wt	lb	weight %
O ₂	21.0	32	672	23.17
N ₂ *	79.0	28.2	2228	76.83
Total	100		2900	100.00

*Includes Ar, CO₂, Kr, Ne, Xe, and is called atmospheric nitrogen. The molecular weight is 28.2. Table 1.4 lists the detailed composition of air.

The average molecular weight is 2900 lb/100 lb mole = 29.00.

TABLE 1.4 COMPOSITION OF CLEAN, DRY AIR NEAR SEA LEVEL

Component	Percent by volume = mole percent
Nitrogen	78.084
Oxygen	20.9476
Argon	0.934
Carbon dioxide	0.0314
Neon	0.001818
Helium	0.000524
Methane	0.0002
Krypton	0.000114
Nitrous oxide	0.00005
Hydrogen	0.00005
Xenon	0.0000087
Ozone	Summer: 0-0.000007 Winter: 0-0.000002
Ammonia	0-trace
Carbon monoxide	0-trace
Iodine	0-0.000001
Nitrogen dioxide	0-0.000002
Sulfur dioxide	0-0.0001

1.3-6 Basis. Have you noted in the previous examples that the word *basis* has appeared at the top of the computations? This concept of basis is vitally important both to your understanding of how to solve a problem and also to your solving it in the most expeditious manner. The basis is the reference chosen by you for the calculations you plan to make in any particular problem and a proper choice of basis frequently makes the problem much easier to solve. The basis may be a period of time—for example, hours, or a given weight of material—such as 5 lb of CO₂ or some other convenient quantity. In selecting a sound basis (which in many problems is predetermined for you but in some

Unit of air

lb	weight %
572	23.17
228	76.83
1000	100.00

aspheric nitrogen. The molecular air.

mole = 29.00.

At Sea Level

Percent by volume
= mole percent

78.084
20.9
0.
0.1
0.001818
0.000524
0.0002
0.000114
0.00005
0.00005
0.0000087
0-0.000007
0-0.000002
0-trace
0-trace
0-0.000001
0-0.000002
0-0.0001

vious examples that the word basis? This concept of basis is now to solve a problem another. The basis is the reference point in any particular problem. A problem much easier to solve. hours, or a given weight of convenient quantity. In selecting a basis is determined for you but in some

problems is not so clear), you should ask yourself the following questions:

- (a) What do I have to start with?
- (b) What do I want to find out?
- (c) What is the most convenient basis to use?

These questions and their answers will suggest suitable bases. Sometimes, when a number of bases seem appropriate, you may find it is best to use a unit basis of 1 or 100 of something, as, for example, pounds, hours, moles, cubic feet, etc. Many times for liquids and solids when a weight analysis is used, a convenient basis is 1 or 100 lb or kg; similarly, 1 or 100 moles is often a good choice if a mole analysis is used for a gas. The reason for these choices is that the fraction or percent automatically equals the number of pounds, kg, or moles, respectively, and one step in the calculations is saved.

EXAMPLE 1.13 Choosing a basis

Aromatic hydrocarbons form 15 to 30 percent of the components of leaded fuels and as much as 40 percent of nonleaded gasoline. The carbon to hydrogen ratio helps to characterize the fuel components. If a fuel is 80 percent C and 20 percent H by weight, what is the C/H ratio in moles?

Solution:

If a basis of 100 lb or kg of oil is selected, then the percent = pounds or kg.

Basis: 100 lb of oil (or 100 kg of oil)

component	kg = % or lb = %	mol. wt	kg moles or lb moles
C	80	12.0	6.67
H	20	1.008	19.84
	100		

Consequently the C/H ratio in moles is

$$\text{C}/\text{H} = 6.67/19.84 = 0.33$$

EXAMPLE 1.14 Choosing a basis

Most processes for producing high energy content gas or gasoline from coal include some type of gasification step to make hydrogen or synthesis gas. Pressure gasification is preferred because of its greater yield of methane and higher rate of gasification.

Given that a 50.0 lb test run of gas averages 10.0 percent H_2 , 40.0 percent CH_4 , 30.0 percent CO , and 20.0 percent CO_2 , what is the average molecular weight of the gas?

Solution:

The obvious basis is 50.0 lb of gas ("What I have to start with") but a little reflection will show that such a basis is of no use. You cannot multiply mole percent

of this gas times pounds and expect the answer to mean anything. Thus the next step is to choose a "convenient basis" which is 100 lb or kg moles of gas, and proceed as follows:

Basis: 100 lb moles of gas			
composition	% = lb moles	mol. wt	lb
CO ₂	20.0	44.0	880
CO	30.0	28.0	840
CH ₄	40.0	16.04	642
H ₂	10.0	2.02	20
	100.0		2382

$$\text{average molecular weight} = \frac{2382 \text{ lb}}{100 \text{ lb moles}} = 23.8 \text{ lb/lb mole}$$

It is important that your basis be indicated at the beginning of the problem so that you will keep clearly in mind the real nature of your calculations and so that anyone checking your problem will be able to understand on what basis they are performed. If you change bases in the middle of the problem, a new basis should be indicated at that time. Many of the problems which we shall encounter will be solved on one basis and then at the end will be shifted to another basis to give the desired answer. The significance of this type of manipulation will become considerably clearer as you accumulate more experience. The ability to choose the basis that requires the fewest steps in solution can only come with practice. You can quickly accumulate the necessary experience if, as you look at each problem illustrated in this text, you determine first in your own mind what the basis should be and then compare your choice with the selected basis. By this procedure you will quickly obtain the knack of choosing a sound basis.

1.3-7 Concentrations. Concentration means the quantity of some solute per fixed amount of solvent or solution in a mixture of two or more components, as, for example,

- (a) Weight per unit volume (lb_m of solute/ft³, g of solute/l, lb_m of solute/bbl, kg of solute/m³).
- (b) Moles per unit volume (lb mole of solute/ft³, g mole of solute/l, g mole of solute/cm³).
- (c) Parts per million—a method of expressing the concentration of extremely dilute solutions. Ppm is equivalent to a weight fraction for solids and liquids because the total amount of material is of a much higher order of magnitude than the amount of solute; it is essentially a mole fraction for gases.
- (d) Other methods of expressing concentration with which you should be familiar are molarity (mole/l), normality (equivalents/l), and molality (mole/1000 g of solvent).

anything. Thus the next step is to convert moles of gas, and proceed as follows:

lb
880
840
642
20
<hr/>
2382

23.8 lb/lb mole

In the beginning of the problem you will have to decide on what basis they will be calculated. In order to understand on what basis they will be calculated, a new basis must be chosen. This basis will be shifted to another basis as required. The manipulation will be explained. The ability to manipulate can only come with experience if, as you look first in your own mind, you can make a choice with the selected basis. The art of choosing a sound basis.

means the quantity of some substance in a mixture of two or more substances.

of solute/l, lb_m of solute/bbl, g/m³, g ft³, g mole of solute/l, g mole of solute/bbl.

The concentration of a solution is expressed as a weight fraction for solids or a mole fraction for liquids. The material is of a much higher molecular weight; it is essentially a mole fraction.

The concentration with which you should be concerned is expressed in equivalents/l, and molality.

A typical example of the use of these concentration measures is the set of guidelines by which the Environmental Protection Agency defined the extreme levels at which the five most common air pollutants could harm individuals over periods of time.

- (a) Sulfur dioxide: $2620 \mu\text{g}/\text{m}^3$, equal to 1 ppm averaged over a 24-hr period.
- (b) Particulate matter: $1000 \mu\text{g}/\text{m}^3$, or a "coefficient of haze" equal to 8, whichever is stricter, averaged over 24 hr. (Total absence of haze, if it could occur in the earth's atmosphere, would be equal to a zero haze coefficient.)
- (c) Carbon monoxide: $57.5 \text{ mg}/\text{m}^3$ (50 ppm) when averaged over an 8-hr period; $86.3 \text{ mg}/\text{m}^3$ (75 ppm) over a 4-hr average; $144 \text{ mg}/\text{m}^3$ (125 ppm) when averaged over 1 hr.
- (d) Photochemical oxidants: $800 \mu\text{g}/\text{m}^3$ (0.4 ppm) when averaged over 4 hr; $1200 \mu\text{g}/\text{m}^3$ (0.6 ppm) when averaged over 2 hr; $1400 \mu\text{g}/\text{m}^3$ (0.7 ppm) when averaged over 1 hr.
- (e) Nitrogen dioxide: $3750 \mu\text{g}/\text{m}^3$ (2 ppm) averaged over 1 hr, $938 \mu\text{g}/\text{m}^3$ (0.5 ppm), 24-hr average.

It is important to remember that in an ideal solution, such as in gases or in a simple mixture of hydrocarbon liquids or compounds of like chemical nature, the volumes of the components may be added without great error to get the total volume of the mixture. For the so-called nonideal mixtures this rule does not hold, and the total volume of the mixture is bigger or smaller than the sum of the volumes of the pure components.

1.4 Temperature

Our concept of temperature probably originated with our physical sense of hot or cold. Attempts to be more specific and quantitative led to the idea of a temperature scale and the thermometer—a device to measure how hot or cold something is. We are all familiar with the thermometer used in laboratories which holds mercury sealed inside a glass tube or the alcohol thermometer used to measure outdoor temperatures.

Although we do not have the space to discuss in detail the many methods of measuring temperature, we can point out some of the other more common techniques with which you are probably already familiar:

- (a) The voltage produced by a junction of two dissimilar conductors changes with temperature and is used as a measure of temperature (the thermocouple).
- (b) The property of changing electrical resistance with temperature gives us a device known as the *thermistor*.

- (c) Two thin strips of metal bonded together at one end expand at different rates with change of temperature. These strips assist in the control of the flow of water in the radiator of an automobile and in the operation of air conditioners and heating systems.
- (d) High temperatures can be measured by devices called *pyrometers* which note the radiant energy leaving a hot body.

Figure 1.3 illustrates the appropriate ranges for various temperature-measuring devices.

As you also know, temperature is a measure of the thermal energy of the random motion of the molecules of a substance at thermal equilibrium. Temperature is normally measured in degrees Fahrenheit or Celsius (Centigrade). The common scientific scale is the *Celsius scale*,⁸ where 0° is the ice point of water and 100° is the normal boiling point of water. In the early 1700s Fahrenheit a glassblower by trade, was able to build mercury thermometers that gave temperature measurements in reasonable agreement with each other. The *Fahrenheit scale* is the one commonly used in everyday life in the United States. Its reference points are of more mysterious origin, but it is reported that the fixed starting point, or 0° on Fahrenheit's scale, was the temperature of an ice-salt mixture, and 96° , the temperature of the blood of a healthy man, was selected as the upper point because it is easily divisible by 2, 3, 4, 6, and 8, whereas 100° is not. In any case, as now standardized, 32°F represents the ice point and 212°F represents the normal boiling point of water. In the SI system, temperature is measured in kelvins, a unit named after the famous Lord Kelvin. Note that in the SI system the degree symbol is suppressed; i.e., the boiling point of water is 373 K .

The Fahrenheit and Celsius scales are *relative* scales; that is, their zero points were arbitrarily fixed by their inventors. Quite often it is necessary to use *absolute* temperatures instead of relative temperatures. Absolute temperature scales have their zero point at the lowest possible temperature which man believes can exist. As you may know, this lowest temperature is related both to the ideal gas laws and to the laws of thermodynamics. The absolute scale, which is based on degree units the size of those in the Celsius (Centigrade) scale, is called the *Kelvin scale*; the absolute scale which corresponds to the Fahrenheit degree scale is called the *Rankine scale* in honor of a Scottish engineer. The relations between relative temperature and absolute temperature are illustrated in Fig. 1.4. We shall round off absolute zero on the Rankine scale of -459.58°F to -460°F ; similarly, -273.15°C will be rounded off to -273°C .

You should recognize that the unit degree, i.e., the unit temperature difference on the Kelvin-Celsius scale, is not the same size as that on the Rankine-Fahrenheit scale. If we let $\Delta^\circ\text{F}$ represent the unit temperature difference in the Fahrenheit scale, $\Delta^\circ\text{R}$ be the unit temperature difference in the Rankine scale,

⁸As originally devised by Celsius in 1742, the freezing point was designated as 100. Officially, ${}^\circ\text{C}$ now stands for *degrees Celsius*.

Chap. 1

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devices called *pyrometers* which say.

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of the thermal energy of the thermal equilibrium. Temperature of Celsius (Centigrade).

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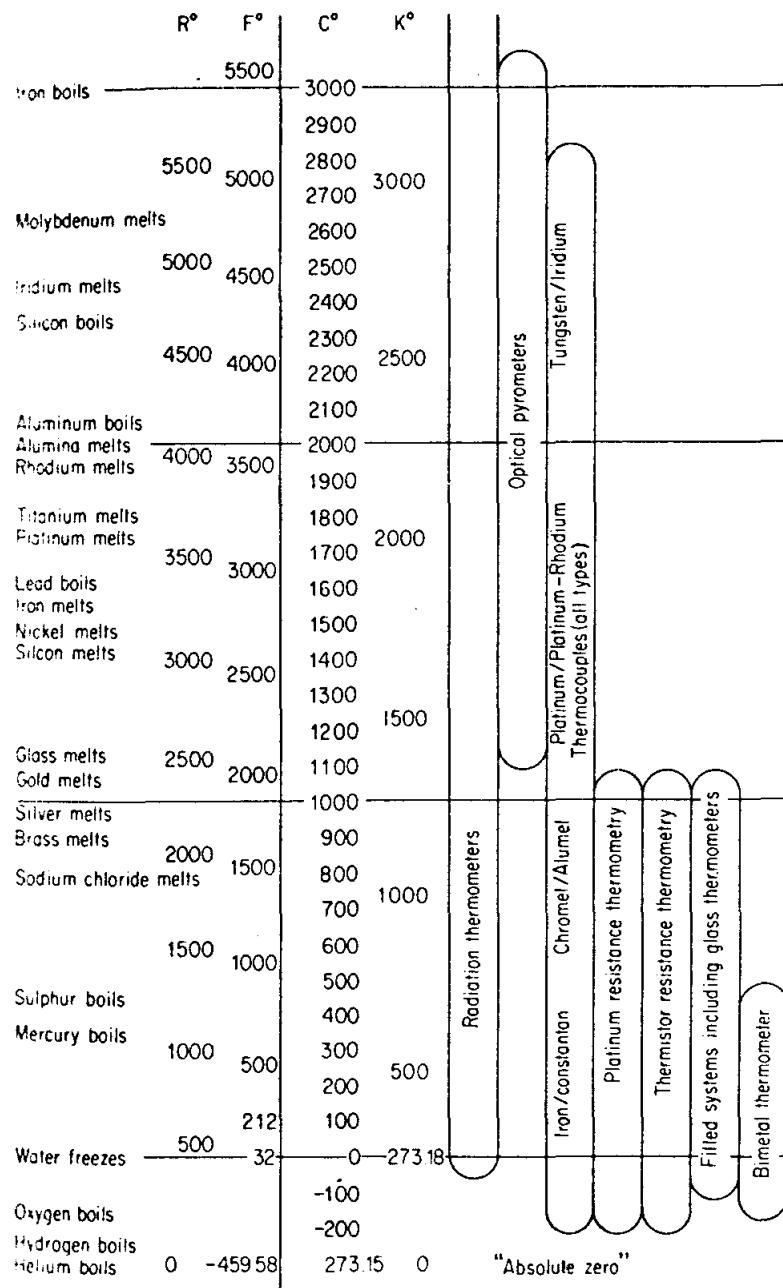


Fig. 1.3. Temperature measuring instruments span the range from near absolute zero to beyond 3000 K. The chart indicates the preferred methods of thermal instrumentation for various temperature regions.

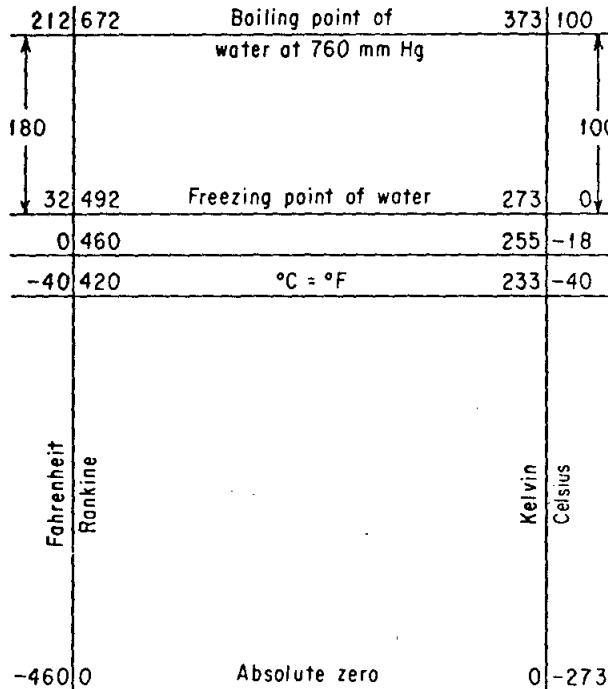


Fig. 1.4. Temperature scales.

and $\Delta^\circ\text{C}$ and $\Delta^\circ\text{K}$ be the analogous units in the other two scales, you should be aware that

$$\Delta^\circ\text{F} = \Delta^\circ\text{R} \quad (1.13)$$

$$\Delta^\circ\text{C} = \Delta^\circ\text{K} \quad (1.14)$$

Also, if you keep in mind that the $\Delta^\circ\text{C}$ is larger than the $\Delta^\circ\text{F}$,

$$\frac{\Delta^\circ\text{C}}{\Delta^\circ\text{F}} = 1.8 \quad \text{or} \quad \Delta^\circ\text{C} = 1.8 \Delta^\circ\text{F} \quad (1.15)$$

$$\frac{\Delta^\circ\text{K}}{\Delta^\circ\text{R}} = 1.8 \quad \text{or} \quad \Delta^\circ\text{K} = 1.8 \Delta^\circ\text{R} \quad (1.16)$$

Unfortunately, the symbols $\Delta^\circ\text{C}$, $\Delta^\circ\text{F}$, $\Delta^\circ\text{K}$, and $\Delta^\circ\text{R}$ are not in standard usage, and consequently the proper meaning of the symbols ${}^\circ\text{C}$, ${}^\circ\text{F}$, ${}^\circ\text{K}$, and ${}^\circ\text{R}$, as either the temperature or the temperature difference, *must be interpreted* from the context of the equation or sentence being examined.

You should learn how to convert one temperature to another with ease. The relations between ${}^\circ\text{R}$ and ${}^\circ\text{F}$ and between ${}^\circ\text{K}$ and ${}^\circ\text{C}$ are, respectively,

$$T_{^\circ\text{R}} = T_{^\circ\text{F}} \left(\frac{1 \Delta^\circ\text{R}}{1 \Delta^\circ\text{F}} \right) + 460 \quad (1.17)$$

$$T_{^\circ\text{K}} = T_{^\circ\text{C}} \left(\frac{1 \Delta^\circ\text{K}}{1 \Delta^\circ\text{C}} \right) + 273 \quad (1.18)$$



Because the relative temperature scales do not have a common zero at the same temperature, as can be seen from Fig. 1.4, the relation between °F and °C is

$$T_{\circ F} - 32 = T_{\circ C} \left(\frac{1.8 \Delta^{\circ F}}{1 \Delta^{\circ C}} \right) \quad (1.19)$$

After you have used Eqs. (1.17)–(1.19) a bit, they will become so familiar that temperature conversion will become an automatic reflex. During your “learning” period,” in case you forget them, just think of the appropriate scales side by side as in Fig. 1.4, and put down the values for the freezing and boiling points of water.

From Fig. 1.4 you will notice that −40° is a common temperature on both the Centigrade and Fahrenheit scales. Therefore the following relationships hold:

$$T_{\circ F} = (T_{\circ C} + 40) \left(\frac{1.8 \Delta^{\circ F}}{1 \Delta^{\circ C}} \right) - 40 \quad (1.20)$$

$$T_{\circ C} = (T_{\circ F} + 40) \left(\frac{1 \Delta^{\circ C}}{1.8 \Delta^{\circ F}} \right) - 40 \quad (1.21)$$

In Fig. 1.4 all the values of the temperatures have been rounded off, but more significant figures can be used. 0°C and its equivalents are known as *standard conditions of temperature*.

EXAMPLE 1.15 Temperature conversion

Convert 100°C to (a) °K, (b) °F, (c) °R.

Solution:

$$(a) (100 + 273)^\circ C \frac{1 \Delta^{\circ K}}{1 \Delta^{\circ C}} = 373^\circ K$$

or with suppression of the Δ symbol

$$(100 + 273)^\circ C \frac{1^\circ K}{1^\circ C} = 373^\circ K$$

$$(b) (100^\circ C) \frac{1.8^\circ F}{1^\circ C} + 32 = 212^\circ F$$

$$(c) (212 + 460)^\circ F \frac{1^\circ R}{1^\circ F} = 672^\circ R$$

$$\text{or } (373^\circ K) \frac{1.8^\circ R}{1^\circ K} = 672^\circ R$$

EXAMPLE 1.16 Temperature conversion

The thermal conductivity of aluminum at 32°F is 117 Btu/(hr)(ft²)(°F/ft). Find the equivalent value at 0°C in terms of Btu/(hr)(ft²)(°K/ft).

Solution:

Since 32°F is identical to 0°C, the value is already at the proper temperature. The “°F” in the denominator of the thermal conductivity actually stands for Δ°F

so that the equivalent value is

$$\frac{117 \text{ (Btu)(ft)}}{(\text{hr})(\text{ft}^2)(\Delta^\circ\text{F})} \left| \frac{1.8 \Delta^\circ\text{F}}{1 \Delta^\circ\text{C}} \right| \left| \frac{1 \Delta^\circ\text{C}}{1 \Delta^\circ\text{K}} \right| = 211 \text{ (Btu)/(hr)(ft}^2)(^\circ\text{K}/\text{ft})$$

or with the Δ symbol suppressed

$$\frac{117 \text{ (Btu)(ft)}}{(\text{hr})(\text{ft}^2)(^\circ\text{F})} \left| \frac{1.8^\circ\text{F}}{1^\circ\text{C}} \right| \left| \frac{1^\circ\text{C}}{1^\circ\text{K}} \right| = 211 \text{ (Btu)/(hr)(ft}^2)(^\circ\text{K}/\text{ft})$$

1.5 Pressure

Pressures, like temperatures, can also be expressed by either absolute or relative scales. Pressure is defined as "force per unit area." Figure 1.5 shows a column of mercury held in place by a sealing plate. Suppose that the column of mercury

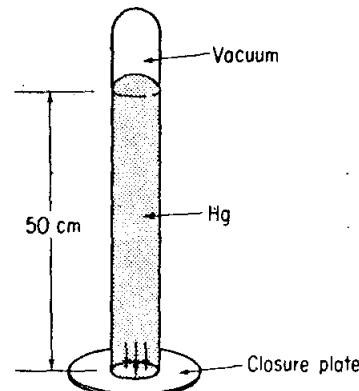


Fig. 1.5. Pressure.

has an area of 1 cm^2 and is 50 cm high. From Table D.1 we can find that the sp gr at 20°C and hence the density, essentially, of the Hg is 13.55 g/cm^3 . Thus the force exerted on the 1 cm^2 section of that plate by the column of mercury is

$$F = \frac{13.55 \text{ g}}{\text{cm}^3} \left| \frac{50 \text{ cm}}{1 \text{ cm}^2} \right| \left| \frac{1 \text{ kg}}{(\text{sec})^2} \right| \left| \frac{980 \text{ cm}}{1000 \text{ g}} \right| \left| \frac{1 \text{ m}}{100 \text{ cm}} \right| \left| \frac{1 \text{ N}}{1 \text{ (kg)(m)}} \right| \left| \frac{1}{\text{sec}^2} \right|$$

$$= 6.64 \text{ N}$$

The pressure on the section of the plate covered by the mercury is

$$p = \frac{6.64 \text{ N}}{1 \text{ cm}^2} \left| \frac{(100 \text{ cm})^2}{1 \text{ m}} \right| = 6.64 \times 10^4 \frac{\text{N}}{\text{m}^2}$$

If we had started with units in the American engineering system, the pressure could be similarly computed as

$$P = \frac{846 \text{ lb}_m}{1 \text{ ft}^3} | 50 \text{ cm} | 1 \text{ in.} | 1 \text{ ft} | 32.2 \text{ ft} |$$

$\frac{32.147(\text{ft})(\text{lb}_m)}{(\text{sec})^2(\text{lb}_f)}$

$$= 1387 \frac{\text{lb}_f}{\text{ft}^2}$$

Whether relative or absolute pressure is measured in a pressure-measuring device depends on the nature of the instrument used to make the measurements. For example, an open-end manometer (Fig. 1.6) would measure a relative pressure, since the reference for the open end is the pressure of the atmosphere at the open end of the manometer. On the other hand, closing off the end of the manometer (Fig. 1.7) and creating a vacuum in the end results in a measurement against a complete vacuum, or against "no pressure." This measurement is called *absolute pressure*. Since absolute pressure is based on a complete vacuum, a fixed reference point which is unchanged regardless of location or temperature or weather or other factors, absolute pressure then establishes a precise, invariable value which can be readily identified. Thus the zero point for an absolute pres-

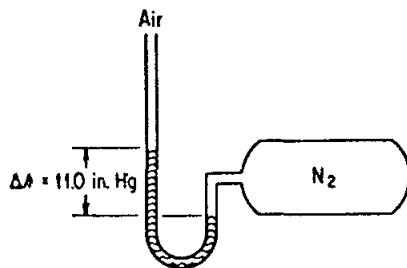


Fig. 1.6. Open-end manometer showing a pressure above atmospheric pressure.

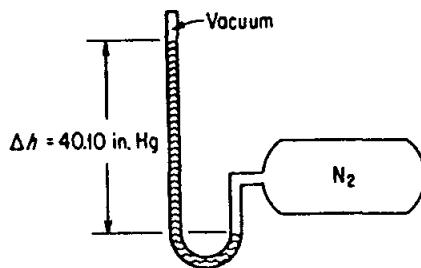


Fig. 1.7. Absolute pressure manometer.

sure scale corresponds to a perfect vacuum, whereas the zero point for a relative pressure scale usually corresponds to the pressure of the air which surrounds us at all times, and as you know, varies slightly.

If the mercury reading is set up as in Fig. 1.8, the device is called a *barometer* and the reading of atmospheric pressure is termed *barometric pressure*.

An understanding of the principle upon which a manometer operates will aid you in recognizing the nature of the pressure measurement taken from it. As shown in Fig. 1.6 for an open-end, U-tube manometer, if the pressure measured is greater than atmospheric, the liquid is forced downward in the leg to which the pressure source is connected and upward in the open leg. Eventually a point of hydrostatic balance is reached in which the manometer fluid stabilizes, and the difference in height of the fluid in the open leg relative to that in the leg attached to the pressure source is exactly equal to

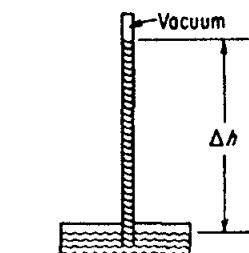


Fig. 1.8. A barometer.

the difference between the atmospheric pressure and the applied pressure in the other leg. If vacuum were applied instead of pressure to the same leg of the manometer, the fluid column would rise on the vacuum side. Again, the difference in pressure between the pressure source in the tank and atmospheric pressure is balanced by the difference in the height of the two columns of fluid. Water and mercury are commonly used indicating fluids for manometers; the readings thus can be expressed in "inches of water" or "inches of mercury." (In ordinary engineering calculations we ignore the vapor pressure of mercury and minor changes in the density of mercury due to temperature changes in making pressure measurements.)

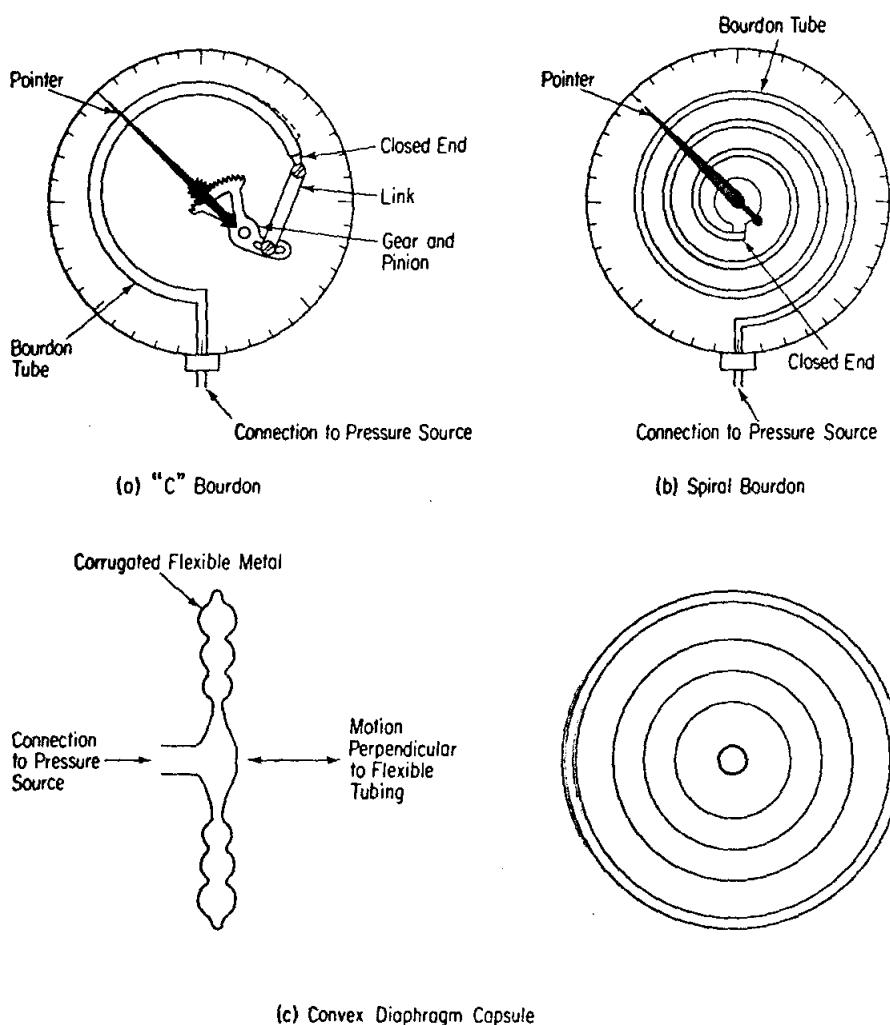
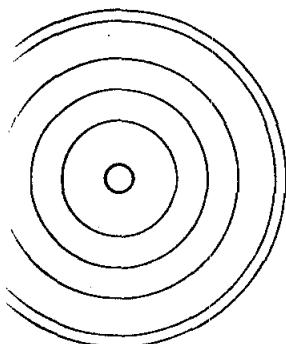
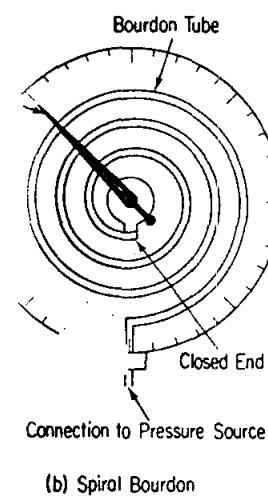


Fig. 1.9. Bourdon and diaphragm pressure-measuring devices.

the applied pressure in the tank is added to the same leg of the manometer side. Again, the difference between tank and atmospheric pressure is the two columns of fluid. This is the basis for manometers; the unit of pressure is "inches of mercury." The vapor pressure of mercury is affected by temperature changes in



Another type of common measuring device is the visual *Bourdon gauge* (Fig. 1.9), which normally (but not always) reads zero pressure when open to the atmosphere. The pressure-sensing device in the *Bourdon* gauge is a thin metal tube with an elliptical cross section closed at one end which has been bent into an arc. As the pressure increases at the open end of the tube, it tries to straighten out, and the movement of the tube is converted into a dial movement by gears and levers. Figure 1.9 also illustrates a diaphragm capsule gauge. Figure 1.10 indicates the pressure ranges for the various pressure-measuring devices.

Pressure scales may be temporarily somewhat more confusing than temperature scales since the reference point or zero point for the relative pressure scales is not constant, whereas in the temperature scales the boiling point or the freezing point of water is always a fixed value. However, you will become accustomed to this feature of the pressure scale with practice.

The relationship between relative and absolute pressure is illustrated in Figs. 1.11 and 1.12 and is also given by the following expression:

$$\text{gauge pressure} + \text{barometer pressure} = \text{absolute pressure} \quad (1.22)$$

Equation (1.22) can be used only with consistent units. Note that you must add the atmospheric pressure, i.e., the barometric pressure, to the gauge, or relative

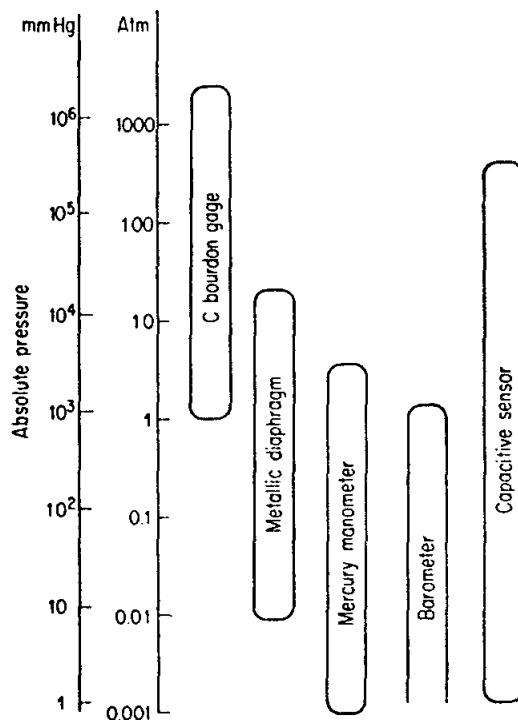


Fig. 1.10. Ranges of application for pressure-measuring devices.

Pounds per square inch		Inches mercury		Newton's per square meter
5.0	19.3	39.3	10.2	0.34×10^5
0.4	14.7	29.92	0.82	0.024×10^5
0.0	14.3	29.1	0.0	0.98×10^5
-2.45	11.85	24.1	-50.50	0.17×10^5
				0.82×10^5
14.3	0.0	0	-29.1	-0.98×10^5
				0.00

Gage pressure Absolute pressure Absolute pressure Gage pressure
 Perfect vacuum 0 Vacuum Absolute pressure

Fig. 1.11. Pressure comparisons when barometer reading is 29.1 in Hg.

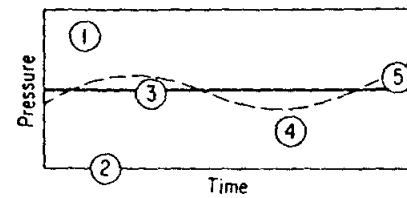


Fig. 1.12. Pressure terminology. The standard atmosphere is shown by the heavy horizontal line. The broken line illustrates the atmospheric (barometric) pressure which changes from time to time. 1 in the figure is a pressure of 19.3 psi referred to a complete vacuum or 5 psi referred to the barometric pressure. 2 is the complete vacuum, while 3 represents the standard atmosphere. 4 illustrates a negative relative pressure or a pressure less than atmospheric. This type of measurement is described in the text as a vacuum type of measurement. 5 also indicates a vacuum measurement, but one which is equivalent to an absolute pressure above the standard atmosphere.

pressure (or manometer reading if open on one end), in order to get the absolute pressure.

Another term applied in measuring pressure which is illustrated in Figs. 1.11 and 1.12 is *vacuum*. In effect, when you measure pressure as "inches of mercury vacuum," you reverse the usual direction of measurement and measure from the barometric pressure down to the vacuum, in which case a perfect vacuum would be the highest pressure that you could achieve. This procedure would be the same as evacuating the air at the top of a mercury barometer and watching the mercury rise up in the barometer as the air is removed. The vacuum system of measurement of pressure is commonly used in apparatus which operate at pressures less than atmospheric—such as a vacuum evaporator or vacuum filter. A pressure which is only slightly below barometric pressure may sometimes be expressed as a "draft" (which is identical to the vacuum system) in inches of water, as, for example, in the air supply to a furnace or a water cooling tower.

As to the units of pressure, we have shown in Fig. 1.11 two common systems: pounds per square inch (psi) and inches of mercury (in. Hg). Pounds per square inch absolute is normally abbreviated "psia," and "psig" stands for "pounds per square inch gauge." Figure 1.11 compares the relative and absolute pressure scales in terms of these two systems of measurement when the barometric pressure is 29.1 in. Hg (14.3 psia) with the SI system of units. Other systems of expressing pressure exist; in fact you will discover there are as many different units of pressure as there are means of measuring pressure. Some of the other most frequently used systems are

- Millimeters of mercury (mm Hg)
- Feet of water (ft H₂O)
- Atmospheres (atm)
- Bars (bar)
- Newton's per square meter (N/m²)

To sum up our discussion of pressure and its measurement, you should now be acquainted with

- (a) Atmospheric pressure—the pressure of the air and the atmosphere surrounding us which changes from day to day.
- (b) Barometric pressure—the same as atmospheric pressure, called "barometric pressure" because a barometer is used to measure atmospheric pressure.
- (c) Absolute pressure—a measure of pressure referred to a complete vacuum, or zero pressure.
- (d) Gauge pressure—pressure expressed as a quantity measured from (above) atmospheric pressure (or some other reference pressure).

Newtons per square meter	
0.34 x 10 ⁵	1.33 x 10 ⁵
0.024 x 10 ⁵	1.01 x 10 ⁵
0.00	0.98 x 10 ⁵
0.17 x 10 ⁵	0.82 x 10 ⁵
Gage pressure	Absolute pressure
-0.98 x 10 ⁵	0.00

is 29.1 in Hg.

- (e) Vacuum—a method of expressing pressure as a quantity below atmospheric pressure (or some other reference pressure).

You definitely must not confuse the standard atmosphere with atmospheric pressure. The *standard atmosphere* is defined as the pressure (in a standard gravitational field) equivalent to 14.696 psi or 760 mm Hg at 0°C or other equivalent value, whereas atmospheric pressure is a variable and must be obtained from a barometer each time you need it. The standard atmosphere may not actually exist in any part of the world except perhaps at sea level on certain days, but it is extremely useful in converting from one system of pressure measurement to another (as well as being useful in several other ways to be considered later).

Expressed in various units, the *standard atmosphere* is equal to

1.000	atmospheres (atm)
33.91	feet of water (ft H ₂ O)
14.7	(14.696, more exactly) pounds per square inch absolute (psia)
29.92	(29.921, more exactly) inches of mercury (in. Hg)
760.0	millimeters of mercury (mm Hg)
1.013×10^5	newtons per square meter (N/m ²)

To convert from one set of pressure units to another, it is convenient to use the relationships among the standard pressures as shown in the examples below.

If pressures are measured by means of the height of a column of liquid⁹ other than mercury or water (for which the standard pressure is known), it is easy to convert from one liquid to another by means of the following expression:

$$p = \rho gh \quad (1.23)$$

where ρ = density of the liquid

g = acceleration of gravity

By equating the same pressure yielded by two liquids with different densities, you will get the ratio between the heights of two columns of liquid. If one of these liquids is water, it is then easy to convert to any of the more commonly used liquids as follows:

$$\rho_1 gh_1 = \rho_{H_2O} g h_{H_2O} \quad \text{or} \quad \frac{h}{h_{H_2O}} = \frac{\rho_{H_2O}}{\rho}$$

EXAMPLE 1.17 Pressure conversion

Convert 35 psia to in. Hg.

Solution:

It is desirable to use the ratio of 14.7 psia to 29.92 in. Hg, an identity, to carry out this conversion.

⁹Sometimes these liquid columns are referred to as "heads" of liquid.

entity below atmos-

phere with atmos-
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at 0°C or other
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(1.23)

different densities,
of liquid. If one of
are more commonly

Basis: 35 psia

$$\frac{35 \text{ psia}}{14.7 \text{ psia}} = \frac{29.92 \text{ in. Hg}}{\text{an identity}} = 71.25 \text{ in. Hg}$$

EXAMPLE 1.18 Pressure conversion

The density of the atmosphere decreases with increasing altitude. When the pressure is 340 mm Hg, how many inches of water is it? How many kilonewtons per square meter?

Solution:

Basis: 340 mm Hg

$$\frac{340 \text{ mm Hg}}{760 \text{ mm Hg}} = \frac{33.91 \text{ ft H}_2\text{O}}{1 \text{ ft}} = 182 \text{ in. H}_2\text{O}$$

$$\frac{340 \text{ mm Hg}}{760.0 \text{ mm Hg}} = \frac{1.013 \times 10^5 \text{ N/m}^2}{1000 \text{ N}} = 45.4 \text{ kN/m}^2$$

EXAMPLE 1.19 Pressure conversion

The pressure gauge on a tank of CO₂ used to fill soda water bottles reads 51.0 psi. At the same time the barometer reads 28.0 in. Hg. What is the absolute pressure in the tank in psia? See Fig. E1.19.

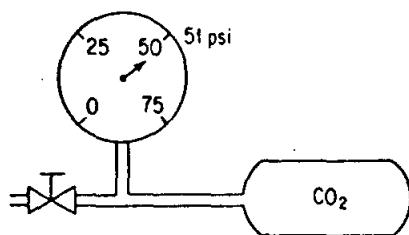


Fig. E1.19.

Solution:

The pressure gauge is reading psig, not psia.

From Eq. (1.22) the absolute pressure is the sum of the gauge pressure and the atmospheric (barometric) pressure expressed in the same units.

Basis: Barometric pressure = 28.0 in. Hg

$$\text{atmospheric pressure} = \frac{28.0 \text{ in. Hg}}{29.92 \text{ in. Hg}} = 14.7 \text{ psia}$$

(Note: Atmospheric pressure does not equal 1 standard atm.) The absolute pressure in the tank is

$$51.0 + 13.78 = 64.78 \text{ psia}$$

EXAMPLE 1.20 Pressure conversion

Air is flowing through a duct under a draft of 4.0 in. H₂O. The barometer indicates that the atmospheric pressure is 730 mm Hg. What is the absolute pressure of the gas in inches of Hg? See Fig. E1.20.

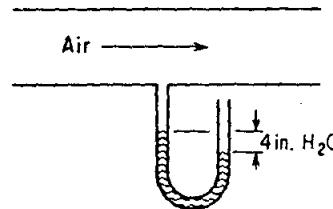


Fig. E1.20.

Solution:

Again we have to employ consistent units, and it appears in this case that the most convenient units are those of inches of mercury.

Basis: 730 mm Hg of pressure

$$\text{atmospheric pressure} = \frac{730 \text{ mm Hg}}{760 \text{ mm Hg}} \left| \frac{29.92 \text{ in. Hg}}{1 \text{ ft}} \right| = 28.9 \text{ in. Hg}$$

Basis: 4.0 in. H₂O draft (under atmospheric)

$$\frac{4 \text{ in. H}_2\text{O}}{12 \text{ in.}} \left| \frac{1 \text{ ft}}{33.91 \text{ ft H}_2\text{O}} \right| \left| \frac{29.92 \text{ in. Hg}}{1 \text{ ft}} \right| = 0.29 \text{ in. Hg}$$

Since the reading is 4.0 in. H₂O draft (under atmospheric), the absolute reading in uniform units is

$$28.9 - 0.29 = 28.6 \text{ in. Hg absolute}$$

EXAMPLE 1.21 Vacuum Pressure Reading

Small animals such as mice can live at reduced air pressures down to 3.0 psia (although not comfortably). In a test a mercury manometer attached to a tank as shown in Fig. E1.21 reads 25.4 in. Hg and the barometer reads 14.79 psia. Will the mice survive?

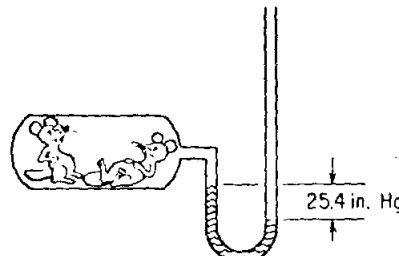


Fig. E1.21.

Solution:

Basis: 25.4 in. Hg below atmospheric

We shall assume that $g/g_c \approx 1.00$ and ignore any temperature corrections to convert the mercury to 0°C . Then, since the vacuum reading on the tank is 25.4 in. Hg below atmospheric, the absolute pressure in the tank is

$$14.79 \text{ psia} - \frac{25.4 \text{ in. Hg}}{29.92 \text{ in. Hg}} | 14.7 \text{ psia} = 14.79 - 12.49 = 2.3 \text{ psia}$$

The mice probably will not survive.

1.6 Physical and chemical properties of compounds and mixtures

Publications of industrial associations provide a tremendous storehouse of data. For example, the American Petroleum Institute publishes both the *Manual on Disposal of Refinery Wastes*¹⁰ and the *Technical Data Book-Petroleum Refining*¹¹. Tables 1.5, 1.6 and 1.7 are typical of the tables that can be found in the former on p. 2-4, and p. 13-11.

If you know the chemical formula for a pure compound, you can look up many of its physical properties in standard reference books, such as

- (a) Perry's *Chemical Engineers' Handbook*¹²
- (b) *Handbook of Physics and Chemistry*¹³
- (c) Lange's *Handbook*¹⁴
- (d) *The Properties of Gases and Liquids*.¹⁵

Also, specialized texts in your library frequently list properties of compounds. For example, the book *Fuel Flue Gases*¹⁶ lists considerable data on gas mixtures which are primarily of concern in the gas utility field. Appendix D in this text tabulates the chemical formula, molecular weight, melting point, boiling point, etc., for most, but not all, of the compounds involved in the problems you will find at the end of the chapters.

Many of the materials we talk about and use every day are not pure com-

¹⁰American Petroleum Institute, Div. of Refining, 1271 Ave. of the Americas, New York, N.Y., 1969.

¹¹*ibid.*, 2nd ed., 1970.

¹²J. H. Perry, ed, *Chemical Engineers' Handbook*, 4th ed., McGraw-Hill, New York, 1963.

¹³*Handbook of Chemistry and Physics*, Chemical Rubber Publishing Co., Cleveland, Ohio, annually.

¹⁴N. A. Lange, *Handbook of Chemistry*, McGraw-Hill, New York, annually.

¹⁵R. C. Reid and T. K. Sherwood, *The Properties of Gases and Liquids*, 2nd ed., McGraw-Hill, New York, 1966.

¹⁶*Fuel Flue Gases*, American Gas Association, New York, 1941.

pounds, and it is considerably more trouble to obtain information about the properties of these materials. Fortunately, for materials such as coal, coke, petroleum products, and natural gas—which are the main sources of energy in this country—tables and formulas are available in reference books and handbooks which list some of the specific gross properties of these mixtures. Some typical examples of natural gas analyses and ultimate analyses of petroleum and petroleum products as shown in Tables 1.5, 1.6, 1.7, 1.8, and 1.9 point out the variety of materials that can be found.

TABLE 1.5 DISSOLVED SOLIDS IN FRESH WATERS OF THE UNITED STATES

Component	Concentration (mg/l)		
	In 5% of the waters is less than	In 50% of the waters is less than	In 95% of the waters is less than
Total dissolved solids	72.0	169.0	400.0
Bicarbonate, HCO_3	40.0	90.0	180.0
Sulfate, SO_4	11.0	32.0	90.0
Chloride, Cl	3.0	9.0	170.0
Nitrate, NO_3	0.2	0.9	4.2
Calcium, Ca	15.0	28.0	52.0
Magnesium, Mg	3.5	7.0	14.0
Sodium, Na, and Potassium, K	6.0	10.0	85.0
Iron, Fe	0.1	0.3	0.7

SOURCE: *Manual on Disposal of Refinery Wastes*, Amer. Pet. Inst., Div. of Refining, pp. 2-4; New York, 1969.

TABLE 1.6 CHARACTERISTICS OF WATERS WHICH SUPPORT A VARIED AND PROFUSE FISH FAUNA—A CRITERION OF QUALITY

Characteristic	Value of Characteristic		
	In 5% of the waters is less than	In 50% of the waters is less than	In 95% of the waters is less than
pH value	6.7	7.6	8.3
Concentration (mg/l)			
Dissolved oxygen, O_2	5.0	6.8	9.8
Carbon dioxide, CO_2			
Free	0.1	1.5	5.0
Fixed	8.0	45.0	95.0
Ammonia, NH_3	0.5	1.5	2.5
Mho (25°C)			
Specific conductivity	$(50)(10^{-6})$	$(270)(10^{-6})$	$(1100)(10^{-6})$

SOURCE: *Manual on Disposal of Refinery Wastes*, Amer. Pet. Inst., Div. of Refining, pp. 2-4; New York, 1969.

formation about the sources of energy in such as coal, coke, sources of energy in books and handbooks and hand-mixtures. Some sources of petroleum and some point out the

STATES

mg/l)

In 95% of the waters is less than

400.0
180.0
90.0
170.0
4.2
52.0
14.0
85.0
0.7

Inst., Div. of Refining,

VARIED

In 95% of the waters is less than

8.3

9.8

5.0

95.0

2.5

(1100)(10⁻⁶)

Inst., Div. of Refining,

TABLE 1.7 REFINERY BIOLOGICAL TREATMENT UNIT FEED CHARACTERISTICS

	Ranges reported*
Chlorides, mg/l	200-960
COD, mg/l	140-640
BOD ₅ , mg/l	97-280
Suspended solids, mg/l	80-450
Alkalinity, mg/l as CaCO ₃	77-210
Temperature, °F	69-100
Ammonia nitrogen, mg/l	56-120
Oil, mg/l	23-130
Phosphate, mg/l	20-97
Phenolics, mg/l	7.6-61
pH	7.1-9.5
Sulfides, mg/l	1.3-38
Chromium, mg/l	0.3-0.7

SOURCE: *Manual on Disposal of Refinery Wastes*, Amer. Pet. Inst., Div. of Refining, pp. 2-4. New York, 1969.

*Values are the averages of the minima and maxima reported by 12 refineries treating total effluent. Individual plants have reported data well outside many of these ranges.

TABLE 1.8 TYPICAL DRY GAS ANALYSES

Type	Analysis (vol. %—excluding water vapor)									
	CO ₂	O ₂	N ₂	CO	H ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₅ H ₁₂ +
Natural gas	6.5					77.5	16.0			
Natural gas, dry*	0.2		0.6			99.2				
Natural gas, wet*	1.1					87.0	4.1	2.6	2.0	3.4
Natural gas, sour† (H ₂ S 6.4)						58.7	16.5	9.9	5.0	3.5
Butane						2.0	3.5	75.4	n-butane 18.1 isobutane	
Illuminants										
Reformed refinery oil	2.3	0.7	4.9	20.8	49.8	12.3	5.5		3.7	
Coal gas, by-product	2.1	0.4	4.4	13.5	51.9	24.3			3.4	
Producer gas	4.5	0.6	50.9	27.0	14.0	3.0				
Blast furnace gas	5.4	0.7	8.3	37.0	47.3	1.3				
Sewage gas	22.0		6.0		2.0	68.0				

SOURCE: *Fuel Flue Gases*, American Gas Association, New York, 1941, p. 20.

*Dry gas contains much less propane (C₃H₈) and higher hydrocarbons than wet gas does.

†Sour implies that the gas contains significant amounts of hydrogen sulfide.

TABLE 1.9 ULTIMATE ANALYSIS OF PETROLEUM CRUDE

Type	Sp gr	At °C	Weight %				
			C	H	N	O	S
Pennsylvania	0.862	15	85.5	14.2			
Humbolt, Kan.	0.921		85.6	12.4			0.37
Beaumont, Tex.	0.91		85.7	11.0	2.61		0.70
Mexico	0.97	15	83.0	11.0	1.7		
Baku, U.S.S.R.	0.897		86.5	12.0			1.5

SOURCE: Data from W. L. Nelson, *Petroleum Refinery Engineering*, 4th ed., McGraw-Hill, New York, 1958.

Since petroleum and petroleum products represent complex mixtures of hydrocarbons and other organic compounds of various types together with various impurities, if the individual components cannot be identified, then the mixture is treated as a uniform compound. Usually, the components in natural gas can be identified, and thus their individual physical properties can be looked up in the reference books mentioned above or in the Appendix in this text. As will be discussed in Chap. 3 under gases, many times the properties of a pure gas when mixed with another gas are the sum of the properties of the pure components. On the other hand, liquid petroleum crude oil and petroleum fractions are such complicated mixtures that their physical properties are hard to estimate from the pure components (even if known) unless the mixture is very simple. As a result of the need for methods of predicting the behavior of petroleum stocks, empirical correlations have been developed in recent years for many of the physical properties we want to use. These correlations are based upon the °API, the Universal Oil Products characterization factor *K*, the boiling point, and the apparent molecular weight of the petroleum fraction. These parameters in turn are related to five or six relatively simple tests of the properties of oils. Some of the details of these tests, the empirical parameters, and the properties that can be predicted from these parameters will be found in the *API Technical Data Book* and in Appendix K.

1.7 *Technique of solving problems*

If you can form good habits of problem solving early in your career, you will save considerable time and avoid many frustrations in all aspects of your work, in and out of school. In solving material and energy balance problems, you should

- (a) Read the available information through thoroughly and understand what is required for an answer. Sometimes, as in life, the major obstacle is to find out what the problem really is.

CRUDE

Weight %

N	O	S
2.61	0.37	
1.7	0.70	
	1.5	

Engineering, 4th ed., McGraw-Hill,

ent complex mixtures of various types together with must be identified, then the components in natural properties can be looked Appendix in this text. As the properties of a pure gas expert the pure components and petroleum fractions properties are hard to estimate mixture is very simple. The behavior of petroleum recent years for many of tions are based upon the factor K , the boiling point, action. These parameters of the properties of oils. meters, and the properties and in the *API Technical*

in your career, you will all aspects of your work, balance problems, you

coughly and understand life, the major obstacle

- (b) Determine what additional data are needed, if any, and obtain this information.
- (c) Draw a simplified picture of what is taking place and write down the available data. You may use boxes to indicate processes or equipment, and lines for the flow streams.
- (d) Pick a basis on which to start the problem, as discussed in Sec. 1.3-6.
- (e) If a chemical equation is involved, write it down and make sure it is balanced.

By this time you should have firmly in mind what the problem is and a reasonably clear idea of what you are going to do about it; however, if you have not seen exactly how to proceed from what is available to what is wanted, then you should

- (f) Decide what formulas or principles are governing in this specific case and what types of calculations and intermediate answers you will need to get the final answer. If alternative procedures are available, try to decide which are the most expedient. If an unknown cannot be found directly, give it a letter symbol, and proceed as if you knew it.
- (g) Make the necessary calculations in good form, being careful to check the arithmetic and units as you proceed.
- (h) Determine whether the answer seems reasonable in view of your experience with these types of calculations.

Problems which are long and involved should be divided into parts and attacked systematically piece by piece.

If you can assimilate this procedure and make it a part of yourself—so that you do not have to think about it step by step—you will find that you will be able to materially improve your speed, performance, and accuracy in problem solving.

The major difference between problems solved in the classroom and in the plant lies in the quality of the data available for the solution. Plant data may be of poor quality, inconclusive, inadequate, or actually conflicting, depending on the accuracy of sampling, the type of analytical procedures employed, the skill of the technicians in the operation of analytical apparatus, and many other factors. The ability of an engineer to use the stoichiometric principles for the calculation of problems of material balance is only partly exercised in the solution of problems, even of great complexity, if solved from adequate and appropriate data. The remainder of the test lies in his ability to recognize poor data, to request and obtain usable data, and, if necessary, to make accurate estimates in lieu of incorrect or insufficient data.¹⁷

¹⁷B. E. Lauer, *The Material Balance*, Work Book Edition, 1954, p. 89.

1.8 The chemical equation and stoichiometry

As you already know, the chemical equation provides a variety of qualitative and quantitative information essential for the calculation of the combining weights of materials involved in a chemical process. Take, for example, the combustion of heptane as shown below. What can we learn from this equation?



First, make sure that the equation is balanced. Then we can see that 1 mole (*not* lb_m or kg) of heptane will react with 11 moles of oxygen to give 7 moles of carbon dioxide plus 8 moles of water. These may be lb moles, g moles, kg moles, or any other type of mole, as shown in Fig. 1.13. One mole of CO₂ is formed from each $\frac{1}{7}$ mole of C₇H₁₆. Also, 1 mole of H₂O is formed with each $\frac{7}{8}$ mole of CO₂. Thus the equation tells us in terms of moles (*not* mass) the ratios among reactants and products.

Stoichiometry (stoi-ki-om-e-tri)¹⁸ deals with the combining weights of elements and compounds. The ratios obtained from the numerical coefficients in the chemical equation are the stoichiometric ratios that permit you to calculate the moles of one substance as related to the moles of another substance in the chemical equation. If the basis selected is to be mass (lb_m, kg) rather than moles, you should use the following method in solving problems involving chemical equations: (a) Calculate the number of moles of the substance equivalent to the basis using the molecular weight; (b) change this quantity into the moles of the desired product or reactant by multiplying by the proper stoichiometric ratio, as determined by the chemical equation; and (c) then change the moles of product or reactant to a weight basis. These steps are indicated in Fig. 1.14 for the above reaction. You can combine these steps in a single dimensional equation, as shown in the examples below, for ease of slide rule calculations; however, the order of operations should be kept the same.

An assumption implicit in the above is that the reaction takes place exactly as written in the equation and proceeds to 100 percent completion. When reactants, products, or degree of completion of the actual reaction differ from the assumptions of the equation, additional data must be made available to indicate the actual status or situation.

EXAMPLE 1.22 Stoichiometry

In the combustion of heptane, CO₂ is produced. Assuming that it is desired to produce 500 lb of dry ice per hour and that 50 percent of the CO₂ can be converted into dry ice, how many pounds of heptane must be burned per hour?

¹⁸From the Greek *stoicheion*, basic constituent, and *metrein*, to measure.

Chap. I

C_7H_{16}	+	$11O_2$	\rightarrow	$7CO_2$	+	$8H_2O$
<i>Qualitative information</i>						
heptane	reacts with	oxygen	to give	carbon dioxide	and	water
<i>Quantitative information</i>						
1 molecule of heptane	reacts with	11 molecules of oxygen	to give	7 molecules of carbon dioxide	and	8 molecules of water
6.023×10^{23} molecules of C_7H_{16}	+	$11(6.023 \times 10^{23})$ molecules of O_2	\rightarrow	$7(6.023 \times 10^{23})$ molecules of CO_2	+	$8(6.023 \times 10^{23})$ molecules of H_2O
1 g mole of C_7H_{16}	+	11 g moles of O_2	\rightarrow	7 g moles of CO_2	+	8 g moles of H_2O
1 kg mole of C_7H_{16}	+	11 kg moles of O_2	\rightarrow	7 kg moles of CO_2	+	8 kg moles of H_2O
1 lb mole of C_7H_{16}	+	11 lb moles of O_2	\rightarrow	7 lb moles of CO_2	+	8 lb moles of H_2O
1 ton mole of C_7H_{16}	+	11 ton moles of O_2	\rightarrow	7 ton moles of CO_2	+	8 ton moles of H_2O
1(100) g of C_7H_{16}	+	$11(32)$ g of O_2	$=$	7(44) g of CO_2	+	8(18) g of H_2O
<u>100 g</u>		<u>352 g</u>		<u>308 g</u>		<u>144 g</u>
			$=$		<u>452 g</u>	
			$=$		<u>452 kg</u>	
			$=$		<u>452 ton</u>	
			$=$		<u>452 lb</u>	

Fig. 1.13. The chemical equation.

Basis: 10.0 lb C_7H_{16}	
Component	Mol. wt
C_7H_{16}	100.1
O_2	32.0
CO_2	44.0
H_2O	18.0
1 lb mole	7 lb mole
C_7H_{16}	$+ 11O_2 \rightarrow 7CO_2 + 8H_2O$
$\frac{10.0 \text{ lb } C_7H_{16}}{100.1 \text{ lb } C_7H_{16}} = 0.100 \text{ lb mole } C_7H_{16} \rightarrow$	$\frac{0.700 \text{ lb mole } CO_2}{1 \text{ lb mole } CO_2} = 30.8 \text{ lb } CO_2$
$44.0 \text{ lb } CO_2$	
10.0 lb C_7H_{16} yields 30.8 lb CO_2	

Fig. 1.14. Stoichiometry.

Solution:

Basis: 500 lb dry ice (or 1 hr)

Mol. wt heptane = 100

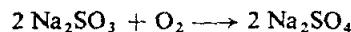
Chemical equation as in Fig. 1.13

500 lb dry ice	1 lb CO ₂	1 lb mole CO ₂	1 lb mole C ₇ H ₁₆
	0.5 lb dry ice	44 lb CO ₂	7 lb mole CO ₂
			$\frac{100 \text{ lb C}_7\text{H}_{16}}{1 \text{ lb mole C}_7\text{H}_{16}} = 325 \text{ lb C}_7\text{H}_{16}$

Since the basis of 500 lb dry ice is identical to 1 hr, 325 lb of C₇H₁₆ must be burned per hour. Note that pounds are converted first to moles, then the chemical equation is applied, and finally moles are converted to pounds again for the final answer.

EXAMPLE 1.23 Stoichiometry

Corrosion of pipes in boilers by oxygen can be alleviated through the use of sodium sulfite. Sodium sulfite removes oxygen from boiler feedwater by the following reaction:



How many pounds of sodium sulfite are theoretically required to remove the oxygen from 8,330,000 lb of water (10⁶ gal) containing 10.0 parts per million (ppm) of dissolved oxygen and at the same time maintain a 35 percent excess of sodium sulfite? See Fig. E1.23.

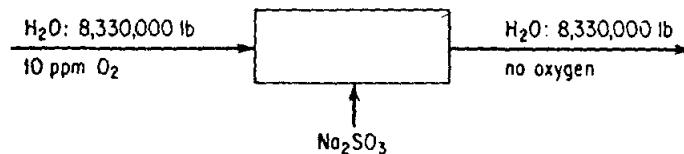


Fig. E1.23.

Solution:

Additional data: mol. wt of Na₂SO₃ is 126.

Chemical equation: 2 Na₂SO₃ + O₂ → 2 Na₂SO₄

Basis: 8,330,000 lb H₂O with 10 ppm O₂ or 83.3 lb O₂

8,330,000 lb H ₂ O	10 lb O ₂	$\frac{10 \text{ lb O}_2}{(1,000,000 - 10 \text{ lb O}_2) \text{ lb H}_2\text{O}}$	= 83.3 lb O ₂
effectively same as 1,000,000			

8,330,000 lb H ₂ O	10 lb O ₂	1 lb mole O ₂	2 lb mole's Na ₂ SO ₃
	$10^6 \text{ lb H}_2\text{O}$	32 lb O ₂	1 lb mole O ₂
			$\frac{126 \text{ lb Na}_2\text{SO}_3}{1 \text{ lb mole Na}_2\text{SO}_3} \cdot \frac{1.35}{1} = 885 \text{ lb Na}_2\text{SO}_3$

EXAMPLE 1.24 Stoichiometry

A limestone analyzes

CaCO ₃	92.89
MgCO ₃	5.41
Insoluble	1.70

- (a) How many pounds of calcium oxide can be made from 5 tons of this limestone?
 (b) How many pounds of CO₂ can be recovered per pound of limestone?
 (c) How many pounds of limestone are needed to make 1 ton of lime?

Solution:

Read the problem carefully to fix in mind exactly what is required. Lime will include all the impurities present in the limestone which remain after the CO₂ has been driven off. Next draw a picture of what is going on in this process. See Fig. E1.24.

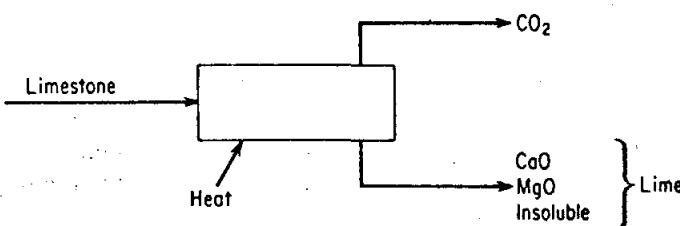
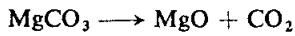
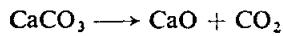


Fig. E1.24.

To complete the preliminary analysis you need the following chemical equations:



Additional data are

Mol. wt	CaCO ₃	MgCO ₃	CaO	MgO	CO ₂
	100	84.3	56.0	40.3	44

Basis: 100 lb limestone

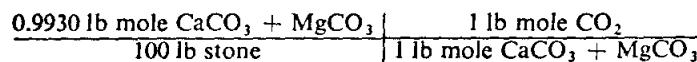
This basis was selected because lb = %.

comp.	lb = %	lb mole	lime	lb	CO ₂ (lb)
CaCO ₃	92.89	0.9289	CaO	52.0	40.9
MgCO ₃	5.41	0.0641	MgO	2.59	2.82
Insol.	1.70		Insol.	1.70	
Total	100.00	0.9930	Total	56.3	43.7

Note that the total pounds of products equal the 100 lb of entering limestone. Now to calculate the quantities originally asked for:

$$(a) \text{ CaO produced} = \frac{52.0 \text{ lb CaO}}{100 \text{ lb stone}} \times 2000 \text{ lb} \times \frac{5 \text{ ton}}{1 \text{ ton}} = 5200 \text{ lb CaO}$$

(b) $\text{CO}_2 \text{ recovered} = \frac{43.7 \text{ lb CO}_2}{100 \text{ lb stone}} = 0.437 \text{ lb, or,}$



$$\boxed{\frac{44 \text{ lb CO}_2}{1 \text{ lb mole CO}_2}} = 0.437 \text{ lb}$$

(c) limestone required = $\frac{100 \text{ lb stone}}{56.3 \text{ lb lime}} \mid \frac{2000 \text{ lb}}{1 \text{ ton}} = 3560 \text{ lb stone}$

In industrial reactions you will rarely find exact stoichiometric amounts of materials used. To make a desired reaction take place or to use up a costly reactant, excess reactants are nearly always used. This excess material comes out together with, or perhaps separately from, the product—and sometimes can be used again. Even if stoichiometric quantities of reactants are used, but if the reaction is not complete or there are side reactions, the products will be accompanied by unused reactants as well as side-products or reactants. In these circumstances some new definitions must be understood:

- (a) *Limiting reactant* is the reactant which is present in the smallest stoichiometric amount.
- (b) *Excess reactant* is a reactant in excess of the limiting reactant. The *percent excess* of a reactant is based on the amount of any excess reactant above the amount required to react with the limiting reactant according to the chemical equation, or

$$\% \text{ excess} = \frac{\text{moles in excess}}{\text{moles required to react with limiting reactant}} \times 100$$

where the moles in excess frequently can be calculated as the total available moles of a reactant less the moles required to react with the limiting reactant. A common term, *excess air*, is used in combustion reactions; it means the amount of air available to react that is in excess of the air theoretically required to *completely* burn the combustible material. The *required* amount of a reactant is established by the limiting reactant and is for all other reactants the corresponding stoichiometric amount. Even if only part of the limiting reactant actually reacts, the required and excess quantities are based on the entire amount of the limiting reactant.

Three other terms that are used in connection with chemical reactions have less clear-cut definitions: conversion, selectivity, and yield. No universally agreed upon definitions exist for these terms—in fact, quite the contrary. Rather than cite all the possible usages of these terms, many of which conflict, we shall define them as follows:

- (c) *Conversion* is the fraction of the feed or some material in the feed that is converted into products. What the basis in the feed is and into what

products the basis is being converted must be clearly specified or endless confusion results. Conversion is somewhat related to the *degree of completion* of a reaction, which is usually the percentage or fraction of the limiting reactant converted into products.

- Selectivity* expresses the amount of a desired product as a fraction or percent of the theoretically possible amount from the feed material converted. Often the quantity defined here as selectivity is called efficiency, conversion efficiency, specificity, yield, ultimate yield, or recycle yield.
- Yield*, for a single reactant and product, is the weight or moles of final product divided by the weight or moles of initial reactant (P lb of product A per R lb of reactant B). If more than one product and more than one reactant are involved, the reactant upon which the yield is to be based must be clearly stated.

The employment of these concepts can best be illustrated by examples.

EXAMPLE 1.25 Limiting reactant and incomplete reaction

Antimony is obtained by heating pulverized stibnite with scrap iron and drawing off the molten antimony from the bottom of the reaction vessel:



0.600 kg of stibnite and 0.250 kg of iron turnings are heated together to give 0.200 kg of Sb metal.

Calculate:

- The limiting reactant.
- The percentage of excess reactant.
- The degree of completion (fraction).
- The percent conversion.
- The selectivity (percent).
- The yield.

Solution:

The molecular weights needed to solve the problem and the g moles forming the basis are

	<i>g</i>	<i>mol. wt</i>	<i>g mole</i>
Sb_2S_3	600	339.7	1.77
Fe	250	55.8	4.48
Sb	200	121.8	1.64
FeS		87.9	

- To find the limiting reactant, we examine the chemical reaction equation and note that if 1.77 g mole of Sb_2S_3 reacts, it requires $3(1.77) = 5.31$ g mole of Fe, whereas if 4.48 g mole of Fe react, it requires $(4.48/3) = 1.49$ g mole of Sb_2S_3 to be

available. Thus Fe is present in the smallest stoichiometric amount and is the limiting reactant; Sb_2S_3 is the excess reactant.

(b) The percentage of excess reactant is:

$$\% \text{ excess} = \frac{(1.77 - 1.49)}{1.49}(100) = 18.8\% \text{ excess } Sb_2S_3$$

(c) Although Fe is the limiting reactant, not all the limiting reactant reacts. We can compute from the 1.64 g moles of Sb how much Fe actually does react:

$$\frac{1.64 \text{ g mole Sb}}{2 \text{ g mole Sb}} \mid \frac{3 \text{ g mole Fe}}{1 \text{ g mole Fe}} = 2.46 \text{ g mole Fe}$$

If by the fractional degree of completion is meant the fraction conversion of Fe to FeS , then

$$\text{fractional degree of completion} = \frac{2.46}{4.48} = 0.55$$

(d) The percent conversion can be arbitrarily based on the Sb_2S_3 if our interest is mainly in the stibnite:

$$\frac{1.64 \text{ g mole Sb}}{2 \text{ g mole Sb}} \mid \frac{1 \text{ g mole } Sb_2S_3}{3 \text{ g mole } Sb_2S_3} = 0.82 \text{ g mole } Sb_2S_3$$

$$\% \text{ conversion of } Sb_2S_3 \text{ to Sb} = \frac{0.82}{1.77}(100) = 46.3\%$$

(e) The selectivity refers to the conversion of Sb_2S_3 (we assume) based on the theoretical amount that can be converted, 1.49 g mole:

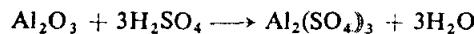
$$\text{selectivity} = \frac{0.82}{1.49}(100) = 55\%$$

(f) The yield will be stated as kilograms of Sb formed per kilogram of Sb_2S_3 that was fed to the reaction:

$$\text{yield} = \frac{0.200 \text{ kg Sb}}{0.600 \text{ kg } Sb_2S_3} = \frac{1}{3} \frac{\text{kg Sb}}{\text{kg } Sb_2S_3}$$

EXAMPLE 1.26 Limiting reactant and incomplete reactions

Aluminum sulfate can be made by reacting crushed bauxite ore with sulfuric acid, according to the following equation:



The bauxite ore contains 55.4 weight percent aluminum oxide, the remainder being impurities. The sulfuric acid solution contains 77.7 percent H_2SO_4 , the rest being water.

To produce crude aluminum sulfate containing 1798 lb of pure aluminum sulfate, 1080 lb of bauxite ore and 2510 lb of sulfuric acid solution are used.

- (a) Identify the excess reactant.
- (b) What percentage of the excess reactant was used?
- (c) What was the degree of completion of the reaction?

amount and is the limiting

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bie Fe

ction conversion of Fe to

$= 0.55$

the Sb_2S_3 if our interest is

ie Sb_2S_3

$= 46.3\%$

we are based on the

per kilogram of Sb_2S_3 that

exite ore with sulfuric acid,

H_2O

xide, the remainder being
nt H_2SO_4 , the rest being

of pure aluminum sulfate,
on are used.

Solution:

The pound moles of substances forming the basis of the problem can be computed
as follows:

$$\frac{1798 \text{ lb } \text{Al}_2(\text{SO}_4)_3}{342.1 \text{ lb } \text{Al}_2(\text{SO}_4)_3} \mid \frac{1 \text{ lb mole } \text{Al}_2(\text{SO}_4)_3}{1 \text{ lb mole } \text{Al}_2(\text{SO}_4)_3} = 5.26 \text{ lb mole}$$

$$\frac{1080 \text{ lb bauxite}}{1 \text{ lb bauxite}} \mid \frac{0.554 \text{ lb } \text{Al}_2\text{O}_3}{101.9 \text{ lb } \text{Al}_2\text{O}_3} = 5.87 \text{ lb mole}$$

$$\frac{2510 \text{ lb acid}}{1 \text{ lb acid}} \mid \frac{0.777 \text{ lb } \text{H}_2\text{O}}{98.1 \text{ lb } \text{H}_2\text{SO}_4} = 19.88 \text{ lb mole}$$

(a) Assume that Al_2O_3 is the limiting reactant. Then $5.87 \times 3 = 17.61$ lb mole
of H_2SO_4 would be required, which is present. Hence H_2SO_4 is the excess reactant.

(b) The $\text{Al}_2(\text{SO}_4)_3$ actually formed indicates that:

$$\frac{5.26 \text{ lb mole } \text{Al}_2(\text{SO}_4)_3}{1 \text{ lb mole } \text{Al}_2(\text{SO}_4)_3} \mid \frac{3 \text{ lb mole } \text{H}_2\text{SO}_4}{15.78 \text{ lb mole } \text{H}_2\text{SO}_4} = 15.78 \text{ lb mole } \text{H}_2\text{SO}_4 \text{ was used}$$

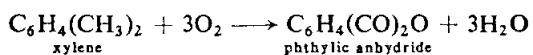
$$\frac{15.78}{19.88} (100) = 79.4\%$$

(c) The fractional degree of completion was

$$\frac{5.26}{5.87} = 0.90$$

EXAMPLE 1.27 The meaning of yield

Your assistant has rushed into your office with a glowing tale of a yield of 108
percent in the manufacture of phthalic anhydride from xylene by the reaction



Should you compliment him or deflate his accomplishment?

Solution:

If the claim is that 108 lb of phthalic anhydride (Ph) are produced per 100 lb
of xylene (X), the selectivity is not especially good.

Basis: 100 lb xylene

$$\frac{100 \text{ lb X}}{106 \text{ lb X}} \mid \frac{1 \text{ lb mole X}}{1 \text{ lb mole X}} = 0.944 \text{ lb mole X}$$

$$\frac{108 \text{ lb Ph}}{148 \text{ lb Ph}} \mid \frac{1 \text{ lb mole X}}{1 \text{ lb mole Ph}} = 0.730 \text{ lb mole Ph}$$

$$(100) \frac{0.730 \text{ lb mole X}}{0.944 \text{ lb mole Ph}} = 77.3\%$$

If the claim is that 108 percent selectivity is achieved, the claim must be erroneous.

You should remember that the chemical equation does not indicate the
true mechanism of the reaction or how fast or to what extent the reaction will

take place. For example, a lump of coal in air will sit unaffected at room temperature, but at higher temperatures it will readily burn. All the chemical equation indicates is the stoichiometric amounts required for the reaction and obtained from the reaction if it proceeds in the manner in which it is written. Also remember to make sure that the chemical equation is balanced before using it.

1.9 Digital computers in solving problems

High-speed digital computers have made a considerable impact on problem solving both in industry and in education. There is no question that a good fraction of today's engineering graduates (who may well be working as engineers in the year 2000) will see the use of computers in their technical work expand dramatically. Consequently, you should know how to use computers in your computations and if possible apply your knowledge to solving some of the more complicated problems in this book. Many routes of approach are used in engineering education to familiarize students with the role of the computer in solving engineering problems. On the one hand, library computer programs ("canned" programs) can be employed to solve specific types of problems, absolving you of most of the programming chores. On the other hand, you can prepare the complete computer code to solve a problem from scratch. Problems marked with an asterisk in this book indicate problems that are especially appropriate for computer solutions by canned programs, and at the end of each chapter are a few problems for which the complete computer program is to be written. Wide differences in computers and the proliferation of programming languages have made the inclusion of detailed computer codes in this text less than particularly meaningful except for one or two solved examples.

You should not attempt to justify the use of a computer as a time-saving device per se when working with a single problem. It is much better to look on the computer and the program as a tool which will enable you, after some experience, to solve complex problems expediently and which may save time and trouble for a simple problem, but may not. Modern, high-speed computers can eliminate repetitive, time-consuming routine calculations that would take years to complete with a slide rule or a desk calculator. Also, computers can essentially eliminate numerical errors once the programs are verified. Typical problems encountered in this text that are most susceptible to computer solution are (a) the solution of simultaneous equations, (b) the solution of one or more nonlinear equations, (c) statistical data fitting, and (d) various types of iterative calculations. Typical industrial problems routinely solved are:

- (a) Heat and mass transfer coefficient correlations.
- (b) Correlation of chemical structure with physical properties.
- (c) Analysis of gaseous hydrocarbon mixtures.

ected at room temperature, the chemical equations of the reaction and which it is written, balanced before using

impact on problem solution that a good working as engineers technical work expand computers in your some of the more often are used in engineering computer in solving programs ("canned" programs, saving you of time, etc., the commands marked with an appropriate for common chapter are a few to be written. Wide programming languages have less than particularly

as a time-saving can better to look on, after some experience may save time and speed computers can it would take years computers can essentially

Typical problems for solution are (a) one or more nonlinear equations of iterative calculations.

properties.

- (d) Particle size analysis.
- (e) Granular fertilizer formulation.
- (f) Evaluation of infrared analysis.
- (g) Optimum operating conditions.
- (h) Comprehensive economic evaluations.
- (i) Chemical-biological coordination and correlation.
- (j) Vapor-liquid equilibrium calculations.
- (k) Mass spectrometer matrix inversion.
- (l) Equipment design.
- (m) Preparation of tables for platinum resistance thermometer.

One of the most significant changes in the use of computers has been in the meaning of the word *solution*. It is widely recognized that a mathematical closed-form solution, while unquestionably pleasing aesthetically and relatively universal in application, may not necessarily be interpreted easily. Curves and graphs may constitute a more desirable format for a solution, but a computer and a program essentially consist of a procedure whereby a numerical answer can be obtained to a specific problem. Repetitive solutions must be obtained to prepare tables, graphs, etc., but these, of course, can be prepared automatically with an appropriate computer code.

The use of a guaranteed canned computer program saves the user considerable time and effort relative to programming his own code. Every major computer center has, or should have, an extensive subroutine library, often stored on an on-line library tape, for effecting extensive numerical calculations and/or simulation. Of course, such programs may still be fallible. When an unexpected answer appears, the user of the program must know enough about the problem to be able to account for the discrepancy. Often the trouble lies in the interpretation of what the program is intended to do, or it is caused by improper entry of parameters or data. If you can avoid these difficulties, you can concentrate on stating the problem correctly and estimating the expected answer; the mechanics of obtaining the answer would be left to the computer. Considerably more complex and realistic problems can be solved, furnishing a deeper understanding of the principles involved, if the latter are not obscured by concern with the problem-solving technique.

If you do use the computer, you will be forced to be far more precise than you have been accustomed to being in the past. Because of the nature of the computer languages, i.e., the necessity for very precise grammar and punctuation, it is unusual to solve completely correctly an engineering problem on the first approach. Experience has shown that, even in the most carefully prepared programs, there will be a certain percentage of errors, which may include programming logic, actual coding, data preparation, or the card punching. For this reason, processing of a problem requires prior program verification in which a computer run of a sample problem is executed for which the results are known, can be estimated, or can be calculated by manual methods. To facilitate such a

check-out as well as to guard against undetected and possible future data errors, a good program should include self-checking features strategically located in the program. If physically impossible conditions are created, the calculation should be stopped and the accumulated results printed out. You no doubt will require many tries before achieving success. The turn-around time, i.e., the time elapsed between submission of a program to the computer and its return for checking and possible resubmission in the case of error, must be fairly short if problems are to be solved in a reasonable amount of time. The use of remote time-sharing terminals can assist in the speedy resolution of programming errors. You will also be forced to think more logically and in greater detail than you have been accustomed to doing, if you do your own programming, about the problem and how to solve it. The computer is a rigid task master that requires precision in the statement of the problem and the flow of information needed to effect a solution. No ambiguity is permitted.

WHAT YOU SHOULD HAVE LEARNED FROM THIS CHAPTER

1. You should have memorized the common conversion units.
2. You should be able to convert units from the American engineering system to the cgs and SI systems and vice versa with ease, and understand the significance of g_c .
3. You should understand *moles, molecular weights, density, specific gravity, mole and weight fraction, temperature, and pressure*, and be able to work problems involving these concepts.
4. You should have well in mind the proper approach to problem solving and be able to effectively put into practice the principles discussed in the chapter.
5. You should know how to apply the principles of stoichiometry to problems involving chemical reactions.

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PROBLEMS

- 1.1. Plot a graph of the relationship between the number of moles of water and the number of moles of carbon dioxide in a mixture of the two gases at 25°C and 1 atm. Assume the total pressure is constant.
- 1.2. Plot a graph of the relationship between the number of moles of water and the number of moles of carbon dioxide in a mixture of the two gases at 25°C and 1 atm. Assume the total pressure is constant.

the future data errors, which are generally located in the time calculation should no doubt will require i.e., the time elapsed to return for checking. It is short if problems are remote time-sharing timing errors. You will than you have been about the problem and requires precision in on needed to effect a

IS CHAPTER

units.

in engineering system
understand the significancedensity, specific gravity,
and be able to workproblem solving and
discussed in the chapter.
stoichiometry to problems

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PROBLEMS¹⁹

- 1.1. Electrically driven automobiles have been proposed as one solution to the problem of excessive automobile emissions in large cities. The Ghia Rowan is a sleek Italo-American prototype, an electrically driven system which converts the kinetic energy produced by the car's natural momentum into chemically stored battery energy via the car's braking system. The vehicle is roughly 3 m long, weighs 596 kg, and has a range of about 320 km at a speed of 41-43.5 mi/hr. Powered by two 9-hp electric motors placed under the rear seats and connected to the control box, the Rowan has no differential, transmission system, or clutch assembly.

Rewrite the specifications given so that they are all consistent in (a) the SI system and (b) in the American engineering system.

- 1.2. Hollywood (AP)—Blonde Jan Eastlund from Europe, a loser in last year's Miss Universe pageant, came up a winner this week with a studio contract and a starring role in her first movie. Jan speaks English with a slight accent, and is baffled by our units of measure. Asked for her measurements, she answered, "My bust is 92, waist 58, and my hips 92." A studio press agent gave an imitation of a

¹⁹An asterisk designates problems appropriate for computer solution. Also refer to the computer problems after Problem 1.104.

Chap. 1

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dense than water),

Material Balances

2

Conservation laws occupy a special place in science and engineering. Common statements of these laws take the form of "mass (energy) is neither created nor destroyed," "the mass (energy) of the universe is constant," "the mass (energy) of any isolated system is constant," or equivalent statements. To refute a conservation law, it would be sufficient to find just one example of a violation. However, Lavoisier and many of the scientists who followed in his path studied chemical changes quantitatively and found invariably that the sum of the weights of the substances entering into a reaction equaled the sum of the weights of the products of the reaction. Thus man's collective experience has been summed up and generalized as the law of the conservation of matter. The only "proof" we have for this law is of a negative type—never in our previous experience has any process been observed that upon thorough examination (including consideration of the precision of the data) has been found to contradict the principle. Of course, we must exclude processes involving nuclear transformations, or else extend our law to include the conservation of both energy and matter. (Insofar as we shall be concerned here, the word *process* will be taken to mean a series of physical operations on or physical or chemical changes in some specified material.)

In this chapter we shall discuss the principle of the conservation of matter and how it can be applied to engineering calculations, making use of the background information discussed in Chap. 1. Figure 2.0 shows the relations between the topics discussed in this chapter and the general objective of making material and energy balances. In approaching the solution of material balance problems, we shall first consider how to analyze them in order to clarify the method and

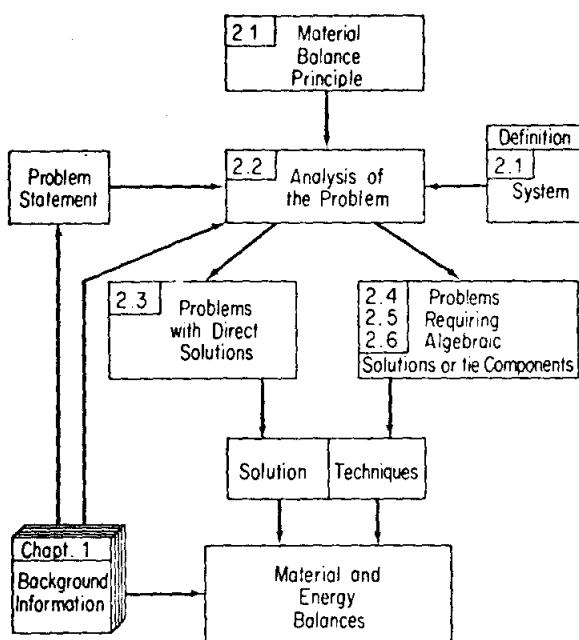


Fig. 2.0. Heirarchy of topics to be studied in this chapter (section numbers are in the upper left-hand corner of the boxes).

the procedure of solution. The aim will be to help you acquire a generalized approach to problem solving so that you may avoid looking upon each new problem, unit operation, or process as entirely new and unrelated to anything you have seen before. As you scrutinize the examples used to illustrate the principles involved in each section, explore the method of analysis, but avoid memorizing each example by rote, because, after all, they are only samples of the myriad problems which exist or could be devised on the subject of material balances. Most of the principles we shall consider are of about the same degree of complexity as the law of compensation devised by some unknown, self-made philosopher who said, "Things are generally made even somewhere or some place. Rain always is followed by a dry spell, and dry weather follows rain. I have found it an invariable rule that when a man has one short leg, the other is always longer!"

In working these problems you will find it necessary to employ some engineering judgment. You think of mathematics as an exact science. For instance, suppose that it takes 1 man 10 days to build a brick wall; then 10 men can finish it in 1 day. Therefore 240 men can finish the wall in 1 hr, 14,400 can do the job in 1 min, and with 864,000 men the wall will be up before a single brick is in place! Your password to success is the famous IBM motto: THINK.

2.1 Material balance

To take into account the law of the conservation of mass, we say that material balance is nothing more than an inventory of mass for a system over a period of time. The principle of the material balance applies to any system, whether it is a reaction:

$$\left\{ \begin{array}{l} \text{accumulation} \\ \text{within} \\ \text{the} \\ \text{system} \end{array} \right\} = \left\{ \begin{array}{l} \text{input} \\ \text{through} \\ \text{system} \\ \text{boundaries} \end{array} \right\}$$

In Eq. (2.1) the generation of mass is represented by accumulation and loss by chemical reaction. We must understand what is meant by a system. We should understand in reading this book that a system is a part of the world selected for study. It is defined by boundaries which are real or imaginary. A system is a time interval of any duration, from a few seconds to a differential time.

Equation (2.1) reduces to the basic equation of material balance if there is no generation or usage of material within the system.

and reduces further to $\dot{m}_i = \dot{m}_o$ if there is no generation or usage of material within the system,

If there is no flow in and out of the system, Eq. (2.1) reduces to the basic equation of material balance:

Inherent in the formalism of material balance is the concept of a system for which the balance is concerned. This is called a closed system. Fig. 2.1 shows a system in which there is no exchange of material with the surroundings.

2.1 Material balance

To take into account the flow of material in and out of a system, the generalized law of the conservation of mass is expressed as a material balance. A *material balance* is nothing more than an accounting for mass flows and changes in inventory of mass for a system. Equation (2.1) describes in words the principle of the material balance applicable to processes both with and without chemical reaction:

$$\left\{ \begin{array}{l} \text{accumulation} \\ \text{within} \\ \text{the} \\ \text{system} \end{array} \right\} = \left\{ \begin{array}{l} \text{input} \\ \text{through} \\ \text{system} \\ \text{boundaries} \end{array} \right\} - \left\{ \begin{array}{l} \text{output} \\ \text{through} \\ \text{system} \\ \text{boundaries} \end{array} \right\} + \left\{ \begin{array}{l} \text{generation} \\ \text{within} \\ \text{the} \\ \text{system} \end{array} \right\} - \left\{ \begin{array}{l} \text{consumption} \\ \text{within} \\ \text{the} \\ \text{system} \end{array} \right\} \quad (2.1)$$

In Eq. (2.1) the generation and consumption terms in this text refer to gain or loss by chemical reaction. The accumulation may be positive or negative. You should understand in reading the words in Eq. (2.1) that the equation refers to a time interval of any desired length, including a year, hour, or second or a differential time.

Equation (2.1) reduces to Eq. (2.2) for cases in which there is no generation (or usage) of material within the system,

$$\text{accumulation} = \text{input} - \text{output} \quad (2.2)$$

and reduces further to Eq. (2.3) when there is, in addition, no accumulation within the system,

$$\text{input} = \text{output} \quad (2.3)$$

If there is no flow in and out of the system and no generation (or usage), Eq. (2.1) reduces to the basic concept of the conservation of one species of matter within an enclosed isolated system.

Inherent in the formulation of each of the above balances is the concept of a system for which the balance is made. By *system* we mean any arbitrary portion or whole of a process as set out specifically by the engineer for analysis. Figure 2.1 shows a system in which flow and reaction take place; note particularly that

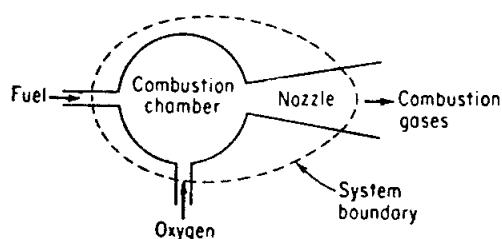


Fig. 2.1. A flow system with combustion.

the system boundary is formally circumscribed about the process itself to call attention to the importance of carefully delineating the system in each problem you work. In nearly all of the problems in this chapter the mass accumulation term will be zero; that is, primarily *steady-state* problems will be considered. (See Chap. 6 for cases in which the mass accumulation is not zero.) For a steady-state process we can say, "What goes in must come out." Illustrations of this principle can be found below.

Material balances can be made for a wide variety of materials, at many scales of size for the system and in various degrees of complication. To obtain a true perspective as to the scope of material balances, examine Figs. 2.2 and 2.3.

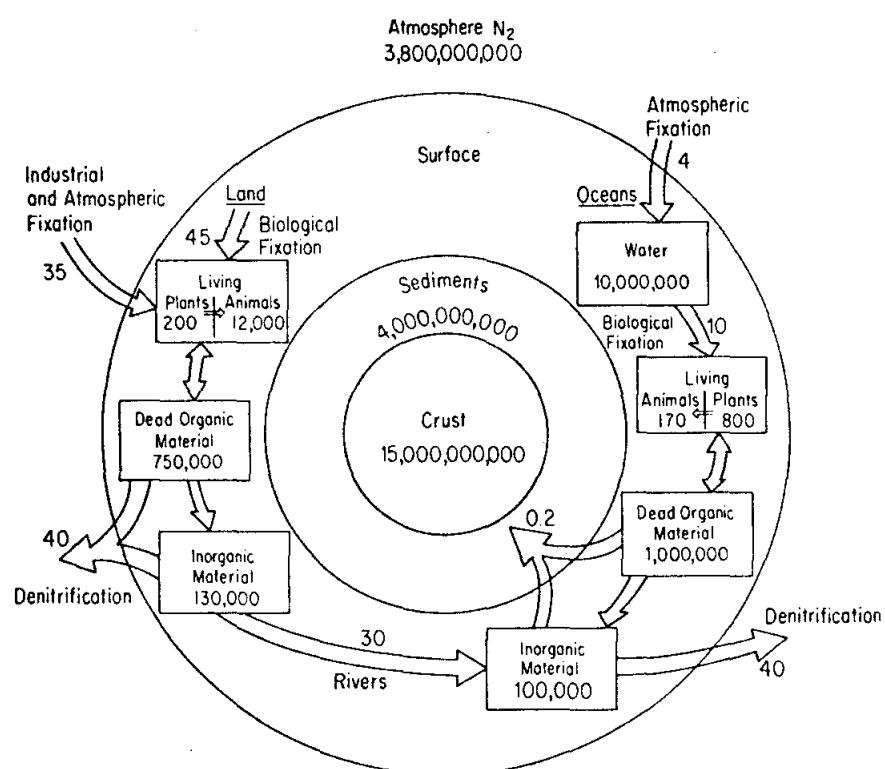


Fig. 2.2. Distribution and annual rates of transfer of nitrogen in the biosphere (in millions of metric tons).

Figure 2.2 delineates the distribution of nitrogen in the biosphere as well as the annual transfer rates, both in millions of metric tons. The two quantities known with high confidence are the amount of nitrogen in the atmosphere and the rate of industrial fixation. The apparent precision of the other figures reflects chiefly an effort to preserve indicated or probable ratios among different inventories. Because of the extensive use of industrially fixed nitrogen, the amount of nitro-

process itself to call them in each problem mass accumulation will be considered. zero.) For a steady- illustrations of this

materials, at many application. To obtain the Figs. 2.2 and 2.3.

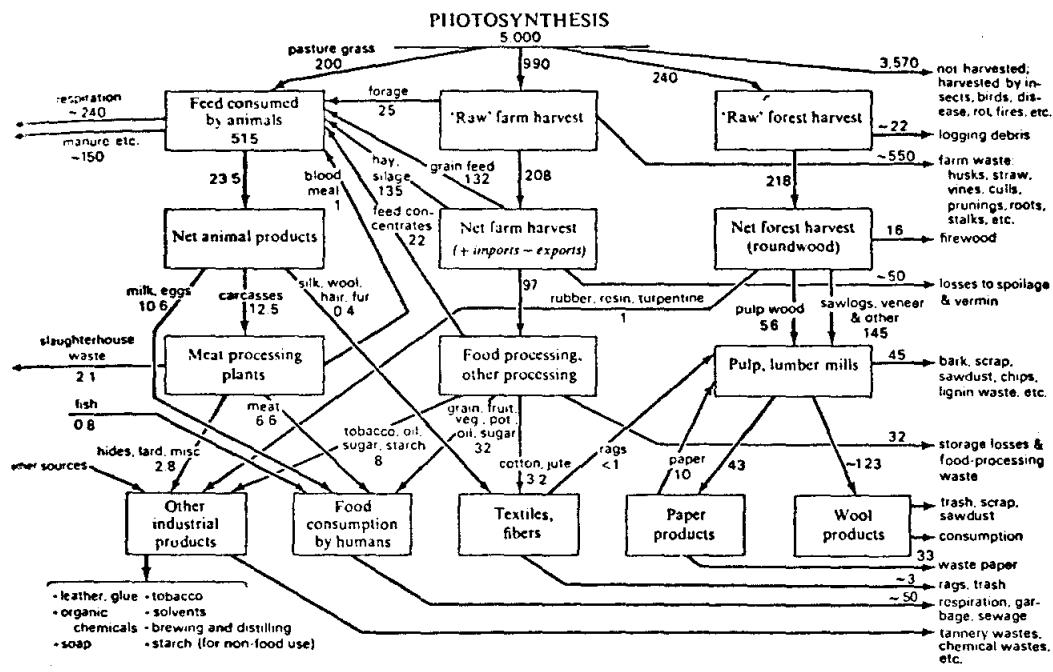


Fig. 2.3. Production and disposal of the products of photosynthesis. (Taken from A. V. Kneese, R. U. Ayres, and R. C. d'Arge, *Economics and the Environment*, Resources for the Future, Inc., 1755 Massachusetts Ave., Washington, D.C., 1970, p. 32.)

gen available to land plants may significantly exceed the nitrogen returned to the atmosphere by denitrifying bacteria in the soil. Figure 2.3 resulted from an analysis of the organic wastes arising from the processing of food and forest products. Changes in any of the streams can pinpoint sources of improvement or deterioration in environmental quality.

We should also note in passing that balances can be made on many other quantities in addition to mass. Balances on dollars are common (your bank statement, for example) as are balances on the number of entities, as in traffic counts, population balances, and social services.

In the process industries, material balances assist in the planning for process design, in the economic evaluation of proposed and existing processes, in process control, and in process optimization. For example, in the extraction of soybean oil from soybeans, you could calculate the amount of solvent required per ton of soybeans or the time needed to fill up the filter press, and use this information in the design of equipment or in the evaluation of the economics of the process. All sorts of raw materials can be used to produce the same end product and quite a few different types of processing can achieve the same end result so that

case studies (simulations) of the processes can assist materially in the financial decisions that must be made.

Material balances also are used in the hourly and daily operating decisions of plant managers. If there are one or more points in a process where it is impossible or uneconomical to collect data, then if sufficient other data are available, by making a material balance on the process it is possible to get the information you need about the quantities and compositions at the inaccessible location. In most plants a mass of data is accumulated on the quantities and compositions of raw materials, intermediates, wastes, products, and by-products that is used by the production and accounting departments and that can be integrated into a revealing picture of company operations. A schematic outline of the material balance control in the manufacture of phenol is shown in Fig. 2.4.

Process mass and energy balance

Basis: 2,000 lb. Phenol @ 60F

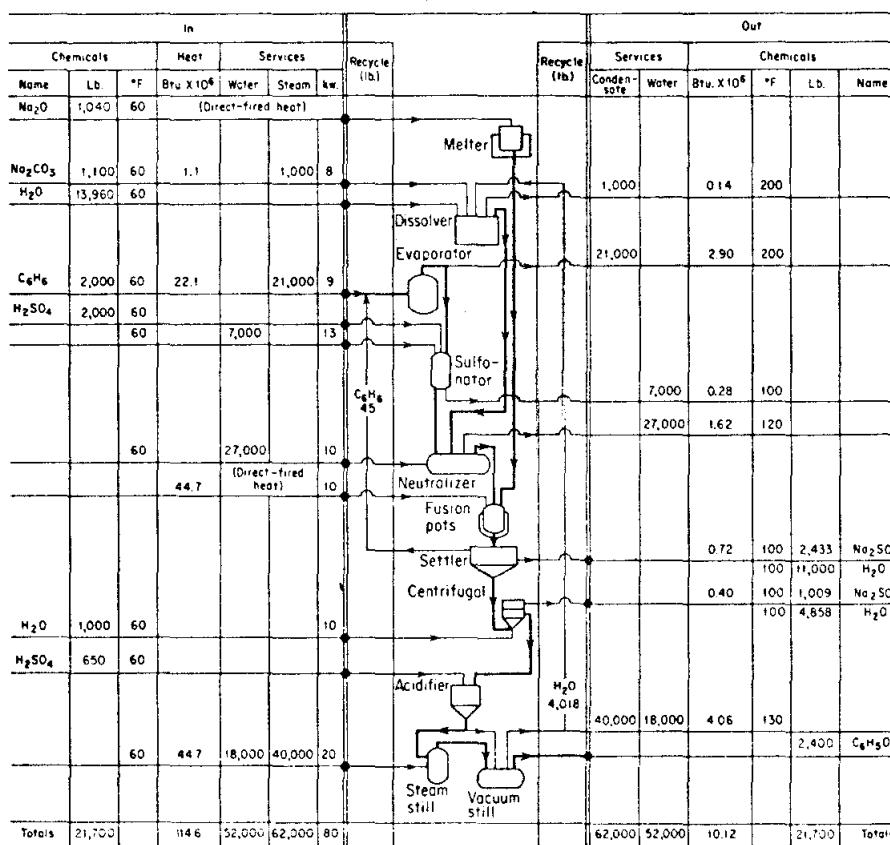


Fig. 2.4. Material (and energy) balances in the manufacture of phenol presented in the form of a ledger sheet. Taken from *Chem. Eng.*, p. 177 (April 1961), by permission.

cially in the financial

operating decisions process where it is important other data are possible to get the at the inaccessible the quantities and facts, and by-products and that can be A schematic outline tool is shown in Fig.

Out			
Chemicals			
Btu X 10 ⁶	*F	Lb.	Name
0.14			
2.90	200		
0.28	100		
1.62	120		
0.72	100	2,433	Na ₂ SO ₃
	100	11,000	H ₂ O
0.40	100	1,009	Na ₂ SO ₃
	100	4,658	H ₂ O
4.06	130		
		2,400	C ₆ H ₅ OH
10.12	21,700	Totals	

of phenol pre-
Eng., p. 177

EXAMPLE 2.1 Water balance for a river basin

Water balances on river basins for a season or for a year can be used to check predicted ground water infiltration, evaporation, or precipitation in the basin. Prepare a water balance, in symbols, for a large river basin, including the physical processes indicated in Fig. E2.1 (all symbols are for 1 yr).

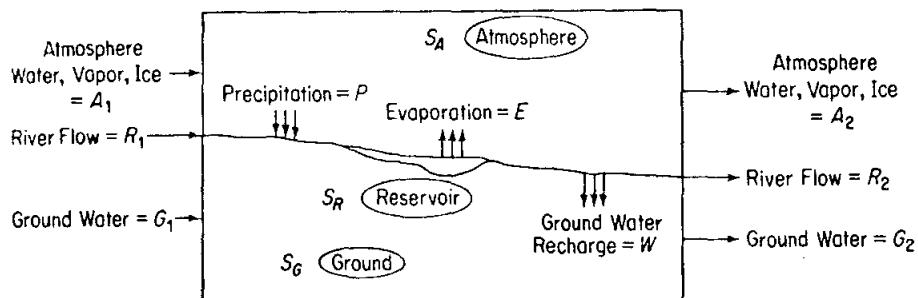


Fig. E2.1.

Solution:

Equation (2.2) applies in as much as there is no reaction in the system. Each term in Eq. (2.2) can be represented by symbols defined in Fig. E2.1. Let the subscript t_2 designate the end of the year and t_1 designate the beginning of the year. If the system is chosen to be the atmosphere plus the river plus the ground, then the accumulation is

$$(S_{At_2} - S_{At_1}) + (S_{Rt_2} - S_{Rt_1}) + (S_{Gt_2} - S_{Gt_1})$$

The inputs are $A_1 + R_1 + G_1$ and the outputs are $A_2 + R_2 + G_2$. Consequently, the material balance is

$$(a) \quad (S_{At_2} - S_{At_1}) + (S_{Rt_2} - S_{Rt_1}) + (S_{Gt_2} - S_{Gt_1}) \\ = (A_1 - A_2) + (R_1 - R_2) + (G_1 - G_2)$$

If the system is chosen to be just the river (including the reservoir), then the material balance would be

$$(b) \quad (S_{Rt_2} - S_{Rt_1}) = (R_1 + P) - (R_2 + E + W)$$

and analogous balances could be made for the water in the atmosphere and in the ground.

One important point to always keep in mind is that the material balance is a balance on mass, not on volume or moles. Thus, in a process in which a chemical reaction takes place so that compounds are generated and/or used up, you will have to employ the principles of stoichiometry discussed in Chap. 1 in making a material balance.

Let us analyze first some very simple examples in the use of the material balance.

EXAMPLE 2.2 Material balance

Hydrogenation of coal to give hydrocarbon gases is one method of obtaining gaseous fuels with sufficient energy content for the future. Figure E2.2 shows how a free-fall fluid bed reactor can be set up to give a product gas of high methane content.

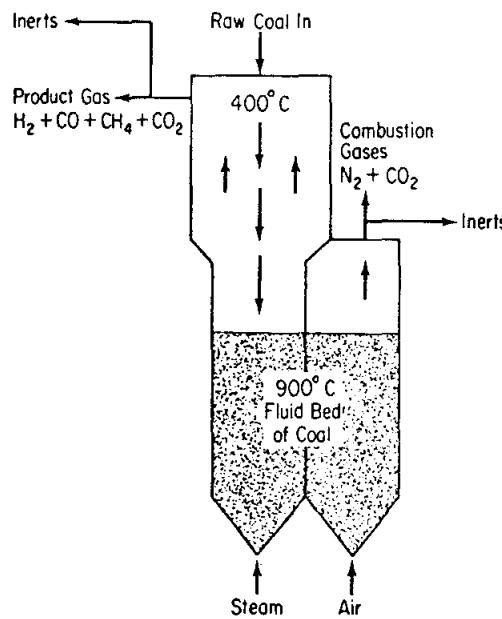


Fig. E2.2.

Suppose, first, that the gasification unit is operated without steam at room temperature (25°C) to check the air flow rates and that cyclones separate the solids from the gases effectively at the top of the unit so that no accumulation (build up) of coal, or air, occurs in the unit. If 1200 kg of coal per hour (assume that the coal is 80 percent C, 10 percent H, and 10 percent inert material) is dropped through the top of the reactor,

- How many kilograms of coal leave the reactor per hour?
- If 15,000 kg of air per hour is blown into the reactor, how many kilograms of air per hour leave the reactor?
- If the reactor operates at the temperatures shown in Fig. E2.2 and with the addition of 2000 kg of steam (H_2O vapor) per hour, how many kilograms per hour of combustion and product gases leave the reactor per hour.

Solution:

Basis: 1 hr

- Since 1200 kg/hr of coal enter the reactor, and none remains inside, 1200 kg/hr must leave the reactor.
- Similarly, 15,000 kg/hr of air must leave the reactor.

obtaining gases shows how a free-
ane content.

- (c) All the material except the inert portion of the coal leaves as a gas. Consequently, we can add up the total mass of material entering the unit, subtract the inert material, and obtain the mass of combustion gases by difference:

$$\frac{1200 \text{ kg coal} + 10 \text{ kg inert}}{100 \text{ kg coal}} = 120 \text{ kg inert}$$

entering material	kg
Coal	1,200
Air	15,000
Steam	2,000
Total	$18,200 - 120 = 18,080 \text{ kg/hr of gases}$

EXAMPLE 2.3 Material balance

- (a) If 300 lb of air and 24.0 lb of carbon are placed in a reactor (see Fig. E2.3) at 600°F and after complete combustion no material remains in the reactor, how many pounds of carbon will come out? How many pounds of oxygen? How many pounds total?

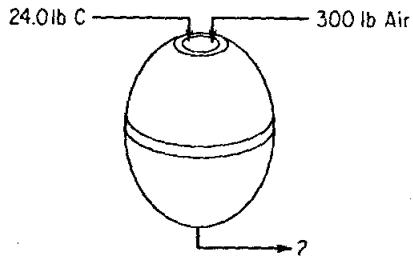


Fig. E2.3.

- (b) How many moles of carbon and oxygen enter? How many leave the reactor?
(c) How many total moles enter the reactor and how many leave the reactor?

Solution:

- (a) The total material leaving the reactor would be 324 lb. Since air has 21.0 percent O₂ and 79.0 percent N₂,

Basis: 300 lb air

$$\frac{300 \text{ lb air} + 1 \text{ lb mole air}}{29.0 \text{ lb air} + 100 \text{ lb mole air}} = 2.18 \text{ lb mole O}_2$$

$$\frac{24 \text{ lb C} + 1 \text{ lb mole C}}{12.0 \text{ lb C}} = 2.00 \text{ lb mole C}$$

The oxygen required to completely burn 24.0 lb of C is 2.00 lb mole; consequently

$$2.18 - 2.00 = 0.18$$

is the number of moles of unused oxygen, and this is equivalent to $(0.18)(32) = 5.76 \text{ lb}$ of O_2 as such leaving the reactor. In addition, 88 lb of CO_2 leave and

$$\frac{2.18 \text{ lb mole } \text{O}_2}{21.0 \text{ lb mole } \text{O}_2} \mid \frac{79.0 \text{ lb mole } \text{N}_2}{1 \text{ lb mole } \text{N}_2} \mid \frac{28.2 \text{ lb } \text{N}_2}{28.2 \text{ lb } \text{N}_2} = 230 \text{ lb } \text{N}_2$$

The moles of N_2 are

$$\frac{230 \text{ lb } \text{N}_2}{28.2 \text{ lb } \text{N}_2} \mid \frac{1 \text{ lb mole } \text{N}_2}{28.2 \text{ lb } \text{N}_2} = 8.20 \text{ lb mole } \text{N}_2$$

Summing up all input and exit streams, we have

<i>in</i>	<i>lb</i>	<i>lb mole</i>	<i>out</i>	<i>lb</i>	<i>lb mole</i>
O_2	70	2.18	O_2	5.76	0.18
N_2	230	8.20	N_2	230	8.20
C	24	2.00	CO_2	88	2.00
Total	324	12.38		324	10.38

There will be no carbon leaving as carbon because all the carbon burns to CO_2 ; the carbon leaves in a combined form with some of the oxygen.

- (b) The moles of C and O_2 entering the reactor are shown in part (a); no moles of C, as such, leave.
- (c) 12.38 total moles enter the reactor and 10.38 total moles leave.

Note that in the example above, although the total pounds put into a process and the total pounds recovered from a process have been shown to be equal, there is no such equality on the part of the *total* moles in and out, if a chemical reaction takes place. What is true is that the number of atoms of an element (such as C, O, or even oxygen expressed as O_2) put into a process must equal the atoms of the same element leaving the process. In Example 2.3 the total moles in and out are shown to be unequal:

<i>total moles in</i>	<i>total moles out</i>
O_2 2.18	O_2 0.18
N_2 8.20	N_2 8.20
C 2.00	CO_2 2.00
12.38	10.38

although the atoms of O in (expressed as moles of O_2) equal the atoms of O (similarly expressed as O_2) leaving:

<i>component moles in</i>		<i>component moles out</i>	
O_2 :	O_2 2.18	O_2 0.18	
		O_2 in CO_2 2.00	
	Total = O_2 2.18	Total = O_2 2.18	
N_2 :	N_2 8.20	N_2 8.20	
C:	C 2.00	C in CO_2 2.00	

Keeping in mind the above remarks for processes involving chemical reactions, we can summarize the circumstances under which the input equals the

If you want to make a material balance for a system, in general you have to have on hand information dealing with two fundamental concepts. One of these is the mass (weight) in all streams of the material entering and leaving the system and present in the system. The other information required is the composition of all the streams entering and leaving the system and the composition of the material in the system. Of course, if a chemical reaction takes place inside the system, the equation for the reaction and/or the extent of the reaction are important pieces of information.

Let us look at some problems in general by means of the "black box" technique. All we do is draw a black box or line around the process and consider what is going into the process and what comes out of the process. This procedure defines the system, i.e., the process or body of matter set out to be analyzed. As previously mentioned, we shall assume that the process is taking place in the steady state, i.e., that there is no accumulation or depletion of material. Even if the process is of the batch type in which there is no flow in and out, let us pretend that the initial material is pushed into the black box and that the final material is removed from the black box. By this hypothesis we can imagine a batch process converted into a fictitious flow process, and talk about the "streams" entering and leaving even though in the real process nothing of the sort happens (except over the entire period of time under consideration). After you do this three or four times, you will see that it is a very convenient technique, although at the beginning it may seem a bit illogical.

Let us start with a box with just three streams entering or leaving (all three cannot enter or leave, of course, in a steady-state process). In the examples in Figs. 2.5 and 2.6, F stands for the feed stream, P stands for product, and W stands for the third stream or "change," but any other symbols would do as well. The procedure of solution depends to some extent on which of the compositions and weights you know. All the problems in Figs. 2.5 and 2.6 have sufficient information shown to effect their solutions, except Fig. 2.5(d).

With respect to Fig. 2.5(a) we could use a total mass balance to compute the value of W :

$$\begin{aligned} F &= P + W \\ 100 &= 60 + W \quad \text{or} \quad W = 40 \end{aligned} \tag{2.4}$$

To determine the composition of W , because no reaction takes place, we can write a mass balance for each of the components: EtOH, H₂O, MeOH [ω = mass ("weight") fraction].

balance in = *out*

$$\omega_F F = \omega_P P + \omega_W W$$

$$\text{EtOH} \quad (0.50)(100) = (0.80)(60) + \omega_{\text{EtOH},W}(40) \tag{2.4a}$$

$$\text{H}_2\text{O} \quad (0.40)(100) = (0.05)(60) + \omega_{\text{H}_2\text{O},W}(40) \tag{2.4b}$$

$$\text{MeOH} \quad (0.10)(100) = (0.15)(60) + \omega_{\text{MeOH},W}(40) \tag{2.4c}$$

Composition
50% EtOH
40 H₂O
10 MeOH

* The third
† A stream

Fig. 2

Because

by definition
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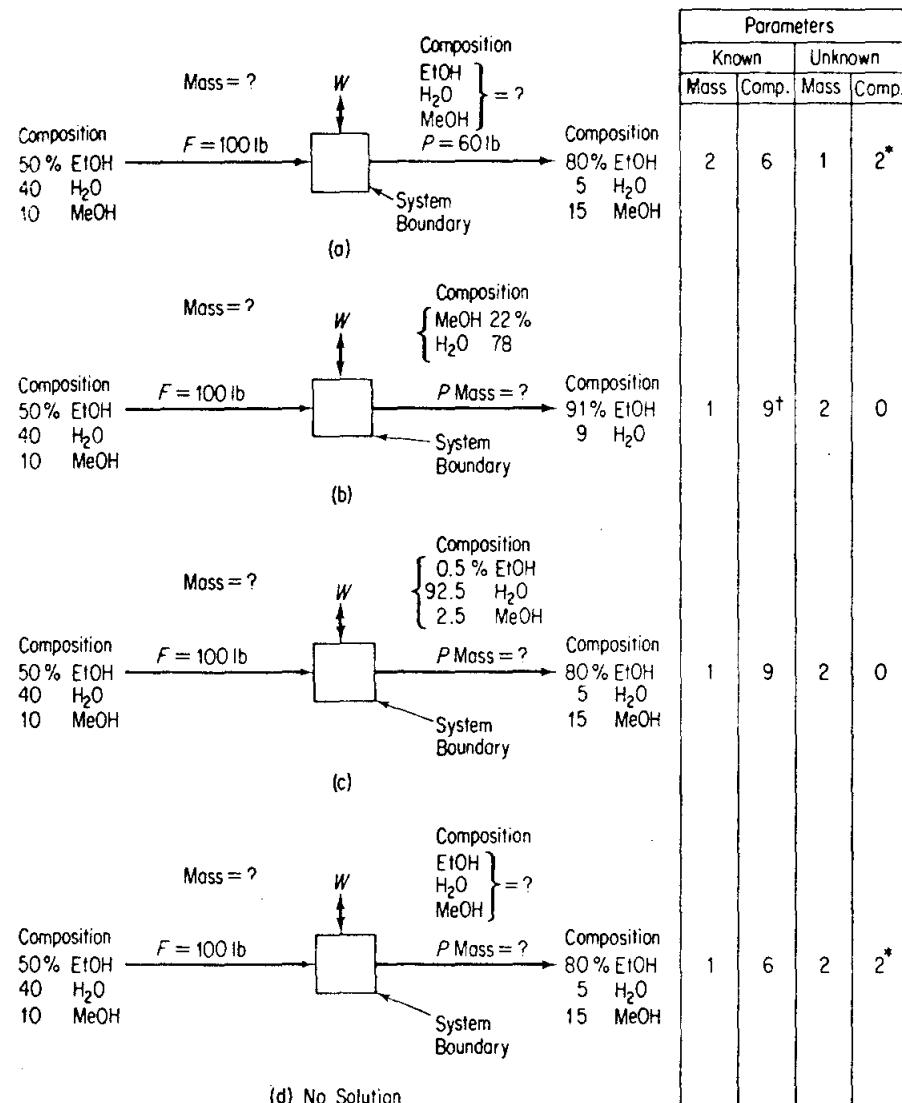
In general you have three concepts. One of entering and leaving the system required is the composition and the composition taking place inside the reaction are

the "black box" technique and consider process. This procedure must be analyzed. is taking place in the system of material. Even if we look at the final material we can imagine a batch about the "streams" of the sort happens . After all, if you do this technique, although

or leaving (all three In the examples in or product, and W would do as well. of the compositions have sufficient information balance to compute

(2.4)

akes place, we can H_2O , MeOH [$\omega =$



* The third percent can be obtained by difference.

† A stream with only two components has 0% for the third component.

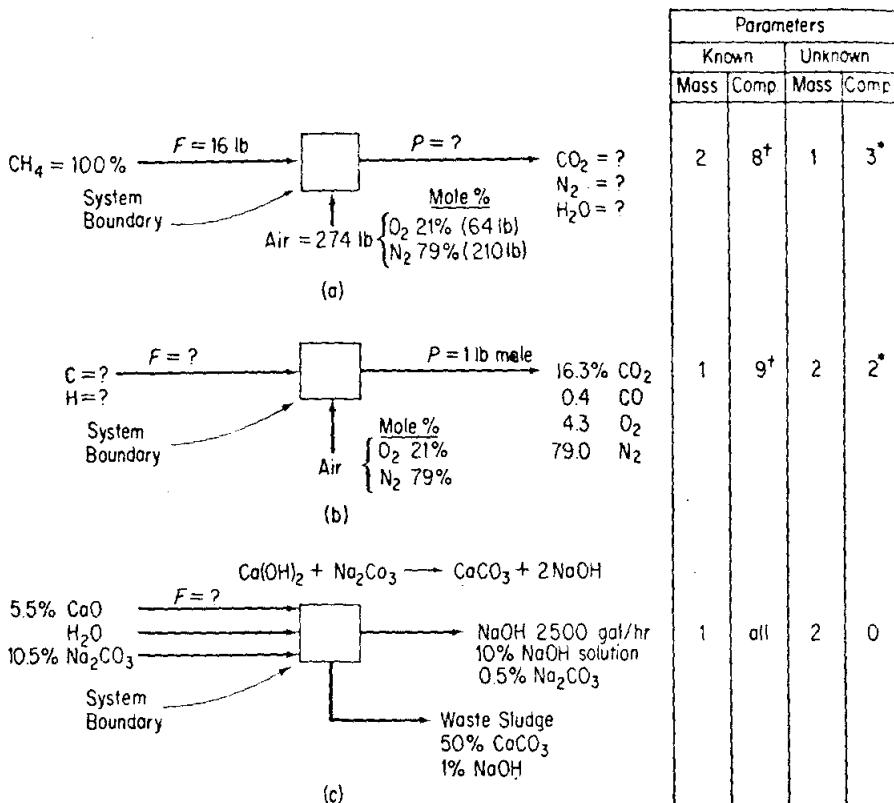
Fig. 2.5. Typical material balance problems (no chemical reaction involved).

Because

$$\omega_{\text{EtOH}} + \omega_{\text{H}_2\text{O}} + \omega_{\text{MeOH}} = 1 \quad (2.5)$$

by definition, only two of the mass fractions are unknown; the third can be computed by difference. Consequently, only two of the component material balances have to be solved simultaneously, and in this particular instance the equations are not coupled so that they can be solved independently.

- 0) (2.4a)
1) (2.4b)
2) (2.4c)



* The third percent can be obtained by difference.

[†] Components not listed are present in 0%.

Fig. 2.6. Typical material balance problems (with chemical reaction).

You should recognize that not all of the four mass balances, Eq. (2.4)-(2.4c), are independent equations. Note how the sum of the three component balances (2.4a), (2.4b), and (2.4c) equals the total mass balance. Consequently, the number of degrees of freedom or the number of independent equations will be equal to the number of components. In many problems you can substitute the total material balance for any one of the component material balances if you plan to solve two or more equations simultaneously.

Since many of the problems you will encounter involving the use of material balances require you to solve for more than one unknown, you should remember that for each unknown you need to have at least one independent material balance or other independent piece of information. Otherwise, the problem is indeterminate. For example, a problem such as illustrated in Fig. 2.5(c) in which the compositions of all the streams are known and the weights of two streams are unknown requires two independent material balances for its solution. What to do when more, or fewer, independent material balance equations are available than unknowns is discussed in Sec. 2.4.

The columns on the right-hand side of Fig. 2.5 tabulate the number of

known and unknowns. The asterisk (*) indicates that the value can be obtained from the total mass balance. The number of degrees of freedom (number of streams minus the number of components times 100 percent).

For problems with more than one unknown, write the equations for each unknown as separate equations. i.e., hydrogen and oxygen balance, carbon and oxygen balance. The number of degrees of freedom is the number of independent equations. Also keep in mind that mass and energy are conserved.

Figure 2.6 illustrates typical material balance problems. However, in many problems the system boundary must be assumed. This depends on the nature of the problem.

The structure of the problem determines the number of degrees of freedom.

- (a) Degrees of freedom
- (b) Number of unknowns
- (c) Number of equations
- (d) Number of streams
- (e) Number of components
- (f) Number of reactions

After this section you should be able to solve most material balance problems.

- (a) A simple problem
- (b) A more complex problem

Not all the problems in this section are solvable. Problem 2.10 is an example of a problem with more unknowns than equations.

Parameters			
Known	Unknown		
Mass	Comp.	Mass	Comp.
8*	1	3*	
9†	2	2*	
all	2	0	

known and unknown parameters, for both the total mass and the compositions. The asterisk designates that one of the three unknown compositions can always be obtained by using the equivalent of Eq. (2.5). Hence in a three-component stream of unknown composition, only two of the three mass fractions (or percents) really need to be evaluated. The dagger indicates that in a stream with only one or two components, the composition of the other components is known to be 0 percent. Note how for each of the first three figures in Fig. 2.5 the number of independent material balances (three in each case) does not exceed the number of unknown quantities.

For problems involving chemical reaction, a total mass balance can be written as well as a mass balance for each atomic species or multiple thereof, i.e., hydrogen expressed as H₂. For example, in Fig. 2.6(a) you can write a total mass (*not* moles) balance and a carbon, a hydrogen, a nitrogen, and an oxygen balance. The carbon balance might be in terms of C, and the hydrogen, nitrogen, and oxygen balances in terms of H₂, N₂, and O₂, respectively. Depending on the problem statement, you would not necessarily have to use each of the balances. Also keep in mind that in using balances on atomic species, both mass and moles are conserved.

Figure 2.6(c) illustrates a case in which the chemical equation is given. However, in solving problems related to Fig. 2.6(a) and (b), chemical equation(s) must be assumed to apply, or else some information given or assumed about the nature of the reaction that takes place.

The strategy to be used in solving material balance problems is very simple. As a general rule, before making any calculations you should

- Draw a picture of the process.
- Place all the available data in the picture.
- See what compositions are known or can be immediately calculated for each stream.
- See what masses (weights) are known or can easily be found for each stream. [One mass (weight) can be assumed as a basis.]
- Select a suitable basis for the calculations. Every addition or subtraction *must* be made with the material on the *same* basis.
- Make sure the system is well defined.

After this has been accomplished, you are ready to make the necessary number of material balances.

As explained previously, you can write

- A *total* material balance.
- A *component* material balance for each component present.

Not all the balances, however, will be independent.

Problems in which the mass (weight) of one stream and the composition of one stream are unknown can be solved without difficulty by direct addition or

direct subtraction. Problems in which all the compositions are known and two or more of the weights are unknown require some slightly more detailed calculations. If a tie component exists which makes it possible to establish the relationship between the unknown weights and the known weights, the problem solution may be simplified. (The tie component will be discussed in detail in Sec. 2.5.) When there is no direct or indirect tie component available, algebra must be used to relate the unknown masses to the known masses.

2.3 Problems with direct solutions

Problems in which one mass (weight) and one composition are unknown can be solved by direct addition or subtraction, as shown in the examples below. There is no need to use formal algebraic techniques. You may find it necessary to make some brief preliminary calculations in order to decide whether or not all the information about the compositions and weights that you would like to have is available. Of course, in a stream containing just one component, the composition is known, because that component is 100 percent of the stream.

In dealing with problems involving combustion, you should become acquainted with a few special terms:

- (a) *Flue or Stack gas*—all the gases resulting from a combustion process including the water vapor, sometimes known as *wet basis*.
- (b) *Orsat analysis* or *dry basis*—all the gases resulting from the combustion process not including the water vapor. (Orsat analysis refers to a type of gas analysis apparatus in which the volumes are measured over water; hence each component is saturated with water vapor. The net result of the analysis is to eliminate water as a component being measured.)

Pictorially, we can express this classification for a given gas as in Fig. 2.7. To convert from one analysis to another, you have to ratio the percentages for the components as shown in Example 2.9.

- (c) *Theoretical air* (or *theoretical oxygen*)—the amount of air (or oxygen) required to be brought into the process for *complete* combustion. Sometimes this quantity is called the *required* air (or oxygen).

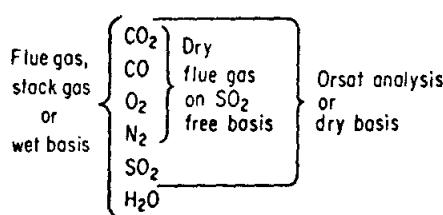


Fig. 2.7. Comparison of gas analyses on different bases.

are known and two more detailed calculations to establish the heights, the problem discussed in detail in available, algebra classes.

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the percentages for

of air (or oxygen) combustion. Some-
gen).

(d) *Excess air* (or *excess oxygen*)—in line with the definition of excess reactant given in Chap. 1, excess air (or oxygen) would be the amount of air (or oxygen) in excess of that required for complete combustion as computed in (c).

Even if only partial combustion takes place, as, for example, C burning to both CO and CO₂, the excess air (or oxygen) is computed as if the process of combustion produced only CO₂. The percent excess air is identical to the percent excess O₂ (a more convenient method of calculation):

$$\% \text{ excess air} = 100 \frac{\text{excess air}}{\text{required air}} = 100 \frac{\text{excess O}_2/0.21}{\text{required O}_2/0.21} \quad (2.6)$$

Note that the ratio 1/0.21 of air to O₂ cancels out in Eq. (2.6). Percent excess air may also be computed as

$$\% \text{ excess air} = 100 \frac{\text{O}_2 \text{ entering process} - \text{O}_2 \text{ required}}{\text{O}_2 \text{ required}} \quad (2.7)$$

or

$$= 100 \frac{\text{excess O}_2}{\text{O}_2 \text{ entering} - \text{excess O}_2}$$

since

$$= \Omega_{\text{req}} \text{ required for complete combustion} + \text{excess } \Omega \quad (28)$$

The precision of these different relations for calculating the percent excess air may not be the same. If the percent excess air and the chemical equation are given in a problem, you know how much air enters with the fuel, and hence the number of unknowns is reduced by one.

EXAMPLE 2.4 Excess air

A man comes to the door selling a service designed to check "chimney rot." He explains that if the CO₂ content of the gases leaving the chimney rises above 15 percent, it is dangerous to your health, is against the city code, and causes your chimney to rot. On checking the flue gas from the furnace he finds it is 30 percent CO₂. Suppose that you are burning natural gas which is about 100 percent CH₄ and that the air supply is adjusted to provide 130 percent excess air. Do you need his service?

Solution:

Let us calculate the actual percentage of CO_2 in the gases from the furnace assuming that complete combustion takes place. See Fig. E2.4. The 130 percent

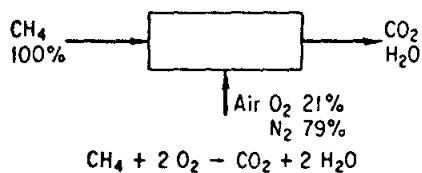
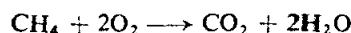


Fig. E2.4.

excess air means 130 percent of the air required for complete combustion of CH_4 . The chemical reaction is



Basis: 1 mole CH_4

By picking a basis, the quantity of the CH_4 stream is fixed. The quantity of air is fixed by the specification of the excess air and is computed as follows: On the basis of 1 mole of CH_4 , 2 moles of O_2 are required for complete combustion, or

$$\frac{2\text{O}_2}{0.21\text{ O}_2} = 9.54 \text{ moles air required}$$

composed of 2 moles O_2 and 7.54 moles N_2 . The excess air is $9.54(1.30) = 12.4$ moles air, composed of 2.60 moles O_2 and 9.80 moles N_2 .

Summing up our calculations so far we have entering the furnace:

	air	O_2	N_2
Required	9.54	2.00	7.54
Excess	12.4	2.60	9.80
Total	21.94	4.60	17.34

Since 2 moles of the 4.60 moles of entering O_2 combine with the C and H of the CH_4 to form CO_2 and H_2O , respectively, the composition of the gases from the furnace should contain the following:

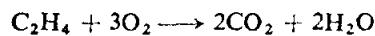
	moles	%
CH_4	0	0
CO_2	1.00	4.4
H_2O	2.00	8.7
O_2	2.60	11.3
N_2	{ 7.54 9.80	75.6
	22.94	100.0

The salesman's line seems to be rot all the way through.

EXAMPLE 2.5 Excess air

Fuels for motor vehicles other than gasoline are being eyed because they generate lower levels of pollutants than does gasoline. Compressed ethane has been suggested as a source of economic power for vehicles. Suppose that in a test 20 lb of C_2H_4 are burned with 400 lb of air to 44 lb of CO_2 and 12 lb of CO. What was the percent excess air?

Solution:



Basis: 20 lb C_2H_4

Since the percentage of excess air is based on the complete combustion of C_2H_4 to CO_2 and H_2O , the fact that combustion is not complete was no influence on the

Combustion of CH_4 .

The quantity of air follows: On the basis combustion, or

is $95.54(1.30) = 12.4$

in excess:

the C and H of the
the from the

definition of "excess air." The required O_2 is

$$\frac{20 \text{ lb } \text{C}_2\text{H}_4}{28 \text{ lb } \text{C}_2\text{H}_4} \mid \frac{1 \text{ lb mole } \text{C}_2\text{H}_4}{1 \text{ lb mole } \text{C}_2\text{H}_4} \mid \frac{3 \text{ lb moles } \text{O}_2}{100 \text{ lb moles air}} = 2.14 \text{ lb moles } \text{O}_2$$

The entering O_2 is

$$\frac{400 \text{ lb air}}{29 \text{ lb air}} \mid \frac{1 \text{ lb mole air}}{100 \text{ lb moles air}} \mid \frac{21 \text{ lb moles } \text{O}_2}{100 \text{ lb moles air}} = 2.90 \text{ lb moles } \text{O}_2$$

The percent excess air is

$$100 \times \frac{\text{excess } \text{O}_2}{\text{required } \text{O}_2} = 100 \frac{\text{entering } \text{O}_2 - \text{required } \text{O}_2}{\text{required } \text{O}_2}$$

$$\% \text{ excess air} = \frac{2.90 \text{ lb moles } \text{O}_2 - 2.14 \text{ lb moles } \text{O}_2}{2.14 \text{ lb moles } \text{O}_2} \mid 100 = 35.5\%$$

EXAMPLE 2.6 Drying

A wet paper pulp is found to contain 71 percent water. After drying it is found that 60 percent of the original water has been removed. Calculate the following:

- The composition of the dried pulp.
- The mass of water removed per kilogram of wet pulp.

Solution:

Basis: 1 kg wet pulp

Initially we know only the composition and mass (the chosen basis) of the wet pulp. However, we can easily calculate the composition (100 percent H_2O) and mass of water removed; examine Fig. E2.6.

$$\text{H}_2\text{O removed} = 0.60(0.71) = 0.426 \text{ kg}$$

Thus in essence we now know two masses and two compositions.

(1) By a pulp balance the final amount of pulp in the dried pulp is 0.29 kg and the associated water is

$$\text{in} - \text{loss} = \text{remainder}$$

$$0.71 - 0.426 = 0.284 \text{ kg } \text{H}_2\text{O} \quad \text{water balance}$$

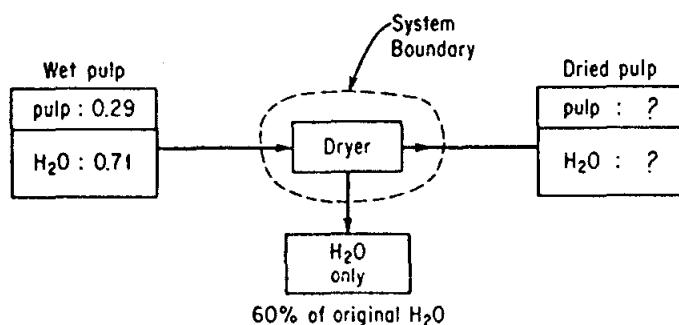


Fig. E2.6.

or, alternatively, since 40 percent of the H_2O was left in pulp,

$$0.40(0.71) = 0.284 \text{ kg } H_2O$$

(2) The composition of the dried pulp is

	kg	%
Pulp (dry)	0.29	50.5
H_2O	0.284	49.5
Total	<u>0.574</u>	<u>100.0</u>

EXAMPLE 2.7 Crystallization

A tank holds 10,000 lb of a saturated solution of $NaHCO_3$ at $60^\circ C$. You want to crystallize 500 lb of $NaHCO_3$ from this solution. To what temperature must the solution be cooled?

Solution:

A diagram of the process is shown in Fig. E2.7.

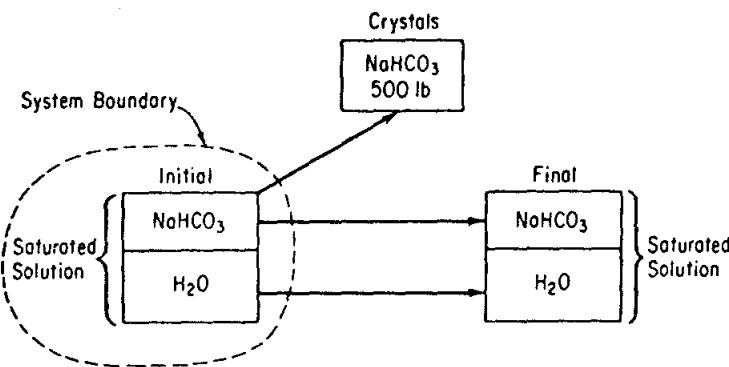


Fig. E2.7.

Additional data are needed on the solubility of $NaHCO_3$ as a function of temperature. From any handbook you can find

temp. ($^\circ C$)	solubility g $NaHCO_3$ /100 g H_2O
60	16.4
50	14.45
40	12.7
30	11.1
20	9.6
10	8.15

Basis: 10,000 lb saturated $NaHCO_3$ solution at $60^\circ C$

We know both the weight of the initial solution and the weight of the crystals; we know the composition of both the initial solution and the crystals (100% $NaHCO_3$). Thus the weight and composition of the final solution can be calculated by subtraction.

(a) Initial composition:

$$\frac{16.4 \text{ lb NaHCO}_3}{16.4 \text{ lb NaHCO}_3 + 100 \text{ lb H}_2\text{O}} = 0.141 \text{ or } 14.1\% \text{ NaHCO}_3$$

$$100 - 14.1 = 85.9\% \text{ HO}$$

(b) Material balance (component balance on the NaHCO₃):

$$\begin{array}{rcl} \text{initial NaHCO}_3 - \text{crystals NaHCO}_3 & = & \text{final NaHCO}_3 \\ 0.141(10,000) - & = & 910 \text{ lb} \end{array}$$

(c) Final composition and weight:

$$\begin{array}{rcl} \text{H}_2\text{O} & = & (0.859)10,000 = 8590 \text{ lb} \\ \text{NaHCO}_3 & = & \frac{910 \text{ lb}}{9500 \text{ lb}} \\ \text{Total} & & \end{array}$$

Since the final solution is still saturated and has

$$\frac{910 \text{ lb NaHCO}_3}{8590 \text{ lb H}_2\text{O}} = \frac{10.6 \text{ g NaHCO}_3}{100 \text{ g H}_2\text{O}}$$

the temperature to which the solution must be cooled is (using a linear interpolation)

$$30^\circ\text{C} - \left[\frac{11.1 - 10.6}{11.1 - 9.6} \right] [10^\circ\text{C}] = 27^\circ\text{C}$$

EXAMPLE 2.8 Distillation

A moonshiner is having a bit of difficulty with his still. The operation is shown in Fig. E2.8. He finds he is losing too much alcohol in the bottoms (waste). Calculate the composition of the bottoms for him and the weight of alcohol lost in the bottoms.

Solution:

The information provided gives us the composition and weight of feed and distillate. The composition of the bottoms can be obtained by subtracting the distillate from the feed.

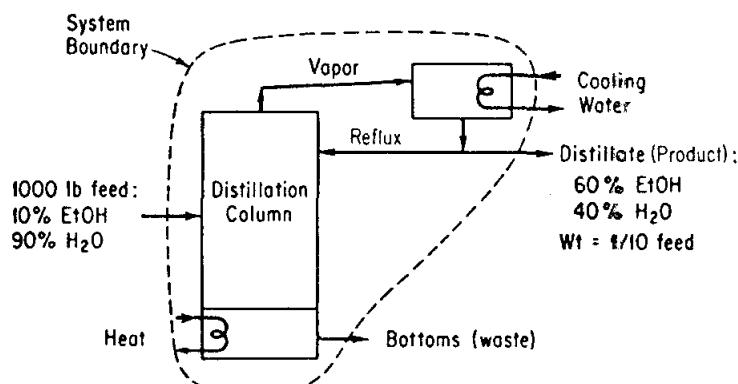


Fig. E2.8.

Basis: 1000 lb feed

component	in		out	
	wt %	lb	distillate (lb)	bottoms (lb) (by subtraction)
EtOH	10	100	60	40*
H ₂ O	90	900	40	860
Total	100	1000	100	900

*Alcohol lost.

$$\frac{1000 \text{ lb feed}}{10 \text{ lb feed}} = 100 \text{ lb distillate}$$

$$\frac{40 \text{ lb EtOH}}{900 \text{ lb bottoms}} = 4.4\% \text{ EtOH}$$

$$\frac{860 \text{ lb H}_2\text{O}}{900 \text{ lb bottoms}} = 95.6\% \text{ H}_2\text{O}$$

EXAMPLE 2.9 Combustion

The same ethane as used in Example 2.5 is initially mixed with oxygen to obtain a gas containing 80 percent C₂H₆ and 20 percent O₂ that is then burned with 200 percent excess air. Eighty percent of the ethane goes to CO₂, 10 percent goes to CO, and 10 percent remains unburned. Calculate the composition of the exhaust gas on a wet basis.

Solution:

We know the composition of the air and fuel gas; if a weight of fuel gas is chosen as the basis, the weight of air can easily be calculated. However, it is wasted effort to convert to a weight basis for this type of problem. Since the total moles entering and leaving the boiler are not equal, if we look at any one component and employ the stoichiometric principles previously discussed in Chap. 1 together with Eq. (2.1), we can easily obtain the composition of the stack gas. The net generation term in Eq. (2.1) can be evaluated from the stoichiometric equations listed below. The problem can be worked in the simplest fashion by choosing a basis of 100 moles of entering gas. See Fig. E2.9.

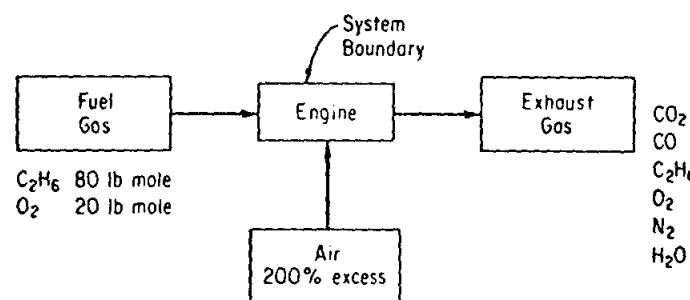
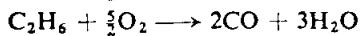


Fig. E2.9.

bottoms (lb)
by subtraction
40*
860
—
900

Basis: 100 lb moles of fuel



The total O_2 entering is 3.00 times the required O_2 (100 percent required plus 200 percent excess). Let us calculate the required oxygen:

O_2 (for complete combustion):

$$\frac{80 \text{ lb mole C}_2\text{H}_6 | 3.5 \text{ lb mole O}_2}{1 \text{ lb mole C}_2\text{H}_6} = 280 \text{ lb mole O}_2$$

Required O_2 :

$$280 - 20 = 260 \text{ lb mole O}_2$$

(Note: The oxygen used to completely burn the fuel is reduced by the oxygen already present in the fuel to obtain the oxygen required in the entering air.)

Next we calculate the input of O_2 and N_2 to the system:

O_2 entering with air:

$$3(260 \text{ lb mole O}_2) = 780 \text{ lb mole O}_2$$

N_2 entering with air:

$$\frac{780 \text{ mole O}_2 | 79 \text{ lb mole N}_2}{21 \text{ lb mole O}_2} = 2930 \text{ lb mole N}_2$$

Now we apply our stoichiometric relations to find the components generated within the system:

$$\frac{80 \text{ lb mole C}_2\text{H}_6 | 2 \text{ lb mole CO}_2 | 0.8}{1 \text{ lb mole C}_2\text{H}_6} = 128 \text{ lb mole CO}_2$$

$$\frac{80 \text{ lb mole C}_2\text{H}_6 | 3 \text{ lb mole H}_2\text{O} | 0.8}{1 \text{ lb mole C}_2\text{H}_6} = 192 \text{ lb mole H}_2\text{O}$$

$$\frac{80 \text{ lb mole C}_2\text{H}_6 | 2 \text{ lb mole CO} | 0.1}{1 \text{ lb mole C}_2\text{H}_6} = 16 \text{ lb mole CO}$$

$$\frac{80 \text{ lb mole C}_2\text{H}_6 | 3 \text{ lb mole H}_2\text{O} | 0.1}{1 \text{ lb mole C}_2\text{H}_6} = 24 \text{ lb mole H}_2\text{O}$$

To determine the O_2 remaining in the exhaust gas, we have to find how much of the available (800 lb mole) O_2 combines with the C and H.

$$\frac{80 \text{ lb mole C}_2\text{H}_6 | 3.5 \text{ lb mole O}_2 | 0.8}{1 \text{ lb mole C}_2\text{H}_6} = 224 \text{ lb mole O}_2 \text{ to burn to CO}_2 \text{ and H}_2\text{O}$$

$$\frac{80 \text{ lb moles C}_2\text{H}_6 | 2.5 \text{ lb moles O}_2 | 0.1}{1 \text{ lb mole C}_2\text{H}_6} = \frac{20 \text{ lb mole O}_2 \text{ to burn to CO and H}_2\text{O}}{244 \text{ lb mole O}_2 \text{ total "used up" by reaction}}$$

By an oxygen (O_2) balance we get

$$\text{O}_2 \text{ out} = 780 \text{ lb mole} + 20 \text{ lb mole} - 244 \text{ lb mole} = 556 \text{ lb mole O}_2$$

From a water balance we find

$$\text{H}_2\text{O out} = 192 \text{ lb mole} + 24 \text{ lb mole} = 216 \text{ lb mole H}_2\text{O}$$

fuel gas is chosen
is wasted effort to
moles entering and
and employ the
er with Eq. (2.1),
tation term in Eq.
ow. The problem
es of entering gas.

CO₂
CO
C₂H₆
O₂
N₂
H₂O

EXAMPLE 2.9 Alternative manner of presentation

Initial Component	lb mole = %	lb mole O ₂ Required	Actual lb mole O ₂ Used	lb mole formed of			C ₂ H ₆ left	Reactions
				CO ₂	H ₂ O	CO		
C ₂ H ₆	64			3(64) = 224	128	192		
C ₂ H ₆	8			3(8) = 24	24	16		
C ₂ H ₆	8						8	C ₂ H ₆ + $\frac{7}{2}$ O ₂ → 2CO ₂ + 3H ₂ O
O ₂	20							C ₂ H ₆ + $\frac{3}{2}$ O ₂ → 2CO + 3H ₂ O
	100		260	244	128	216	16	C ₂ H ₆ → C ₂ H ₆
O ₂ entering with air:	3(260) = 780							
N ₂ entering with air:	780 $\frac{7}{11}$ = 2930							
O ₂ in exit gas:	air fuel used							
	780 + 20 - 244 = 556							

Summary of Material Balances

Total mole in ≠ total mole out

Total lb in = total lb out: (each compound has to be multiplied by its molecular weight)

balances on atomic species

$$\left\{ \begin{array}{l} \text{lb mole C in} = \text{lb mole C out: } 2(80) = 128 + 16 + 2(8) \\ \text{lb mole H}_2\text{ in} = \text{lb mole H}_2\text{ out: } 3(80) = 216 + 3(8) \\ \text{lb mole O}_2\text{ in} = \text{lb mole O}_2\text{ out: } 20 + 780 = 128 + \frac{1}{2}(216) + \frac{1}{2}(16) + 556 \\ \text{lb mole N}_2\text{ in} = \text{lb mole N}_2\text{ out: } 2930 = 2930 \end{array} \right.$$

balances on compounds

$$\left\{ \begin{array}{l} \text{lb mole C}_2\text{H}_6\text{ in} = \text{lb mole C}_2\text{H}_6\text{ out} + \text{lb mole C}_2\text{H}_6\text{ consumed: } 80 = 8 + 72 + 0 \\ \text{lb mole CO}_2\text{ in} = \text{lb mole CO}_2\text{ out} - \text{lb mole CO}_2\text{ generated: } 0 = 128 - 128 \\ \text{lb mole CO in} = \text{lb mole CO out} - \text{lb mole CO generated: } 0 = 16 - 16 \\ \text{lb mole H}_2\text{O in} = \text{lb mole H}_2\text{O out} - \text{lb mole H}_2\text{O generated: } 0 = 216 - 216 \\ \text{lb mole N}_2\text{ in} = \text{lb mole N}_2\text{ out} + \text{lb mole N}_2\text{ consumed: } 2930 = 2930 + 0 \\ \text{lb mole O}_2\text{ in} = \text{lb mole O}_2\text{ out} + \text{lb mole O}_2\text{ consumed: } 800 = 556 + 244 \end{array} \right.$$

Sec. 2.4

The balances on the formally listed here.
Summarizing the

component
C ₂ H ₆
O ₂
N ₂
CO ₂
CO
H ₂ O

On a dry basis we

Once you have
the tabular form of
convenient form to use

2.4 Material balance

As illustrated in Fig. 2.1, different ways depend on streams and their respective sections were quite often words into numbers per stream. Only simple quantities. Other types of the balance formal quantities. Each unknown the unknown value involved in the problem is to have a unique value as the case may be, however, have to write one index is to have a unique value involved in the problem.

The balances on the other compounds— C_2H_6 , CO_2 , CO , N_2 —are too simple to be formally listed here.

Summarizing these calculations, we have

component	lb mole			% in exhaust gas
	fuel	air	exhaust gas	
C_2H_6	80	—	8	0.21
O_2	20	780	556	14.42
N_2	—	2930	2930	76.01
CO_2	—	—	128	3.32
CO	—	—	16	0.42
H_2O	—	—	216	5.62
	100	3710	3854	100.00

On a dry basis we would have (the water is omitted)

component	lb mole	%
C_2H_6	8	0.23
O_2	556	15.29
N_2	2930	80.52
CO_2	128	3.52
CO	16	0.44
	3638	100.00

Once you have become familiar with these types of problems, you will find the tabular form of solution illustrated in Example 2.9, on the facing page, a very convenient form to use.

2.4 Material balances using algebraic techniques

As illustrated in Figs. 2.5 and 2.6, problems can be posed or formulated in different ways depending on the type of information available on the process streams and their respective compositions. The problems treated in the previous section were quite easy to solve, once the problem had been converted from words into numbers, because the missing information pertained to a single stream. Only simple addition or subtraction was required to find the unknown quantities. Other types of material balance problems can be solved by writing the balance formally, and assigning letters or symbols to represent the unknown quantities. Each unknown stream, or component, is assigned a letter to replace the unknown value in the total mass balance or the component mass balance, as the case may be. Keep in mind that for each unknown so introduced you will have to write one independent material balance if the set of equations you form is to have a unique solution.

If more than one piece of equipment or more than one junction point is involved in the problem to be solved, you can write material balances for each

$$\begin{aligned}
 & 0 = 128 - 128 \\
 & 0 = 16 - 16 \\
 & 0 = 216 - 216 \\
 & 2930 = 2930 + 0 \\
 & 800 = 556 + 244
 \end{aligned}$$

piece of equipment and a balance around the whole process. However, since the overall balance is nothing more than the sum of the balances about each piece of equipment, not all the balances will be independent. Appendix L discusses how you can determine whether sets of linear equations are independent or not.

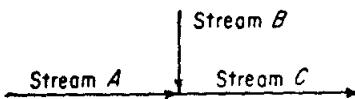
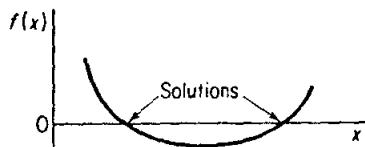


Fig. 2.8. A mixing point.

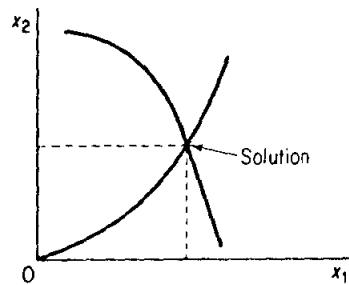
other piece of equipment.

Some brief comments are now appropriate as to how to solve sets of coupled simultaneous equations. If only two or three linear material balances are written, the unknown variables can be solved for by substitution. If the material balances consist of large sets of linear equations, you will find suggestions for solving them in Appendix L. If the material balance is a nonlinear equation, it can be plotted by hand or by using a computer routine, and the root(s), i.e., the crossings of the horizontal axis, located. See Fig. 2.9. If two material balances have to be solved, the equations can be plotted and their intersection(s) located. With many simultaneous nonlinear equations to be solved, the use of computer routines is essential; for linear equations, computer routines are quick and prevent human error. Making a balance for each component for each defined sys-

Under some circumstances, particularly if you split a big problem into smaller parts to make the calculations easier, you may want to make a material balance about a *mixing point*. As illustrated in Fig. 2.8, a mixing point is nothing more than a junction of three or more streams and can be designated as a system in exactly the same fashion as any



(a) Single Nonlinear Equation



(b) Two Nonlinear Equations

Fig. 2.9. Solution of nonlinear material balances by graphical techniques.

ever, since the about each piece index L discusses dependent or not. ces, particularly to smaller parts you may want about a *mixing* a mixing point ion of three or designated as a fashion as any

sets of coupled balances are written, material balances ions for solving equation, it can be i.e., the cross-balances have to be located. With the of outer quite pre-defined sys-

tem, a set of independent equations can be obtained whether linear or nonlinear. Total mass balances may be substituted for one of the component mass balances. Likewise, an overall balance around the entire system may be substituted for one of the subsystem balances. By following these rules, you should encounter no difficulty in generating sets of independent material balances for any process.

Illustrations of the use of algebraic techniques to solve material balance problems can be found below in this section and in the next section (on tie components).

EXAMPLE 2.10 Mixing

Dilute sulfuric acid has to be added to dry charged batteries at service stations in order to activate a battery. You are asked to prepare a batch of new acid as follows. A tank of old weak battery acid (H_2SO_4) solution contains 12.43 percent H_2SO_4 (the remainder is pure water). If 200 kg of 7.77 percent H_2SO_4 are added to the tank, and the final solution is 18.63 percent H_2SO_4 , how many kilograms of battery acid have been made? See Fig. E2.10.

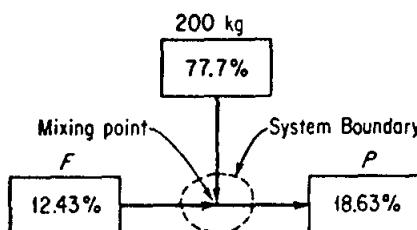


Fig. E2.10.

Solution:

In this problem one mass and three compositions are known; two masses are missing. To assist us, we shall arbitrarily label the masses of the two unknown solutions F and P . With two unknowns it is necessary to set up two independent equations. However, we can write three material balances, any pair of which are independent equations.

Basis: 200 kg of 77.7 percent H_2SO_4 solution

type of balance	in	=	out	
Total	$F + 200$	=	P	(a)
component				
H_2SO_4	$F(0.1243) + 200(0.777) = P(0.1863)$			(b)
H_2O	$F(0.8757) + 200(0.223) = P(0.8137)$			(c)

Use of the total mass balance and one of the others is the easiest way to find P :

$$(P - 200)(0.1243) + 200(0.777) = P(0.1863)$$

$$P = 2110 \text{ kg acid}$$

$$F = 1910 \text{ kg acid}$$

EXAMPLE 2.11 Distillation

A typical distillation column is shown in Fig. E2.11 together with the known information for each stream. Calculate the pounds of distillate per pound of feed and per pound of waste.

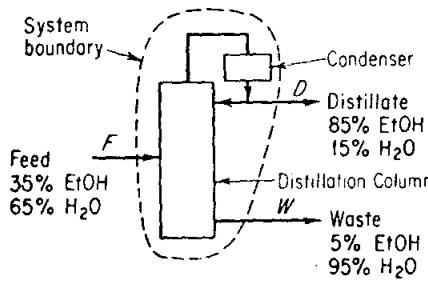


Fig. E2.11.

Solution:

Inspection of Fig. E2.11 shows that all compositions are known, but three weights are unknown. Because only two independent balances can be written, one weight must be chosen as the basis for the problem to effect an algebraic solution.

Basis: 1.00 lb feed

type of balance	in	=	out
total	1.00	=	$D + W$
EtOH	$1.00(0.35)$	=	$D(0.85) + W(0.05)$
H ₂ O	$1.00(0.65)$	=	$D(0.15) + W(0.95)$

Solving for D with $W = (1.00 - D)$,

$$1.00(0.35) = D(0.85) + (1.00 - D)(0.05)$$

$$D = 0.375 \text{ lb/lb feed}$$

Since $W = 1 - 0.375 = 0.625 \text{ lb}$,

$$\frac{D}{W} = \frac{0.375}{0.625} = \frac{0.60 \text{ lb}}{\text{lb}}$$

EXAMPLE 2.12 Multiple equipment

In your first problem as a new company engineer you have been asked to set up an acetone recovery system to remove acetone from gas that was formerly vented but can no longer be handled that way, and to compute the cost of recovering acetone. Your boss has provided you with the design of the proposed system, as shown in Fig. E2.12. From the information given, list the flow rates (in pounds per hour) of all the streams so that the size of the equipment can be determined, and calculate the composition of the feed to the still.

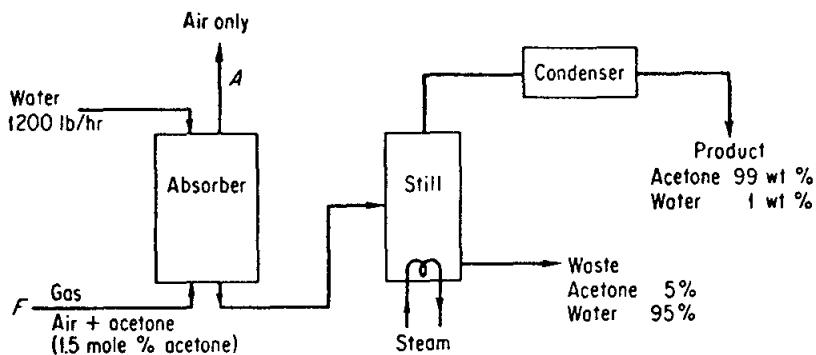


Fig. E2.12.

Solution:

Convert mole percent of the air-acetone feed to weight percent because all the other compositions are given in weight percent:

$$\text{mol. wt acetone} = 58, \quad \text{mol. wt air} = 29$$

Basis: 100 lb moles gas feed

composition	lb mole	mol. wt	lb	wt %
Acetone	1.5	58	87	2.95
Air	98.5	29	2860	97.05
	100.0		2947	100.00

Now we know the compositions (on a weight basis) of all the streams. There are five streams entering and leaving the entire system (excluding the steam), and the weight of only one is known, leaving four weights as unknowns.

Basis: 1 hr

Balances on complete system (overall balances):

Let

$$\left. \begin{array}{l} F = \text{feed to absorber, lb} \\ A = \text{air leaving absorber, lb} \\ P = \text{product, lb} \\ W = \text{waste, lb} \end{array} \right\} \text{the four unknowns}$$

$$\text{total} \quad F + 1200 = P + W + A$$

$$\text{acetone} \quad F(0.0295) = P(0.99) + W(0.05)$$

$$\text{water} \quad 1200 = P(0.01) + W(0.95)$$

$$\text{air} \quad F(0.9705) = A$$

We now have four balances and four unknowns; however, only three of the equations are independent equations, as you can easily discover by adding up the component balances to get the overall balance. What is wrong? It seems as if there is not enough information available to solve this problem.

One additional bit of information would be enough to solve the problem as originally stated. This information might be, for example,

- (a) The weight of entering gas per hour product per hour, or waste per hour.
 (b) The composition of the feed into the still.

With an extra piece of pertinent information available, a complete solution is possible; without it, only a partial solution can be effected. Observe that making additional balances about the individual pieces of equipment will not resolve the problem, since as many new unknowns are added as independent equations.

EXAMPLE 2.13 Countercurrent stagewise mass transfer

In many commercial processes such as distillation, extraction, absorption of gases in liquids, and the like, the entering and leaving streams represent two different phases that flow in opposite directions to each other, as shown in Fig. E2.13(a). (The figure could just as well be laid on its side.)

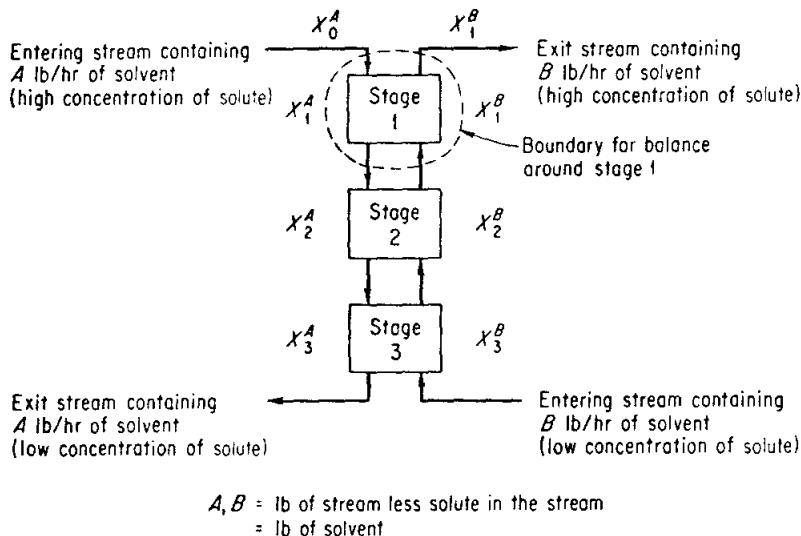


Fig. E2.13(a).

This type of operation is known as *countercurrent* operation. If equilibrium is attained between each stream at each stage in the apparatus, calculations can be carried out to relate the flow rates and concentration of products to the size and other design features of the apparatus. We shall illustrate how a material balance can be made for such type of equipment. The letter X stands for the weight concentration of solute in pounds of solute per pound of stream, solute-free. The streams are assumed immiscible as in a liquid-liquid extraction process.

Around stage 1 the solute material balance is

$$\frac{A \text{ lb}}{\text{hr}} \left| \begin{array}{c} X_0^A \text{ lb} \\ \hline \text{lb } A \end{array} \right. + \frac{B \text{ lb}}{\text{hr}} \left| \begin{array}{c} X_1^B \text{ lb} \\ \hline \text{lb } B \end{array} \right. = \frac{A \text{ lb}}{\text{hr}} \left| \begin{array}{c} X_1^A \text{ lb} \\ \hline \text{lb } A \end{array} \right. + \frac{B \text{ lb}}{\text{hr}} \left| \begin{array}{c} X_2^B \text{ lb} \\ \hline \text{lb } B \end{array} \right.$$

or

$$A(X_0^A - X_1^A) = B(X_1^B - X_2^B) \quad (\text{a})$$

per hour.

is possible;
additional
problem,option of
different
E2.13(a).

rate)

Around stage 2 the solute material balance is

$$\begin{array}{c} \text{in} \qquad \qquad \qquad \text{out} \\ \hline A \text{ lb} & X_1^A \text{ lb} & + & B \text{ lb} & X_2^B \text{ lb} \\ \text{hr} & \text{lb } A & & \text{hr} & \text{lb } B \\ \end{array} = \begin{array}{c} \text{in} \qquad \qquad \qquad \text{out} \\ \hline A \text{ lb} & X_1^A \text{ lb} & + & B \text{ lb} & X_2^B \text{ lb} \\ \text{hr} & \text{lb } A & & \text{hr} & \text{lb } B \\ \end{array}$$

or

$$A(X_1^A - X_2^A) = B(X_2^B - X_1^B)$$

We could generalize that for any stage number n

$$A(X_{n-1}^A - X_n^A) = B(X_n^B - X_{n+1}^B) \quad (\text{b})$$

Also a solute material balance could be written about the sum of stage 1 and stage 2 as follows:

$$\begin{array}{c} \text{in} \qquad \qquad \qquad \text{out} \\ \hline A(X_0^A) + B(X_1^B) & = A(X_2^A) + B(X_1^B) \\ \end{array} \quad (\text{c})$$

or to generalize for an overall solute material balance between the top end and the n th stage,

$$A(X_0^A - X_n^A) = B(X_1^B - X_{n+1}^B)$$

or for the $(n-1)$ th stage,

$$A(X_0^A - X_{n-1}^A) = B(X_1^B - X_n^B)$$

Changing signs,

$$A(X_{n-1}^A - X_0^A) = B(X_n^B - X_1^B) \quad (\text{d})$$

If we rearrange Eq. (d) assuming that A, B, X_0^A , and X_1^B are constants (i.e., steady-state operation) and X^A and X^B are the variables as we go from stage to stage, we can write

$$X_{n-1}^A = \frac{B}{A} X_n^B + \left(X_0^A - \frac{B}{A} X_1^B \right) \quad (\text{e})$$

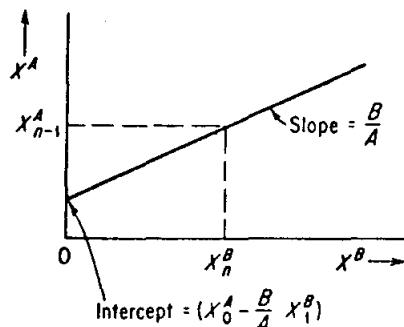
Equations (a)–(e) represent an unusual type of equation, one that gives the relationship between discrete points rather than continuous variables; it is called a *difference equation*. In Eq. (e) the locus of these points will fall upon a line with the slope B/A and an intercept $[X_0^A - (B/A)X_1^B]$, as shown in Fig. E2.13(b).

Fig. E2.13(b).

2.5 Problems involving tie components (elements)

A *tie component (element)* is material which goes from one stream into another without changing in any respect or having like material added to it or lost from it. If a tie component exists in a problem, in effect you can write a material balance that involves *only two streams*. Furthermore, the material balance has a particularly simple form, that of a ratio. For example, in Fig. 2.5(b) all the MeOH in stream *F* goes into stream *W*. Consequently, streams *F* and *W* can be related by a MeOH material balance:

$$\omega_{\text{MeOH}, F} F = \omega_{\text{MeOH}, W} W \quad \text{or} \quad \frac{\omega_{\text{MeOH}, W}}{\omega_{\text{MeOH}, F}} = \frac{F}{W}$$

$$0.10(100) = 0.22W \quad \text{or} \quad W = \frac{0.10}{0.22}(100)$$

To select a tie element, ask yourself the question, What component passes from one stream to another unchanged with constant weight (mass)? The answer is the tie component. Frequently several components pass through a process with continuity so that there are many choices of tie elements. Sometimes the amounts of these components can be added together to give an overall tie component that will result in a smaller percentage error in your calculations than if an individual tie element had been used. It may happen that a minor constituent passes through with continuity, but if the percentage error for the analysis of this component is large, you should not use it as a tie component. Sometimes you cannot find a tie component by direct examination of the problem, but you still may be able to develop a hypothetical tie component or a man-made tie component which will be equally effective as a tie component for a single material. A tie component is useful even if you do not know all the compositions and weights in any given problem because the tie component enables you to put two streams on the same basis. Thus a *partial solution* can be effected even if the entire problem is not resolved.

In solutions of problems involving tie components it is not always advantageous to select as the basis "what you have." Frequently it turns out that the composition of one stream is given as a percentage composition, and then it becomes convenient to select as the basis 100 lb (or other mass) of the material because then pounds equal percentage and the same numbers can be used to represent both. After you have carried out the computations on the basis of 100 lb (or another basis), then the answer can be transformed to the basis of the amount of material actually given by using the proper conversion factor. For example, if you had 32.5 lb of material and you knew its composition on the basis of percentage, you then could take as your basis 100 lb of material, and at the end of the calculations convert your answer to the basis of 32.5 lb.

Tie component problems can, of course, be worked by algebraic means, but in combustion problems and in some of the more complicated types of industrial chemical calculations so many unknowns and equations are involved that the

use of a tie component greatly simplifies the calculations. Use of a tie component also clarifies the internal workings of a process. Consequently, the examples below illustrate the use of both tie-component and algebraic solutions. Become proficient in both techniques, as you will have to draw upon both of them in your career as an engineer.

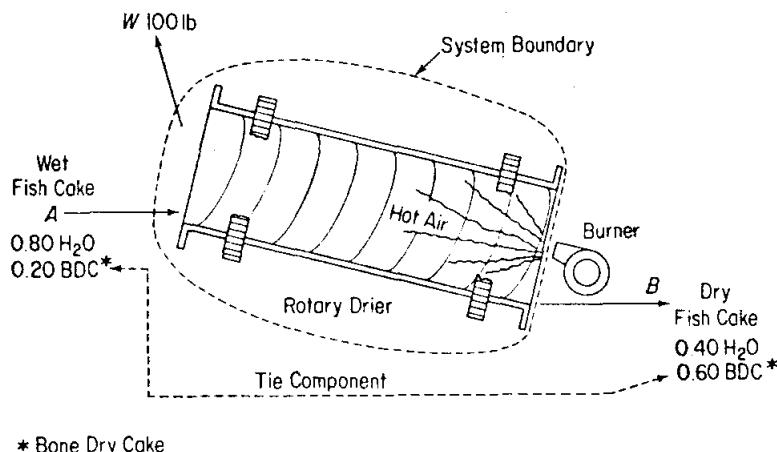
EXAMPLE 2.14 Drying

Fish caught by man can be turned into fish meal, and the fish meal can be used as feed to produce meat for man or used directly as food. The direct use of fish meal significantly increases the efficiency of the food chain. However, fish-protein concentrate, primarily for aesthetic reasons, is used as a supplementary protein food. As such, it competes with soy and other oilseed proteins.

In the processing of the fish, after the oil is extracted, the fish cake is dried in rotary drum dryers, finely ground, and packed. The resulting product contains 65 percent protein. In a given batch of fish cake that contains 80 percent water (the remainder is dry cake), 100.0 lb of water is removed, and it is found that the fish cake is then 40 percent water. Calculate the weight of the fish cake originally put into the dryer.

Solution:

From Fig. E2.14 we see that all the compositions and one weight are known and that there is a tie component of BDC.



* Bone Dry Cake

Fig. E2.14.

To solve the problem by use of algebra requires the use of two independent material balance equations since there are two unknowns—*A* and *B*.

Basis: 100 lb water evaporated

in = out

$$\begin{aligned} \text{Total balance } A &= B + W = B + 100 \\ \text{BDC balance } 0.20A &= 0.60B \end{aligned} \quad \left. \begin{array}{l} \text{mass balances} \end{array} \right\}$$

Notice that because the bone dry cake balance involves only two streams, you can set up a direct ratio of A to B , which is the essence of the tie component:

$$B = \frac{0.20A}{0.60} = \frac{1}{3}A$$

Introduction of this ratio into the total balance gives

$$A = \frac{1}{3}A + 100$$

$$\frac{2}{3}A = 100$$

$$A = 150 \text{ lb initial cake}$$

To solve the same problem by use of the tie component, take as a basis 100 lb of initial material (the 100 lb of H_2O will not serve as a useful basis).

Basis: 100 lb initial fish cake

initial -- loss = final

component	% = lb	lb*	lb	%
H_2O	80	100	?	40
BDC	20	← tie →	20	60
	100		?	100

*All H_2O .

To make either a total or a water material balance for this problem, all streams must be placed on the same basis (100 lb initial cake) by use of the tie component.

Tie final cake to initial cake by a tie component:

$$\frac{20 \text{ lb BDC}}{100 \text{ lb initial cake}} \mid \frac{100 \text{ lb final cake}}{60 \text{ lb BDC}} = 33.3 \text{ lb final cake}/100 \text{ lb initial cake}$$

Notice that the BDC is the same (the tie component) in both the initial and final stream and that the units of BDC can be cancelled. We have now used one independent material balance equation, the BDC balance. Our second balance will be total balance:

$$100 \text{ lb initial} - 33.3 \text{ lb final} = 66.7 \text{ lb of } H_2O \text{ evap.}/100 \text{ lb initial cake}$$

An alternative way to obtain this same value is to use a water balance

$$\frac{20 \text{ lb BDC}}{100 \text{ lb initial cake}} \mid \frac{40 \text{ lb } H_2O \text{ in dry cake}}{60 \text{ lb BDC in dry cake}} = 13.3 \text{ lb } H_2O \text{ left}/100 \text{ lb initial cake}$$

$$80 \text{ lb initial } H_2O - 13.3 \text{ lb final } H_2O = 66.7 \text{ lb } H_2O \text{ evap.}/100 \text{ lb initial cake}$$

Next a shift is made to the basis of 100 lb H_2O evaporated as required by the problem statement:

$$\frac{100 \text{ lb initial cake}}{66.7 \text{ lb } H_2O \text{ evap.}} \mid \frac{100 \text{ lb } H_2O \text{ evap.}}{100 \text{ lb initial cake}} = 150 \text{ lb initial cake}$$

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a basis 100 lb

Another suitable starting basis would be to use 1 lb of bone dry cake as the basis.

Basis: 1 lb BDC

component	initial fraction	- loss lb	= final fraction
H ₂ O	0.80	100	0.40
BDC	0.20		0.60
	1.00		1.00

$$\text{initial HO} - \text{final H}_2\text{O} = \text{H}_2\text{O lost} \quad \text{water balance}$$

$$\frac{0.80 \text{ lb H}_2\text{O}}{0.20 \text{ lb BDC}} - \frac{0.40 \text{ lb H}_2\text{O}}{0.60 \text{ lb BDC}} =$$

$$4.0 - 0.67 = 3.33 \text{ lb H}_2\text{O/lb BDC}$$

Again we have to shift bases to get back to the required basis of 100 lb of H₂O evaporated:

$$\frac{1 \text{ lb BDC}}{3.33 \text{ lb H}_2\text{O}} \mid \frac{100 \text{ lb H}_2\text{O evap.}}{} \mid \frac{1.0 \text{ lb initial cake}}{0.2 \text{ lb BDC}} = 150 \text{ lb initial cake}$$

You can see that the use of the tie component makes it quite easy to shift from one basis to another. If you now want to compute the pounds of final cake, all that is necessary is to write

$$\begin{array}{r} 150 \text{ lb initial cake} \\ - 100 \text{ lb H}_2\text{O evaporated} \\ \hline 50 \text{ lb final cake} \end{array}$$

Now that we have examined some of the correct methods of handling tie components let us look at another method frequently attempted (not for long!) by some students before they become completely familiar with the use of the tie component. They try to say that

$$0.80 - 0.40 = 0.40 \text{ lb H}_2\text{O evaporated}$$

$$\frac{100 \text{ lb}}{0.40 \text{ lb}} = 250 \text{ lb cake}$$

On the surface this looks like an easy way to solve the problem—what is wrong with the method? More careful inspection of the calculation shows that two different bases were used in subtracting (0.80 - 0.40). The 0.80 is on the basis of 1.00 lb of initial cake, while the 0.40 is on the basis of 1.00 lb of final cake. You would not say $0.80/A - 0.40/B = 0.40/A$, would you? From our early discussion about units you can see that this subtraction is not a legitimate operation.

EXAMPLE 2.15 Dilution

Trace components can be used to measure flow rates in pipelines, process equipment, and rivers that might otherwise be quite difficult to measure. Suppose that the

water analysis in a flowing creek shows 180 ppm Na_2SO_4 . If 10 lb of Na_2SO_4 are added to the stream uniformly over a 1-hr period and the analysis downstream where mixing is complete indicates 3300 ppm Na_2SO_4 , how many gallons of water are flowing per hour? See Fig. E2.15.

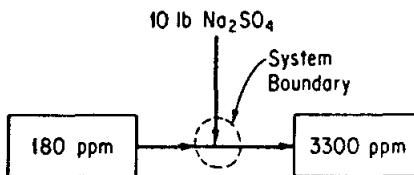


Fig. E2.15.

Tie-component Solution:

Basis: 100 lb initial solution (water + Na_2SO_4 initially present)

After choosing a basis of 100 lb of initial solution, we know three compositions and one weight. A tie component, the water, is present.

composition	initial	final
	lb = %	%
H_2O	99.982	99.670
Na_2SO_4	0.018	0.330
	100.000	100.000

$$\begin{array}{c|c} 0.33 \text{ lb } \text{Na}_2\text{SO}_4 & 99.982 \text{ lb } \text{H}_2\text{O} \\ \hline 99.67 \text{ lb } \text{H}_2\text{O} & 100 \text{ lb initial solution} \end{array} = 0.331 \text{ lb } \text{Na}_2\text{SO}_4 / 100 \text{ lb initial solution}$$

The tie component of water comprises our first material balance. Now that the exit Na_2SO_4 concentration is on the same basis as the entering Na_2SO_4 concentration, by an Na_2SO_4 balance (our second balance) we find that the Na_2SO_4 added on the same basis is

$$0.331 - 0.0180 = 0.313 \text{ lb}/100 \text{ lb initial solution}$$

Basis: 1 hr

$$\begin{array}{c|c|c} 100 \text{ lb initial solution} & 10 \text{ lb added} & 1 \text{ gal} \\ \hline 0.313 \text{ lb } \text{Na}_2\text{SO}_4 \text{ added} & 1 \text{ hr} & 8.35 \text{ lb} \end{array} = 383 \text{ gal/hr}$$

Algebraic Solution:

Let

$$x = \text{total lb flowing/hr initially}$$

$$y = \text{total lb flowing/hr after addition of } \text{Na}_2\text{SO}_4$$

$$\begin{aligned} \text{total balance} \quad x + 10 &= y \\ \text{water balance} \quad 0.99982x &= 0.99670y \end{aligned} \quad \left. \begin{array}{l} \\ \end{array} \right\} \text{mass balances}$$

$$x + 10 = \frac{0.99982x}{0.99670}$$

The water balance involves only two streams and provides a direct ratio between x and y . One of the difficulties in the solution of this problem using a water balance

Na_2SO_4 are added
in where mixing
are flowing per

is that the quantity

$$\left[\frac{0.99982}{0.99670} - 1 \right] = 0.00313$$

has to be determined quite accurately. It would be more convenient to use an Na_2SO_4 balance,

$$0.00018x + 10 = 0.00330y$$

Solving the total balance and the Na_2SO_4 balance simultaneously,

$$x = 3210 \text{ lb/hr}$$

$$\frac{3210 \text{ lb}}{\text{hr}} \mid \frac{1 \text{ gal}}{8.35 \text{ lb}} = 385 \text{ gal/hr}$$

EXAMPLE 2.16 Crystallization

The solubility of barium nitrate at 100°C is 34 g/100 g H_2O and at 0°C is 5.0 g/100 g H_2O . If you start with 100 g of $\text{Ba}(\text{NO}_3)_2$ and make a saturated solution in water at 100°C , how much water is required? If this solution is cooled to 0°C , how much $\text{Ba}(\text{NO}_3)_2$ is precipitated out of solution?

Tie-component Solution:

Basis: 100 g $\text{Ba}(\text{NO}_3)_2$

The maximum solubility of $\text{Ba}(\text{NO}_3)_2$ in H_2O at 100°C is a saturated solution, or 34 g/100 g H_2O . Thus the amount of water required at 100°C is

$$\frac{100 \text{ g } \text{H}_2\text{O}}{34 \text{ g } \text{Ba}(\text{NO}_3)_2} \mid \frac{100 \text{ g } \text{Ba}(\text{NO}_3)_2}{= 295 \text{ g } \text{H}_2\text{O}}$$

If the 100°C solution is cooled to 0°C , the $\text{Ba}(\text{NO}_3)_2$ solution will still be saturated, and the problem now can be pictured as in Fig. E2.16. The tie element is the water.

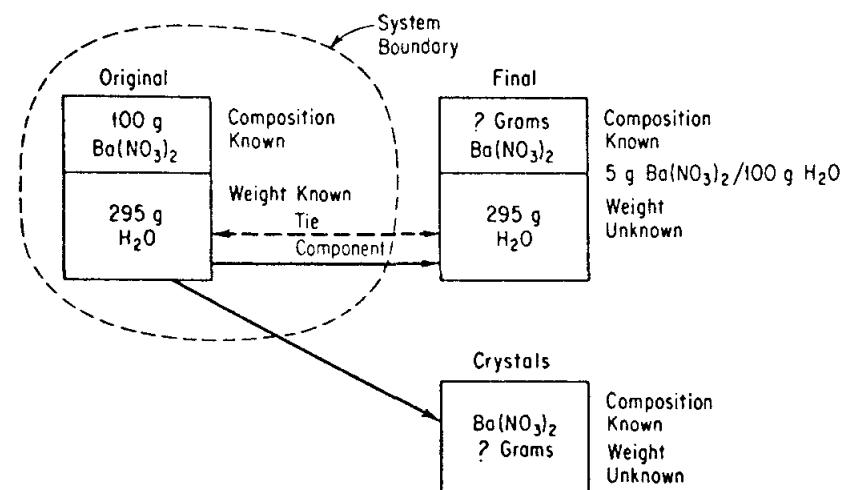


Fig. E2.16.

$$\frac{295 \text{ g H}_2\text{O}}{100 \text{ g H}_2\text{O}} \mid 5 \text{ g Ba}(\text{NO}_3)_2 = 14.7 \text{ g Ba}(\text{NO}_3)_2 \text{ in final solution}$$

original — final = crystals

$$100 \text{ g Ba}(\text{NO}_3)_2 - 14.7 \text{ g Ba}(\text{NO}_3)_2 = 85.3 \text{ g Ba}(\text{NO}_3)_2 \text{ precipitated}$$

Algebraic Solution:

Let

$$x = \text{g crystals}$$

$$y = \text{g final solution}$$

$$\text{H}_2\text{O balance} \quad 295 = y \left(\frac{100}{100 + 5} \right) \frac{\text{g H}_2\text{O}}{\text{g final solution}}$$

$$\text{Total balance} \quad 395 = x + y$$

$$y = 295 \left(\frac{105}{100} \right) = 310$$

$$x = 395 - y = 85 \text{ g Ba}(\text{NO}_3)_2 \text{ crystals}$$

EXAMPLE 2.17 Combustion

The main advantage of catalytic incineration of odorous gases or other obnoxious substances over direct combustion is the lower cost. Catalytic incinerators operate at lower temperatures—500°–900°C compared with 1100°–1500°C for thermal incinerators—and use substantially less fuel. Because of the lower operating temperatures, materials of construction do not need to be as heat resistant, reducing installation and construction costs.

In a test run, a liquid having the composition 88 percent C and 12 percent H₂ is vaporized and burned to a flue gas (fg) of the following composition:

CO ₂	13.4
O ₂	3.6
N ₂	83.0
<hr/>	

100.0%

To compute the volume of the combustion device, determine how many pound moles of dry fg are produced per 100 lb of liquid feed. What was the percentage of excess air used? See Fig. E2.17.

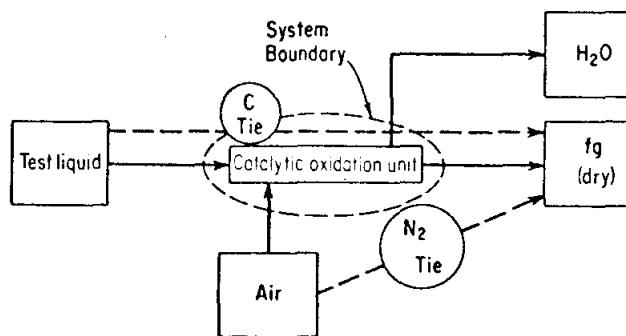


Fig. E2.17.

Tie-Components

In this problem we have two entering air streams (if we choose one as a tie component). If there are questions about the amount of air entering the system, we can use the data to determine the amount from the test data. If there is another tie component, we can use available data to determine the oxidation air required.

We can say the following about leaving the process: leaving the process, leaving the process, leaving the process.

In step (a) below, In the dry flue gas, In the test.

In the test.

(a₁) Using lb C

100 lb C

(a₂) Using lb O₂

100 lb O₂

(b) The N₂ stream must know the value of N₂ to be computed.

Tie-Component Solution:

In this problem four streams are present all of whose compositions are known, two entering and two leaving. We have the weights of three streams as unknown, (if we choose one weight as the basis). However, since we do not have to answer any questions about the water stream, two tie elements to relate the test fluid, dry flue gas, and air streams to each other would be sufficient to solve the problem. In examining the data to determine whether a tie element exists, we see that the carbon goes directly from the test fluid to the dry flue gas, and nowhere else, and so carbon will serve as one tie component. The N₂ in the air all shows up in the dry flue gas so N₂ can be used as another tie component. As explained before, there is no reason to convert all the available data to a weight basis, even though the moles of material entering and leaving the oxidation unit are not the same. Let us consider the moles of each atomic species present. Then we have in 100 lb of test fluid:

$$C: \frac{88}{12} = 7.33 \text{ lb mole}$$

$$H_2: \frac{12}{2} = 6.00 \text{ lb mole}$$

We can say the pound moles of C entering the process equal the pound moles of C leaving the process since the molecular weight is a constant factor in both inlet and outlet material and can be canceled out. Thus

$$lb \text{ C in} = lb \text{ C out}$$

$$lb \text{ mole C in} = lb \text{ mole C out}$$

In step (a) below both of these methods of attack are employed.

In the dry flue gas

Basis: 100 lb mole dry fg

$$\frac{13.4 \text{ lb mole C}}{1 \text{ lb mole C}} \mid \frac{12 \text{ lb C}}{1 \text{ lb mole C}} = 161 \text{ lb C}$$

In the test fluid

Basis: 100 lb test fluid

$$\frac{88 \text{ lb C}}{12 \text{ lb C}} \mid \frac{1 \text{ lb mole C}}{1 \text{ lb mole C}} = 7.33 \text{ lb mole C}$$

(a₁) Using lb C = lb C as the tie component,

$$\frac{100 \text{ lb mole dry fg}}{161 \text{ lb C}} \mid \frac{88 \text{ lb C}}{100 \text{ lb test fluid}} = \frac{54.6 \text{ lb mole dry fg}}{100 \text{ lb test fluid}}$$

(a₂) Using lb mole C = lb mole C as the tie component,

$$\frac{100 \text{ lb mole dry fg}}{13.4 \text{ lb mole C}} \mid \frac{7.33 \text{ lb mole C}}{100 \text{ lb test fluid}} = \frac{54.6 \text{ lb mole dry fg}}{100 \text{ lb test fluid}}$$

(b) The N₂ serves as the tie component to tie the air to the dry flue gas, and since we know the excess O₂ in the dry flue gas, the percentage of excess air can be computed.

Basis: 100 lb mole dry fg

$$\frac{83.0 \text{ lb mole N}_2}{0.79 \text{ lb mole N}_2} \mid \frac{1.00 \text{ lb mole air}}{105.0 \text{ lb mole air}} = \frac{105.0 \text{ lb mole air}}{100 \text{ lb mole dry fg}}$$

$$(105.0)(0.21) = O_2 \text{ entering} = 22.1 \text{ lb mole O}_2$$

Or, saving one step,

$$\frac{83.0 \text{ lb mole N}_2}{0.79 \text{ lb mole N}_2 \text{ in air}} \mid \frac{0.21 \text{ lb mole O}_2 \text{ in air}}{100 \text{ lb mole dry fg}} = \frac{22.1 \text{ lb mole O}_2 \text{ entering}}{100 \text{ lb mole dry fg}}$$

$$\% \text{ excess air} = 100 \frac{\text{excess O}_2}{\text{O}_2 \text{ entering} - \text{excess O}_2} = \frac{(100)3.6}{22.1 - 3.6} = 19.4\%$$

To check this answer, let us work part (b) of the problem using as a basis

Basis: 100 lb test fluid

The required oxygen for complete combustion is

comp.	lb	lb mole	lb mole O ₂ required
C	88	7.33	7.33
H ₂	12	6	3
			<u>10.33</u>

The excess oxygen is

$$\frac{3.6 \text{ lb mole O}_2}{100 \text{ lb mole fg}} \mid \frac{54.6 \text{ lb mole dry fg}}{100 \text{ lb oil}} = 1.97 \text{ lb mole}$$

$$\% \text{ excess air} = \frac{\text{excess O}_2}{\text{required O}_2} 100 = \frac{1.97(100)}{10.33} = 19.0\%$$

The answers computed on the two different bases agree reasonably well here, but in many combustion problems slight errors in the data will cause large differences in the calculated percentage of excess air. Assuming no mathematical mistakes have been made (it is wise to check), the better solution is the one involving the use of the most precise data. Frequently this turns out to be the method used in the check here—the one with a basis of 100 lb of test fluid.

If the dry flue-gas analysis had shown some CO, as in the following hypothetical analysis,

CO ₂	11.9%
CO	1.6
O ₂	4.1
N ₂	82.4

then, on the basis of 100 moles of dry flue gas, we would calculate the excess air as follows:

O₂ entering with air:

$$\frac{82.4 \text{ lb moles N}_2}{0.79 \text{ lb mole N}_2} \mid \frac{0.21 \text{ lb mole O}_2}{100 \text{ lb mole dry fg}} = 21.9 \text{ lb mole O}_2$$

Excess O₂:

$$4.1 - \frac{1.6}{2} = 3.3 \text{ lb mole}$$

$$\% \text{ excess air} = 100 \frac{3.3}{21.9 - 3.3} = 17.7\%$$

Note that to get the true excess oxygen, the apparent excess oxygen in dry flue gas, 4.1 lb moles, has to be reduced by the amount of the theoretical oxygen not combining with the CO. According to the reactions



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EXAMPLE 2.

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for each mole of CO in the dry flue gas, $\frac{1}{2}$ mole of O₂ which should have combined with the carbon to form CO₂ did not do so. This $\frac{1}{2}$ mole carried over into the flue gas and inflated the value of the true excess oxygen expected to be in the flue gas. In this example, 1.6 lb moles of CO are in the flue gas, so that (1.6/2) lb mole of theoretical oxygen are found in the flue gas in addition to the true excess oxygen.

Algebraic Solution:

An algebraic solution of the originally stated problem would proceed as follows:
Let

$$x = \text{lb of test fluid}$$

$$y = \text{lb moles of dry fg}$$

$$z = \text{lb moles of air}$$

$$w = \text{lb moles of H}_2\text{O associated with the flue gas}$$

One of these unknowns can be replaced by the basis, say $x = 100 \text{ lb of test fluid}$. Since three unknowns will remain, it will be necessary to use in the solution three independent material balances from among the four component and one total balance that can be written. The balances are

total

$$100 + 29z = 30.25y + 18w \quad \text{where } 30.25 = \text{average mol. wt. of fg}$$

component

$$\text{C} \quad 100(0.88) = \frac{y \text{ lb mole dry fg}}{1 \text{ lb mole dry fg}} \mid \frac{0.134 \text{ lb mole C}}{1 \text{ lb mole C}} \mid \frac{12 \text{ lb C}}{1 \text{ lb mole C}}$$

$$\text{H}_2 \quad 100(0.12) = \frac{w \text{ lb mole H}_2\text{O}}{1 \text{ lb mole H}_2\text{O}} \mid \frac{1 \text{ lb mole H}_2}{1 \text{ lb mole H}_2\text{O}} \mid \frac{2.016 \text{ lb H}_2}{1 \text{ lb mole H}_2}$$

$$\text{N}_2 \quad 0.79z = 0.83y$$

$$\text{O}_2 \quad 0.21z = \frac{w \text{ lb mole H}_2\text{O}}{1 \text{ lb mole H}_2\text{O}} \mid \frac{0.5 \text{ lb mole O}_2}{1 \text{ lb mole H}_2\text{O}} \mid \frac{y \text{ lb mole dry fg}}{1 \text{ lb mole dry fg}} \mid \frac{0.036 \text{ lb mole O}_2 + 0.134 \text{ mole O}_2}{1 \text{ lb mole dry fg}}$$

Note that the balances for the tie components C and N₂ (as well as H₂) involve only two streams, whereas the O₂ (and total) balance involves three streams. We shall use the C and N₂ balances.

Basis: 100 lb of test fluid

$$y = \frac{88}{(0.134)(12)} = 54.6 \text{ lb mole dry fg}$$

$$z = \frac{0.83}{0.79}y = 57.5 \text{ lb mole air}$$

$$\text{O}_2 \text{ entering} = 57.5(0.21) = 12.1 \text{ lb mole}$$

The remainder of the calculations follow those described above. Can you demonstrate that the dry flue-gas analysis is slightly inaccurate?

EXAMPLE 2.18 Distillation

A continuous still is to be used to separate acetic acid, water, and benzene from each other. On a trial run the calculated data were as shown in Fig. E2.18. Data record-

Take a new basis:

$$\frac{67.4 \text{ lb Bz}}{75.9 \text{ lb HAc}}$$

Algebraic Solution:

To employ algebraic material balance for each

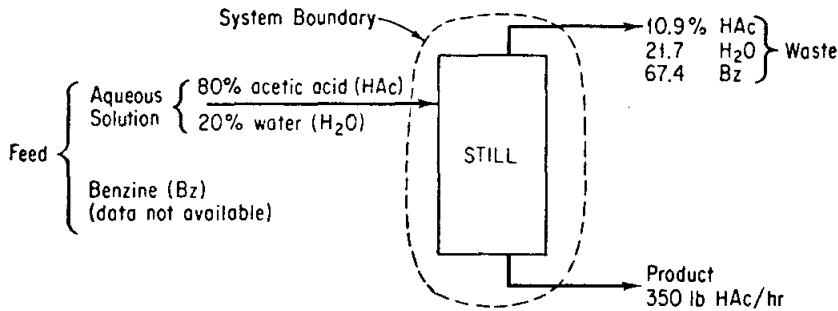


Fig. E2.18.

ing the benzene composition of the feed were not taken because of an instrument defect. Calculate the benzene flow in the feed per hour.

A quick inspection of the flow diagram shows that enough information about weights and compositions would be available to work this problem if only the benzene composition in the feed were known, but it is not. However, we have one added source of information not readily apparent on the surface, and that is that there are *two* tie components from the feed to the waste: water and benzene. A choice now must be made in procedure: the problem can be calculated using the tie components or using algebraic techniques.

Tie-Component Solution:

Take a convenient basis of 100 lb of waste (100 lb of feed would involve more work since the benzene composition is unknown, but 100 lb of aqueous solution—80 percent HAc, 20 percent H₂O—would be a sound basis). Let x = lb of benzene in the feed/100 lb feed.

Basis: 100 lb waste

composition	feed lb	waste % = lb	product %
HAc	(100 - x).080	10.9	100
H ₂ O	(100 - x).20	21.7	
Bz	x	67.4	
Total	100	100	

For an initial step let us calculate the quantity of feed per 100 lb of waste. We have the water in the feed (21.7 lb) and the benzene in the feed (67.4 lb); these two materials appear only in the waste and not in the product and can act as tie components. All that is needed is the HAc in the feed. We can use water as the tie component to find this quantity.

$$\frac{21.7 \text{ lb H}_2\text{O}}{100 \text{ lb waste}} \left| \begin{array}{l} 0.80 \text{ lb HAc} \\ 0.20 \text{ lb H}_2\text{O} \end{array} \right. = 86.8 \text{ lb HAc/100 lb waste}$$

The product now is

$$\text{HAc in feed} - \text{HAc in waste} = \text{HAc in product} \quad \text{HAc balance}$$

$$86.8 - 10.9 = 75.9$$

The equations are

Total balan

H₂O balan

HAc balan

Bz balan

Any three will be independent. Three equations involves three unknowns.

EXAMPLE 2.19 Economic Basis

A chemical company has a contract to supply a certain amount of moisture and job assignment is as follows: you are to supply a contract for 10 carloads of coal at \$3.20 per ton (3.2 percent moisture and a maximum of 10 percent ash). You accept this contract and buy coal as reported by your supplier. The billed price for this coal is \$3.00 per ton outside your plant. The coal is delivered to your plant correct. Calculate the cost per ton.

Solution:

What you really pay is the allowable content of ash times the cost of the combustible material.

com

Combust

Moisture

% HAc
H₂O } Waste
Bz

Take a new basis:

Basis: 350 lb HAc product ≡ 1 hr

$$\frac{67.4 \text{ lb Bz in feed}}{75.9 \text{ lb HAc in product}} \mid \frac{350 \text{ lb HAc product}}{\text{hr}} = 311 \text{ lb Bz/hr}$$

Algebraic Solution:

To employ algebra in the solution of this problem, we need an independent material balance for each unknown. The unknowns are

W = waste, lb

F = feed, lb

x = lb benzene/100 lb feed

Basis: 1 hr ≡ 350 lb HAc product

The equations are

$$\text{Total balance} \quad F = W + 350$$

$$\text{H}_2\text{O balance} \quad F \left[\frac{0.20(100 - x)}{100} \right] = W(0.217)$$

$$\text{HAc balance} \quad F \left[\frac{0.80(100 - x)}{100} \right] = W(0.109) + 350$$

$$\text{Bz balance} \quad F \left[\frac{x}{100} \right] = W(0.674)$$

Any three will be independent equations, but you can see the simultaneous solution of three equations involves more work than the use of tie components.

EXAMPLE 2.19 Economics

A chemical company buys coal at a contract price based on a specified maximum amount of moisture and ash. Since you have married the boss's daughter, your first job assignment is as purchasing agent. The salesman for the Higrade Coal Co. offers you a contract for 10 carloads/month of coal with a maximum moisture content of 3.2 percent and a maximum ash content of 5.3 percent at \$4.85/ton (weighed at delivery). You accept this contract price. In the first delivery the moisture content of the coal as reported by your laboratory is 4.5 percent and the ash content is 5.6 percent. The billed price for this coal is \$4.85/ton—as weighed by the railroad in the switchyards outside your plant. The accounting department wants to know if this billing price is correct. Calculate the correct price.

Solution:

What you really pay for is 91.5 percent combustible material with a maximum allowable content of ash and water. Based on this assumption, you can find the cost of the combustible material in the coal actually delivered.

Basis: 1 ton coal as delivered

composition	delivered	contract coal
Combustible	0.899	0.915
Moisture plus ash	0.101	0.085
	1.000	1.000

The contract calls for

$$\frac{\$4.85}{\text{ton contract}} \left| \begin{array}{c} 1 \text{ ton contract} \\ 0.915 \text{ ton comb.} \end{array} \right| \frac{0.899 \text{ ton comb.}}{1 \text{ ton del.}} = \$4.76/\text{ton del.}$$

The billed price is wrong.

If the ash content had been below 5.3 percent but the water content above 3.2 percent, presumably an adjustment should have been made in the billing for excess moisture even though the ash was low.

2.6 Recycle, bypass, and purge calculations

Processes involving *feedback* or recycle of part of the product are frequently encountered in the chemical and petroleum industry as well as in nature. Figure 2.10 shows by a block diagram the character of the recycle stream. Figures 2.3 and 2.4 indicate some typical recycle streams in the world at large. As another example, in planning long space missions, all the food and water will have to be provided from stores on board the spacecraft. Table 2.1 lists the daily intake and output per man of solid and water. Since the average internal water consumption amounts to some 5.50 lb/man/day, this leaves an additional requirement of 4.69 lb that must be made up from stores or reclaimed from waste products containing water. Figure 2.11 shows the sources of water and how by the use of several recycle streams the 5.50 lb/day is proposed to be collected.

Many industrial processes employ recycle streams. For example, in some drying operations, the humidity in the air is controlled by recirculating part of the wet air which leaves the dryer. In chemical reactions, the unreacted material may be separated from the product and recycled, as in the synthesis of ammonia. Another example of the use of recycling operations is in fractionating columns where part of the distillate is refluxed through the column to maintain the quantity of liquid within the column.

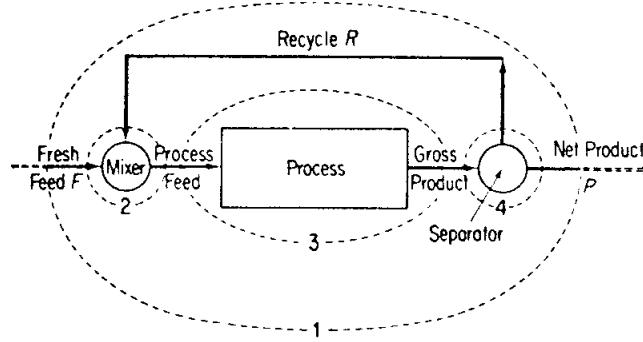


Fig. 2.10. A process with recycle (the numbers designate possible material balances—see text).

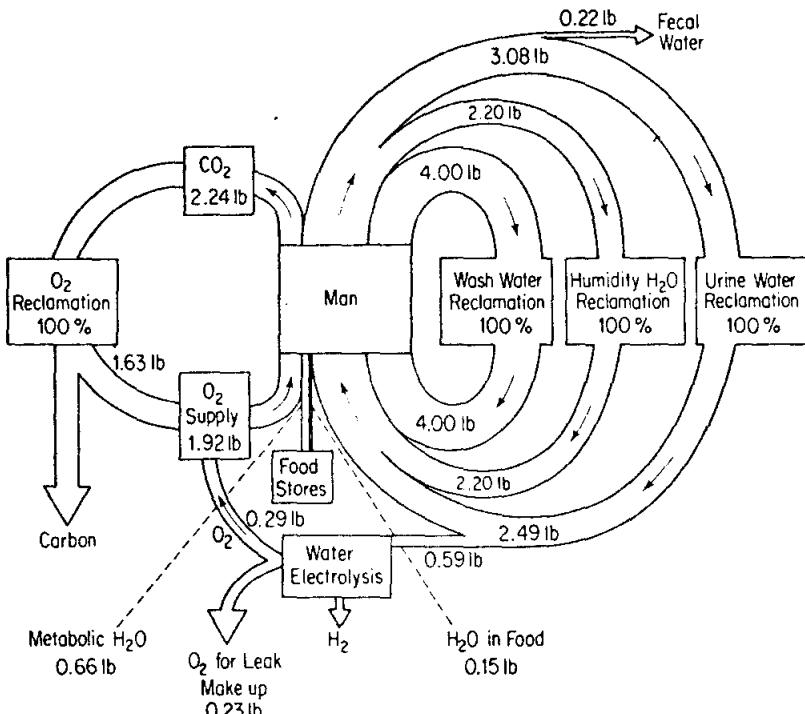


Fig. 2.11. Water and oxygen recycle in a space vehicle.

TABLE 2.1 MAN'S DAILY BALANCE

		Total balance (lb)	Water balance (lb)
<i>Output</i>	Urine (95% H ₂ O)	3.24	3.08
	Feces (75.8% H ₂ O)	0.29	0.22
	Transpired	2.20	2.20
	Carbon dioxide (1.63 lb O ₂)	2.24	
	Other losses	0.14	
		8.11	5.50
<i>Input</i>	Food	1.5	0.15
	Oxygen	1.92	
	Metabolic water		0.66
	Water	4.69	4.69
		8.11	5.50

Recycle streams initially may be confusing to you, but with a little practice in solving problems involving recycle you should thereafter experience little difficulty. The first point you should grasp concerning recycle calculations is that the process shown in Fig. 2.10 is in the *steady state*—no buildup or deple-

tion of material takes place inside the process or in the recycle stream. The values of F , P , and R are *constant*. The feed to the process itself is made up of two streams, the fresh feed and the recycle material. The gross product leaving the process is separated into two streams, the net product and the material to be recycled. In some cases the recycle stream may have the same composition as the gross product stream, while in other instances the composition may be entirely different depending on how the separation takes place and what happens in the process.

Recycle problems have certain features in common, and the techniques you should use in solving these problems are the familiar ones previously encountered in this chapter in the use of material balances. You can make a material balance on a total basis or for each component. Depending on the information available concerning the amount and composition of each stream, you can determine the amount and composition of the unknowns. If tie components are available, they simplify the calculations. If they are not available, then algebraic methods should be used.

A balance can be written in several ways, four of which are shown by dashed lines in Fig. 2.10:

- About the entire process including the recycle stream, as indicated by the dashed lines marked 1 in Fig. 2.10.
- About the junction point at which the fresh feed is combined with the recycle stream (marked 2 in Fig. 2.10).
- About the process only (marked 3 in Fig. 2.10).
- About the junction point at which the gross product is separated into recycle and net product (marked 4 in Fig. 2.10).

Only three of the four balances are independent. However, balance 1 will not include the recycle stream, so that the balance will not be directly useful in calculating a value for the recycle R . Balances 2 and 4 to include R . It would also be possible to write a material balance for the combination of 2 and 3 or 3 and 4 and include the recycle stream.

If a chemical reaction occurs in the process, the stoichiometric equation, the limiting reactant, and the degree of completion all should be considered before beginning your calculations. As discussed in Chap. 1, the term *conversion* as applied to Fig. 2.10 may be either the fraction or percentage of the fresh feed which reacts or the fraction of the feed plus recycle. If 100 lb of substance A in the fresh feed is converted on an overall basis into 40 lb of desired product, 30 lb of waste, 20 lb of a secondary product, and 10 lb of A pass through the process unchanged, the total conversion of A is 90 percent based on the fresh feed. However, the *yield* of primary and secondary products is only 60 lb of products per 100 lb of A . If, in addition, the recycle stream contains 100 lb of A , the total conversion of A on a once-through basis is only 45 percent. You can see that the basis on which the conversion and yield are calculated must always be clearly specified. When the fresh feed consists of more than one

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You should carefully analyze a problem to ascertain whether there is a simplified method of solution (as illustrated in the following examples), but if such a simplification escapes you, or if there is none, then the standard procedure of setting up algebraic material balances will always be effective, although perhaps long and involved. One psychological stumbling block is the stream of unknown weight or composition which is found to be essential for the solution and for which you have no information. By labeling this stream with a letter—*R*, *X*, or whatever—you can proceed to make material balances in the ordinary way and solve for the unknown stream. Of course, for each unknown you set up, you must write an independent equation, and so from the viewpoint of the economic use of your time, it is advisable to minimize the number of unknowns. Some illustrations follow.

EXAMPLE 2.20 Recycle without chemical reaction

A distillation column separates 10,000 lb/hr of a 50 percent benzene-50 percent toluene mixture. The product recovered from the condenser at the top of the column contains 95 percent benzene, and the bottoms from the column contain 96 percent toluene. The vapor stream entering the condenser from the top of the column is 8000 lb/hr. A portion of the product is returned to the column as reflux, and the rest is withdrawn for use elsewhere. Assume the compositions of the streams at the top of the column (*V*), the product withdrawn (*D*), and the reflux (*R*) are identical. Find the ratio of the amount refluxed to the product withdrawn.

Solution:

See Fig. E2.20. All the compositions are known and two weights are unknown. No tie components are evident in this problem; thus an algebraic solution is mandatory.

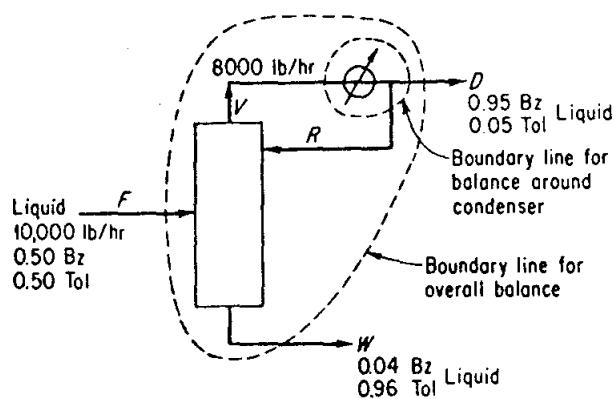


Fig. E2.20.

By making an overall balance (ignoring the reflux stream for the moment), we can find D . With D known, a balance around the condenser will give us R .

Basis: 1 hr

Overall material balances:

Total material:

$$F = D + W$$

$$10,000 = D + W \quad (a)$$

Component (benzene):

$$FX_F = DX_D + WX_W$$

$$10,000(0.50) = D(0.95) + W(0.04) \quad (b)$$

Solving (a) and (b) together,

$$5000 = (0.95)(10,000 - W) + 0.04W$$

$$W = 4950 \text{ lb/hr}$$

$$D = 5050 \text{ lb/hr}$$

Balance around the condenser:

Total material:

$$V = R + D$$

$$8000 = R + 5050$$

$$R = 2950 \text{ lb/hr}$$

$$\frac{R}{D} = \frac{2950}{5050} = 0.584$$

EXAMPLE 2.21 Recycle without chemical reaction

Data are presented in Fig. E2.21(a) for an evaporator. What is the recycle stream in pounds per hour?

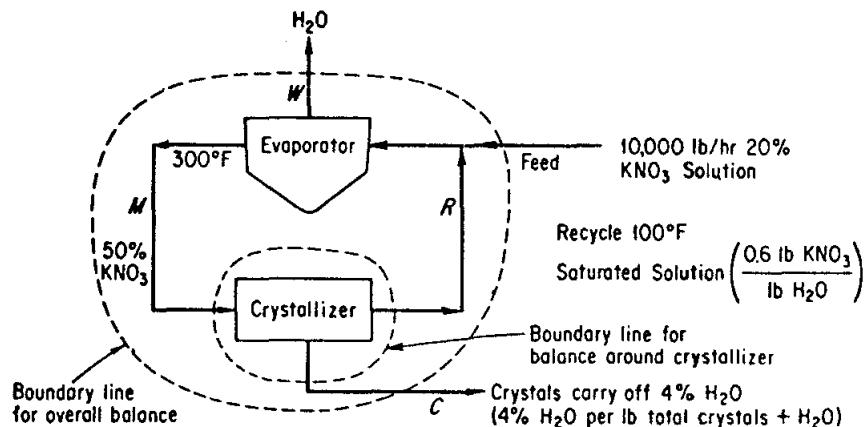


Fig. E2.21(a).

component), we can
R.

(a)

(b)

Solution:

In this problem the compositions are all known except for the recycle stream, but this can be easily calculated. On the basis of 1 lb of water, the saturated recycle stream contains $(1.0 \text{ lb H}_2\text{O} + 0.6 \text{ lb KNO}_3) = 1.6 \text{ lb}$ total. The recycle stream composition is

$$\frac{0.6 \text{ lb KNO}_3}{1 \text{ lb H}_2\text{O}} \mid \frac{1 \text{ lb H}_2\text{O}}{1.6 \text{ lb solution}} = 0.375 \text{ lb KNO}_3/\text{lb solution}$$

With all compositions known, a search for a tie component shows that one exists for an overall balance—the KNO_3 . Temporarily ignoring the interior streams, we can draw a picture as in Fig. E2.21(b). Now we can calculate the amount of crystals (and H_2O evaporated, if wanted).

Basis: 1 hr \equiv 10,000 lb feed

$$\frac{10,000 \text{ lb } F}{1 \text{ lb } F} \mid \frac{0.20 \text{ lb KNO}_3}{0.96 \text{ lb KNO}_3} \mid \frac{1 \text{ lb crystals}}{0.80 \text{ lb H}_2\text{O}} = 2080 \text{ lb/hr crystals}$$

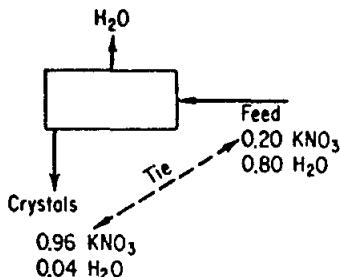


Fig. E2.21(b).

To determine the recycle stream R we need, in the absence of an additional tie component, either

- (a) A balance around the evaporator—or
- (b) A balance around the crystallizer.

The latter is easier since only three rather than four (the recycle added to the feed is the fourth stream) streams are involved.

Total balance on crystallizer:

$$M = C + R$$

$$M = 2080 + R$$

Component (KNO_3) balance on crystallizer:

$$Mx_M = Cx_C + Rx_R$$

$$0.5M = 0.96C + R(0.375)$$

Solving these two equations,

$$0.5(2080 + R) = 0.375R + 2000$$

$$R = 7680 \text{ lb/hr}$$

EXAMPLE 2.22 Recycle with a chemical reaction

In a proposed process for the preparation of methyl iodide, 2000 lb/day of hydroiodic acid are added to an excess of methanol:



If the product contains 81.6 percent CH_3I along with the unreacted methanol, and the waste contains 82.6 percent hydroiodic acid and 17.4 percent H_2O , calculate, assuming that the reaction is 40 percent complete in the process vessel:

- (a) The weight of methanol added per day.
- (b) The amount of HI recycled.

Solution:

In this problem all the compositions are known (in weight percent) as well as one weight—the HI input stream. The unknown quantities are the weights of the CH_3OH (M), the product (P), the waste (W), and the recycle stream. An overall balance about the whole process is all that is needed to calculate the M stream, but it will not include the recycle stream—see the dashed line in Fig. E2.22.

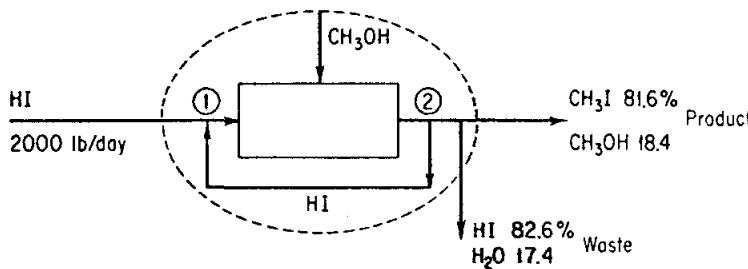


Fig. E2.22.

We first need to convert the product and waste streams to a mole composition in order to make use of the chemical equation. A basis of 100 lb of waste is convenient, although 100 lb of product would also be a satisfactory basis.

Basis: 100 lb waste

comp.	$lb = \%$	MW	$lb \text{ mole}$
HI	82.6	128	0.646
H_2O	17.4	18	0.968
	100.0		

Basis: 100 lb product

comp.	$lb = \%$	MW	$lb \text{ mole}$	equivalent lb $\text{mole of } \text{CH}_3\text{OH}$
CH ₃ I	81.6	142	0.575	0.575
CH ₃ OH	18.4	32	0.575	0.575
				1.150

(a) From the chemical equation we observe that associated with each pound mole of H_2O in the waste is 1 lb mole of CH_3I . Consequently the entering HI is (per 100 lb waste).

Reacted

$$\frac{0.968 \text{ lb mole } \text{H}_2\text{O}}{100 \text{ lb waste}} \mid \frac{1 \text{ lb mole } \text{CH}_3\text{I}}{1 \text{ lb mole } \text{H}_2\text{O}} \mid \frac{1 \text{ lb mole HI}}{1 \text{ lb mole } \text{CH}_3\text{I}} \mid \frac{128 \text{ lb HI}}{1 \text{ lb mole HI}} = \frac{124 \text{ lb HI}}{100 \text{ lb waste}}$$

Total HI = reacted + unreacted = $124 + 82.6 = 206.6 \text{ lb HI}/100 \text{ lb waste}$
On the same basis the CH_3OH entering is,

$$\frac{0.968 \text{ lb mole } \text{H}_2\text{O}}{100 \text{ lb waste}} \mid \frac{1 \text{ lb mole } \text{CH}_3\text{I}}{1 \text{ lb mole } \text{H}_2\text{O}} \mid \frac{1.150 \text{ lb mole } \text{CH}_3\text{OH}}{0.575 \text{ lb mole } \text{CH}_3\text{I}} \mid \frac{32 \text{ lb } \text{CH}_3\text{OH}}{1 \text{ lb mole } \text{CH}_3\text{OH}} \\ = \frac{61.9 \text{ lb } \text{CH}_3\text{OH}}{100 \text{ lb waste}}$$

Basis: 1 day

$$\frac{2000 \text{ lb HI}}{1 \text{ day}} \mid \frac{100 \text{ lb waste}}{206.6 \text{ lb HI}} \mid \frac{61.9 \text{ lb } \text{CH}_3\text{OH}}{100 \text{ lb waste}} = 600 \text{ lb } \text{CH}_3\text{OH/day}$$

(b) To obtain the value of the recycle stream R , a balance must be made about a junction point or about just the reactor itself so as to include the stream R . A balance about junction 1 indicates that (all subsequent bases are 1 day)

$$200 + R = \text{reactor feed}$$

but this equation is not of much help since we do not know the rate of feed to the reactor. Similarly, for a balance on junction 2,

$$\text{gross product} = R + P + W$$

we can compute the value of the product and waste but not that of the gross product.

The only additional information available to us that has not yet been used is the fact that the reaction is 40 percent complete on one pass through the reactor. Consequently, 60 percent of the HI in the gross feed passes through the reactor unchanged. We can make an HI balance, then, about the reactor:

$$(2000 + R)(0.60) = R + 800$$

$$400 = 0.40R$$

$$R = 1000 \text{ lb/day}$$

Our material balance around the reactor for the HI is known as a *once-through balance* and says that 60 percent of the HI that enters the reactor (as fresh feed plus recycle) leaves the reactor unchanged in the gross product (recycle plus product).

Two additional commonly encountered types of process streams are shown in Figs. 2.12 and 2.13:

- (a) A bypass stream—one which skips one or more stages of the process and goes directly to another stage.
- (b) A purge stream—a stream bled off to remove an accumulation of inert or unwanted material that might otherwise build up in the recycle

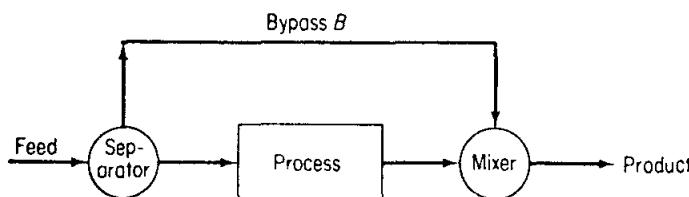


Fig. 2.12. Bypass stream.

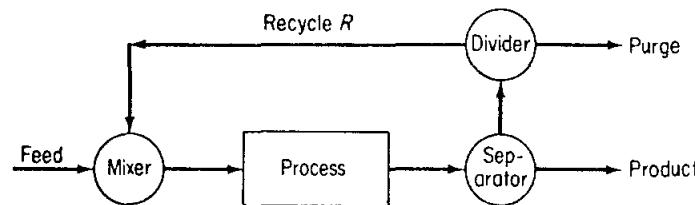


Fig. 2.13. A recycle stream with purge.

stream. The purge rate is adjusted so that the amount of purged material remains below a specified level or so that the

$$\left\{ \begin{array}{l} \text{rate of} \\ \text{accumulation} \end{array} \right\} = 0 = \left\{ \begin{array}{l} \text{rate of entering material} \\ \text{and/or production} \end{array} \right\} - \left\{ \begin{array}{l} \text{rate of purge} \\ \text{and/or loss} \end{array} \right\}$$

Calculations for bypass and purge streams introduce no new principles or techniques beyond those presented so far. An example will make this clear.

EXAMPLE 2.23 Bypass calculations

In the feed-stock preparation section of a plant manufacturing natural gasoline, isopentane is removed from butane-free gasoline. Assume for purposes of simplification that the process and components are as shown in Fig. E2.23. What fraction of the butane-free gasoline is passed through the isopentane tower?

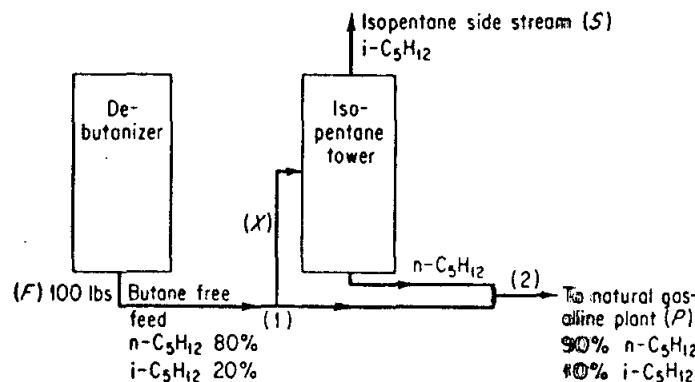


Fig. E2.23.

Solution:

By examining the flow diagram you can see that part of the butane-free gasoline bypasses the isopentane tower and proceeds to the next stage in the natural gasoline plant. All the compositions are known. What kind of balances can we write for this process? We can write the following (each stream is designated by the letter F , S , or P):

Basis: 100 lb feed

- (a) *Overall balances* (all compositions are known; a tie component exists):
Total material balance:

$$\begin{aligned} \text{in} &= \text{out} \\ 100 &= S + P \end{aligned} \quad (1)$$

Component balance ($n\text{-C}_5$):

$$\begin{aligned} \text{in} &= \text{out} \\ 100(0.80) &= S(0) + P(0.90) \end{aligned} \quad (2)$$

Using (2),

$$P = 100 \left(\frac{0.80}{0.90} \right) = 89 \text{ lb}$$

$$S = 100 - 89 = 11 \text{ lb}$$

The overall balances will not tell us the fraction of the feed going to the isopentane tower; for this we need another balance.

- (b) *Balance around isopentane tower*: Let x = lb of butane-free gas going to isopentane tower.

Total material:

$$\begin{aligned} \text{in} &= \text{out} \\ x &= 11 + n\text{-C}_5\text{H}_{12} \text{ stream (another unknown, } y) \end{aligned} \quad (3)$$

Component ($n\text{-C}_5$):

$$x(0.80) = y \quad (\text{a tie component}) \quad (4)$$

Consequently, combining (3) and (4),

$$x = 11 + 0.8x$$

$$x = 55 \text{ lb, or the desired fraction is 0.55}$$

Another approach to this problem is to make a balance at points (1) or (2) called *mixing points*. Although there are no pieces of equipment at those points, you can see that streams enter and leave the junction.

- (c) *Balance around mixing point (2)*:

material into junction = material out

Total material:

$$(100 - x) + y = 89 \quad (5)$$

Component (iso-C_5):

$$(100 - x)(0.20) + 0 = 89(0.10) \quad (6)$$

Equation (6) avoids the use of y . Solving,

$$20 - 0.2x = 8.9$$

$$x = 55 \text{ lb, as before}$$

After a little practice you can size up a problem and visualize the simplest types of balances to make.

Up to now we have discussed material balances of a rather simple order of complexity. If you try to visualize all the operations which might be involved in even a moderate-sized plant, as illustrated in Fig. 2.4, the stepwise or simultaneous solution of material balances for each phase of the entire plant is truly a staggering task, but a task that can be eased considerably by the use of computer codes. Keep in mind that a plant can be described by a number of individual, interlocking material balances which, however tedious they are to set up and solve, can be set down according to the principles and techniques discussed in this chapter. In a practical case there is always the problem of collecting suitable information and evaluating its accuracy, but this matter calls for detailed familiarity with any specific process and is not a suitable topic for discussion here. We can merely remark that some of the problems you will encounter have such conflicting data or so little useful data that the ability to perceive what kind of data are needed is the most important attribute you can bring to bear in their solution. By now, from working with simple problems, you should have some insight into the requirements for the solution of more complicated problems. In Chap. 5 you will encounter some of these more complex problems.

WHAT YOU SHOULD HAVE LEARNED FROM THIS CHAPTER

1. You should be able to analyze a material balance problem in order to
 - (a) Find out what the problem is.
 - (b) Draw a picture of the process.
 - (c) Put down all the compositions of the entering and leaving streams.
 - (d) Decide which masses (weights) are known and unknown.
 - (e) Find a tie component and/or set up algebraic mass balances involving the unknowns.
 - (f) Solve for the required values.
2. You should understand the once-through balance for recycle problems involving chemical reactions.

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PROBLEMS¹

- 2.1. The steady-state hydrology of the Great Lakes based on average flow values for the period 1900–1960 is shown in Fig. P2.1. Compute the return into lake St. Clair and the evaporation from Lake Ontario based on the data shown. Would the balance for 1 year be a steady-state balance? For 1 month?

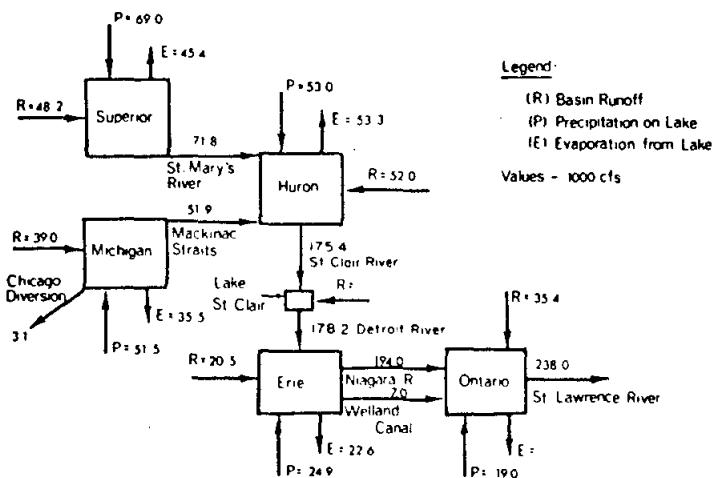


Fig. P2.1.

- 2.2. By use of an overall steady-state material balance determine whether or not the petrochemical process indicated in Fig. P2.2 has been properly formulated. The block diagrams represent the steam cracking of naphtha into various products, and all flows are on an annual basis, i.e., per year.

¹An asterisk designates problems appropriate for computer solution. Also refer to the computer problem after Problem 2.68.

Gases, Vapors, Liquids, and Solids

3

In planning and decision making for our modern technology, the engineer and scientist must know with reasonable accuracy the properties of the fluids and solids with which he deals. If you are engaged in the design of equipment, say the volume required for a process vessel, you need to know the specific volume or density of the gas or liquid that will be in the vessel as a function of temperature and pressure. If you are interested in predicting the possibility or extent of rainfall, you have to know something about the relation between the vapor pressure of water and the temperature. Whatever your current or future job, you need to have an awareness of the character and sources of information concerning the physical properties of fluids.

Clearly it is not possible to have reliable detailed experimental data on all the useful pure compounds and mixtures that exist in the world. Consequently, in the absence of experimental information, we estimate (predict) properties based on modifications of well-established principles, such as the *ideal* gas law, or based on empirical correlations. Thus the foundation of the estimation methods ranges from quite theoretical to completely empirical and their reliability ranges from excellent to terrible.

In this chapter we shall first discuss ideal and real gas relationships including some of the gas laws for pure components and mixtures of ideal gases. You will learn about methods of expressing the p - V - T properties of real gases by means of equations of state and, alternatively, by compressibility factors. Next we shall introduce the concepts of vaporization, condensation, and vapor pressure and illustrate how material balances are made for saturated and partially

color, shape, the fluids design equipment, to know the specific vessel as a function of being the possibility or relation between the our current or future sources of information experimental data on all world. Consequently, (predict) properties such as the *ideal* gas law of the estimation ideal and their reliability of ideal gases. You ties of real gases by sibility factors. Next ion, and vapor pres- saturated and partially

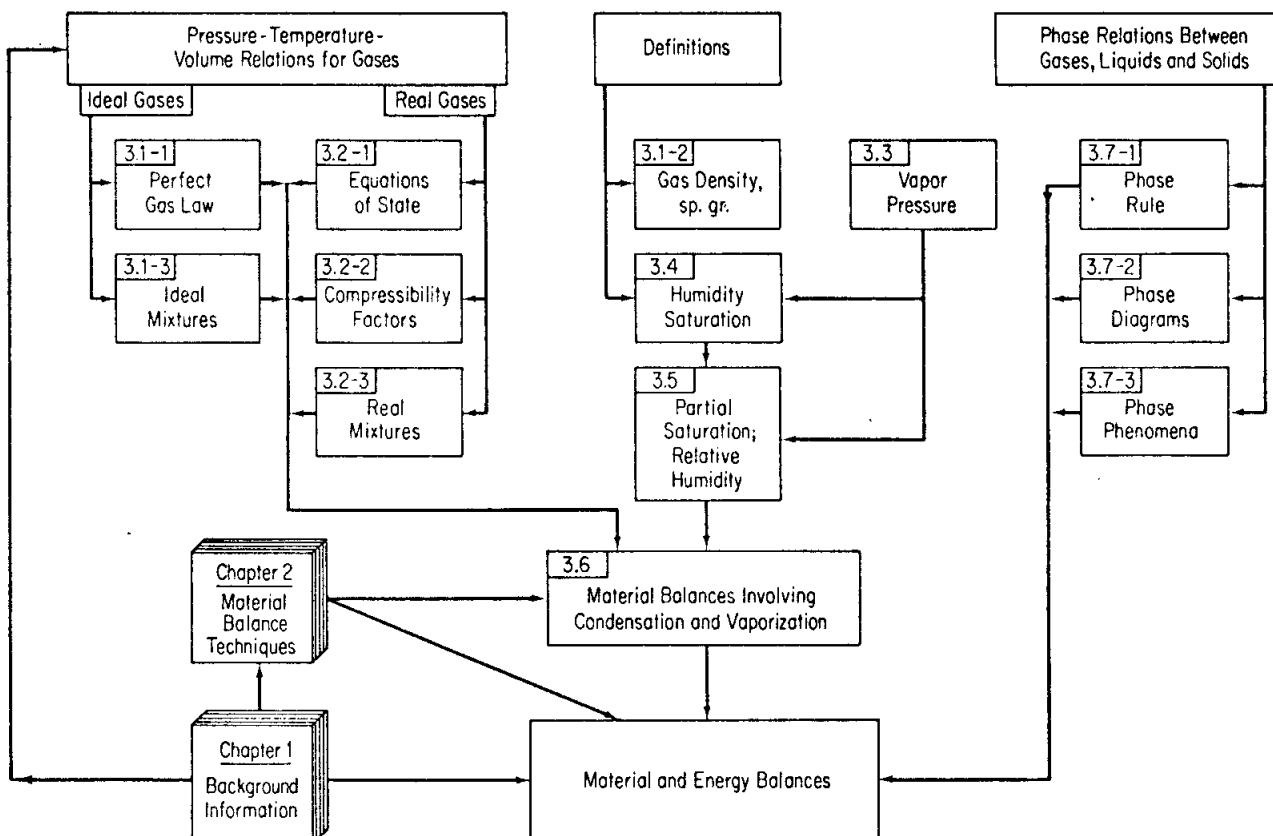


Fig. 3.0. Hierarchy of topics to be studied in this chapter (section numbers are in the upper left-hand corner of the boxes).

saturated gases. Finally, we shall examine the qualitative characteristics of gas-liquid-solid phases with the aid of diagrams. Figure 3.0 shows the interrelationships among the topics discussed in this chapter and how they relate to the making of material and energy balances.

3.1 *Ideal gas laws*

In 1787, Jacques Charles, a French chemist and physicist, published his conclusions about the relationship between the volume of gases and temperature. He demonstrated that the volume of a dry gas varies directly with temperature if the pressure remains constant. Charles, Boyle, Gay-Lussac, Dalton, and Amagat, the investigators who originally developed correlating relations among gas temperature, pressure, and volume, worked at temperatures and pressures such that the average distance between the molecules was great enough to neglect the effect of the intermolecular forces and the volume of the molecules themselves. Under these conditions a gas came to be termed an *ideal gas*. More properly, an *ideal gas* is an imaginary gas which obeys exactly certain simple laws such as the laws of Boyle, Charles, Dalton, and Amagat. No real gas obeys these laws exactly over all ranges of temperature and pressure, although the "lighter" gases (hydrogen, oxygen, air, etc.) under ordinary circumstances obey the ideal gas laws with but negligible deviations. The "heavier" gases such as sulfur dioxide and hydrocarbons, particularly at high pressures and low temperatures, deviate considerably from the ideal gas laws. Vapors, under conditions near the boiling point, deviate markedly from the ideal gas laws. However, at low pressures and high temperatures, the behavior of a vapor approaches that of an ideal gas. Thus for many engineering purposes, the ideal gas laws, if properly applied, will give answers that are correct within a few percent or less. But for liquids and solids with the molecules compacted relatively close together, we do not have such general laws.

In order that the volumetric properties of various gases may be compared, several arbitrarily specified standard states (usually known as *standard conditions*, or S.C.) of temperature and pressure have been selected by custom. The most common standard conditions of temperature and pressure are

Universal Scientific 32°F and 760 mm Hg (and their equivalents)

Natural Gas Industry 60°F and 14.7 psia

The first set of standard conditions, the Universal Scientific, is the one you have previously encountered in Chap. 1 and is by far the most common in use. Under these conditions the following volumetric data are true for any *ideal gas*:

$$1 \text{ g mole} = 22.41 \text{ ft}^3 \text{ at S.C.}$$

$$1 \text{ lb mole} = 359 \text{ ft}^3 \text{ at S.C.}$$

$$1 \text{ kg mole} = 22.4 \text{ m}^3 \text{ at S.C.}$$

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The fact that a substance cannot exist as a gas at 32°F and 29.92 in. Hg is immaterial. Thus, as we shall see later, water vapor at 32°F cannot exist at a pressure greater than its saturation pressure of 0.18 in. Hg without condensation occurring. However, the imaginary volume at standard conditions can be calculated and is just as useful a quantity in the calculation of volume-mole relationships as though it could exist. In the following, the symbol V will stand for total volume, and the symbol \bar{V} for volume per mole, or per unit mass.

EXAMPLE 3.1 Use of standard conditions

Calculate the volume, in cubic feet, occupied by 88 lb of CO₂ at standard conditions.

Solution:

Basis: 88 lb CO₂

$$\frac{88 \text{ lb CO}_2}{44 \text{ lb CO}_2} \left| \frac{1 \text{ lb mole CO}_2}{1 \text{ lb mole CO}_2} \right| \frac{359 \text{ ft}^3 \text{ CO}_2}{1 \text{ lb mole CO}_2} = 718 \text{ ft}^3 \text{ CO}_2 \text{ at S.C.}$$

Notice how in this problem the information that 359 ft³ at S.C. = 1 lb mole is applied to transform a known number of moles into an equivalent number of cubic feet. Incidentally, whenever you use cubic feet, you must establish the conditions of temperature and pressure at which the cubic feet are measured, since the term "ft³," standing alone, is really not any particular quantity of material.

3.1.1 Perfect Gas Law. Boyle found that the volume of a gas is inversely proportional to the absolute pressure at constant temperature. Charles showed that, at constant pressure, the volume of a given mass of gas varies directly with the absolute temperature. From the work of Boyle and Charles scientists developed the relationship now called the *perfect gas law* (or sometimes *the ideal gas law*):

$$pV = nRT \quad (3.1)$$

In applying this equation to a process going from an initial set of conditions to a final set of conditions, you can set up ratios of similar terms which are dimensionless as follows:

$$\left(\frac{p_1}{p_2} \right) \left(\frac{V_1}{V_2} \right) = \left(\frac{n_1}{n_2} \right) \left(\frac{T_1}{T_2} \right) \quad (3.2)$$

Here the subscripts 1 and 2 refer to the initial and final conditions. This arrangement of the perfect gas law has the convenient feature that the pressures may be expressed in any system of units you choose, such as in. Hg, mm Hg, N/m², atm, etc., so long as the same units are used for both conditions of pressure (do not forget that the pressure must be *absolute* pressure in both cases). Similarly, the grouping together of the *absolute* temperature and the volume terms gives ratios that are dimensionless.

Let us see how we can use the perfect gas law both in the form of Eq. (3.2) and Eq. (3.1).

Formal

EXAMPLE 3.2 Perfect gas law

An oxygen cylinder used as a standby source of oxygen contains 1.000 ft³ of O₂ at 70°F and 200 psig. What will be the volume of this O₂ in a dry-gas holder at 90°F and 4.00 in. H₂O above atmospheric? The barometer reads 29.92 in. Hg. See Fig. E3.2.

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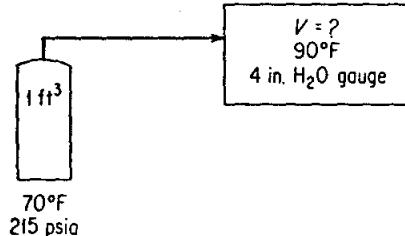


Fig. E3.2.

Solution:

You must first convert the temperatures and pressures into absolute units:

$$460 + 70 = 530^{\circ}\text{R}$$

$$460 + 90 = 550^{\circ}\text{R}$$

$$\text{atmospheric pressure} = 29.92 \text{ in. Hg} = \text{std atm} = 14.7 \text{ psia}$$

$$\text{initial pressure} = \frac{200 \text{ psig} + 14.7 \text{ psia}}{14.7 \text{ psia}} | \frac{29.92 \text{ in. Hg}}{14.7 \text{ psia}} = 437 \text{ in. Hg}$$

$$\begin{aligned} \text{final pressure} &= 29.92 \text{ in. Hg} + \frac{4 \text{ in. H}_2\text{O}}{12 \text{ in. H}_2\text{O}} | \frac{29.92 \text{ in. Hg}}{33.91 \text{ ft H}_2\text{O}} \\ &= 29.92 + 0.29 = 30.21 \text{ in. Hg} \end{aligned}$$

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Notice h

The simplest way to proceed, now that the data are in good order, is to apply the laws of Charles and Boyle, and, in effect, to apply the perfect gas law.

From Charles' law, since the temperature *increases*, the volume *increases*; hence the ratio of the temperatures *must* be greater than 1. The pressure *decreases*; therefore from Boyle's law, the volume will *increase*; hence the ratio of pressures will be *greater* than 1.

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Basis: 1 ft³ of oxygen at 70°F and 200 psig

$$\begin{aligned} \text{final volume} &= \frac{1.00 \text{ ft}^3}{530^{\circ}\text{R}} | \frac{550^{\circ}\text{R}}{30.21 \text{ in. Hg}} | \frac{437 \text{ in. Hg}}{30.21 \text{ in. Hg}} \\ &= 15.0 \text{ ft at } 90^{\circ}\text{F and } 4 \text{ in. H}_2\text{O gauge} \end{aligned}$$

form of Eq. (3.2)

lens 1.000 ft³ of O₂
gas holder at 90°F
2 in. Hg. See Fig.

absolute units:

= 437 in. Hg

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Formally, the same calculation can be made using Eq. (3.2),

$$V_2 = V_1 \left(\frac{P_1}{P_2} \right) \left(\frac{T_2}{T_1} \right) \quad \text{since } n_1 = n_2$$

EXAMPLE 3.3 Perfect gas law

Probably the most important constituent of the atmosphere that fluctuates is the water. Rainfall, evaporation, fog, and even lightning are associated with water as a vapor or a liquid in air. To obtain some feeling for how little water vapor there is at higher altitudes, calculate the mass of 1.00 m³ of water vapor at 15.5 mm Hg and 23°C. Assume that water vapor is an ideal gas under these conditions.

Solution:

First visualize the information available to you, and then decide how to convert it into the desired mass. If you can convert the original amount of water vapor to S.C. by use of the ideal gas law and then make use of the fact that 22.4 m³ = 1 kg mole, you can easily get the desired mass of water vapor. See Fig. E3.3.

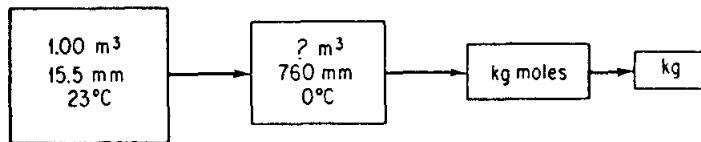


Fig. E3.3.

Basis: 1.00 m³ H₂O vapor at 15.5 mm Hg and 23°C

$$\frac{1.00 \text{ m}^3 | 15.5 \text{ mm} | (273 + 0)^\circ\text{K}}{760 \text{ mm} | (273 + 23)^\circ\text{K}} | \frac{1 \text{ kg mole}}{22.4 \text{ m}^3} | \frac{18 \text{ kg H}_2\text{O}}{1 \text{ kg mole}} = 1.51 \times 10^{-2} \text{ kg H}_2\text{O}$$

Notice how the entire calculation can be carried out in a single dimensional equation.

EXAMPLE 3.4 Perfect gas law

You have 10 lb of CO₂ in a 20-ft³ fire extinguisher tank at 30°C. Assuming that the ideal gas laws hold, what will the pressure gauge on the tank read in a test to see if the extinguisher is full? See Fig. E3.4.

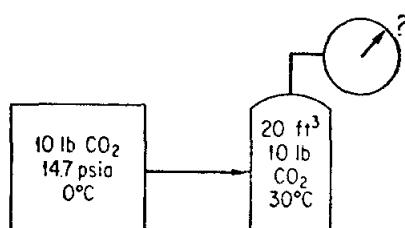


Fig. E3.4.

Solution:

Employing Eq. (3.2), we can write (the subscript 1 stands for standard conditions, 2 for the conditions in the tank)

$$p_2 = p_1 \left(\frac{V_1}{V_2} \right) \left(\frac{T_2}{T_1} \right)$$

$\overbrace{p_1}$	14.7 psia	10 lb CO ₂	1 lb mole CO ₂	359 ft ³	20 ft ³	$\overbrace{\frac{303^\circ\text{K}}{273^\circ\text{K}} = p_2 = 66 \text{ psia}}$
		$\underbrace{44 \text{ lb CO}_2}_{V_1}$	$\underbrace{1 \text{ lb mole}}_{V_2}$		$\uparrow \frac{T_2}{T_1}$	

Hence the gauge on the tank will read (assuming that it reads gauge pressure and that the barometer reads 14.7 psia) $66 - 14.7 = 51.3$ psig.

We have not used the gas constant R in the solution of any of the example problems so far, but you can use Eq. (3.1) to solve for one unknown as long as all the other variables in the equation are known. However, such a calculation requires that the units of R be expressed in units corresponding to those used for the quantities $p-V-T$. There are so many possible units you can use for each variable that a very large table of R values will be required. But, if you want to use R , you can always determine R from the $p-V-T$ data at standard conditions which you have already memorized and used; R merely represents a pV/T relation at some fixed condition of temperature and pressure.

EXAMPLE 3.5 Calculation of R

Find the value for the universal gas constant R for the following combinations of units:

- For 1 lb mole of ideal gas when the pressure is expressed in psia, the volume is in ft³/lb mole, and the temperature is in °R.
- For 1 g mole of ideal gas when the pressure is in atm, the volume in cm³, and the temperature in °K.
- For 1 kg mole of ideal gas when the pressure is in N/m², the volume is in m³/kg mole, and the temperature is in °K.

Solution:

- At standard conditions

$$p = 14.7 \text{ psia}$$

$$\hat{V} = 359 \text{ ft}^3/\text{lb mole}$$

$$T = 492^\circ\text{R}$$

Then

$$R = \frac{p\hat{V}}{T} = \frac{14.7 \text{ psia}}{492^\circ\text{R}} \left| \frac{359 \text{ ft}^3}{1 \text{ lb mole}} \right. = 10.73 \frac{(\text{psia})(\text{ft}^3)}{(\text{R})(\text{lb mole})}$$

for standard conditions,

$$\frac{5^{\circ}\text{K}}{273^{\circ}\text{K}} = p_2 = 66 \text{ psia}$$

gauge pressure and that

of any of the example unknown as long as it, such a calculation leading to those used for you can use for each. But you want to stand. conditions represents a pV/T re.

showing combinations

ed in psia, the volume

the volume in cm^3 ,

m^2 , the volume is in

(b) Similarly, at standard conditions,

$$p = 1 \text{ atm}$$

$$\hat{V} = 22,400 \text{ cm}^3/\text{g mole}$$

$$T = 273^{\circ}\text{K}$$

$$R = \frac{p\hat{V}}{T} = \frac{1 \text{ atm}}{273^{\circ}\text{K}} \left| \frac{22,400 \text{ cm}^3}{1 \text{ g mole}} \right. = 82.06 \frac{(\text{cm}^3)(\text{atm})}{(^{\circ}\text{K})(\text{g mole})}$$

(c) In the SI system of units standard conditions are

$$p = 1.013 \times 10^5 \text{ N/m}^2$$

$$\hat{V} = 22.4 \text{ m}^3/\text{kg mole}$$

$$T = 273^{\circ}\text{K}$$

$$R = \frac{p\hat{V}}{T} = \frac{1.013 \times 10^5 \text{ N/m}^2}{273^{\circ}\text{K}} \left| \frac{22.4 \text{ m}^3}{1 \text{ kg mole}} \right. = 8.30 \times 10^3 \frac{(\text{N})(\text{m})}{(^{\circ}\text{K})(\text{kg mole})}$$

We want to emphasize that R does not have a universal value even though it is called the *universal gas constant*. The value of R depends on the units of p , V , and T . Similarly, you should realize that R is not a dimensionless quantity; i.e., there is no value of $R = 21.9$, but there is a value of

$$R = 21.9 \frac{(\text{in. Hg})(\text{ft}^3)}{(\text{lb mole})(^{\circ}\text{R})}$$

EXAMPLE 3.6 Perfect gas law

Calculate the volume occupied by 88 lb of CO_2 at a pressure of 32.2 ft of water and at 15°C .

Solution:

See Fig. E3.6.

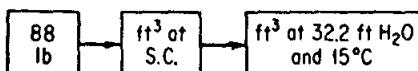


Fig. E3.6.

Solution No. 1 (using Boyle's and Charles' laws):

At S.C.:

$$p = 33.91 \text{ ft H}_2\text{O}$$

$$\hat{V} = 359 \frac{\text{ft}^3}{\text{lb mole}}$$

$$T = 273^{\circ}\text{K}$$

Basis: 88 lb of CO_2

88 lb CO_2	$\left \begin{array}{c} 359 \text{ ft}^3 \\ 44 \text{ lb } \text{CO}_2 \\ \hline 1 \text{ lb mole } \text{CO}_2 \end{array} \right $	288	33.91	$= 798 \text{ ft}^3 \text{ CO}_2$
		273	32.2	at 32.2 ft H_2O and 15°C

Solution No. 2 (using gas constant R):

First, the value of R must be obtained in the same units as the variable p , \hat{V} , and T . For 1 lb mole,

$$R = \frac{p\hat{V}}{T}$$

and at S.C.,

$$p = 33.91 \text{ ft H}_2\text{O}$$

$$\hat{V} = 359 \text{ ft}^3/\text{lb mole}$$

$$T = 273^\circ\text{K}$$

$$R = \frac{33.91}{273} \left| \frac{359}{1} \right| = 44.6 \frac{(\text{ft H}_2\text{O})(\text{ft}^3)}{(\text{lb mole})(^\circ\text{K})}$$

Now, using Eq. (3.1), inserting the given values, and performing the necessary calculations, we get

Basis: 88 lb CO₂

$$V = \frac{nRT}{p} = \frac{88 \text{ lb CO}_2}{44 \text{ lb CO}_2} \left| \frac{(44.6 \text{ ft H}_2\text{O})(\text{ft}^3)}{1 \text{ lb mole CO}_2} \right| \left| \frac{288^\circ\text{K}}{(1 \text{ lb mole})(^\circ\text{K})} \right| \left| \frac{32.2 \text{ ft H}_2\text{O}}{1} \right|$$

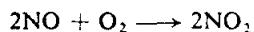
$$= 798 \text{ ft}^3 \text{ CO}_2 \text{ at } 32.2 \text{ ft H}_2\text{O and } 15^\circ\text{C}$$

If you will inspect both solutions closely, you will observe that in both cases the same numbers appear and that both are identical except that in the second solution using R two steps are required to obtain the solution.

EXAMPLE 3.7 Perfect gas law

One important source of emissions from gasoline-powered automobile engines that causes smog is the nitrogen oxides NO and NO₂. They are formed whether combustion is complete or not as follows: At the high temperatures which occur in an internal combustion engine during the burning process, oxygen and nitrogen combine to form nitric oxide (NO). The higher the peak temperatures and the more oxygen available, the more NO is formed. There is insufficient time for the NO to decompose back to O₂ and N₂ because the burned gases cool too rapidly during the expansion and exhaust cycles in the engine. Although both NO and nitrogen dioxide (NO₂) are significant air pollutants (together termed NO_x), the NO₂ is formed in the atmosphere as NO is oxidized.

Suppose that you collect a sample of a NO-NO₂ mixture (after having removed the other combustion gas products by various separations procedures) in a 100-cm³ standard cell at 30°C. Certainly some of the NO will have been oxidized to NO₂.



during the collection, storage, and processing of the combustion gases so that measurement of NO alone will be misleading. If the standard cell contains 0.291 g of NO₂ plus NO and the pressure measured in the cell is 1265 mm Hg, what percent of the NO + NO₂ is in the form of NO? See Fig. E3.7.

Solution:
The gas ideal gas law the chemical in the cell.

$R =$

$n =$

If the we know the grams of NO

The sum

$x \text{ g N}$

The weight p

and the mole

3.1.2 defined as the foot, grams volume variation, you otherwise sp calculated by the containe

s the variable p , V , and

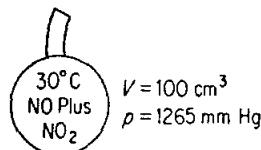


Fig. E3.7.

Solution:

The gas in the cell is composed partly of NO and partly of NO₂. We can use the ideal gas law to calculate the total gram moles present in the cell and then, by using the chemical equation and the principles of stoichiometry, compute the composition in the cell.

Basis: 100 cm³ gas at 1265 mm Hg and 30°C

$$R = \frac{760 \text{ mm Hg}}{273^\circ\text{K}} \left| \frac{22.4 \text{ l}}{1 \text{ g mole}} \right| \left| \frac{1000 \text{ cm}^3}{1 \text{ l}} \right| = 6.24 \times 10^4 \frac{(\text{mm Hg})(\text{cm}^3)}{(\text{K})(\text{g mole})}$$

$$n = \frac{pV}{RT} = \frac{1265 \text{ mm Hg}}{6.24 \times 10^4 \frac{(\text{mm Hg})(\text{cm}^3)}{(\text{K})(\text{g mole})}} \left| \frac{100 \text{ cm}^3}{303^\circ\text{K}} \right| = 0.00670 \text{ g mole}$$

If the mixture is composed of NO (MW = 30) and NO₂ (MW = 46), because we know the total mass in the cell we can compute the fraction of, say, NO. Let x = grams of NO; then $(0.291 - x)$ = g NO₂.

Basis: 0.291 g total gas

The sum of the moles is

$$\frac{x \text{ g NO}}{30 \text{ g NO}} + \frac{(0.291 - x) \text{ g NO}_2}{46 \text{ g NO}_2} = 0.00670$$

$$0.0333x + (0.291 - x)(0.0217) = 0.00670$$

$$x = 0.033 \text{ g}$$

The weight percent NO is

$$\frac{0.033}{0.291}(100) \cong 11\%$$

and the mole percent NO is

$$\frac{(0.033)(0.033)}{(0.00670)}(100) \cong 17\%$$

3.1.2 Gas Density and Specific Gravity. The density of a gas is defined as the mass per unit volume and can be expressed in pounds per cubic foot, grams per liter, or other units. Inasmuch as the mass contained in a unit volume varies with the temperature and pressure, as we have previously mentioned, you should always be careful to specify these two conditions. Unless otherwise specified, the volumes are presumed to be at S.C. Density can be calculated by selecting a unit volume as the basis and calculating the mass of the contained gas.

EXAMPLE 3.8 Gas density

What is the density of N₂ at 80°F and 745 mm Hg expressed in

- (a) American engineering units?
- (b) cgs units?
- (c) SI units?

Solution:

(a)

Basis: 1 ft³ N₂ at 80°F and 745 mm Hg

$$\frac{1 \text{ ft}^3}{540^\circ\text{R}} \left| \begin{array}{|l|l|l|l|l|} \hline 492^\circ\text{R} & 745 \text{ mm Hg} & 1 \text{ lb mole} & 28 \text{ lb} \\ \hline 760 \text{ mm Hg} & 359 \text{ ft}^3 & 1 \text{ lb mole} & \\ \hline \end{array} \right. = 0.0696 \text{ lb}$$

density = 0.0696 lb/ft³ of N₂ at 80°F and 745 mm Hg

(b)

Basis: 1 l N₂ at 80°F and 745 mm Hg

$$\frac{1 \text{ l}}{540^\circ\text{R}} \left| \begin{array}{|l|l|l|l|l|} \hline 492^\circ\text{R} & 745 \text{ mm Hg} & 1 \text{ g mole} & 28 \text{ g} \\ \hline 760 \text{ mm Hg} & 22.4 \text{ l} & 1 \text{ g mole} & \\ \hline \end{array} \right. = 1.115 \text{ g}$$

density = 1.115 g/l of N₂ at 80°F (27°C) and 745 mm Hg

(c)

Basis: 1 m³ N₂ at 80°F and 745 mm Hg

$$\frac{1 \text{ m}^3}{540^\circ\text{R}} \left| \begin{array}{|l|l|l|l|l|} \hline 492^\circ\text{R} & 745 \text{ mm Hg} & 1 \text{ kg mole} & 28 \text{ kg} \\ \hline 760 \text{ mm Hg} & 22.4 \text{ m}^3 & 1 \text{ kg mole} & \\ \hline \end{array} \right. = 1.115 \text{ kg}$$

density = 1.115 kg/m³ of N₂ at 80°F (300°K) and 745 mm Hg (9.94 × 10⁴ N/m²)

The *specific gravity* of a gas is usually defined as the ratio of the density of the gas at a desired temperature and pressure to that of air (or any specified reference gas) at a certain temperature and pressure. The use of specific gravity occasionally may be confusing because of the manner in which the values of specific gravity are reported in the literature. You must be very careful in using literature values of specific gravity. Be particularly careful to ascertain that the conditions of temperature and pressure are known both for the gas in question and for the reference gas. Among the examples below, several represent inadequate methods of expressing specific gravity.

- (a) *What is the specific gravity of methane?* Actually this question may have the same answer as the question, How many grapes are in a bunch? Unfortunately, occasionally one may see this question and the best possible answer is

$$\text{sp gr} = \frac{\text{density of methane at S.C.}}{\text{density of air at S.C.}}$$

- (b) *What is the specific gravity of methane (H₂ = 1.00)?* Again a poor question. The notation of (H₂ = 1.00) means that H₂ at S.C. is used as

the reference gas, but the question does not even give a hint regarding the conditions of temperature and pressure of the methane. Therefore the best interpretation is

$$\text{sp gr} = \frac{\text{density of methane at S.C.}}{\text{density of H}_2 \text{ at S.C.}}$$

- (c) *What is the specific gravity of ethane (air = 1.00)?* Same as question (b) except that in the petroleum industry the following is used:

$$\text{sp gr} = \frac{\text{density of ethane at } 60^\circ\text{F and 760 mm Hg}}{\text{density of air at S.C. } (60^\circ\text{F, 760 mm Hg})}$$

- (d) *What is the specific gravity of butane at 80°F and 740 mm Hg?* No reference gas nor state of reference gas is mentioned. However, when no reference gas is mentioned, it is taken for granted that air is the reference gas. In the case at hand the best thing to do is to assume that the reference gas and the desired gas are under the same conditions of temperature and pressure:

$$\text{sp gr} = \frac{\text{density of butane at } 80^\circ\text{F and 740 mm Hg}}{\text{density of air at } 80^\circ\text{F and 740 mm Hg}}$$

- (e) *What is the specific gravity of CO₂ at 60°F and 740 mm Hg (air = 1.00)?*

$$\text{sp gr} = \frac{\text{density of CO}_2 \text{ at } 60^\circ\text{F and 740 mm Hg}}{\text{density of air at S.C.}}$$

- (f) *What is the specific gravity of CO₂ at 60°F and 740 mm Hg (ref. air at S.C.)?*

$$\text{sp gr} = \text{same as question (e)}$$

EXAMPLE 3.9 Specific gravity of a gas

What is the specific gravity of N₂ at 80°F and 745 mm Hg compared to

- (a) Air at S.C. (32°F and 760 mm Hg)?
 (b) Air at 80°F and 745 mm Hg?

Solution:

First you must obtain the density of the N₂ and the air at their respective conditions of temperature and pressure, and then calculate the specific gravity by taking a ratio of their densities. Example 3.8 covers the calculation of the density of a gas, and therefore, to save space, no units will appear in the following calculations:

(a)

Basis: 1 ft³ N₂ at 80°F and 745 mm Hg

$$\begin{array}{|c|c|c|c|c} \hline 1 & 492 & 745 & | 28 \\ \hline & 540 & 760 & | 359 & \\ \hline \end{array} = 0.0696 \text{ lb N}_2/\text{ft}^3 \text{ at } 80^\circ\text{F, 745 mm Hg}$$

Basis: 1 ft³ of air at 32°F and 760 mm Hg

$$\begin{array}{|c|c|c|c|c} \hline 1 & 492 & 760 & | 29 \\ \hline & 492 & 760 & | 359 & \\ \hline \end{array} = 0.0808 \text{ lb air}/\text{ft}^3 \text{ at } 32^\circ\text{F, 760 mm Hg}$$

Therefore

$$\text{sp gr} = \frac{0.0696}{0.0808} = 0.863 \frac{\text{lb N}_2/\text{ft}^3 \text{ N}_2 \text{ at } 80^\circ\text{F}, 745 \text{ mm Hg}}{\text{lb air}/\text{ft}^3 \text{ air at S.C.}}$$

Note: specific gravity is not a dimensionless number.

(b)

Basis: 1 ft³ air at 80°F and 745 mm Hg

$$\begin{array}{|c|c|c|c|c|} \hline 1 & 492 & 745 & | & 29 \\ \hline & 540 & 760 & 359 & \\ \hline \end{array} = 0.0721 \text{ lb}/\text{ft}^3 \text{ at } 80^\circ\text{F and } 745 \text{ mm Hg}$$

$$\begin{aligned} (\text{sp gr})_{N_2} &= \frac{0.0696}{0.0721} = 0.965 \frac{\text{lb N}_2/\text{ft}^3 \text{ N}_2 \text{ at } 80^\circ\text{F}, 745 \text{ mm Hg}}{\text{lb air}/\text{ft}^3 \text{ air at } 80^\circ\text{F, } 745 \text{ mm Hg}} \\ &= 0.965 \text{ lb N}_2/\text{lb air} \end{aligned}$$

Note: You can work part (b) by dividing the unit equations instead of dividing the resulting densities:

$$\text{sp gr} = \frac{d_{N_2}}{d_{air}} = \frac{\begin{array}{|c|c|c|c|c|} \hline 1 & 492 & 745 & | & 28 \\ \hline & 540 & 760 & 359 & \\ \hline \end{array}}{\begin{array}{|c|c|c|c|c|} \hline 1 & 492 & 745 & | & 29 \\ \hline & 540 & 760 & 359 & \\ \hline \end{array}} = \frac{28}{29} = 0.965 \text{ lb N}_2/\text{lb air}$$

The latter calculation shows that the specific gravity is equal to the *ratio of the molecular weights* of the gases when the densities of *both* the desired gas and the reference gas are at the same temperature and pressure. This, of course, is true only for ideal gases and should be no surprise to you, since Avogadro's law in effect states that at the same temperature and pressure 1 mole of any ideal gas is contained in identical volumes.

3.1.3 Ideal Gaseous Mixtures. In the majority of cases, as an engineer you will deal with mixtures of gases instead of individual gases. There are three ideal gas laws which can be applied successfully to gaseous mixtures:

- (a) Dalton's law of partial pressures.
- (b) Amagat's law of partial volumes.
- (c) Dalton's law of the summation of partial pressures.

(a) *Dalton's laws.* Dalton postulated that the total pressure of a gas is equal to the sum of the pressures exerted by the individual molecules of each component gas. He went one step further to state that each individual gas of a gaseous mixture can hypothetically be considered to exert a *partial pressure*. A partial pressure is the pressure that would be obtained if this *same mass* of individual gas were alone in the *same total volume* at the *same temperature*. The sum of these partial pressures for each component in the gaseous mixture would be equal to the total pressure, or

$$p_1 + p_2 + p_3 + \cdots + p_n = p_t \quad (3.3)$$

Equation (3.3) is Dalton's law of the summation of the partial pressures.

To illustrate the significance of Eq. (3.3) and the meaning of partial pressure, suppose that you carried out the following experiment with ideal gases. Two tanks of 150 ft^3 volume, one containing gas A at 300 mm Hg and the other gas B at 400 mm of Hg (both gases being at the same temperature of 70°F), are connected together. All the gas in B is forced into tank A isothermally. Now you have a 150-ft^3 tank of A + B at 700 mm of Hg. For this mixture (in the 150-ft^3 tank at 70°F and a total pressure of 700 mm Hg) you could say that gas A exerts a partial pressure of 300 mm and gas B exerts a partial pressure of 400 mm. Of course you cannot put a pressure gauge on the tank and check this conclusion because the pressure gauge will read only the total pressure. These partial pressures are hypothetical pressures that the individual gases would exert and are equivalent to the pressures they actually would have if they were put into the same volume at the same temperature all by themselves.

You can surmise that, at constant volume and at constant temperature, the pressure is a function only of the number of molecules of gas present. If you divide the perfect gas law for component 1, $p_1V_1 = n_1RT_1$, by that for component 2, $p_2V_2 = n_2RT_2$, at *constant temperature and volume*, you can obtain

$$\frac{p_1}{p_2} = \frac{n_1}{n_2} \quad (3.4)$$

which shows that the ratio of the partial pressures is exactly the same numerically as the ratio of the moles of components 1 and 2. Similarly, dividing the ideal gas law for component 1 by the gas law for all the molecules, $p_iV_i = n_iRT_i$, you will get Dalton's law of partial pressures:

$$\frac{p_1}{p_t} = \frac{n_1}{n_t} = \text{mole fraction} = y_1 \quad (3.5)$$

Equation (3.5) shows that the ratio of the partial pressure of an individual component to the total pressure is exactly the same numerically as the ratio of the moles of the individual component to the total moles. With this principle under your belt, if the mole fraction of an individual gaseous component in a gaseous mixture is known and the total pressure is known, then you are able to calculate the partial pressure of this component gas by generalizing Eq. (3.5):

$$p_i = y_i p_t \quad (3.5a)$$

where i stands for any component.

(b) *Amagat's law*: Amagat's law of additive volumes is analogous to Dalton's law of additive pressures. Amagat stated that the total volume of a gaseous mixture is equal to the sum of the volumes of the individual gas components if they were to be measured at the same temperature and at the total pressure of all the molecules. The individual volumes of these individual components at the same temperature and pressure are called the *partial volumes* (or sometimes *pure component volumes*) of the individual components:

$$V_1 + V_2 + V_3 + \cdots + V_n = V_t \quad (3.6)$$

$$\frac{V_1}{V_2} = \frac{n_1}{n_2} \quad (3.7)$$

and

for an ideal gas.

EXAMPLE 3.10 Partial pressures and volumes

A gas-tight room has a volume of 10,000 ft³. This room contains air (considered to be 21 percent O₂ and 79 percent N₂) at 70°F and a total pressure of 760 mm Hg.

Solution:

See Fig. E3.10(a)

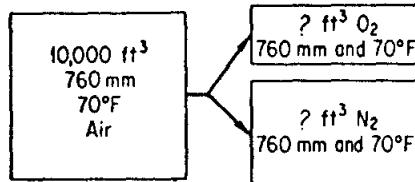


Fig. E3.10(a).

Basis: 10,000 ft³ of air at 70°F and 760 mm Hg

Partial volumes can be calculated by multiplying the total volume by the respective component mole fractions [Eq. (3.8)]:

$$(a) V_{O_2} = (0.21)(10,000) = 2,100 \text{ ft}^3 \text{ O}_2 \text{ at } 70^\circ\text{F}, 760 \text{ mm}$$

$$(b) V_{N_2} = (0.79)(10,000) = 7,900 \text{ ft}^3 \text{ N}_2 \text{ at } 70^\circ\text{F}, 760 \text{ mm}$$

partial pressures, function only of
in the gaseous

(3.7)

Note how the temperature and pressure have to be specified for the partial volumes to make them meaningful.

Partial pressures can be calculated by multiplying the total pressure by the respective component mole fractions [Eq. (3.5a)]; the basis is still the same:

$$(c) \ p_{O_2} = (0.21)(760) = 160 \text{ mm Hg when } V = 10,000 \text{ ft}^3 \text{ at } 70^\circ\text{F}$$

$$(d) p_{N_2} = (0.79)(760) = 600 \text{ mm Hg when } V = 10,000 \text{ ft}^3 \text{ at } 70^\circ\text{F}$$

total pressure = 760 mm Hg when $V = 10,000 \text{ ft}^3$ at 70°F

(3.8)

Fig. E3.10(b).

For use in our subsequent calculations you should clearly understand now that the original room contained:

1. 7,900 ft³ dry N₂ at 760 mm Hg and 70°F
 2. 2,100 ft³ dry O₂ at 760 mm Hg and 70°F
 3. 10,000 ft³ dry air at 760 mm Hg and 70°F
(add 1 and 2)

or

1. 10,000 ft³ dry O₂ at 160 mm Hg and 70°F
 2. 10,000 ft³ dry N₂ at 600 mm Hg and 70°F
 3. 10,000 ft³ dry air at 760 mm Hg and 70°F
(add 1 and 2)

EXAMPLE 3.11 Ideal gas mixtures

A flue gas analyzes CO₂, 14.0 percent; O₂, 6.0 percent; and N₂, 80.0 percent. It is at 400°F and 765.0 mm Hg pressure. Calculate the partial pressure of each component.

Solution:

Basis: 1.00 kg mole flue gas

comp.	kg moles	p (mm Hg)
CO ₂	0.140	107.1
O ₂	0.060	45.9
N ₂	0.800	612.0
	<hr/> 1.000	<hr/> 765.0

On the basis of 1.00 kg mole of flue gas, the mole fraction y of each component, when multiplied by the total pressure, gives the partial pressure of that component. Thus, $V \text{ ft}^3$ of flue gas represents four different things:

$V \text{ ft}^3$ flue gas	at 765.0 mm Hg and 400°F
$V \text{ ft}^3$ carbon dioxide	at 107.1 mm Hg and 400°F
$V \text{ ft}^3$ oxygen	at 45.9 mm Hg and 400°F
$V \text{ ft}^3$ nitrogen	at 612.0 mm Hg and 400°F

3.2 Real gas relationships

We have said that at room temperature and pressure many gases can be assumed to act as ideal gases. However, for some gases under normal conditions, and for most gases under conditions of high pressure, values of the gas properties that you might obtain using the ideal gas law would be at wide variance with the experimental evidence. You might wonder exactly how the behavior of real gases does compare with that calculated from the ideal gas laws. In Fig. 3.1 you can see how the pV product of several gases deviates from that predicted by the ideal gas laws as the pressure increases substantially. Thus it is clear that we need some way of computing the $p\text{-}V\text{-}T$ properties of a gas that is not ideal.

Essentially there are four methods of handling real gas calculations:

- (a) Equations of state.
- (b) Compressibility charts.
- (c) Estimated properties.¹
- (d) Actual experimental data.

Even if experimental data is available, the other three techniques still may be quite useful for certain types of calculations. Of course, under conditions such that part of the gas liquefies, the gas laws apply only to the gas phase portion of the system—you cannot extend these real gas laws into the liquid region any more than you can apply the ideal gas laws to a liquid.

¹Computer programs are available to estimate physical properties of compounds and mixtures based on structural group contributions and other basic parameters; refer to E. L. Meadows, *Chem. Eng. Progr.*, vol. 61, p. 93 (1965).

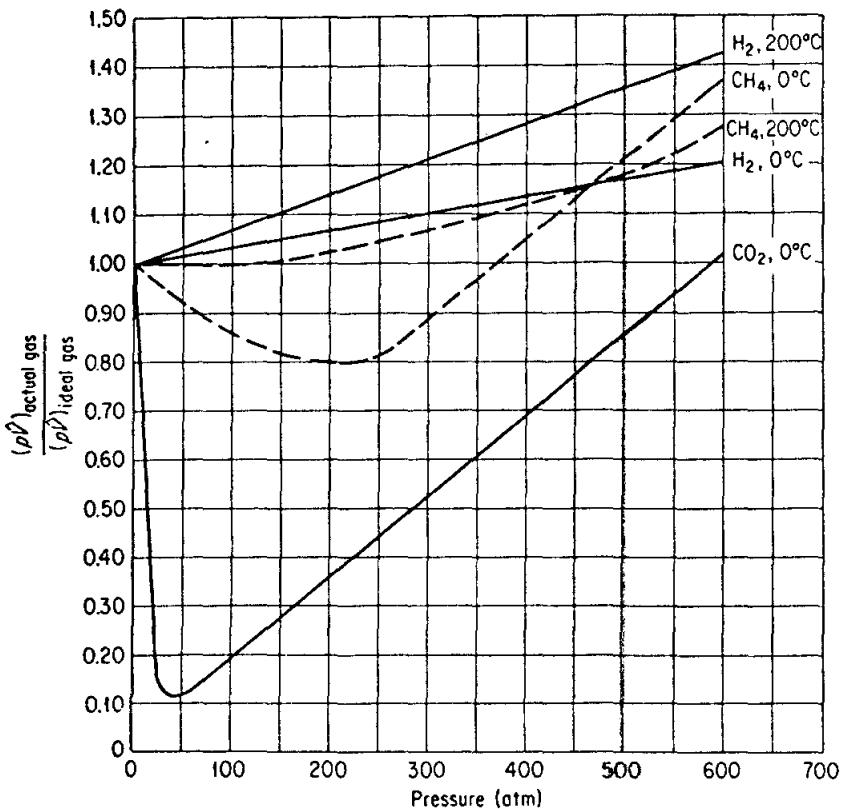
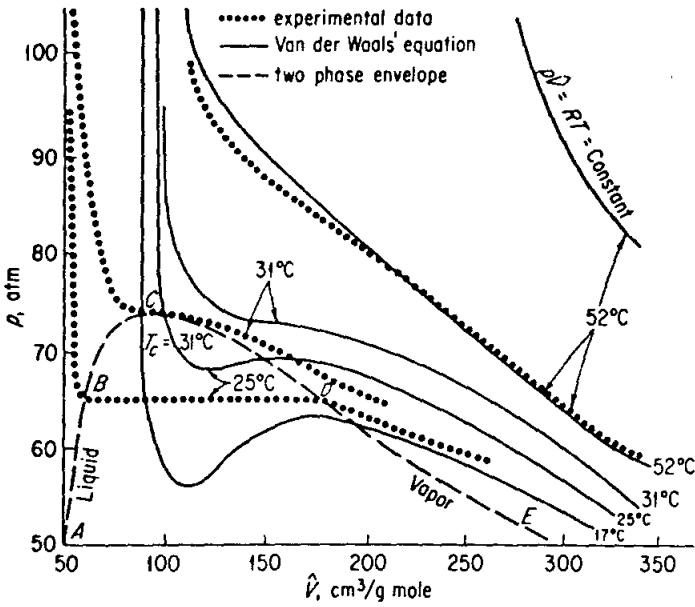


Fig. 3.1. Deviation of real gas from ideal gas laws at high pressures.

3.2.1 Equations of State. Equations of state relate the p - V - T properties of a pure substance (or mixtures) by semitheoretical or empirical relations. By *property* we shall mean any measurable characteristic of a substance, such as pressure, volume, or temperature, or a characteristic that can be calculated or deduced, such as internal energy, to be discussed in Chap. 4. Experimental data for a gas, carbon dioxide, are illustrated in Fig. 3.2, which is a plot of pressure, versus molal volume with absolute temperature (converted to $^{\circ}\text{C}$) as the third parameter. For a constant temperature the perfect gas law, $pV = RT$ (for 1 mole), is, on this plot, a rectangular hyperbola because $pV = \text{constant}$. The experimental data at high temperatures and low pressures is not shown but closely approximate the perfect gas law. However, as we approach the point *C*, called the critical point (discussed in Sec. 3.2.2), we see that the traces of the experimental data are quite different from the lines which would represent the relation $pV = \text{constant}$.

The problem, then, is to predict these experimental points by means of some equation which can, with reasonable accuracy, represent the experimental data throughout the gas phase. Over 100 equations of state have been proposed

Fig. 3.2. p - V - T properties of CO_2 .

to accomplish this task, of which a few are shown in Table 3.1. We would not, of course, expect the function to follow the experimental data within the two-phase region outlined by the area inside the envelope A, B, C, D , and E .

(a) van der Waal's equation.

van der Waals' equation, first proposed in 1893, does not yield satisfactory predictions at low gas temperatures (see Fig. 3.2), but it does have historical interest and is one of the simplest equations of state. Thus it illustrates some of the typical theoretical development that has taken place as well as some of the computational problems involved in using equations of state. Keep in mind that some of the equations listed in Table 3.1 are completely empirical while others, such as van der Waals' equation, are semiempirical; that is, although they were developed from theory, the constants in the equation or portions of the equation are determined by empirical methods.

van der Waals tried to include in the ideal gas law the effect of the attractive forces among the molecules by adding to the pressure term, in the ideal gas law, the term

$$\frac{n^2 a}{V^2} \quad (3.10)$$

where

n = number of moles

V = volume

a = a constant, different for each gas

TABLE 3.1 EQUATIONS OF STATE (for 1 mole)

van der Waals:

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

Lorentz:

$$p = \frac{RT}{V^2} (V + b) - \frac{a}{V^2}$$

Dieterici:

$$p = \frac{RT}{(V - b)} e^{-a/V RT}$$

Berthelot:

$$p = \frac{RT}{(V - b)} - \frac{a}{T V^2}$$

Redlich-Kwong:

$$\left[p + \frac{a}{T^{1/2} V (V + b)}\right] (V - b) = RT$$

$$a = 0.4278 \frac{R^2 T_c^{2.5}}{p_c}$$

$$b = 0.0867 \frac{RT_c}{p_c}$$

Kammerlingh-Onnes:

$$pV = RT \left[1 + \frac{B}{V} + \frac{C}{V^2} + \dots\right]$$

Holborn:

$$pV = RT[1 + B'p + C'p^2 + \dots]$$

Beattie-Bridgeman:

$$pV = RT + \frac{\beta}{V} + \frac{\gamma}{V^2} + \frac{\delta}{V^3}$$

$$\beta = RTB_0 - A_0 - \frac{RC}{T^2}$$

$$\gamma = -RTB_0b + aA_0 - \frac{RB_0c}{T^2}$$

$$\delta = \frac{RB_0bc}{T^2}$$

Benedict-Webb-Rubin:

$$pV = RT + \frac{\beta}{V} + \frac{\sigma}{V^2} + \frac{\eta}{V^4} + \frac{w}{V^5}$$

$$\beta = RTB_0 - A_0 - \frac{C_0}{T^2}$$

$$\sigma = bRT - a + \frac{c}{T^2} \exp\left(-\frac{\gamma}{V^2}\right)$$

$$\eta = cy \exp\left(-\frac{\gamma}{V^2}\right)$$

$$w = \alpha x$$

He also tried to take into account the effect of the volume occupied by the molecules themselves by subtracting a term from the volume in the ideal gas law. These corrections led to the following equation:

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \quad (3.11)$$

where a and b are constants determined by fitting van der Waals' equation to experimental p - V - T data, particularly the values at the critical point. Values of the van der Waals constants for a few gases are given in Table 3.2.

Let us look at some of the computational problems that may arise when using equations of state to compute p - V - T properties by using van der Waals' equation as an illustration. van der Waals' equation can easily be explicitly solved for p as follows:

$$p = \frac{nRT}{(V - nb)} - \frac{n^2 a}{V^2} \quad (3.12)$$

However, if you want to solve for V (or n), you can see that the equation becomes cubic in V (or n), or

$$V^3 - \left(nb + \frac{nRT}{p}\right)V^2 + \frac{n^2 a}{p}V - \frac{n^3 ab}{p} = 0 \quad (3.13)$$

TABLE 3.2 VAN DER WAALS' CONSTANTS FOR GASES
(From the data of the International Critical Tables)

	a^* atm $\left(\frac{\text{cm}^3}{\text{g mole}}\right)^2$	b^{\dagger} $\left(\frac{\text{cm}^3}{\text{g mole}}\right)$
Air	1.33×10^6	36.6
Ammonia	4.19×10^6	37.3
Carbon dioxide	3.60×10^6	42.8
Ethylene	4.48×10^6	57.2
Hydrogen	0.245×10^6	26.6
Methane	2.25×10^6	42.8
Nitrogen	1.347×10^6	38.6
Oxygen	1.36×10^6	31.9
Water vapor	5.48×10^6	30.6

*To convert to psia $\left(\frac{\text{ft}^3}{\text{lb mole}}\right)^2$, multiply table value by 3.776×10^{-3} .

†To convert to $\frac{\text{ft}^3}{\text{lb mole}}$, multiply table value by 1.60×10^{-2} .

Consequently to solve for V (or n) you would have to

- (a) Resort to a trial-and-error method,
- (b) Plot the equation assuming various values of V (or n), and see at what value of V (or n) the curve you plot intersects the abscissa, or
- (c) Use Newton's method or some other method for solving nonlinear equations (refer to Appendix L).

A computer program can be of material help in technique (c). You can obtain a close approximation to V (or n) in many cases from the ideal gas law, useful at least for the first trial, and then you can calculate a more exact value of V (or n) by using van der Waals' equation.

EXAMPLE 3.12 van der Waals' equation

A 5.0-ft³ cylinder containing 50.0 lb of propane (C_3H_8) stands in the hot sun. A pressure gauge shows that the pressure is 665 psig. What is the temperature of the propane in the cylinder? Use van der Waals' equation. See Fig. E3.12.

Solution:

Basis: 50 lb of propane

The van der Waals' constants obtained from any suitable handbook are

$$a = 3.27 \times 10^4 \text{ psia } \left(\frac{\text{ft}^3}{\text{lb mole}}\right)^2$$

$$b = 1.35 \frac{\text{ft}^3}{\text{lb mole}}$$

$$\left(P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

$b \frac{ft^3}{g \text{ mole}}$
36.6
37.3
42.8
57.2
26.6
42.8
38.6
31.9
30.6

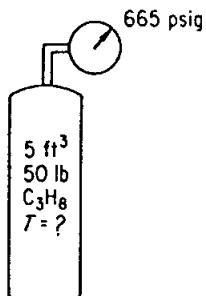


Fig. E3.12.

All the additional information you need is as follows:

$$p = 665 \text{ psig} + 14.7 = 679.7 \text{ psia}$$

$$R \text{ in proper units is } = 10.73 \frac{(\text{psia})(\text{ft}^3)}{(\text{lb mole})(^{\circ}\text{R})}$$

$$n = \frac{50 \text{ lb}}{44 \text{ lb/lb mole}} = 1.137 \text{ lb moles propane}$$

$$\left[679.7 + \frac{(1.137)^2(3.27 \times 10^4)}{(5)^2} \right] [5 - (1.137)(1.35)] = 1.137(10.73)T$$

$$T = 673^{\circ}\text{R} = 213^{\circ}\text{F}$$

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You can obtain
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are

(b) Other equations of state.

Among the numerous other equations of state which have been proposed in addition to van der Waals' equation are those shown in Table 3.1. The form of these equations is of interest inasmuch as they are attempts to fit the experimental data with as few constants in the equation as possible. One form of the equation known as the *virial* form is illustrated by the equations of Kammerlingh-Onnes and Holborn. These are essentially power series in $1/V$ or in p , and the quantities B , C , D , etc., are known as *virial coefficients*. These equations reduce to $pV = RT$ at low pressures. The virial form of an equation of state is the best we have today; however, it is not possible to solve theoretically by statistical thermodynamics for the constants beyond the first two. Therefore, fundamentally, these equations are semiempirical, the constants being determined by fitting the equation to experimental data. The Beattie-Bridgeman equation, which has five constants (exclusive of R), and the Benedict-Webb-Rubin equation, which has eight constants, are among the best we have at the present time. The two-constant Redlich-Kwong equation also appears to be quite good according to a study of Thodos and Shah.² Naturally, the use of these equations involves time-consuming calculations, particularly when carried

²G. Thodos and K. K. Shah, *Ind. Eng. Chem.*, v. 57, p. 30 (1965).

out by hand rather than on the computer, but the results will frequently be more accurate than those obtained by other methods to be described shortly.

In spite of the complications involved in their use, equations of state are important for several reasons. They permit a concise summary of a large mass of experimental data and also permit accurate interpolation between experimental data points. They provide a continuous function to facilitate thermodynamic calculations involving differentiation and integration. Finally, they provide a point of departure for the treatment of thermodynamic properties of mixtures. However, for instructional purposes, and for many engineering calculations, the techniques of predicting p - V - T values discussed in the next section are considerably more convenient to use and are usually just as accurate as equations of state.

3.2.2 Compressibility Factors. In the attempt to devise some truly universal gas law for high pressures, the idea of corresponding states was developed. Early experimenters found that at the critical point all substances are in approximately the same state of molecular dispersion. Consequently, it was felt that their thermodynamic and physical properties should be similar. The *law of corresponding states* expresses the idea that in the critical state all substances should behave alike.

Now that we have mentioned *critical state* several times, let us consider exactly what the term means. You can find many definitions, but the one most suitable for general use with pure component systems as well as with mixtures of gases is the following:

The *critical state* for the gas-liquid transition is the set of physical conditions at which the density and other properties of the liquid and vapor become identical.

Referring to Fig. 3.3, note how as the pressure increases the specific volumes of the liquid and gas approach each other and finally become the same at the point *C*. This point, for a pure component (only), is the highest temperature at which liquid and vapor can exist in equilibrium. From a slightly different view a critical point is a limiting point that marks the disappearance of a state.

Consider Fig. 3.2. When gaseous carbon dioxide is compressed at 25°C its pressure rises until a certain density is reached (*D*). On further compression the pressure remains constant and the gas condenses, liquid and vapor being in coexistence. Only after all vapor is condensed to liquid (*B*) does the pressure rise again. If the temperature is raised a little, the vapor reaches a higher density before it starts condensing; on the other hand, the condensation is completed at lower liquid density. Thus the coexisting phases have a smaller difference in density at the higher temperature. Above 30°C this density range diminishes very rapidly with temperature and finally, just above 30°C, the two densities at which condensation is initiated and completed coincide. Vapor and liquid are no longer distinguishable; the separating meniscus disappears. Below the

frequently be more useful shortly. Equations of state are usually of a large mass advantage between experimental and theoretical thermodynamics. Finally, they dynamic properties of engineering calculated in the next section are just as accurate.

Devise some truly interesting states was point all substances on. Consequently, should be similar. The critical state all

es, let us consider but the one most as with mixtures

of physical conditions and vapor become

the specific volumes are the same at the highest temperature at only different view appearance of a state. Compressed at 25°C either compression and vapor being in as the pressure rise a higher density condition is completed smaller difference range diminishes the two densities vapor and liquid becomes low the

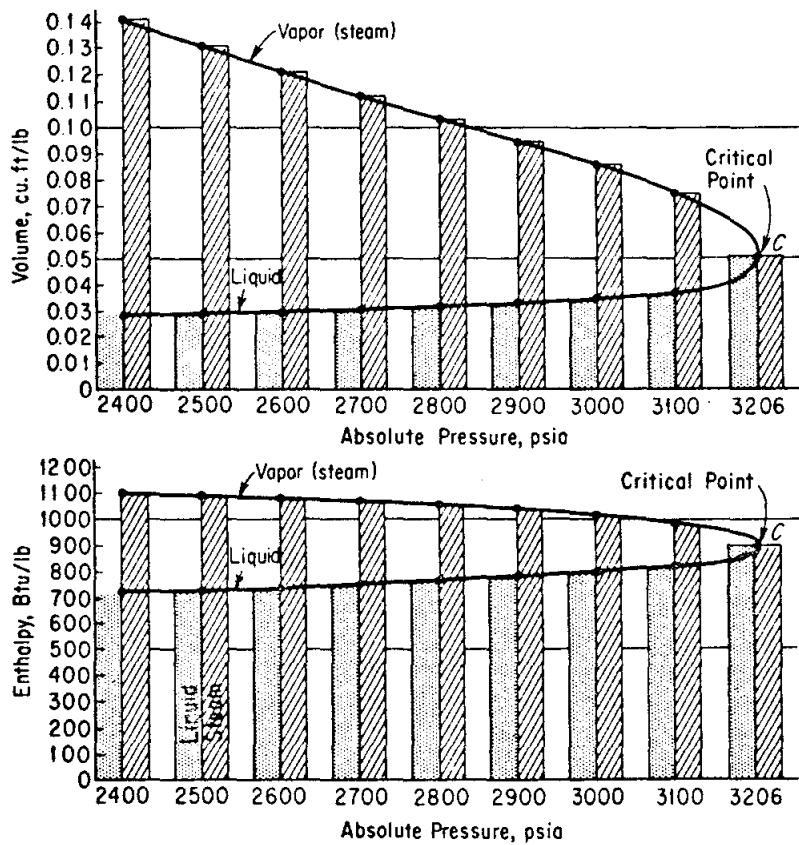


Fig. 3.3. The critical point for a pure substance (water).

critical temperature, the system can exhibit two coexisting phases; above, it goes from the dilute to the dense state without a phase transition. The critical point marks the highest temperature on the coexistence curve.

Experimental values of the critical temperature (T_c) and the critical pressure (p_c) for various compounds will be found in Appendix D. If you cannot find a desired critical value in this text or in a handbook, you can always consult Reid and Sherwood³ or Hakata and Hirata,⁴ which describe and evaluate methods of estimating critical constants for various compounds.

The gas-liquid transition described above is only one of several possible transitions exhibiting a critical point. Critical phenomena are observed in liquids and solids as well. For example, at low temperatures water is only partially miscible in phenol and vice versa. Thus, if equal amounts of water and phenol

³R. C. Reid and T. K. Sherwood, *The Properties of Gases and Liquids*, 2nd ed., McGraw-Hill, New York, 1965.

⁴T. Hakata and M. Hirata, *J. Chem. Engr. of Japan*, 3, p. 5 (1970).

are shaken together, they will separate in two phases, one consisting of water with some phenol and the other of phenol with some water dissolved in it. If the temperature is increased, the concentration of phenol in water increases and also that of water in phenol. Finally (if the initial composition is chosen correctly) a critical temperature of the binary liquid mixture is reached at which the two phases become equal in composition, so that the interface disappears and the phases can no longer be distinguished from one another. Above the critical temperature, the system cannot coexist in two phases. A plot of the coexisting compositions against temperature would give a coexistence curve closely analogous to the coexistence curves for the gas-liquid transition.

Another set of terms with which you should immediately become familiar are the *reduced* conditions. These are *corrected*, or *normalized*, conditions of temperature, pressure, and volume and are expressed mathematically as

$$T_r = \frac{T}{T_c} \quad (3.14)$$

$$p_r = \frac{p}{p_c} \quad (3.15)$$

$$V_r = \frac{V}{V_c} \quad (3.16)$$

The idea of using the reduced variables to correlate the *p-V-T* properties of gases, as suggested by van der Waals, is that all substances behave alike in their reduced, i.e., their corrected, states. In particular, any substance would have the same *reduced* volume at the same *reduced* temperature and pressure. If a relationship does exist involving the reduced variables that can be used to predict p_r , T_r , and V_r , what would the equation be? Certainly the simplest form of such an equation would be to imitate the ideal gas law, or

$$p_r V_r = \gamma T_r \quad (3.17)$$

where γ is some constant.

Now, how does this concept work out in practice? If we plot p_r vs. T_r , with a third parameter of constant V_r ,

$$\frac{p_r}{T_r} = \frac{\gamma}{V_r} \quad (3.18)$$

we should get straight lines for constant V_r . That this is actually what happens can be seen from Fig. 3.4 for various hydrocarbons. Furthermore, this type of correlation works in the region where $pV = nRT$ is in great error. Also, at the critical point ($p_r = 1.0$, $T_r = 1.0$), V_r should be 1.0 as it is in the diagram.

However, the ability of Eq. (3.18) to predict gas properties breaks down for most substances as they approach the perfect gas region (the area of low pressures somewhat below $p_r = 1.0$). If this concept held in the perfect gas region

consisting of water dissolved in it. If water increases its position is chosen at which surface disappears altogether. Above the plot of the concurrence curve closely follows.

become familiar with conditions of equation as

$$(3.14)$$

$$(3.15)$$

$$(3.16)$$

n -V-T properties of all substances behave alike in that they are proportional to temperature and pressure. This can be used to obtain the simplest form of the equation:

$$(3.17)$$

we plot p_r vs. T_r ,

$$(3.18)$$

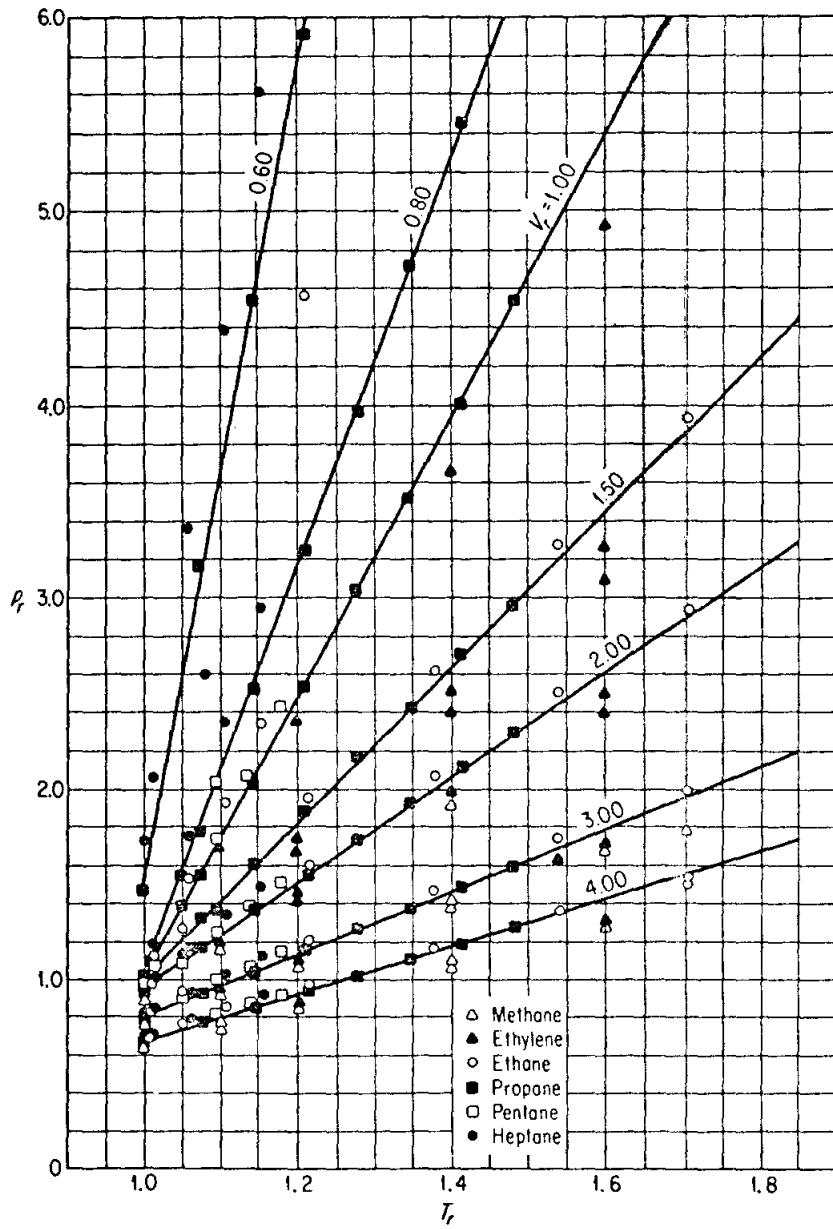


Fig. 3.4. A test of the relation $p_r/T_r = \gamma/V_r$.

for all gases, then for 1 mole

$$p\hat{V} = RT \quad (3.1a)$$

should hold as well as Eq. (3.17)

$$p_r V_r = \gamma T_r$$

For both of these relations to be true would mean that

$$\frac{p\hat{V}}{RT} = \frac{p_r V_r}{\gamma T_r} = \frac{(p/p_c)(\hat{V}/\hat{V}_c)}{\gamma(T/T_c)} \quad (3.19)$$

or

$$\frac{p_c \hat{V}_c}{RT_c} = \text{constant} \quad (3.20)$$

for all substances. If you look at Table 3.3 you can see from the experimental data that Eq. (3.20) is not quite true, although the range of values for most substances is not too great (from 0.24 to 0.28). He (0.305) and HCN (0.197) represent the extremes of the range.

TABLE 3.3 EXPERIMENTAL VALUES OF $p_c \hat{V}_c / RT_c$ FOR VARIOUS GASES

NH ₃	0.243	HCN	0.197	CH ₄	0.290	C ₂ H ₄	0.270
Ar	0.291	H ₂ O	0.233	C ₂ H ₆	0.285	CH ₃ OH	0.222
CO ₂	0.279	N ₂	0.292	C ₃ H ₈	0.277	C ₂ H ₅ OH	0.248
He	0.305	Toluene	0.270	C ₆ H ₁₄	0.264	CCl ₄	0.272

A more convenient and accurate way that has been developed to tie together the concepts of the law of corresponding states and the ideal gas law is to revert to a correction of the ideal gas law, i.e., a generalized equation of state expressed in the following manner:

$$pV = znRT \quad (3.21)$$

where the dimensionless quantity z is called the *compressibility factor* and is a function of the pressure and temperature:

$$z = \psi(p, T) \quad (3.22)$$

One way to look at z is to consider it to be a factor which makes Eq. (3.21) an equality. If the compressibility factor is plotted for a given temperature against the pressure for different gases, we obtain something like Fig. 3.5(a). However, if the compressibility is plotted against the reduced pressure as a function of the reduced temperature,

$$z = \psi(p_r, T_r) \quad (3.23)$$

then for most gases the compressibility values at the same reduced temperature and reduced pressure fall at about the same point, as illustrated in Fig. 3.5(b).

This permits the use of what is called a generalized compressibility factor, and Figs. 3.6(a) and (b) through 3.10 are the *generalized compressibility charts* or z -factor charts prepared by Nelson and Obert.³ These charts are based on

³L. C. Nelson and E. F. Obert, *Chem. Eng.*, vol. 61, no. 7, pp. 203-208 (1954). O. A. Hougen and K. M. Watson, *Chemical Process Principles*, J. Wiley, New York, 1943, also presents z -factor charts, as do many articles in the literature for specialized gases, such as natural gases.

(3.19)

(3.20)

the experimental values for most
and HCN (0.197)

GASES

H ₂	0.270
CH ₃ OH	0.222
H ₃ OH	0.248
Cl ₂	0.272

ed to gether
s law is to revert
state expressed

(3.21)

factor and is a

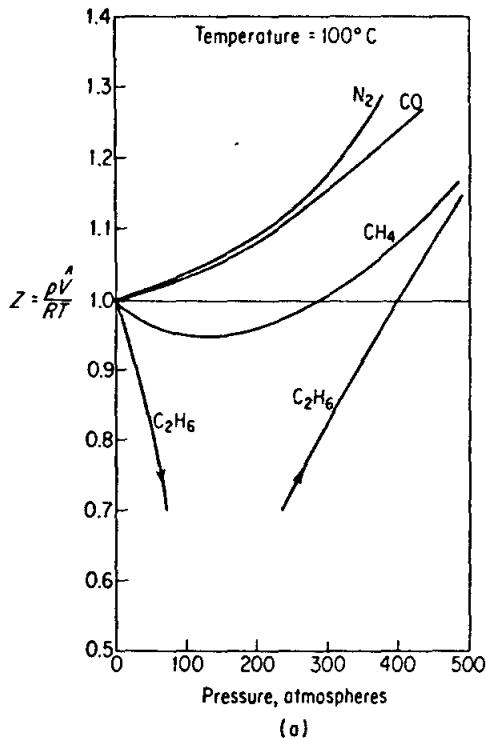
(3.22)

takes Eq. (3.21)
perature against
Fig. 3.5(a). However,
is a function of

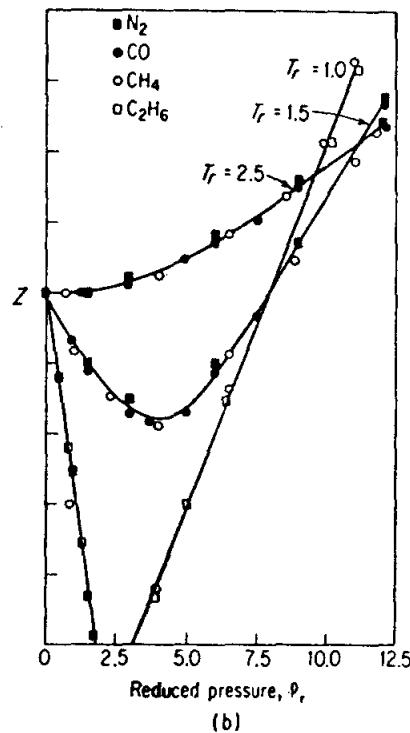
(3.23)

ed temperature
in Fig. 3.5(b).
sibility factor,
sibility charts
are based on

4). O. A. Hougen
& R. H. Watson
as gases.



(a)



(b)

Fig. 3.5(a). Compressibility factor as a function of temperature and pressure.

Fig. 3.5(b). Compressibility as a function of reduced temperature and reduced pressure.

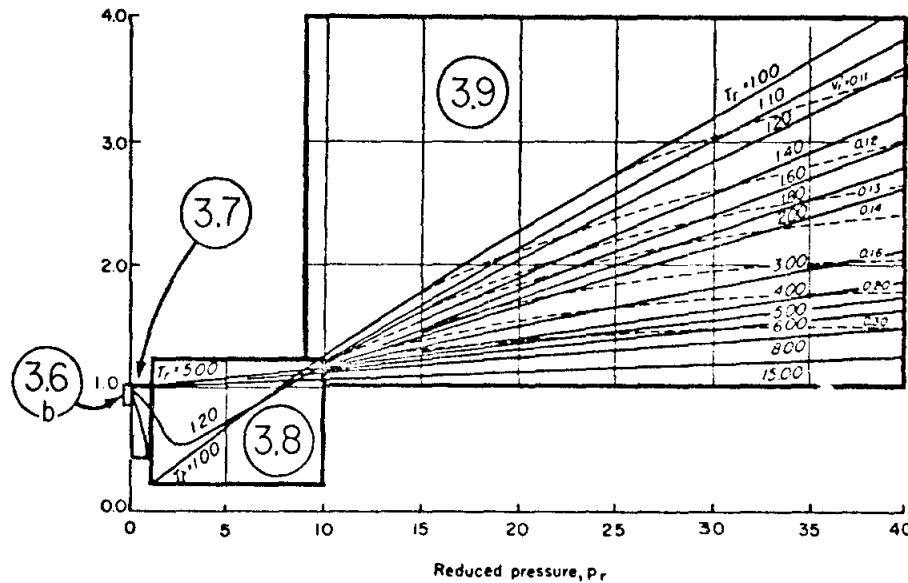


Fig. 3.6(a). General compressibility chart.

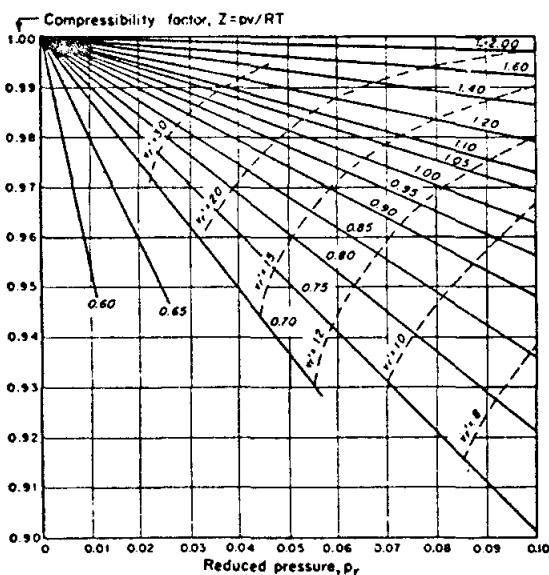


Fig. 3.6(b). General compressibility chart, very low temperatures.

30 gases. Figures 3.6(b) and 3.7 represent z for 26 gases (excluding H_2 , He, NH_3 , H_2O) with a maximum deviation of 1 percent, and H_2 and H_2O within a deviation of 1.5 percent. Figure 3.8 is for 26 gases and is accurate to 2.5 percent, while Fig. 3.9 is for nine gases and errors can be as high as 5 percent. For H_2 and He only, Newton's corrections to the actual critical constants are used to give pseudocritical constants

$$T'_c = T_c + 8^\circ K \quad (3.24)$$

$$p'_c = p_c + 8 \text{ atm} \quad (3.25)$$

which enable you to use Figs. 3.6 through 3.10 for these two gases as well with minimum error. Figure 3.10 is a unique chart which, by having several parameters plotted simultaneously on it, helps you avoid trial-and-error solutions or graphical solutions of real gas problems. One of these helpful factors is the ideal reduced volume defined as

$$V_{r_i} (\text{or } V'_r \text{ in the Nelson and Obert charts}) = \frac{\hat{V}}{\hat{V}_{c_i}} \quad (3.26)$$

\hat{V}_{c_i} is the ideal critical volume, or

$$\hat{V}_{c_i} = \frac{RT_c}{p_c} \quad (3.27)$$

Both V_{r_i} and \hat{V}_{c_i} are easy to calculate since T_c and p_c are presumed known. The development of the generalized compressibility chart is of considerable practical as well as pedagogical value because it enables engineering calculations to be made with considerable ease and also permits the development of thermodynamic functions for gases for which no experimental data are available. All you need to know to use these charts are the critical temperature and the critical

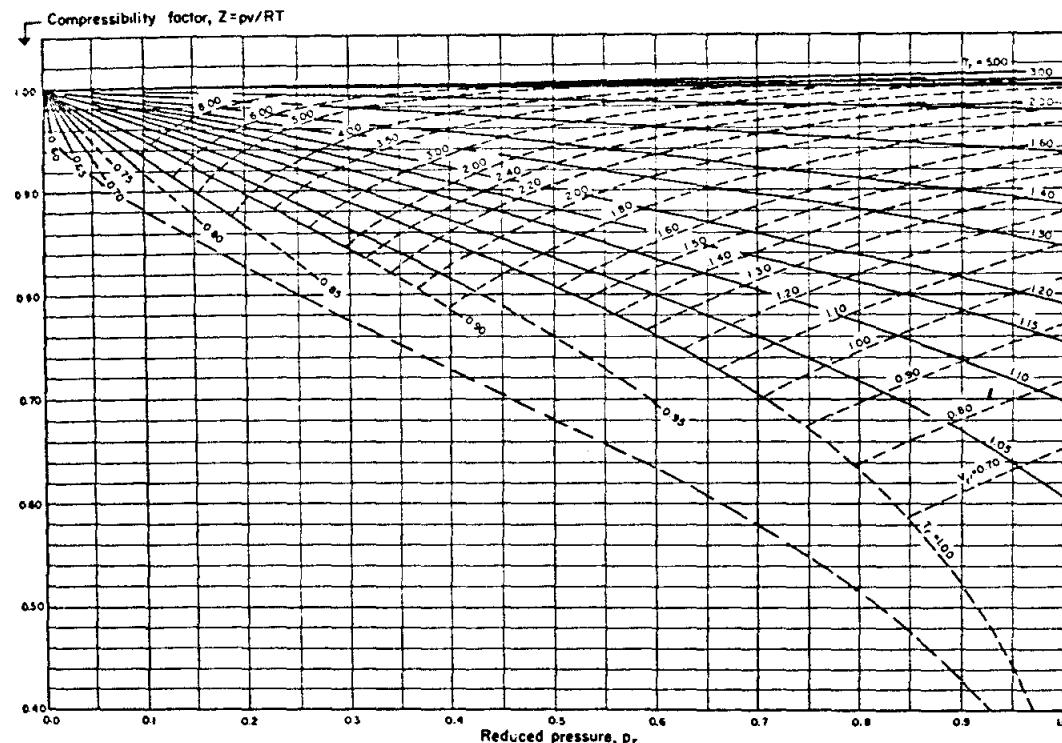


Fig. 3.7. General compressibility chart, low pressures.

excluding H₂, He, and H₂O within rate to 2.5 percent, 5 percent. For H₂ constants are used to

$$(3.24)$$

$$(3.25)$$

gases as well with several para-nd-error solutions useful factors is the

$$(3.26)$$

$$(3.27)$$

umed known. The considerable practical calculations to be made thermodynamic available. All you are and the critical

pressure for a pure substance (or the pseudovalue for a mixture, as we shall see later). The value $z = 1$ represents ideality, and the value $z = 0.27$ is the compressibility factor at the critical point.

Quite a few authors have suggested that the generalized compressibility relation, Eq. (3.23), could provide better accuracy if another parameter for the gas were included in the argument on the right-hand side (in addition to p_r and T_c). Clearly, if a third parameter is used, adding a third dimension to p_r and T_c , you have to employ a set of tables or charts rather than a single table or chart. Lydersen et al.⁶ developed tables of z that included as the third parameter the critical compressibility factor, $z_c = p_c \bar{f}_c / RT_c$. Pitzer⁷ used a different third parameter termed the *acentric* factor, defined as being equal to $-\ln p_{rs} - 1$, where p_{rs} is the value of the reduced vapor pressure at $T_c = 0.70$.

Viswanath and Su⁸ compared the z factors from the Nelson and Obert charts, the Lydersen-Greenkorn-Hougen charts, and the two-parameter (T_c and p_r) Viswanath and Su chart with the experimental z 's for T_c 's of 1.00–15.00

⁶A. L. Lydersen, R. A. Greenkorn, and O. A. Hougen, *University of Wisconsin Engineering Experimental Station Report no. 4*, Madison, Wis., 1955.

⁷K. S. Pitzer, *J. Amer. Chem. Soc.*, v. 77, p. 3427 (1955).

⁸D. S. Viswanath and G. J. Su, *A.I.Ch.E. J.*, v. 11, p. 202 (1965).

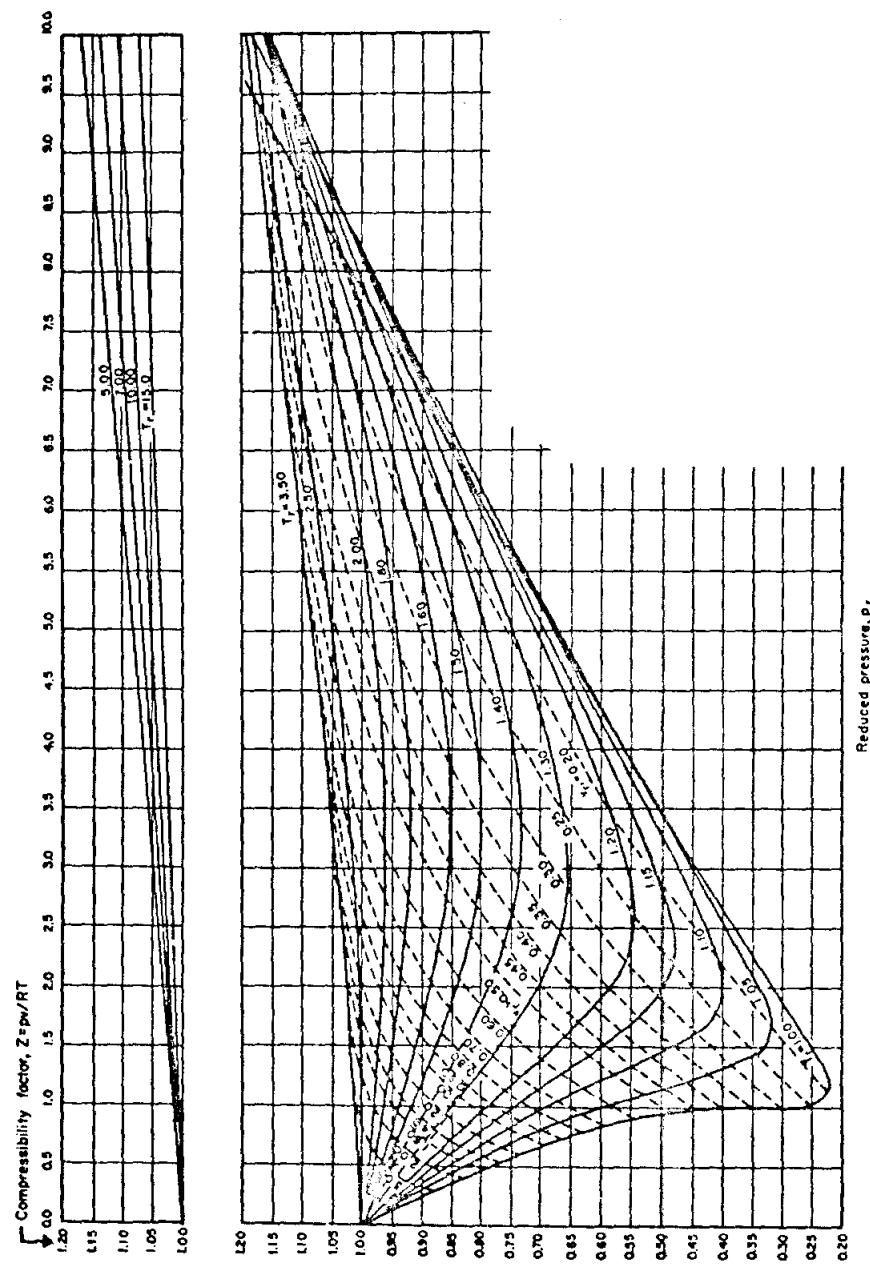


Fig. 3.8. General compressibility chart, medium pressures.

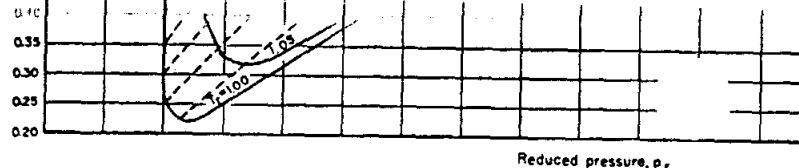


Fig. 3.8. General compressibility chart, medium pressures.

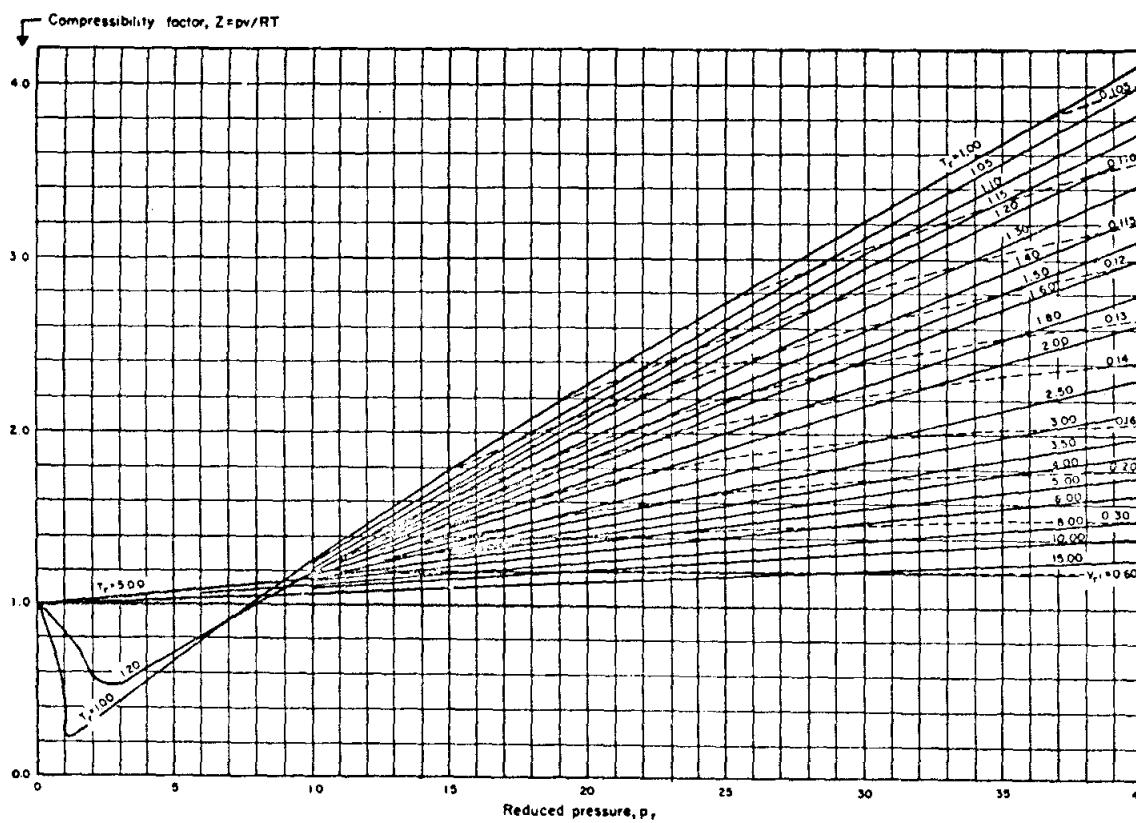


Fig. 3.9. Generalized compressibility chart, high pressures.

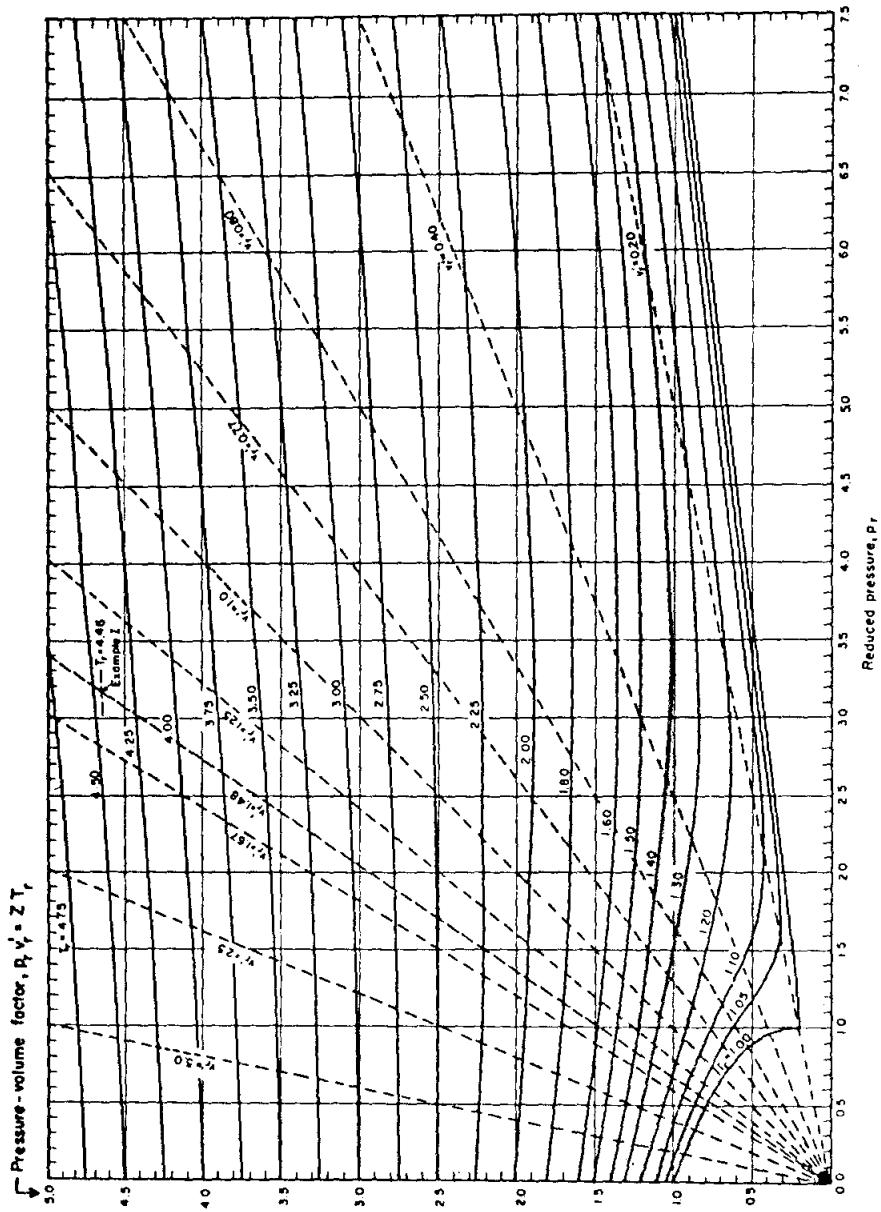


Fig. 3.10. Generalized compressibility chart, with special scales.

and p_r 's of 0–40 for 19 gases with the following results:

	Viswanath-Su	Nelson-Obert	Lyderson-Greenkorn-Hougen
Number of points	415	355	339
Average deviation (%) in z	0.61	0.83	1.26

It is seen that all these charts yield quite reasonable values for engineering purposes. Because the use of a third parameter does not necessarily yield gas calculations of greater accuracy and because the presentation of z values so as to include the third parameter is considerably more cumbersome, we shall not show the three-parameter tables here.

EXAMPLE 3.13 Use of the compressibility factor

In spreading liquid ammonia fertilizer, the charges for the amount of NH_3 are based on the time involved plus the pounds of NH_3 injected into the soil. After the liquid has been spread, there is still some ammonia left in the source tank (volume = 120 ft^3), but in the form of a gas. Suppose that your weight tally, which is obtained by difference, shows a net weight of 125 lb of NH_3 left in the tank as a gas at 292 psig. Because the tank is sitting in the sun, the temperature in the tank is 125°F .

Your boss complains that his calculations show that the specific volume of the gas is $1.20 \text{ ft}^3/\text{lb}$ and hence that there are only 100 lb of NH_3 in the tank. Could he be correct? See Fig. E3.13.

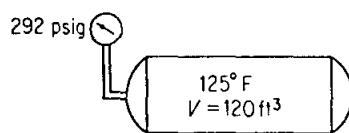


Fig. E3.13.

Solution:

Basis: 1 lb of NH_3

Apparently your boss used the ideal gas law in calculating his figure of $1.20 \text{ ft}^3/\text{lb}$ of NH_3 gas:

$$R = 10.73 \frac{(\text{psia})(\text{ft}^3)}{(\text{lb mole})(^\circ\text{R})}$$

$$T = 125^\circ\text{F} + 460 = 585^\circ\text{R}$$

$$p = 292 + 14.7 = 307 \text{ psia}$$

$$n = \frac{1 \text{ lb}}{17 \text{ lb/lb mole}}$$

$$\hat{V} = \frac{nRT}{p} = \frac{(1/17)(10.73)(585)}{307} = 1.20 \text{ ft}^3/\text{lb}$$

Fig. 3.10. Generalized compressibility chart, with special scales.

However, he should have used the compressibility factor because NH_3 does not behave as an ideal gas under the observed conditions of temperature and pressure. Let us again compute the mass of gas in the tank this time using

$$pV = znRT$$

What is known and unknown in the equation?

$$p = 307 \text{ psia}$$

$$V = 120 \text{ ft}^3$$

$$z = ?$$

$$n = \frac{1}{17} \text{ lb mole}$$

$$T = 585^\circ\text{R}$$

The additional information needed (taken from Appendix D) is

$$T_c = 405.4^\circ\text{K} \cong 729^\circ\text{R}$$

$$p_c = 111.3 \text{ atm} \cong 1640 \text{ psia}$$

Then, since z is a function of T_r and p_r ,

$$T_r = \frac{T}{T_c} = \frac{585^\circ\text{R}}{729^\circ\text{R}} = 0.803$$

$$p_r = \frac{p}{p_c} = \frac{307 \text{ psia}}{1640 \text{ psia}} = 0.187$$

From the Nelson and Obert chart, Fig. 3.7, you can read $z \cong 0.845$. Now \hat{V} can be calculated as

$$\hat{V} = \frac{znRT}{p}$$

or

$$\hat{V} = \frac{1.20 \text{ ft}^3 \text{ ideal}}{1 \text{ lb}} \left| \frac{0.845 \text{ ft}^3 \text{ actual}}{1 \text{ ft}^3 \text{ ideal}} \right| = 1.01 \text{ ft}^3/\text{lb NH}_3$$

Note in the calculation above that we have added some hypothetical units to z to make the conversion from ideal cubic feet to actual cubic feet clear:

$$\frac{1 \text{ lb NH}_3}{1.01 \text{ ft}^3} \left| \frac{120 \text{ ft}^3}{1 \text{ ft}^3} \right| = 119 \text{ lb NH}_3$$

Certainly 119 lb is a more realistic figure than 100 lb, and it is easily possible to be in error by 6 lb if the residual weight of NH_3 in the tank is determined by difference. As a matter of interest you might look up the specific volume of NH_3 at the conditions in the tank in a handbook—you would find that $\hat{V} = 0.973 \text{ ft}^3/\text{lb}$, and hence the compressibility factor calculation yielded a volume with an error of only about 4 percent.

EXAMPLE 3.14 Use of the compressibility factor

A single-stage-to-orbit vehicle with space-shuttle capabilities may be feasible if the mechanical strength of frozen propellants can be utilized—particularly frozen oxygen, if it could be vaporized at the required rate. During the thrust period, the solid oxygen cylinder would be melted from its bottom surface and the resulting liquid propellant conveyed to a conventional pump-fed rocket engine where the oxygen would be vaporized and combined with vaporized fuel.

ctor because NH_3 does not
temperature and pressure.
using:

D) is

Suppose that 3.500 kg of O_2 is vaporized into a tank of 0.0284-m^3 volume at -25°C . What will the pressure in the tank be; will it exceed 100 atm?

Solution:

See Fig. E3.14.

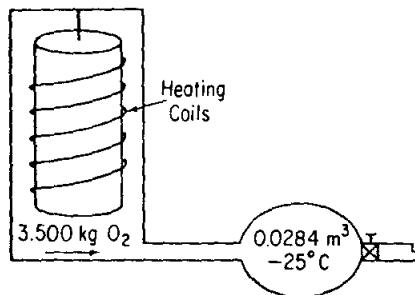


Fig. E3.14.

Basis: 3.500 kg O_2

We do know from Appendix D that

$$T_c = -118.8^\circ\text{C} \quad \text{or} \quad -118.8 + 273.1 = 154.3^\circ\text{K}$$

$$p_c = 49.7 \text{ atm}$$

However, this problem cannot be worked exactly the same way as the previous problem because we do not know the pressure of the O_2 in the tank. Thus we need to use the other parameter, V_{r_i} (i.e., V' on the chart), that is available on the Nelson and Obert charts:

$$\hat{V} \text{ (molal volume)} = \frac{0.0284 \text{ m}^3}{3.500 \text{ kg}} \left| \frac{32 \text{ kg}}{1 \text{ kg mole}} \right. = 0.259 \text{ m}^3/\text{kg mole}$$

Note that the *molal volume* must be used in calculating V_{r_i} since \hat{V}_{c_i} is a volume per mole. Next,

$$\hat{V}_{c_i} = \frac{RT_c}{p_c} = \frac{0.08206(\text{m}^3)(\text{atm})}{(\text{kg mole})(^\circ\text{K})} \left| \frac{154.3^\circ\text{K}}{49.7 \text{ atm}} \right. = 0.255 \frac{\text{m}^3}{\text{kg mole}}$$

Then

$$V_{r_i} = \frac{\hat{V}}{\hat{V}_{c_i}} = \frac{0.259}{0.255} = 1.02$$

Now we know two parameters, V_{r_i} and, with $T = -25^\circ\text{C} + 273 = 248^\circ\text{K}$,

$$T_r = \frac{T}{T_c} = \frac{248^\circ\text{K}}{154.3^\circ\text{K}} = 1.61$$

From the Nelson and Obert chart, Figs. 3.8 or 3.10,

$$p_r = 1.43$$

Then

$$\begin{aligned} p &= p_r p_c \\ &= 1.43(49.7) = 71.0 \text{ atm} \end{aligned}$$

The pressure of 100 atm is not exceeded.

Now \hat{V} can be

numerical units to z to make
it:

easily possible to be in
mined by difference. As
 H_2 at the conditions in
o, and hence the com-
only about 4 percent.

ies may be feasible if
particularly frozen
the thrust period, the
nd the resulting liquid
ere the oxygen would

EXAMPLE 3.15 Use of compressibility factor

Repeat Example 3.12, this time using the compressibility factor, i.e., the equation of state $pV = znRT$. "A 5-ft³ cylinder containing 50.0 lb of propane (C_3H_8) stands in the hot sun. A pressure gauge shows that the pressure is 665 psig. What is the temperature of the propane in the cylinder?"

Solution:

See Fig. E3.15.

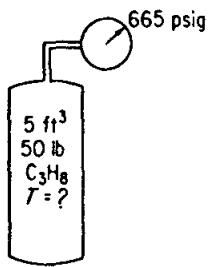


Fig. E3.15.

In the equation $pV = znRT$, we know that

$$V = 5 \text{ ft}^3$$

$$n = \frac{50 \text{ lb}}{44 \text{ lb/lb mole}} = 1.135 \text{ lb moles } C_3H_8$$

$$p = 665 \text{ psig} + 14.7 \approx 680 \text{ psia}$$

However, z as well as T is unknown. Since z is a function of T_r and p_r , we should first calculate the latter two quantities ($T_c = 370^\circ\text{K}$, or 666°R ; $p_c = 42.1 \text{ atm}$, or 617 psia , from Appendix D) but are stopped by the fact that T is unknown. Another parameter available for use, to avoid a trial-and-error or graphical solution, is the factor zT_r (or V'_r could be used, as in the last example):

$$zT = \frac{pV}{nR} \quad \text{or} \quad zT_r = \frac{pV}{nRT_c}$$

$$zT_r = \frac{680 \text{ psia}}{1.135 \text{ lb mole}} \left| \frac{5 \text{ ft}^3}{10.73 \frac{(\text{psia})(\text{ft}^3)}{(\text{lb mole})(^\circ\text{R})}} \right| 666^\circ\text{R} \\ = 0.42$$

From the Nelson and Obert chart, Fig. 3.10, at

$$\left. \begin{aligned} zT_r &= 0.42 \\ p_r &= \frac{680}{617} = 1.10 \end{aligned} \right\}$$

you can find $T_r = 1.02$ and

$$\begin{aligned} T &= T_r T_c = (370)(1.02) = 378^\circ\text{K} \\ &= (666)(1.02) = 680^\circ\text{R} \end{aligned}$$

3.2.3 Gas properties pounds and temperatures and therefore. Thus the question of accuracy for the gas law and saw, as an example, that for ideal gases put together to give the equations prove to be a better develop methods for the properties of the gases discussed below.

(a) Equations

Take, for example, the partial pressures add the individual pressures the total pressure, for component i :

for component i :

for component i :

etc., in total,

This technique, however, the number

(b) Charts

A set of charts is to convert information on the properties of gases for different conditions.

For

sector, i.e., the equation
propane (C_3H_8) stands in
What is the tempera-

3.2.3 Gaseous Mixtures. So far we have discussed only pure compounds and their p - V - T relations. Most practical problems involve gaseous mixtures and there is very little experimental data available for gaseous mixtures. Thus the question is, How can we predict p - V - T properties with reasonable accuracy for gaseous mixtures? We treated ideal gas mixtures in Sec. 3.1.3, and saw, as we shall see later (in Chap. 4 for the thermodynamic properties), that for ideal mixtures the properties of the individual components can be added together to give the desired property of the mixture. But this technique does not prove to be adequate for real gases. The most desirable technique would be to develop methods of calculating p - V - T properties for mixtures based solely on the properties of the pure components. Possible ways of doing this for real gases are discussed below.

(a) Equations of state.

Take, for example, van der Waals' equation, Eq. (3.12). You can compute the partial pressure of each component by van der Waals' equation and then add the individual partial pressures together according to Dalton's law to give the total pressure of the system,

for component A,

$$p_A = \frac{n_A RT}{V - n_A b_A} - \frac{n_A^2 a_A}{V^2} \quad (3.28)$$

for component B,

$$p_B = \frac{n_B RT}{V - n_B b_B} - \frac{n_B^2 a_B}{V^2} \quad (3.29)$$

etc.,
in total,

$$\begin{aligned} p_T &= RT \left[\frac{n_A}{V - n_A b_A} + \frac{n_B}{V - n_B b_B} + \dots \right] \\ &\quad - \frac{1}{V^2} [n_A^2 a_A + n_B^2 a_B + \dots] \end{aligned} \quad (3.30)$$

This technique provides a direct solution for p_T if everything else is known; however, the solution for V or n_A from Eq. (3.30) is quite cumbersome.

(b) Average constants.

A simpler and usually equally effective way to solve gas mixture problems is to use average constants in the equation of state. The problem resolves itself into this question, How should the constants be averaged to give the least error in the whole? For van der Waals' equation, you should proceed as follows.

For:

b (Use linear mole fraction weight):

$$b_{\text{mixture}} = b_A y_A + b_B y_B + \dots \quad (3.31)$$

a (Use linear square root average weight):

$$a_{\text{mixture}}^{1/2} = a_A^{1/2}y_A + a_B^{1/2}y_B + \dots \quad (3.32)$$

If you are puzzled as to the reasoning behind the use of the square root weighting for a , remember that the term in van der Waals' equation involving a is

$$\frac{n^2 a}{V^2}$$

in which the number of moles is squared. The method of average constants can be successfully applied to most of the other equations of state listed in Table 3.1. The average constants can also be calculated from the pseudoreduced constants described below. For example, for van der Waals' equation,

$$a = \frac{27}{64} \frac{R^2 T_c^2}{p_c} \quad \text{and} \quad b = \frac{RT_c}{8p_c}$$

(c) Mean compressibility factor.

Another approach toward the treatment of gaseous mixtures is to say that $pV = z_m nRT$, where z_m can be called the *mean compressibility factor*. With such a relationship the only problem is how to evaluate the mean compressibility factor satisfactorily. One obvious technique that might occur to you is to make z_m a mole average as follows:

$$z_m = z_A y_A + z_B y_B + \dots \quad (3.33)$$

Since z is a function of both the reduced temperature and the reduced pressure, it is necessary to decide what pressure will be used to evaluate p_r .

(1) *Assume Dalton's law of partial pressures.* For each component z is evaluated at T , and the reduced *partial pressure* for each gaseous component. The reduced partial pressure is defined as

$$p_{T,A} = \frac{p_A}{p_{c,A}} = \frac{(p_T)y_A}{p_{c,A}} \quad (3.34)$$

(2) *Assume Amagat's law of pure component volumes.* For each component z is evaluated at T , and the reduced *total pressure* on the system.

(d) Pseudocritical properties.

Many weighting rules have been proposed to combine the critical properties of the components of a real gas mixture in order to get an effective set of critical properties (*pseudocritical*) that enable *pseudoreduced* properties of the mixture to be computed.⁹ The pseudoreduced properties in turn are used in exactly the same way as the reduced properties for a pure compound, and in effect the mixture can be treated as a pure compound. In instances where you know no-

⁹You should still add Newton's corrections for H₂ and He.

thing about it previously.

In fact, on the assumption that the critical values of the components are known, the pseudocritical properties can be calculated directly from the critical properties of the components.

where p'_c is the critical pressure of the pure component c . It has also been found that the pseudoreduced properties of a mixture are the same as those of a mole average of the reduced properties of the pure components at their respective critical points.

If you are familiar with the well-known methods of calculating such as shown in Sec. 3.1.

(3.32)

square root weighting involving a is

average constants can
be listed in Table 3.1.
Pseudoreduced constants

mixtures is to say that
stability factor. With
near possibility
er to you is to make

(3.33)

the reduced pressure,
rate p_r ,
which component z is
gaseous component.

(3.34)

or each component
em.

the critical properties
effective set of critical
ties of the mixture
used in exactly the
and in effect the
here you know no-

thing about the gas mixture this technique is preferable to any of those discussed previously.

In Kay's method pseudocritical values for mixtures of gases are calculated on the assumption that each component in the mixture contributes to the pseudocritical value in the same proportion as the number of moles of that component. Thus the pseudocritical values are computed as follows:

$$p'_c = p_{c_A}y_A + p_{c_B}y_B + \dots \quad (3.35)$$

$$T'_c = T_{c_A}y_A + T_{c_B}y_B + \dots \quad (3.36)$$

where p'_c = pseudocritical pressure, T'_c = pseudocritical temperature. (It has also been found convenient in some problems to calculate similarly a weighted pseudo-ideal-critical volume $V'_{c,i}$.) You can see that these are linearly weighted mole average pseudocritical properties. (In Sec. 3.8 we shall compare the true critical point of gaseous mixture with the pseudocritical point). Then the respective pseudoreduced values are

$$p'_r = \frac{p}{p'_c} \quad (3.37)$$

$$T'_r = \frac{T}{T'_c} \quad (3.38)$$

If you are faced with a complicated mixture of gases whose composition is not well known, you still can estimate the pseudocritical constants from charts¹⁰ such as shown in Figs. 3.11(a) and (b) if you know the gas specific gravity. Figure

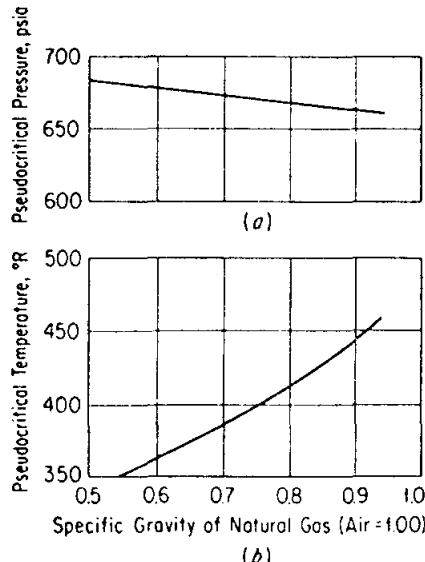


Fig. 3.11. Estimation of critical properties of natural gases.

¹⁰Natural Gasoline Supply Men's Association, *Engineering Data Book*, Tulsa, Okla., 1957, p. 103.

3.11 is good only for natural gases composed mainly of methane which contain less than 5 percent impurities (CO_2 , N_2 , H_2S , etc.).

Kay's method is known as a two-parameter rule since only p_c and T_c for each component are involved in the calculation of z . If a third parameter such as z_c , the Pitzer acentric factor, or $\bar{\gamma}_c$, is included in the determination of the mean compressibility factor, then we would have a three-parameter rule. Reid and Leland¹¹ have shown that all the weighting rules can be obtained from a common base, and all reduce to Kay's rule as limiting cases with the proper assumptions. All the pseudocritical methods do not provide equal accuracy in predicting

TABLE 3.4 PREDICTION OF p -V-T VALUES OF GAS DENSITY BY PSEUDOCRITICAL METHODS

Method	% Root-mean-square deviation of density, 35 systems	% Root-mean-square deviation of density, CO_2 and H_2S free systems
(1) Three-parameter Kay's rule:		
$T'_c = \sum T_{ci} y_i$		
$p'_c = \sum p_{ci} y_i$	10.74	6.82
$z'_c = \sum z_{ci} y_i$		
(2) Empirical:		
$T'_c = \sum T_{ci} y_i$		
$\frac{T'_c}{p'_c} = \sum \frac{T'_{ci} y_i}{p'_{ci}}$	6.06	5.85
$\hat{V}'_c = \sum \hat{V}_{ci} y_i$		
(3) Virial approach (Joffe's method III):		
$\frac{T'_c}{p'_c} = \frac{1}{8} \sum_i \sum_j y_i y_j \left[\left(\frac{T_{ci}}{p_{ci}} \right)^{1/3} + \left(\frac{T_{cj}}{p_{cj}} \right)^{1/3} \right]^3$		
$\frac{T'_c}{\sqrt{p'_c}} = \sum y_i \frac{T_{ci}}{\sqrt{p_{ci}}}$	4.98	4.24
$\hat{V}'_c = \sum \hat{V}_{ci} y_i$		
(4) "Recommended" method:		
$\frac{T'_c}{p'_c} = \frac{1}{3} \sum y_i \frac{T_{ci}}{p_{ci}} + \frac{2}{3} \left[\sum y_i \left(\frac{T_{ci}}{p_{ci}} \right)^{1/2} \right]^2$		
$\frac{T'_c}{\sqrt{p'_c}} = \sum y_i \frac{T_{ci}}{\sqrt{p_{ci}}}$	4.32	3.26
$z'_c = \sum z_{ci} y_i$		

¹¹R. C. Reid and T. W. Leland, *A.I.Ch.E. J.*, vol. 11, p. 228 (1965).

ethane which contain
only p_c and T_c for each
parameter such as
determination of the mean
parameter rule. Reid and
Reid made from a common
proper assumptions.
accuracy in predicting

INTENSITY

% Root-mean-square
deviation of
density,
 CO_2 and H_2S
free systems

6.82

5.85

4.24

3.26

p - V - T properties, however, but most suffice for engineering work. Stewart¹² et al. reviewed 21 different methods of determining the pseudoreduced parameters by three-parameter rules (see Table 3.4). Although Kay's method was not the most accurate, it was easy to use and not considerably poorer than some of the more complex techniques of averaging critical properties.

In summary, to evaluate all the various methods which have been presented for treating p - V - T relationships of gaseous mixtures, we would have to state that no one method will consistently give the best results. Kay's pseudocritical method, on the average, will prove reliable, although other methods of greater accuracy (and of greater complexity) are available in the literature, as brought out in Table 3.4. Some of the longer equations of state, with average constants, are quite accurate. All these methods begin to break down near the true critical point for the mixture.

EXAMPLE 3.16 p - V - T Relations for gas mixtures

A gaseous mixture has the following composition (in mole percent):

Methane	CH_4	20
Ethylene	C_2H_4	30
Nitrogen	N_2	50

at 90 atm pressure and 100°C. Compare the molal volume as computed by the methods of

- (a) Perfect gas law.
- (b) van der Waals' equation plus Dalton's law.
- (c) van der Waals' equation using averaged constants.
- (d) Mean compressibility factor and Dalton's law.
- (e) Mean compressibility factor and Amagat's law.
- (f) Pseudoreduced technique (Kay's method).

Solution:

Basis: 1 g mole of gas mixture

Additional data needed are:

	$a(\text{atm}) \left(\frac{\text{cm}^3}{\text{g mole}} \right)^2$	$b \left(\frac{\text{cm}^3}{\text{g mole}} \right)$	$T_c(\text{°K})$	$p_c(\text{atm})$
CH_4	2.25×10^6	42.8	191	45.8
C_2H_4	4.48×10^6	57.2	283	50.9
N_2	1.35×10^6	38.6	126	33.5

$$R = 82.06 \frac{(\text{cm}^3)(\text{atm})}{(\text{g mole})(\text{°K})}$$

¹²W. E. Stewart, S. F. Burkhardt, and David Voo, Paper given at the A.I.Ch.E. meeting in Kansas City, Mo., May 18, 1959. Also refer to A. Satter and J. M. Campbell, *Soc. Petrol. Engrs. J.*, p. 333 (Dec. 1963); and H. E. Barner and W. C. Quinlan, *I&EC Process Design and Development*, vol. 8, p. 407 (1969).

(a) Perfect gas law:

$$V = \frac{nRT}{P} = \frac{1(82.06)(373)}{90} = 340 \text{ cm}^3 \text{ at } 90 \text{ atm and } 373^\circ\text{K}$$

(b) Combine van der Waals' equation and Dalton's law according to Eq. (3.30):

$$P_T = RT \left[\frac{n_{\text{CH}_4}}{V - n_{\text{CH}_4}b_{\text{CH}_4}} + \frac{n_{\text{C}_2\text{H}_6}}{V - n_{\text{C}_2\text{H}_6}b_{\text{C}_2\text{H}_6}} + \frac{n_{\text{N}_2}}{V - n_{\text{N}_2}b_{\text{N}_2}} \right] - \frac{1}{V^2} [n_{\text{CH}_4}^2 a_{\text{CH}_4} + n_{\text{C}_2\text{H}_6}^2 a_{\text{C}_2\text{H}_6} + n_{\text{N}_2}^2 a_{\text{N}_2}]$$

Substitute the numerical values (in the proper units):

$$90 = 82.06(373) \left[\frac{0.2}{V - 8.56} + \frac{0.3}{V - 17.1} + \frac{0.5}{V - 19.3} \right] - \frac{1}{V^2} [9 \times 10^4 + 40.5 \times 10^4 + 33.8 \times 10^4] \quad (1)$$

The solution to this equation can be obtained by trial and error or graphical means. For the first trial assume ideal conditions. By plotting the right-hand side of Eq. (1) against V until the total is 90, we find the equation converges at about $V = 332 \text{ cm}^3$ at 90 atm and 373°K .

(c) To use average constants in van der Waals' equation, write it in the following fashion:

$$V^3 - \left(\bar{b} + \frac{RT}{P} \right) nV^2 + \left(\frac{\bar{a}}{P} \right) n^2 V - \frac{\bar{a}\bar{b}}{P} n^3 = 0$$

where \bar{a} and \bar{b} are the average constants.

$$(\bar{a})^{1/2} = 0.2a_{\text{CH}_4}^{1/2} + 0.3a_{\text{C}_2\text{H}_6}^{1/2} + 0.5a_{\text{N}_2}^{1/2}$$

$$\bar{a} = 2.30 \times 10^6 \text{ atm} \left(\frac{\text{cm}^3}{\text{g mole}} \right)^2$$

$$\bar{b} = 0.2b_{\text{CH}_4} + 0.3b_{\text{C}_2\text{H}_6} + 0.5b_{\text{N}_2} = 45.0 \frac{\text{cm}^3}{\text{g mole}}$$

$$n = 1 \text{ g mole (the basis)}$$

$$V^3 - \left[45.0 + \frac{(82.06)(373)}{90} \right] V^2 + \left[\frac{2.30 \times 10^6}{90} \right] V - \left[\frac{(2.30 \times 10^6)(45.0)}{90} \right] = 0 \quad (2)$$

Let us work out a method of solving Eq. (2) for V different from the method used in part (b):

$$f(V) = V^3 - 385V^2 + 2.56 \times 10^4 V - 1.15 \times 10^6 = 0$$

$$-V^3 + 385V^2 = 2.56 \times 10^4 V - 1.15 \times 10^6 \quad (3)$$

Splitting this equation into two parts,

$$f_1(V) = 2.56 \times 10^4 V - 1.15 \times 10^6 \quad (4)$$

$$f_2(V) = -V^3 + 385V^2 = V^2(385 - V) \quad (5)$$

and plotting these parts (see Fig. E3.16) to see where they cross is one method of obtaining the real root of the equation. You know V is in the vicinity of 340 cm^3 .

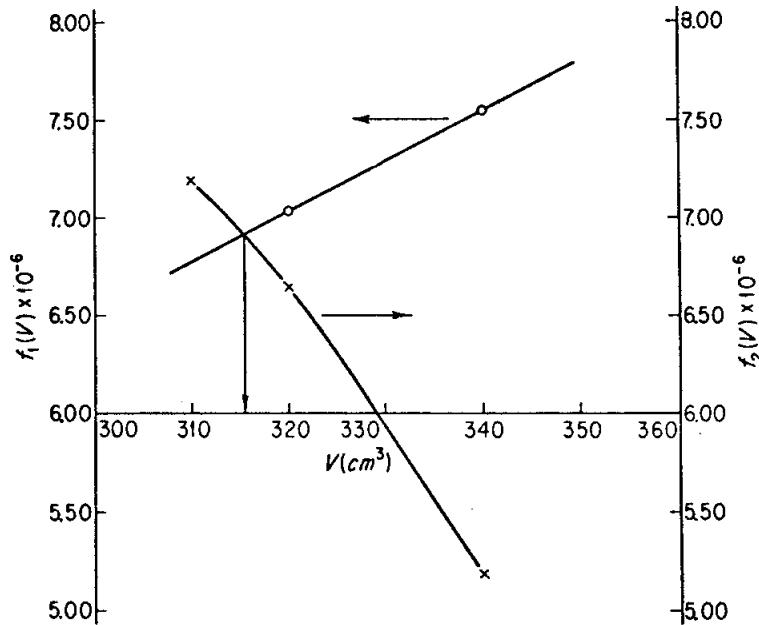


Fig. E3.16.

$V(cm^3)$	$f_1(V)$	$f_2(V)$
340	7.55×10^6	5.20×10^6
320	7.04×10^6	6.65×10^6
310	(only 2 points required for straight line)	7.20×10^6

From the graph $V \cong 316 cm^3$ at 90 atm and 373°K.

(d) The table below shows how Dalton's law can be used to estimate a mean compressibility factor.

Comp.	$p_c(atm)$	$T_c(^{\circ}K)$	y	$(90)y = p$	$p_r = \frac{p}{p_c}$	$T_r = \frac{373}{T_c}$
CH ₄	45.8	191	0.2	18	0.394	1.95
C ₂ H ₄	50.9	283	0.3	27	0.535	1.32
N ₂	33.5	126	0.5	45	1.340	2.95
Comp.	z	$(z)(y)$				
CH ₄	0.99	0.198				
C ₂ H ₄	0.93	0.279				
N ₂	1.00	0.500				
			$z_{\text{mean}} = 0.977$			

Then

$$V = \frac{z_{\text{mean}} RT}{p} = \frac{(0.977)(82.06)(373)}{90}$$

$$= 332 \text{ cm}^3 \text{ at 90 atm and } 373^{\circ}\text{K}$$

(e) Combining Amagat's law and the z factor,

Comp.	$p_c(\text{atm})$	$T_c(^{\circ}\text{K})$	y	$p_r = \frac{90}{p_c}$	$T_r = \frac{373}{T_c}$
CH ₄	45.8	191	0.2	1.97	1.95
C ₂ H ₄	50.9	283	0.3	1.78	1.32
N ₂	33.5	126	0.5	2.68	2.95
Comp.	z	$(z)(y)$			
CH ₄	0.97	0.194			
C ₂ H ₄	0.75	0.225			
N ₂	1.01	0.505			
z_{mean}	=	0.924			

$$V = \frac{0.924(82.06)(373)}{90} = 313 \text{ cm}^3 \text{ at 90 atm and } 373^{\circ}\text{K}$$

(f) According to Kay's method, we first calculate the pseudocritical values for the mixture by Eqs. (3.35) and (3.36).

$$\begin{aligned} & \text{CH}_4 \quad \text{C}_2\text{H}_4 \quad \text{N}_2 \\ p'_c &= p_{c_A}y_A + p_{c_B}y_B + p_{c_C}y_C = (45.8)(0.2) + (50.9)(0.3) + (33.5)(0.5) \\ &= 41.2 \text{ atm} \\ T'_c &= T_{c_A}y_A + T_{c_B}y_B + T_{c_C}y_C = (191)(0.2) + (283)(0.3) + (126)(0.5) \\ &= 186^{\circ}\text{K} \end{aligned}$$

Then we calculate the pseudoreduced values for the mixture by Eqs. (3.37) and (3.38):

$$p'_r = \frac{p}{p'_c} = \frac{90}{41.2} = 2.18, \quad T'_r = \frac{T}{T'_c} = \frac{373}{186} = 2.00$$

With the aid of these two parameters we can find from Fig. 3.8 that $z = 0.965$. Thus

$$V = \frac{zRT}{p} = \frac{(0.965)(82.06)(373)}{90} = 328 \text{ cm}^3 \text{ at 90 atm and } 373^{\circ}\text{K}$$

EXAMPLE 3.17 Use of pseudoreduced ideal molal volume

In instances where the temperature or pressure of a gas mixture is unknown, it is convenient, in order to avoid a trial-and-error solution using the generalized compressibility charts, to compute a pseudocritical ideal volume and a pseudoreduced ideal volume as illustrated below. Suppose we have given that the molal volume of the gas mixture in the previous problem was 326 cm³ at 90.0 atm. What was the temperature?

*Solution:*Basis: 326 cm³ gas at 90.0 atm and $T^{\circ}\text{K}$

Comp.	$T_c(^{\circ}\text{K})$	$p_c(\text{atm})$	y	yT_c	yp_c
CH ₄	190.7	45.8	0.20	38.14	9.16
C ₂ H ₄	283.1	50.9	0.30	84.93	15.27
N ₂	126.2	33.5	0.50	63.10	16.75
				<u>186.2</u>	<u>41.2</u>

Note we have used mole fractions as weighting factors to find an average $T'_c = 186.2$ and $p'_c = 41.2$ as in the previous example. Next we compute V'_{ci} :

$$\hat{V}'_{ci} = \frac{RT'_c}{p'_c} = \frac{(82.06)(186.2)}{41.2} = 371.0 \text{ cm}^3/\text{g mole}$$

$$V'_{ci} = \frac{\hat{V}}{\hat{V}'_{ci}} = \frac{326}{371} = 0.879$$

$$p'_r = \frac{p}{p'_c} = \frac{90.0}{41.2} = 2.19$$

From Fig. 3.8 or Fig. 3.10, $T'_r = 1.98$. Then

$$T = T'_c T'_r = (186.2)(1.98) = 369^\circ\text{K}$$

373°K

critical values for the

 N_2
— (33.5)(0.5)

+ (1 —)

—qs. (3.37) and (3.38):

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3.3 Vapor pressure

The terms *vapor* and *gas* are used very loosely. A gas which exists below its critical temperature is usually called a vapor because it can condense. If you continually compress a pure gas at constant temperature, provided that the temperature is below the critical temperature, some pressure is eventually reached at which the gas starts to condense into a liquid. Further compression does not increase the pressure but merely increases the fraction of gas that condenses. A reversal of the procedure just described will cause the liquid to be transformed into the gaseous state again. From now on, the word *vapor* will be reserved to describe a gas below its critical point in a process in which the phase change is of primary interest, while the word *gas* or *noncondensable gas* will be used to describe a gas above the critical point or a gas in a process in which it cannot condense.

Vaporization and condensation at constant temperature and pressure are *equilibrium* processes, and the equilibrium pressure is called the *vapor pressure*. At a given temperature there is only one pressure at which the liquid and vapor phases of a pure substance may exist in equilibrium. Either phase alone may exist, of course, over a wide range of conditions. By *equilibrium* we mean a state in which there is no tendency toward spontaneous change. Another way to say the same thing is to say equilibrium is a state in which all the rates of attaining and departing from the state are balanced.

You can visualize vapor pressure, vaporization, and condensation more easily with the aid of Fig. 3.12. Figure 3.12 is an expanded *p-T* diagram for pure water. For each temperature you can read the corresponding pressure at which water vapor and water liquid exist in equilibrium. You have encountered this condition of equilibrium many times—for example, in boiling. Any substance has an infinite number of boiling points, but by custom we say the “normal” boiling point is the temperature at which boiling takes place under a pressure of 1 atm (760 mm Hg). Unless another pressure is specified, 1 atm is assumed,

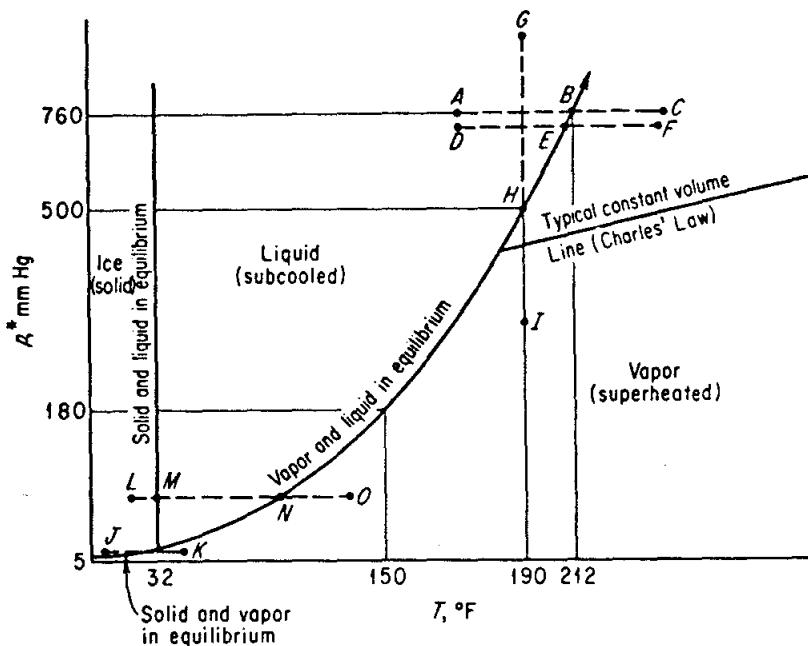


Fig. 3.12. Vapor pressure curve for water.

and the term *boiling point* is taken to mean the "normal boiling point." The normal boiling point for water occurs when the vapor pressure of the water equals the pressure of the atmosphere on top of the water. A piston with a force of 14.7 psia could just as well take the place of the atmosphere, as shown in Fig. 3.13. For example, you know that at 212°F water will boil (vaporize) and the pressure

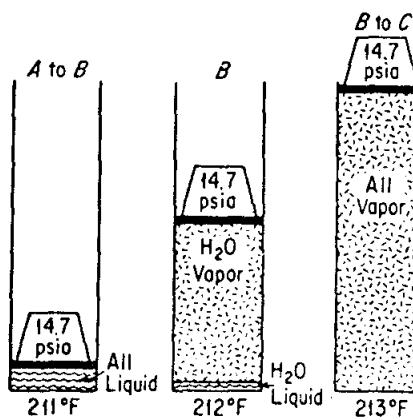


Fig. 3.13. Transformation of liquid water into water vapor at constant pressure.

will be 760 mm Hg at 212°F. Noticeable evaporation of liquid in it had already begun at 211°F.

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will be 760 mm Hg, or 1 atm (point *B*). Suppose that you heat water starting at 170°F (point *A*) in an open pan—what happens? We assume that the water vapor above the pan is at all times in equilibrium with the liquid water. This is a constant-pressure process since the air around the water in the pan acts similarly to a piston in a cylinder to keep the pressure at atmospheric pressure. As the temperature rises and the confining pressure stays constant, nothing particularly noticeable occurs until 212°F is reached, at which time the water begins to boil, i.e., evaporate. It pushes back the atmosphere and will completely change from liquid into vapor. If you heated the water in an enclosed cylinder, and if after it had all evaporated at point *B* you continued heating the water vapor formed at constant pressure, you could apply the gas laws in the region *B-C* (and at higher temperatures). A reversal of this process would cause the vapor to condense at *B* to form a liquid. The temperature at point *B* would in these circumstances represent the *dew point*.

Suppose that you went to the top of Pikes Peak and repeated the experiment—what would happen then? Everything would be the same (points *D-E-F*) with the exception of the temperature at which the water would begin to boil, or condense. Since the pressure of the atmosphere at the top of Pikes Peak would presumably be lower than 760 mm Hg, the water would start to displace the air, or boil, at a lower temperature. However, water still would exert a vapor pressure of 760 mm Hg at 212°F. You can see that (a) at any given temperature water exerts its vapor pressure (at equilibrium); (b) as the temperature goes up, the vapor pressure goes up; and (c) it makes no difference whether water vaporizes into air, into a cylinder closed by a piston, or into an evacuated cylinder—at any temperature it still exerts the same vapor pressure as long as the water is in equilibrium with its vapor.

A process of vaporization or condensation at constant temperature is illustrated by the lines *G-H-I* or *I-H-G*, respectively, in Fig. 3.12. Water would vaporize or condense at constant temperature as the pressure reached point *H* on the vapor-pressure curve (also look at Fig. 3.14.)

The *p-T* conditions at which ice (in its common form) and water vapor are in equilibrium are also seen in Fig. 3.12. When the solid passes directly into the vapor phase without first becoming a liquid (line *J-K* as opposed to line *L-M-N-O*), it is said to *sublime*. Iodine crystals do this at room temperature; water sublimes only below 32°F, as when the frost disappears in the winter when the thermometer reads 20°F.

The vapor-pressure line indicates the separation of both solid and liquid regions from the vapor region and extends well past the conditions shown in Fig. 3.12 all the way to the critical temperature and pressure (not shown). Above the critical temperature, water can exist only as a gas. A term commonly applied to the vapor-liquid portion of the vapor-pressure curve is the word *saturated*. It means the same thing as vapor and liquid in equilibrium with each other. If a gas is just ready to start to condense its first drop of liquid, the gas is called a saturated gas; if a liquid is just about to vaporize, it is called a saturated liquid.

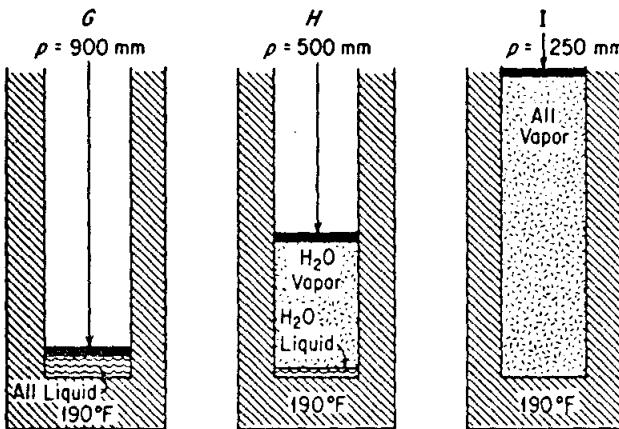


Fig. 3.14. Transformation of liquid water into water vapor at constant temperature.

These two conditions are also known as the *dew point* and *bubble point*, respectively.

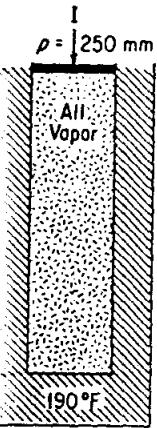
If you have a mixture of liquid and vapor at equilibrium (called a *wet gas*), both the liquid and vapor are said to be saturated at the specified conditions. The vapor-pressure line in Fig. 3.12 thus represents the state of a pure component designated by a number of special terms depending on what aspect of the state is of primary importance:

- The saturated liquid.
- The saturated vapor.
- The bubble point.
- The dew point.

The region to the right of the vapor-pressure curve in Fig. 3.12 is called the *superheated* region and the one to the left of the vapor-pressure curve is called the *subcooled* region. The temperatures in the superheated region, if measured as the difference ($O - N$) between the actual temperature of the superheated vapor and the saturation temperature for the same pressure, are called *degrees of superheat*. For example, steam at 500°F and 100 psia (the saturation temperature for 100 psia is 327.8°F) has $(500 - 327.8) = 172.2^{\circ}\text{F}$ of superheat. Another new term you will find used frequently is the word *quality*. A "wet" vapor consists of saturated vapor and saturated liquid in equilibrium. The weight fraction of vapor is known as the quality.

EXAMPLE 3.18 Properties of wet vapors

The properties of a mixture of vapor and liquid in equilibrium (for a single component) can be computed from the individual properties of the saturated vapor



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Fig. 3.12 is called the pressure curve is called d region, if measured as f the superheated vapor called degrees of superheat. Another new "wet" vapor consists The weight fraction of

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and saturated liquid. The steam tables (Appendix C) are a good source of data to illustrate such computations. At 400°F and 247.3 psia the specific volume of a wet steam mixture is 1.05 ft³/lb. What is the quality of the steam?

Solution:

From the steam tables the specific volumes of the saturated vapor and liquid are

$$\hat{V}_l = 0.0186 \text{ ft}^3/\text{lb}, \quad \hat{V}_v = 1.8633 \text{ ft}^3/\text{lb}$$

Basis: 1 lb wet steam mixture

Let x = weight fraction vapor.

$$\frac{0.0186 \text{ ft}^3}{1 \text{ lb liquid}} \left| (1-x) \text{ lb liquid} \right. + \frac{1.8633 \text{ ft}^3}{1 \text{ lb vapor}} \left| x \text{ lb vapor} \right. = 1.05 \text{ ft}^3$$

$$0.0186 - 0.0186x + 1.8633x = 1.05$$

$$1.845x = 1.03$$

$$x = 0.56$$

Other properties of wet mixtures can be treated in the same manner.

3.3.1 Change of Vapor Pressure with Temperature. A large number of experiments on many substances have shown that a plot of the vapor pressure (p^*) of a compound against temperature does not yield a straight line but a curve, as you saw in Fig. 3.12. Many types of correlations have been proposed to transform this curve to a linear form ($y = mx + b$); a plot of $\log(p^*)$ vs. $(1/T)$, for moderate temperature intervals, is reasonably linear:

$$\underbrace{\log(p^*)}_{y} = \underbrace{m\left(\frac{1}{T}\right) + b}_{mx + b} \quad (3.39)$$

Equation (3.39) is derived from the Clausius-Clapeyron equation (see Chap. 4). Empirical correlations of vapor pressure are frequently given in the following form (refer to Appendix G for values of the constants):

$$\log(p^*) = -\frac{A}{t + C} + B \quad (3.40)$$

where A, B, C = constants different for each substance

t = temperature in °C

Over wide temperature intervals the experimental data are not exactly linear as indicated by Eq. (3.39), but have a slight tendency to curve. This curvature can be straightened out by using a special plot known as a Cox chart.¹³ The log of the vapor pressure of a compound is plotted against a special non-linear temperature scale constructed from the vapor-pressure data for water (called a *reference substance*).

¹³E. R. Cox, *Ind. Eng. Chem.*, v. 15, p. 592 (1923).

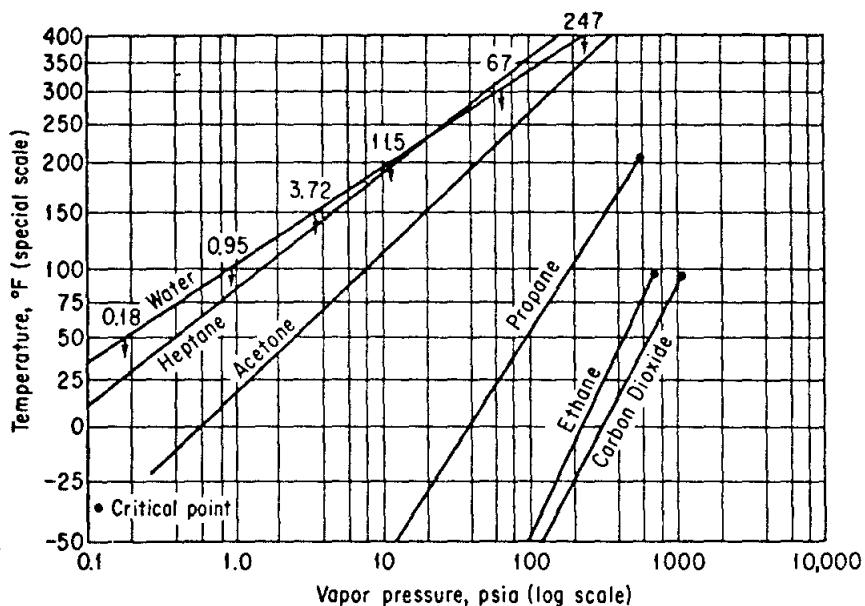


Fig. 3.15. Cox chart.

As illustrated in Fig. 3.15, the temperature scale is established by recording the temperature at a given vapor pressure of water for a number of vapor pressures. The numbers on the line for water indicate the vapor pressures of water for selected values (50, 100, 150, etc.) of temperature. The vapor pressures of other substances plotted on this same graph will yield straight lines over extensive temperature ranges and thus facilitate the extrapolation and interpolation of vapor-pressure data. It has been found that lines so constructed for closely related compounds, such as hydrocarbons, all meet at a common point. Since straight lines can be obtained on a Cox chart only two sets of vapor-pressure data are needed to provide complete information about the vapor pressure of a substance over a considerable temperature range. We shall discuss in Chap. 4 under the topic of the Clausius-Clapeyron equation other information that can be obtained from vapor-pressure plots.

3.3.2 Change of Vapor Pressure with Pressure. The equation for the change of vapor pressure with total pressure at constant temperature in a system is

$$\left(\frac{\partial(p^*)}{\partial p_T} \right)_T = \frac{\hat{V}_l}{\hat{V}_s} \quad (3.41)$$

where \hat{V} = molal volume of saturated liquid or gas

p_T = total pressure on the system

Under normal conditions the effect is negligible.

EXAMPLE 3.19 Extrapolation of vapor-pressure data

The control of existing solvents is described in the Federal Register, v. 36, no. 158, dated August 14, 1971, under Title 42, Chapter 4, Appendix B, Section 4.0, Control of Organic Compound Emissions. Section 4.6 indicates that reductions of at least 85 percent can be accomplished by (a) incineration or (b) carbon adsorption.

Chlorinated solvents and many other solvents used in industrial finishing and processing, dry-cleaning plants, metal degreasing, printing operations, and so forth, can be recycled and reused by the introduction of carbon adsorption equipment. To predict the size of the adsorber, you first need to know the vapor pressure of the compound being adsorbed at the process conditions.

The vapor pressure of chlorobenzene is 400 mm Hg at 110.0°C and 5 atm at 205°C. Estimate the vapor pressure at 245°C and at the critical point (359°C).

Solution:

The vapor pressures will be estimated by use of a Cox chart. See Fig. E3.19. The temperature scale is constructed by using the following data from the steam tables:

$p^* \text{ H}_2\text{O (psia)}$	$t (\text{°F})$
0.95	100
3.72	150
11.5	200
29.8	250
67.0	300
247	400
680	500
1543	600
3094	700

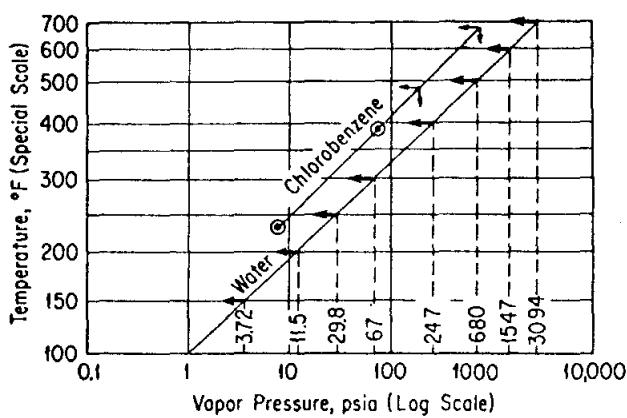


Fig. E3.19.

The vapor pressures from 1 to 3100 psia are marked on the horizontal logarithmic scale. Next, draw a line representing the vapor pressure of water at any suitable angle on the graph so as to stretch the desired temperature range from the bottom to the top of the vertical axis. For each vapor pressure, the temperature is marked and a hori-

(3.41)

horizontal line drawn to the ordinate. This establishes the temperature scale (which looks almost logarithmic in nature).

Now convert the two vapor pressures of chlorobenzene into psia,

$$\begin{array}{c|cc} 400 \text{ mm} & 14.7 \text{ psia} \\ \hline 760 \text{ mm} & 7.74 \text{ psia} \end{array} \quad \begin{array}{l} 110^\circ\text{C} = 230^\circ\text{F} \\ \\ \begin{array}{c|cc} 5 \text{ atm} & 14.7 \text{ psia} \\ \hline 1 \text{ atm} & 73.5 \text{ psia} \end{array} \quad \begin{array}{l} 205^\circ\text{C} = 401^\circ\text{F} \end{array} \end{array}$$

and plot these two points on the graph paper. Next draw a straight line between them, and extrapolate to 471°F (245°C) and 678°F (359°C). At these two temperatures read off the estimated vapor pressures:

	471°F (245°C)	678°F (359°C)
Estimated	150 psia	700 psia
Experimental	147 psia	666 psia

Experimental values given for comparison.

An alternative way to extrapolate vapor pressure data would be to use the Othmer¹⁴ plot as explained in Sec. 4.4.

3.3.3 Estimating Vapor Pressures. Miller¹⁵ recommends the following equation to estimate vapor pressures based on the normal boiling-point temperature (T_b) and the critical temperature and pressure:

$$\log p_r = -\frac{G}{T_c}[1 - T_r^2 + k(3 + T_r)(1 - T_r)^3]$$

where

$$G = 0.210 + 0.200a$$

$$a = \frac{T_{rb} \text{ lb } p_c}{1 - T_{rb}}$$

$$k = \frac{(a/2.306 G) - (1 + T_{rb})}{(3 + T_{rb})(1 - T_{rb})^2}$$

$$T_{rb} = \frac{T_b}{T_c}$$

Other methods of estimating vapor pressures are given by McGowan.¹⁶

3.3.4 Liquid Properties. Considerable experimental data are available for liquid densities of pure compounds as a function of temperature and pressure. Gold¹⁷ reviews 13 methods of estimating liquid densities and provides recommendations for different classes of compounds if you cannot locate experimental data. As to liquid mixtures, it is even more difficult to predict the p - V - T

¹⁴D. F. Othmer and E. S. Yu, *Indus. Engr. Chem.*, v. 60, p. 20 (1968).

¹⁵D. G. Miller, *J. Phys. Chem.*, v. 69, p. 3209 (1965).

¹⁶J. C. McGowan, *Rec. Trav. Chim.*, v. 84, p. 99 (1965).

¹⁷P. I. Gold, *Chem. Engr.*, p. 170 (Nov. 18, 1968).

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into psia,

0°F

1°F

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59°C)

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predict the p - V - T

properties of liquid mixtures than of real gas mixtures. Probably more experimental data (especially at low temperatures) are available than for gases, but less is known about the estimation of the p - V - T properties of liquid mixtures. Corresponding state methods are usually used, but with less assurance than for gas mixtures.

3.4 Saturation

How can you predict the properties of a mixture of a pure vapor (which can condense) and a noncondensable gas? A mixture containing a vapor behaves somewhat differently than does a pure component by itself. A typical example with which you are quite familiar is that of water vapor in air.

Water vapor is a gas, and like all gases its molecules are free to migrate in any direction. They will do so as long as they are not stopped by the walls of a container. Furthermore, the molecules will distribute themselves evenly throughout the entire volume of the container.

When any pure gas (or a gaseous mixture) comes in contact with a liquid, the gas will acquire vapor from the liquid. If contact is maintained for a considerable length of time, equilibrium is attained, at which time the *partial pressure of the vapor* (vaporized liquid) *will equal the vapor pressure* of the liquid at the temperature of the system. Regardless of the duration of contact between the liquid and gas, after equilibrium is reached no more net liquid will vaporize into the gas phase. The gas is then said to be *saturated* with the particular vapor at the given temperature. We can also say that the gas mixture is at its dew point.

As an illustration, assume that you put dry air at 147°F into a container in which liquid water is present. The initial total pressure on the air and water is to be 760 mm Hg. If you keep the total pressure on the container constant at 760 mm Hg (Figs. 3.16 and 3.17), eventually the water will vaporize, and water vapor will enter and mix with the air until the partial pressure of the water in

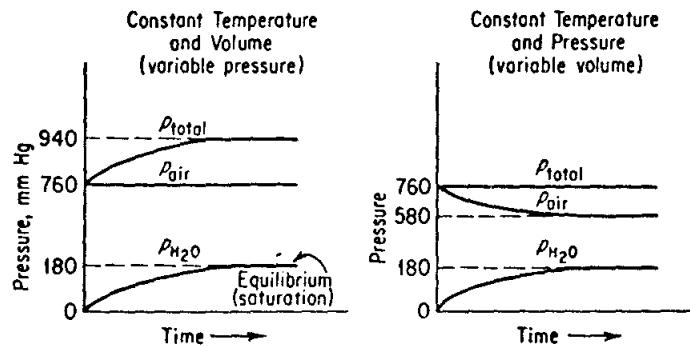


Fig. 3.16. Change of partial and total pressures on vaporization of water into air at constant temperature.

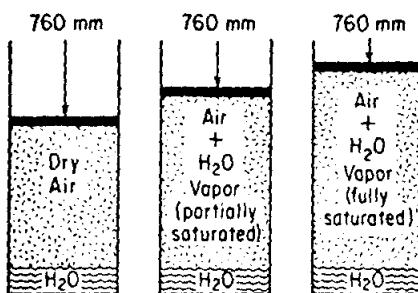


Fig. 3.17. Evaporation of water at constant pressure and temperature.

the air reaches approximately 180 mm Hg (the vapor pressure of water at 147°F). Regardless of the duration of contact between the water and the air (after this partial pressure of water vapor is reached), no more water vapor can enter the air. The air is saturated with respect to water vapor and cannot contain additional water. Of course the volume of the system will change if the total pressure is maintained at 760 mm Hg, or else some air will have to leave the system if the volume and pressure are to stay constant. If the volume of the system is fixed, the total pressure will rise to $760 + 180 = 940$ mm Hg.

Assuming that the ideal gas laws apply to both air and water vapor, as they do with excellent precision, you can calculate the partial pressure of the air as follows *at saturation*:

$$p_{\text{air}} + p_{\text{H}_2\text{O}} = p_{\text{total}}, \quad p_{\text{air}} + 180 \text{ mm} = 760 \text{ mm}$$

$$p_{\text{air}} = 760 - 180 = 580 \text{ mm Hg}$$

From Eq. (3.4), we know that

$$\frac{p_{\text{air}}}{p_{\text{H}_2\text{O}}} = \frac{n_{\text{air}}}{n_{\text{H}_2\text{O}}} \quad \text{at constant temperature}$$

or, from Eq. (3.7),

$$\frac{V_{\text{air}}}{V_{\text{H}_2\text{O}}} = \frac{n_{\text{air}}}{n_{\text{H}_2\text{O}}} \quad \text{at constant temperature}$$

Then

$$\frac{p_{\text{air}}}{p_{\text{H}_2\text{O}}} = \frac{p_{\text{air}}}{p_{\text{total}} - p_{\text{air}}} = \frac{V_{\text{air}}}{V_{\text{total}} - V_{\text{air}}} \quad (3.42)$$

We can generalize these expressions for any two components as follows:

$$\frac{p_1}{p_2} = \frac{p_1}{p_t - p_1} = \frac{n_1}{n_2} = \frac{V_1}{V_t - V_1} = \frac{V_1}{V_2} \quad (3.43)$$

and

$$p_1 = \frac{V_1}{V_2} p_2 \quad \text{or} \quad V_1 = \frac{p_1}{p_2} V_2 \quad (3.44)$$

where the subscripts indicate component 1, component 2, and total.

If the air initially contains no water vapor, graphically

Fig. 3.17

EXAMPLE 3.3

What is the partial pressure of air at 738 mm Hg if the total pressure is to be maintained at 738 mm Hg by adding water vapor to a way that the

Solution

See Fig. 3.17

atc

The most
saturated w-

If the temperature rises in an air-water mixture and the vapor phase is initially saturated with water vapor, the change in the partial pressure of the water and the air and in the total pressure, as a function of temperature, can be graphically shown as in Fig. 3.18.

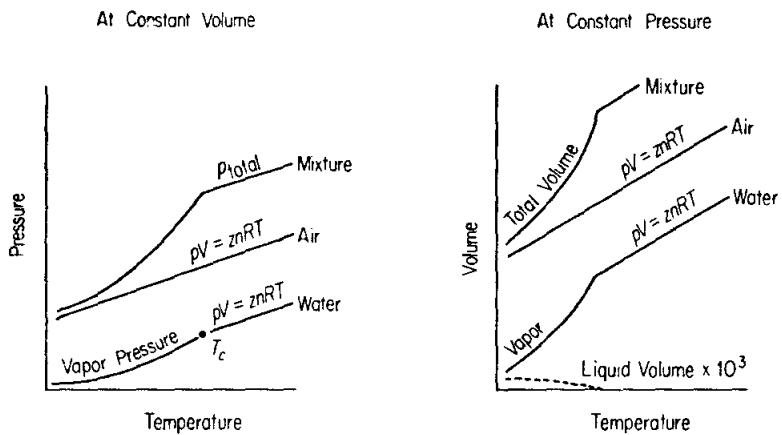


Fig. 3.18. The change of total pressure (volume) and partial pressures (volumes) of air and water in a saturated mixture with increasing temperature.

EXAMPLE 3.20 Saturation

What is the minimum number of cubic feet of dry air at 20°C and 738 mm Hg that are necessary to evaporate 13.1 lb of alcohol if the total pressure remains constant at 738 mm Hg? Assume that the air is blown over the alcohol to evaporate it in such a way that the exit pressure of the air-alcohol mixture is at 738 mm Hg.

Solution:

See Fig. E3.20. Assume that the process is isothermal. The additional data needed are

$$p_{\text{alcohol}}^* \text{ at } 20^\circ\text{C} (68^\circ\text{F}) = 44.5 \text{ mm Hg}$$

(3.42)

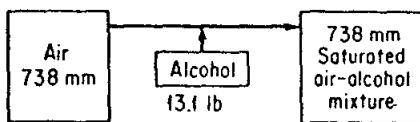


Fig. E3.20.

(3.44)

The most alcohol the air can pick up is a saturated mixture; any condition less than saturated would require more air.

Basis: 13.1 lb alcohol

The ratio of moles of alcohol to moles of air in the final gaseous mixture is the same as the ratio of the partial pressures of these two substances. Since we know the moles of alcohol, we can find the number of moles of air:

$$\frac{P_{\text{alcohol}}}{P_{\text{air}}} = \frac{n_{\text{alcohol}}}{n_{\text{air}}}$$

From Dalton's law,

$$P_{\text{air}} = P_{\text{total}} - P_{\text{alcohol}}$$

$$P_{\text{alcohol}} = 44.5 \text{ mm}$$

$$P_{\text{air}} = (738 - 44.5) \text{ mm}$$

13.1 lb alcohol		1 lb mole alcohol		(738 - 44.5) lb moles air
		46 lb alcohol		44.5 lb moles alcohol
359 ft ³		293°K		760 mm

$\frac{1 \text{ lb mole}}{1 \text{ lb mole}} \frac{293^{\circ}\text{K}}{273^{\circ}\text{K}} \frac{760 \text{ mm}}{738 \text{ mm}} = 1800 \text{ ft}^3 \text{ air}$
at 20°C and 738 mm Hg

EXAMPLE 3.21 Saturation

If 1250 cm³ of wet H₂ are saturated with water at 30°C and 742 mm Hg, what is the volume of dry gas at standard conditions? The vapor pressure water at 30°C is 32 mm Hg.

Solution:

(a) *Long Solution:*

Your first impulse in selecting a basis is probably to ask yourself the question, What do I have or what do I want? The answer might be that you have 1250 cm³ of saturated H₂ at 30°C and 742 mm Hg. See Fig. E3.21.

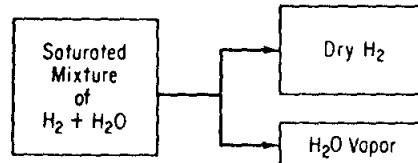


Fig. E3.21.

Basis: 1250 cm³ H₂ saturated with water at 30°C and 742 mm Hg

1250 cm ³ wet gas		(742 - 32) cm ³ dry H ₂		273°K		742 mm
		742 cm ³ wet gas		303°K		760 mm

= 1051 cm³ dry H₂ at S.C.

seous mixture is the
Since we know the

(b) *Shorter Solution:*
You can save a little time by recalling that

$$\begin{aligned}P_{\text{total}} &= P_{\text{H}_2\text{O}} + P_{\text{H}_2} \\742 &= 32 + 710\end{aligned}$$

In the given gas mixture you have *any* of the following:

- (a) 1250 cm³ wet H₂ at 30°C and 742 mm Hg.
- (b) 1250 cm³ dry H₂ at 30°C and 710 mm Hg.
- (c) 1250 cm³ water vapor at 30°C and 32 mm Hg.

Therefore, since the problem asks for the volume of dry H₂, you could take as a basis the dry H₂, and then apply the ideal gas laws to the dry H₂.

Basis: 1250 cm³ dry H₂ at 30°C and 710 mm Hg

$$\frac{1250 \text{ cm}^3 \text{ dry H}_2}{303^\circ\text{K}} \left| \frac{273^\circ\text{K}}{760 \text{ mm}} \right| \frac{710 \text{ mm}}{= 1051 \text{ cm}^3 \text{ dry H}_2 \text{ at S.C.}}$$

You can see that by choosing the second basis you can eliminate one step in the solution.

42 min⁻¹ g, what is
re v 30°C is

EXAMPLE 3.22 Saturation

A telescopic gas holder contains 10,000 ft³ of saturated gas at 80°F and a pressure of 6.0 in. H₂O above atmospheric. The barometer reads 28.46 in. Hg. Calculate the weight of water vapor in the gas.

Solution:

The total pressure of the saturated gas must be calculated first in in. Hg. See Fig. E3.22.

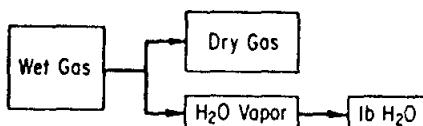


Fig. E3.22.

$$\frac{6.0 \text{ in. H}_2\text{O}}{12 \text{ in.}} \left| \frac{1 \text{ ft}}{33.91 \text{ ft H}_2\text{O}} \right| \frac{29.92 \text{ in. Hg}}{= 0.44 \text{ in. Hg}}$$

$$\text{barometer} = 28.46 \text{ in. Hg}$$

$$P_{\text{total}} = 28.90 \text{ in. Hg}$$

$$P_w = \text{vapor pressure of H}_2\text{O at } 80^\circ\text{F} = 1.03 \text{ in. Hg}$$

$$P_t = P_a + P_w$$

$$28.90 = 27.87 + 1.03$$

mm Hg

dry H₂ at S.C.

There exists

10,000 ft ³ wet gas	at 28.90 in. Hg and 80°F
10,000 ft ³ dry gas	at 27.87 in. Hg and 80°F
10,000 ft ³ water vapor	at 1.03 in. Hg and 80°F

$$^{\circ}\text{R} = 80 + 460 = 540^{\circ}\text{R}$$

From the volume of water vapor present at known conditions, you can calculate the volume at S.C. and hence the pound moles and pounds of water.

Basis: 10,000 ft³ water vapor at 1.03 in. Hg and 80°F

10,000 ft ³ H ₂ O vapor	492°R	1.03 in. Hg	1 lb mole	18 lb H ₂ O
	540°R	29.92 in. Hg	359 ft ³	1 lb mole H ₂ O
				= 15.7 lb H ₂ O

EXAMPLE 3.23 Smokestack emission and pollution

A local pollution-solutions group has reported the Simtron Co. boiler plant as being an air polluter and has provided as proof photographs of heavy smokestack emissions on 20 different days in January and February. As the chief engineer for the Simtron Co., you know that your plant is not a source of pollution because you burn natural gas (essentially methane) and your boiler plant is operating correctly. Your boss believes the pollution-solutions group has made an error in identifying the stack—it must belong to the company next door that burns coal. Is he correct? Is the pollution-solutions group correct? See Fig. E3.23.

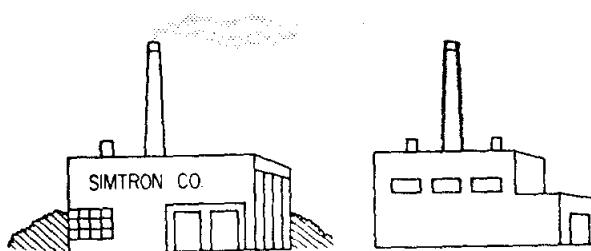


Fig. E3.23.

Solution:

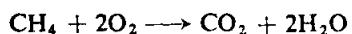
Methane (CH₄) contains 2 lb moles of H₂ per pound mole of C, while coal (see Example 4.24) contains 71 lb of C per 5.6 lb of H₂ in 100 lb of coal. The coal analysis is equivalent to

$$\frac{71 \text{ lb C}}{12 \text{ lb C}} \mid \frac{1 \text{ lb mole C}}{1 \text{ lb mole C}} = 5.9 \text{ lb moles C} \quad \frac{5.6 \text{ lb H}_2}{2.02 \text{ lb H}_2} \mid \frac{1 \text{ lb mole H}_2}{1 \text{ lb mole H}_2} = 2.8 \text{ lb mole H}_2$$

or a ratio of 2.8/5.9 = 0.47 lb mole H₂/lb mole C. Suppose that each fuel burns with 40 percent excess air and that combustion is complete. We can compute the mole fraction of water vapor in each stack gas.

Basis: 1 lb mole C

Natural gas



fuel comp.	lb moles	composition of combustion gases, lb moles			
		CO ₂	excess O ₂	N ₂	H ₂ O
C	1.0	1.0			
H ₂	2.0				2.0
Air		1.0	0.80	10.5	2.0
			0.80	10.5	2.0

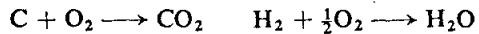
$$\text{Excess O}_2: 2(0.40) = 0.80$$

$$\text{N}_2: (2)(1.40)(79/21) = 10.5$$

The total pound moles of gas produced are 14.3 and the mole fraction H₂O is

$$\frac{2.0}{14.3} \approx 0.14$$

Coal



fuel comp.	lb moles	composition of gas produced, lb moles			
		CO ₂	excess O ₂	N ₂	H ₂ O
C	1	1			
H ₂	0.47				0.47
Air		1	0.49	6.5	0.47
			0.49	6.5	0.47

$$\text{Excess O}_2: \frac{\text{C}}{1(0.40)} = 0.40 \quad \frac{\text{H}_2}{(0.47)(1/2)(0.40)} = 0.094$$

$$\text{N}_2: 1.40(79/21)(1 + 0.47(1/2)) = 6.5$$

The total pound moles of gas produced are 8.46 and the mole fraction H₂O is

$$\frac{0.47}{8.46} \approx 0.056$$

If the barometric pressure is 14.7 psia, then the stack gas becomes saturated at

	natural gas	coal
Pressure	14.7(0.14) = 2.06 psia	14.7(0.056) = 0.083 psia
Equivalent temperature:	127°F	96°F

By mixing the stack gas with air, the mole fraction water vapor is reduced, and hence the condensation temperature is reduced. However, for equivalent dilution, the coal-burning plant will always have a lower condensation temperature. Thus, on cold winter days, the condensation of water vapor will occur more often and to a greater extent from power plants firing natural gas than from those using other fuels.

The public, unfortunately, sometimes concludes that all the emissions they perceive are pollution. Natural gas could appear to the public to be a greater pollutant than either oil or coal when, in fact, the emissions are just water vapor. The sulfur content of coal and oil can be released as sulfur dioxide to the atmosphere, and the polluting capacities of coal and oil are much greater than natural gas when all three are being

burned properly. The sulfur contents as delivered to the consumers are as follows: natural gas, 4×10^{-4} percent (as added mercaptans); number 6 fuel oil, up to 2 percent; and coal, from 0.5 to 5 percent.

What additional steps would you take to resolve the questions that were originally posed?

3.5 Partial saturation and humidity

In the foregoing section we dealt with mixtures of gas and vapor in which the gas was saturated with the vapor. More often, the contact time required between the gas and liquid for equilibrium (or saturation) to be attained is too long, and the gas is not completely saturated with the vapor. Then the vapor is not in equilibrium with a liquid phase, and the partial pressure of the vapor is less than the vapor pressure of the liquid at the given temperature. This condition is called *partial saturation*. What we have is simply a mixture of two or more gases which obey the real gas laws. What distinguishes this case from the previous examples for gas mixtures is that under suitable conditions it is possible to condense part of one of the gaseous components. In Fig. 3.19 you can see how the partial

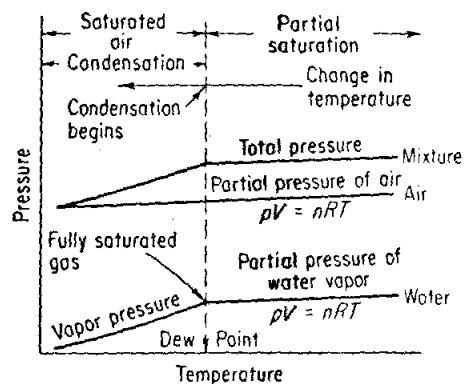


Fig. 3.19. Transformation of a partially saturated water vapor-air mixture into a saturated mixture as the temperature is lowered (volume = constant).

pressure of the water vapor in a gaseous mixture at constant volume obeys the ideal gas laws as the temperature drops until saturation is reached, at which time the water vapor starts to condense. Until these conditions are achieved, you can confidently apply the gas laws to the mixture.

Several ways exist to express the concentration of a vapor in a gas mixture. You sometimes encounter weight or mole fraction (or percent), but more frequently one of the following:

- Relative saturation (relative humidity); Sec. 3.5.1.
- Molal saturation (molal humidity); Sec. 3.5.2.

consumers are as follows:
over 6 fuel oil, up to 2.6
ections that were originally

vapor in which the gas time required between attained is too long, and when the vapor is not in of the vapor is less than This condition is called two or more gases which the previous examples possible to condense part can see how the partial

- (c) "Absolute" saturation ("absolute" humidity) or percent saturation (percent humidity); Secs. 3.5.3 and 5.3.
- (d) Humidity; Sec. 3.5.2 and 5.3.

When the vapor is water vapor and the gas is air, the special term *humidity* applies. For other gases or vapors, the term *saturation* is used.

3.5.1 Relative Saturation.

Relative saturation is defined as

$$\text{RS} = \frac{p_{\text{vapor}}}{p_{\text{satd}}} = \text{relative saturation} \quad (3.45)$$

where p_{vapor} = partial pressure of the vapor in the gas mixture

p_{satd} = partial pressure of the vapor in the gas mixture if the gas were saturated at the given temperature of the mixture, i.e., the vapor pressure of the vapor

Then, for brevity, if the subscript 1 denotes vapor,

$$\text{RS} = \frac{p_1}{p_1^*} = \frac{p_1/p_t}{p_1^*/p_t} = \frac{V_1/V_t}{V_{\text{satd}}/V_t} = \frac{n_1}{n_{\text{satd}}} = \frac{\text{lb}_1}{\text{lb}_{\text{satd}}} \quad (3.46)$$

You can see that relative saturation, in effect, represents the fractional approach to total saturation, as shown in Fig. 3.20. If you listen to the radio or TV and

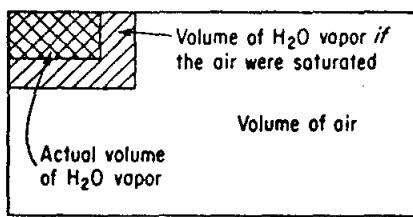


Fig. 3.20. A gas partially saturated with water vapor.

hear the announcer say that the temperature is 70°F and the *relative humidity* is 60 percent, he means that

$$\frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2\text{O}}^*}(100) = \% \text{ RH} \quad (3.47)$$

with both the $p_{\text{H}_2\text{O}}$ and the $p_{\text{H}_2\text{O}}^*$ being measured at 70°F. Zero percent relative saturation means no vapor in the gas; 100 percent relative saturation means that the partial pressure of the vapor is the same as the vapor pressure of the substance that is the vapor.

EXAMPLE 3.24 Relative humidity

The weather man on the radio this morning reported that the temperature this afternoon would reach 94°F, the relative humidity would be 43 percent, the barometer

29.67 in. Hg, partly cloudy to clear, with the wind from SSE at 8 mi/hr. How many pounds of water vapor would be in 1 mi³ of afternoon air? What would be the dew point of this air?

Solution:

The vapor pressure of water at 94°F is 1.61 in. Hg. We can calculate the partial pressure of the water vapor in the air from the given percent relative humidity; from this point forward, the problem is the same as the examples in the previous section.

$$p_w = (1.61 \text{ in. Hg})(0.43) = 0.69 \text{ in. Hg}$$

$$p_{\text{air}} = p_t - p_w = 29.67 - 0.69 = 28.98 \text{ in. Hg}$$

Basis: 1 mi³ water vapor at 94°F and 0.69 in. Hg

$$\frac{1 \text{ mi}^3}{1 \text{ mi}} \left| \frac{\left(5280 \text{ ft}^3\right)^3}{554^\circ \text{R}} \right| \frac{492^\circ \text{R}}{29.92 \text{ in. Hg}} \left| \frac{0.69 \text{ in. Hg}}{359 \text{ ft}^3} \right| \frac{1 \text{ lb mole}}{1 \text{ lb mole}} \left| \frac{18 \text{ lb H}_2\text{O}}{1 \text{ lb mole}} \right. = 1.51 \times 10^8 \text{ lb H}_2\text{O}$$

Now the dew point is the temperature at which the water vapor in the air will first condense on cooling at *constant total pressure and composition*. As the gas is cooled you can see from Eq. (3.47) that the percent relative humidity increases since the partial pressure of the water vapor is constant while the vapor pressure of water decreases with temperature. When the percent relative humidity reaches 100 percent,

$$100 \frac{p_1}{p_1^*} = 100\% \quad \text{or} \quad p_1 = (p_1^*)$$

the water vapor will start to condense. This means that at the dew point the vapor pressure of water will be 0.69 in. Hg. From the steam tables you can see that this corresponds to a temperature of about 69°F.

3.5.2 Molal Saturation. Another way to express vapor concentrations in a gas is to use the ratio of the moles of vapor to the moles of vapor-free gas:

$$\frac{n_{\text{vapor}}}{n_{\text{vapor-free gas}}} = \text{molal saturation} \quad (3.48)$$

If subscripts 1 and 2 represent the vapor and the dry gas, respectively, then for a binary system,

$$p_1 + p_2 = p_t \quad (3.49)$$

$$n_1 + n_2 = n, \quad (3.50)$$

$$\frac{n_1}{n_2} = \frac{p_1}{p_2} = \frac{V_1}{V_2} = \frac{n_1}{n_t - n_1} = \frac{p_1}{p_t - p_1} = \frac{V_1}{V_t - V_1} \quad (3.51)$$

By multiplying by the appropriate molecular weights, you can find the weight of vapor per weight of dry gas:

$$\frac{(n_{\text{vapor}} \times \text{mol. wt}_{\text{vapor}})}{(n_{\text{gas, eq.}} \times \text{mol. wt}_{\text{gas, eq.}})} = \frac{\text{wt}_{\text{vapor}}}{\text{wt}_{\text{gas, eq.}}} \quad (3.52)$$

The special term *humidity* (\mathcal{H}) refers to the pounds of water vapor per pound of bone-dry air and is used in connection with the humidity charts in Sec. 5.3.

SE at 8 mi/hr. How many
? What would be the dew

we can calculate the partial
ent relative humidity; from
es in the previous section.

in. Hg

9 in. Hg

$$\frac{18 \text{ lb H}_2\text{O}}{1 \text{ lb mole}} = 1.51 \times 10^8 \text{ lb H}_2\text{O}$$

water vapor in the air will
position. As the gas is cooled
v increases since the partial
ture of water decreases with
100 percent,

the dew point the vapor
you can see that this corre-

ress vapor concentration
moles of vapor-free gas:

(3.48)

as, respectively, then for

(3.49)

(3.50)

$$\frac{V_1}{V_t - V_1} \quad (3.51)$$

you can find the weight

(3.52)

water vapor per pound
idity charts in Sec. 5.3.

3.5.3 "Absolute" Saturation; Percentage Saturation. "Absolute" saturation is defined as the ratio of the moles of vapor per mole of vapor-free gas to the moles of vapor which would be present per mole of vapor-free gas if the mixture were completely saturated at the existing temperature and total pressure:

$$\alpha s = \text{"absolute saturation"} = \frac{\left(\frac{\text{moles vapor}}{\text{moles vapor-free gas}}\right)_{\text{actual}}}{\left(\frac{\text{moles vapor}}{\text{moles vapor-free gas}}\right)_{\text{saturated}}} \quad (3.53)$$

Using the subscripts 1 for vapor and 2 for vapor-free gas,

$$\text{percent absolute saturation} = \frac{\left(\frac{n_1}{n_2}\right)_{\text{actual}}(100)}{\left(\frac{n_1}{n_2}\right)_{\text{saturated}}} = \frac{\left(\frac{p_1}{p_2}\right)_{\text{actual}}(100)}{\left(\frac{p_1}{p_2}\right)_{\text{saturated}}} \quad (3.54)$$

Since p_1 saturated = p_1^* and $p_t = p_1 + p_2$,

$$\text{percent absolute saturation} = 100 \cdot \frac{\frac{p_1}{p_t - p_1}}{\frac{p_1^*}{p_t - p_1}} = \frac{p_1}{p_1^*} \left(\frac{p_t - p_1^*}{p_t - p_1} \right) 100 \quad (3.55)$$

Now you will recall that $p_1/p_1^* = \text{relative saturation}$. Therefore,

$$\text{percent absolute saturation} = (\text{relative saturation}) \left(\frac{p_t - p_1^*}{p_t - p_1} \right) 100 \quad (3.56)$$

Percent absolute saturation is always less than relative saturation except at saturated conditions (or at zero percent saturation) when percent absolute saturation = percent relative saturation.

EXAMPLE 3.25 Partial saturation

Helium contains 12 percent (by volume) of ethyl acetate. Calculate the percent relative saturation and the percent absolute saturation of the mixture at a temperature of 30°C and a pressure of 740 mm of Hg.

Solution:

The additional data needed are

$$p_{\text{EtAc}}^* \text{ at } 30^\circ\text{C} = 119 \text{ mm Hg} \quad (\text{from any suitable handbook})$$

Using Dalton's laws,

$$\begin{aligned} p_{\text{EtAc}} &= p_t y_{\text{EtAc}} = p_t \left(\frac{n_{\text{EtAc}}}{n_t} \right) = p_t \left(\frac{V_{\text{EtAc}}}{V_t} \right) \\ &= (740)(0.12) = 88.9 \text{ mm Hg} \end{aligned}$$

$$\begin{aligned} p_{\text{He}} &= p_t - p_{\text{EtAc}} \\ &= 740 - 88.9 = 651.1 \text{ mm Hg} \end{aligned}$$

At 30°C the

(a) Percent relative saturation =

$$100 \frac{p_{\text{EtAc}}}{p_{\text{EtAc}}^*} = 100 \frac{88.9}{119} = 74.6\%$$

(b) Percent absolute saturation =

$$100 \frac{\frac{p_{\text{EtAc}}}{p_t - p_{\text{EtAc}}}}{\frac{p_{\text{EtAc}}^*}{p_t - p_{\text{EtAc}}^*}} = \frac{\frac{88.9}{119}}{\frac{740 - 88.9}{119}} 100 = \frac{\frac{88.9}{119}}{\frac{651.1}{621}} 100 \\ = 71.1\%$$

EXAMPLE 3.26 Partial saturation

A mixture of ethyl acetate vapor and air has a relative saturation of 50 percent at 30°C and a total pressure of 740 mm Hg. Calculate the analysis of the vapor and the molal saturation.

Solution:

The vapor pressure of ethyl acetate at 30°C from the previous problem is 119 mm Hg.

$$\% \text{ relative saturation} = 50 = \frac{p_{\text{EtAc}}}{p_{\text{EtAc}}^*} 100$$

From the above relation, the p_{EtAc} is

$$p_{\text{EtAc}} = 0.50(119) = 59.5 \text{ mm Hg}$$

$$(a) \quad \frac{n_{\text{EtAc}}}{n_t} = \frac{p_{\text{EtAc}}}{p_t} = \frac{59.5}{740} = 0.0805$$

Hence the vapor analyzes EtAc, 8.05 percent; air, 91.95 percent.

(b) Molal saturation is

$$\frac{n_{\text{EtAc}}}{n_{\text{air}}} = \frac{p_{\text{EtAc}}}{p_{\text{air}}} = \frac{p_{\text{EtAc}}}{p_t - p_{\text{EtAc}}} = \frac{59.5}{740 - 59.5} \\ = 0.0876 \frac{\text{mole EtAc}}{\text{mole air}}$$

EXAMPLE 3.27 Partial saturation

The percent absolute humidity of air at 86°F and a total pressure of 750 mm of Hg is 20 percent. Calculate the percent relative humidity and the partial pressure of the water vapor in the air. What is the dew point of the air?

Solution:

Data from the steam tables are

$$p_{\text{H}_2\text{O}}^* \text{ at } 86^\circ\text{F} = 31.8 \text{ mm Hg}$$

To get the relative humidity, $p_{\text{H}_2\text{O}}/p_{\text{H}_2\text{O}}^*$, we need to find the partial pressure of the

This equation is

(a)

(b)

(c) The de
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3.6 Materials and variables

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H₂O

86°F

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include the

water vapor in the air. This may be obtained from

$$\alpha \mathcal{R}C = 20 = \frac{\frac{p_{H_2O}}{p_t - p_{H_2O}}}{\frac{p_{H_2O}^*}{p_t - p_{H_2O}^*}} 100 = \frac{\frac{p_{H_2O}}{750 - p_{H_2O}}}{\frac{31.8}{750 - 31.8}} 100$$

This equation can be solved for p_{H_2O}

$$0.00885 = \frac{p_{H_2O}}{750 - p_{H_2O}}$$

$$6.65 - 0.00885p_{H_2O} = p_{H_2O}$$

(a) $p_{H_2O} = 6.6 \text{ mm Hg}$

(b) $\% \mathcal{R}C = 100 \frac{6.6}{31.8} = 20.7\%$

- (c) The dew point is the temperature at which the water vapor in the air would commence to condense. This would be at the vapor pressure of 6.6 mm, or about 41°F.

3.6 Material balances involving condensation and vaporization

The solution of material balance problems involving partial saturation, condensation, and vaporization will now be illustrated. Remember the drying problems in Chap. 2? They included water and some bone-dry material, as shown in the top of Fig. 3.21. To complete the diagram, we can now add the air that is used to remove the water from the material being dried.

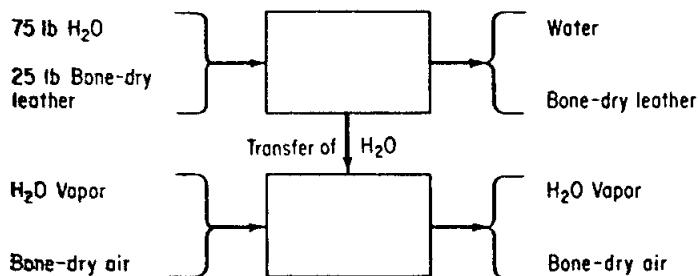


Fig. 3.21. Complete drying schematic.

You can handle material balance problems involving water vapor in air in exactly the same fashion as you handled the material balance problems for the drying of leather (or paper, etc.), depending on the information provided and sought. (You can find additional humidity and saturation problems which include the use of energy balances and humidity charts in Chap. 5.)

We should again stress in connection with the examples to follow that if you know the dew point of a gas mixture, you automatically know the partial pressure of the water vapor in the gas mixture. When a partially saturated gas is cooled at constant pressure, as in the cooling of air containing some water vapor at atmospheric pressure, the volume of the mixture may change slightly, but the partial pressures of the air and water vapor remain constant until the dew point is reached. At this point water begins to condense; the air remains saturated as the temperature is lowered. All that happens is that more water goes from the vapor into the liquid phase. At the time the cooling is stopped, the air is still saturated, and at its dew point.

EXAMPLE 3.28 Material balance with condensation

If the atmosphere in the afternoon during a humid period is at 90°F and 80 percent RH (barometer reads 738 mm Hg) while at night it is at 68°F (barometer reads 745 mm Hg), what percent of the water in the afternoon air is deposited as dew?

Solution:

The data are shown in Fig. E3.28.

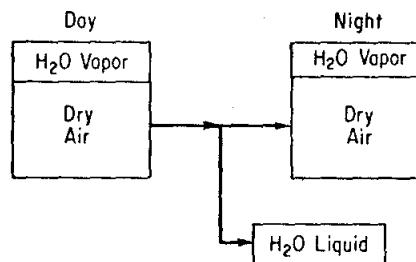


Fig. E3.28.

If any dew is deposited at night, the air must be fully saturated at 68°F. You can easily check the dew point of the day air and find it is 83°F. Thus the air first becomes saturated at 83°F. The partial pressures of air and water vapor during the day and night are

$$p_w \text{ day} = 36(0.80) = 28.8 \text{ mm}$$

$$p_w \text{ night} = 17.5(1.00) = 17.5 \text{ mm}$$

$$p_t = p_{\text{air}} + p_w$$

$$\text{day: } p_{\text{air}} = 738 - 28.8 = 709.2 \text{ mm}$$

$$\text{night: } p_{\text{air}} = 745 - 17.5 = 727.5 \text{ mm}$$

This gives us in effect the compositions of all the streams.

As a basis you could select 1 ft³ of wet air, 1 lb mole wet (or dry) air, or many other suitable bases. The simplest basis to take is

Basis: 738 lb moles moist day air

because then the moles = the partial pressures.

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ay change slightly,
n constant until the
se; the air remains
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at 90°F and 80 percent
barometer reads 745
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saturated at 68°F. You
°F. Thus the air first
water vapor during the

(or dry) air, or many

	<i>initial mixture (day)</i>	<i>final mixture (night)</i>
<i>comp.</i>	<i>lb moles = partial press.</i>	<i>lb moles = partial press.</i>
Air	709.2	$\xleftarrow{\text{tie element}}$ 727.5
H ₂ O	28.8	17.5
Total	738.0	745.0

On the basis of 738 lb moles of moist day air we have the following water in the night air:

$$\frac{17.5 \text{ lb mole H}_2\text{O in night air}}{727.5 \text{ lb mole air}} | 709.2 \text{ lb mole air} = 17.0 \text{ lb mole H}_2\text{O}$$

$$28.8 - 17.0 = 11.8 \text{ lb moles H}_2\text{O deposited as dew}$$

$$100 \frac{11.8}{28.8} = 41\% \text{ of water in day air deposited as dew}$$

This problem could also be solved on the basis of

Basis: 1 lb mole of bone-dry air (BDA)

$$\begin{array}{ccc|c} \text{initial} & - & \text{final} & = \text{change} \\ 28.8 \text{ lb moles H}_2\text{O} & - & 17.5 \text{ lb moles H}_2\text{O} & = \text{change} \\ \hline 709.2 \text{ lb moles BDA} & - & 727.5 \text{ lb moles BDA} & \\ \\ 0.0406 & - & 0.0241 & = 0.0165 \frac{\text{lb mole H}_2\text{O}}{\text{lb mole DBA}} \\ \\ \frac{0.0165}{0.0406} 100 & = 41\% \text{ of water vapor deposited as dew} \end{array}$$

Note especially that the operation

$$\begin{array}{ccc|c} \text{initial} & \text{final} & & \\ 28.8 & 17.5 & & \\ \hline 738 & 745 & & \end{array}$$

is meaningless since two different bases are involved—the wet initial air and the wet final air.

EXAMPLE 3.29 Dehydration

By absorption in silica gel you are able to remove all (0.72 lb) of the H₂O from moist air at 60°F and 29.2 in. Hg. The same air measures 1000 ft³ at 70°F and 32.0 in. Hg when dry. What was the relative humidity of the moist air?

Solution:

See Fig. E3.29.

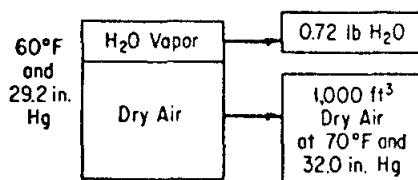


Fig. E3.29.

Basis: 1000 ft³ bone-dry air (BDA) at 70°F and 32.0 in. Hg

$$\frac{1000 \text{ ft}^3 \text{ BDA}}{1 \text{ lb mole}} \left| \begin{array}{c} 492^\circ\text{R} \\ 530^\circ\text{R} \end{array} \right| \frac{32.0 \text{ in. Hg}}{29.92 \text{ in. Hg}} \left| \begin{array}{c} 1 \text{ lb mole} \\ 359 \text{ ft}^3 \end{array} \right| = 2.77 \text{ lb moles dry air}$$

The wet air now appears to have the following composition:

	lb moles
BDA	2.77
H ₂ O	0.040
0.72/18 =	<hr/>
Wet air	2.81

The partial pressure of the water in the moist air was the total pressure times the mole fraction water vapor:

$$\frac{29.2 \text{ in. Hg}}{2.81} \left| \begin{array}{c} 0.04 \\ 2.81 \end{array} \right| = 0.415 \text{ in. Hg}$$

Saturated air at 60°F has a vapor pressure of water of 0.52 in. Hg. Consequently, the relative humidity was

$$\frac{p_{H_2O}}{p_{H_2O}^*} = \frac{0.415}{0.52} 100 = 80\%$$

EXAMPLE 3.30 Humidification

One thousand cubic feet of moist air at 760 mm Hg and 72°F and with a dew point of 53°F enter a process. The air leaves the process at 740 mm Hg with a dew point of 137°F. How many pounds of water vapor are added to each pound of wet air entering the process?

Solution:

See Fig. E3.30.

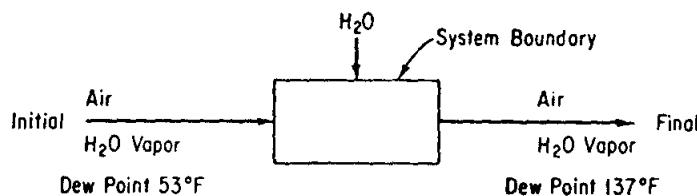


Fig. E3.30.

Additional data are

dew point

<i>t</i> (°F)	<i>p</i> _{H₂O} [*] (mm Hg)
53°F	10.3*
137°F	138.2*

*These give the partial pressures of the water vapor in the initial and final gas mixtures.

62.0 in. Hg

1b moles dry air

pressure times the mole

Hg. Consequently, the

72°F and with a dew
40 mm Hg with a dew
each pound of wet air

We know the initial and final compositions of the air-water vapor mixture, since the partial pressure of the water vapor in the moist air is the pressure of water at the dew point for each case.

Basis: 760 moles initial wet air

component	initial moles	final moles	pressure (mm)
Vapor	10.3		138.2
BDA*	749.9	749.9	601.8
Total	760		740

*Bone-dry air.

In the final gas we can say that there are

$$138.2 \text{ moles vapor}/601.8 \text{ moles BDA}$$

$$138.2 \text{ moles vapor}/740 \text{ moles moist air}$$

$$601.8 \text{ moles BDA}/740 \text{ moles moist air}$$

Since we have a tie element of 750 moles of bone-dry air and want to know how many moles of vapor are present in the final air on our basis of 760 moles initial wet air,

$$\frac{749.7 \text{ moles BDA}}{601.8 \text{ moles BDA in final}} = 172 \text{ moles vapor in final}$$

$$172 \text{ moles final vapor} - 10.3 \text{ moles initial vapor} = 162 \text{ moles of vapor added}$$

But these calculations were all based on 760 moles of initial wet gas. Therefore our answer should be

$$\frac{162 \text{ moles vapor added}}{760 \text{ moles wet gas in}} = \frac{0.213 \text{ moles vapor added}}{1 \text{ mole wet gas in}}$$

Now the molecular weight of water is 18; the average molecular weight of the original wet air has to be calculated:

comp.	moles	mol. wt	lb
BDA	750	29	21,750
H ₂ O	10	18	180
	760		21,930

$$\frac{21,930 \text{ lb}}{760 \text{ lb mole}} = 28.8$$

$$\frac{0.213 \text{ lb mole H}_2\text{O}}{1 \text{ lb mole wet gas}} \left| \frac{18 \text{ lb}}{1 \text{ lb mole H}_2\text{O}} \right| \frac{1 \text{ lb mole wet gas}}{28.8 \text{ lb}} = 0.133 \frac{\text{lb H}_2\text{O}}{\text{lb wet gas}}$$

Comments:

- (a) If the original problem had asked for the moles of final wet gas, we could have used the tie element in the following manner:

$$\frac{750 \text{ moles BDA}}{602 \text{ moles BDA out}} \left| \frac{740 \text{ moles wet gas out}}{602 \text{ moles BDA out}} \right| = 921 \text{ moles wet gas out}$$

(b) If a basis of 1 mole of bone-dry air had been used, the following calculation would apply:

Basis: 1 mole BDA

$$\text{in: } \frac{\text{moles vapor}}{\text{mole BDA}} = \frac{10.3}{749.7} = 0.0138$$

$$\text{out: } \frac{\text{moles vapor}}{\text{mole BDA}} = \frac{138.2}{601.8} = 0.229$$

Since there are more moles of vapor in the final air (per mole of bone-dry air), we know that vapor must have been added:

$$\text{moles vapor added} = 0.229 - 0.0138 = 0.215 \text{ moles}$$

The remainder of the calculations would be the same.

We have gone over a number of examples of condensation and vaporization, and you have seen how a given amount of air at atmospheric pressure can hold only a certain maximum amount of water vapor. This amount depends on the temperature of the air, and any decrease in the temperature will lower the water-bearing capacity of the air. An increase in pressure also will accomplish the same effect. If a pound of saturated air at 75°F is isothermally compressed (with a reduction in volume, of course), liquid water will be deposited out of the air just like water being squeezed out of a wet sponge (Fig. 3.22). This process has been previously described in the *p-T* diagram for water (Fig. 3.12), by line *G-H-J*.

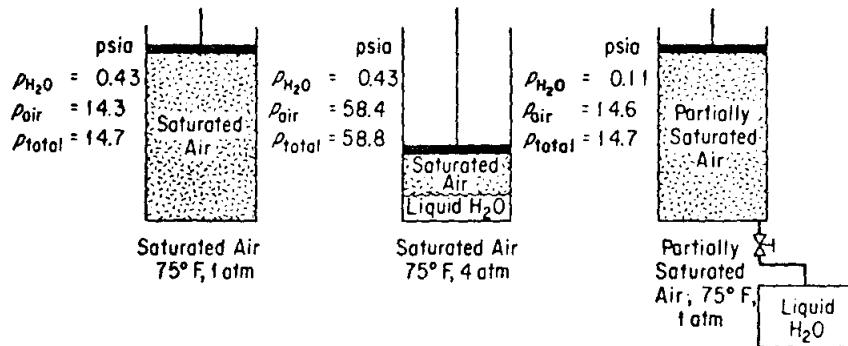


Fig. 3.22. Effect of an increase of pressure on saturated air and a return to the initial pressure.

For example, if a pound of saturated air at 75°F and 1 atm is compressed isothermally to 4 atm (58.8 psia), almost three-quarters of the original content of water vapor now will be in the form of liquid, and the air has a dew point of 75°F at 4 atm. Remove the liquid water, expand the air isothermally back to 1 atm, and you will find the dew point has been lowered to about 36°F. Mathe-

following calculation

matically ($1 = \text{state at } 1 \text{ atm}$, $4 = \text{state at } 4 \text{ atm}$) with $z = 1.00$ for both components:

For saturated air at 75°F and 4 atm,

$$\left(\frac{n_{\text{H}_2\text{O}}}{n_{\text{air}}}\right)_4 = \left(\frac{p_{\text{H}_2\text{O}}^*}{p_{\text{air}}}\right)_4 = \frac{0.43}{58.4}$$

For the same air saturated at 75°F and 1 atm,

$$\left(\frac{n_{\text{H}_2\text{O}}}{n_{\text{air}}}\right)_1 = \left(\frac{p_{\text{H}_2\text{O}}^*}{p_{\text{air}}}\right)_1 = \frac{0.43}{14.3}$$

Since the air is the tie element in the process,

$$\left(\frac{n_4}{n_1}\right)_{\text{H}_2\text{O}} = \frac{\frac{0.43}{58.4}}{\frac{0.43}{14.3}} = \frac{14.3}{58.4} = 0.245$$

24.5 percent of the original water will remain as vapor. After the air-water vapor mixture is returned to a total pressure of 1 atm, the following two familiar equations now apply:

$$p_{\text{H}_2\text{O}} + p_{\text{air}} = 14.7$$

$$\frac{p_{\text{H}_2\text{O}}}{p_{\text{air}}} = \frac{n_{\text{H}_2\text{O}}}{n_{\text{air}}} = \frac{0.43}{58.4} = 0.00737$$

From these two relations you can find that

$$p_{\text{H}_2\text{O}} = 0.108 \text{ psia}$$

$$p_{\text{air}} = \frac{14.6}{0.00737}$$

$$p_{\text{total}} = 14.7 \text{ psia}$$

The pressure of the water vapor represents a dew point of about 36°F , and a relative humidity of

$$100 \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2\text{O}}^*} = \frac{0.108}{0.43} 100 = 25\%$$

3.7 Phase phenomena

We shall now consider briefly some of the qualitative characteristics of vapors, liquids, and solids.

3.7.1 The Phase Rule. You will find the phase rule a useful guide in establishing how many properties, such as pressure and temperature, have to be specified to definitely fix all the remaining properties and number of phases that can coexist for any physical system. The rule can be applied only to systems in *equilibrium*. It says

$$F = C - \varphi + 2 \quad (3.57)$$

where F = number of degrees of freedom, i.e., the number of independent properties which have to be specified to determine all the intensive properties of each phase of the system of interest.

C = number of components in the system. For circumstances involving chemical reactions, C is not identical to the number of chemical compounds in the system but is equal to the number of chemical compounds less the number of independent-reaction and other equilibrium relationships among these compounds.

Φ = number of phases that can exist in the system. A phase is a homogeneous quantity of material such as a gas, a pure liquid, a solution, or a homogeneous solid.

Variables of the kind with which the phase rule is concerned are called *phase-rule variables*, and they are *intensive* properties of the system. By this we mean properties which do not depend on the quantity of material present. If you think about the properties we have employed so far in this text, you have the feeling that pressure and temperature are independent of the amount of material present. So is concentration, but what about volume? The total volume of a system is called an *extensive* property because it does depend on how much material you have; the specific volume, on the other hand, the cubic feet per pound, for example, is an intensive property because it is independent of the amount of material present. In the next chapter we shall take up additional properties such as internal energy and enthalpy; you should remember that the specific (per unit mass) values of these quantities are intensive properties; the total quantities are extensive properties.

An example will clarify the use of these terms in the phase rule. You will remember for a pure gas that we had to specify three of the four variables in the ideal gas equation $pV = nRT$ in order to be able to determine the remaining one unknown. For a single phase $\Phi = 1$, and for a pure gas $C = 1$, so that

$$F = C - \Phi + 2 = 1 - 1 + 2 = 2 \quad \text{variables to be specified}$$

How can we reconcile this apparent paradox with our previous statement? Since the phase rule is concerned with intensive properties only, the following are phase-rule variables in the ideal gas law:

$$\left. \begin{array}{c} P \\ \hat{V} \text{ (specific molar volume)} \\ T \end{array} \right\} \quad \text{3 intensive properties}$$

Thus, the ideal gas law should be written as follows:

$$p\hat{V} = RT$$

and once two of the intensive variables are fixed, the third is also automatically fixed.

An *invariant* system is one in which no variation of conditions is possible without one phase disappearing. An example with which you may be familiar

independent processes all the intensive

instances involving number of chemical reaction and other is.

phase is a homogenous liquid, a solution,

ncerned are called system. By this we material present. If this text, you have of the amount of The total volume depend on how much the cubic feet per acre. t of the make . Additional remember that the ve properties; the

ase rule. You will cur variables in the the remaining one 1, so that e specified evious statement? naly, the following

ties

also automatically ditions is possible u may be familiar

is the ice-water-water vapor system which exists at only one temperature (0.01°C):

$$F = C - \varphi + 2 = 1 - 3 + 2 = 0$$

With the three phases present, none of the physical conditions can be varied without the loss of one phase. As a corollary, if the three phases are present, the temperature, the specific volume, etc., must always be fixed at the same values. This phenomenon is useful in calibrating thermometers and other instruments.

A complete discussion of the significance of the term C and the other terms in the phase rule is beyond the scope of this text; for further information you can read one of the general references on the phase rule listed at the end of this chapter or consult an advanced book on thermodynamics or physical chemistry. We are now going to consider how phase phenomena can be illustrated by means of diagrams.

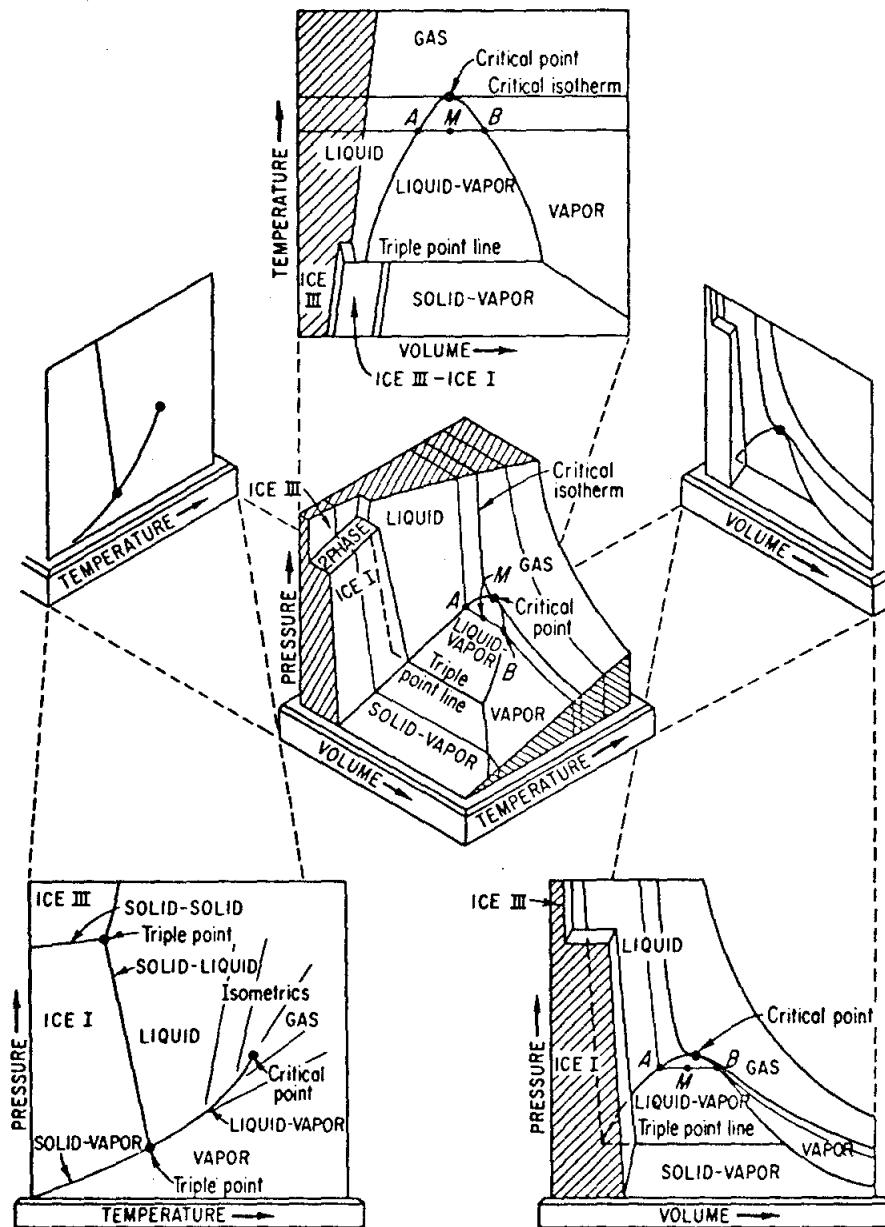
3.7.2 Phase Phenomena of Pure Components. We can show the properties of a single-phase pure component, such as a gas, on two-dimensional plots. According to the phase rule,

$$F = C - \varphi + 2 = 1 - 1 + 2 = 2$$

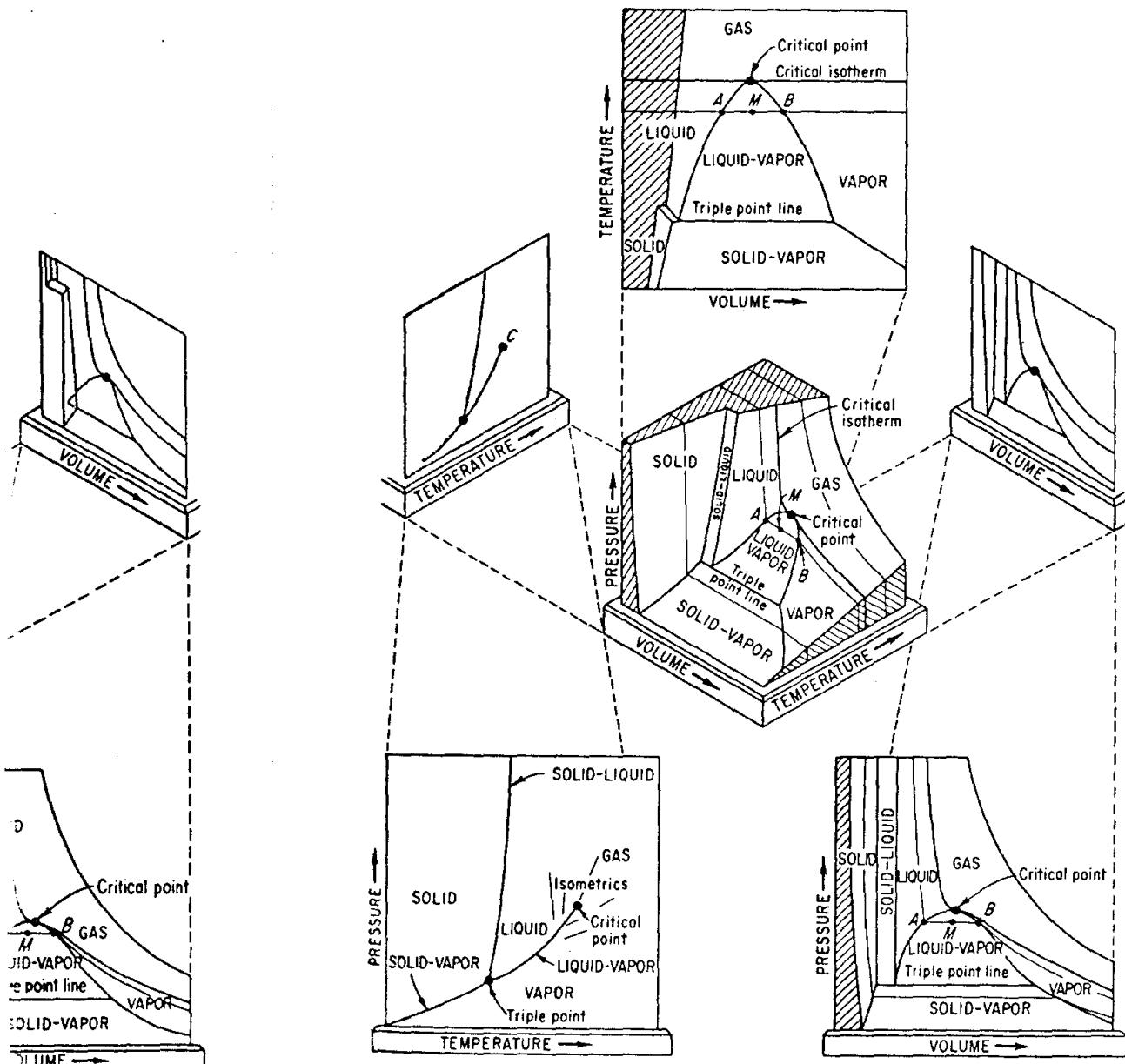
only two physical variables have to be specified to fix the system definitely; i.e., any point on the two-dimensional diagram will be enough to fix the other properties of the system at that point.

Actually, if we are to clearly understand phase phenomena, the properties of a substance should be shown in three dimensions, particularly if there can be more than one phase in the region for which the p - V - T properties are to be presented. We previously overcame the handicap of using two dimensions to present three-dimensional data by showing, on the two-dimensional graph, lines of constant value for the other properties of the system (see Fig. 3.2, which has p and \bar{V} as axes, and lines of constant temperature as the third parameter). In this section we are going to present a more elaborate treatment of these same p - V - T properties. Since the data on water, a substance that expands on freezing (to ice I), and carbon dioxide, a substance that contracts on freezing, are so well known, we have illustrated in Figs. 3.23 and 3.24 the relationships between the three-dimensional presentations of p - V - T data for these two compounds and the conventional two-dimensional diagrams you usually encounter. Be certain that you view Figs. 3.23 and 3.24 as *surfaces* and not as solid figures; only the p - V - T points on the surface exist, and no point exists above or below the surface.

You can see that the two-dimensional diagrams are really projections of the three-dimensional figure onto suitable axes. On the p - \bar{V} diagram, you will observe lines of constant temperature called *isothermal lines*, and on the p - T diagram you will see lines of constant volume, called *isometric lines* or *isochores*. On the T - \bar{V} diagram, we might have put lines of constant pressure known as *isobaric lines*, but these are not shown since they would obscure the more impor-

Fig. 3.23. p - V - T surface and projections for H_2O .

tant features which are shown. The two-phase vapor-liquid region is represented by the heavy envelope in the p - V and the T - V diagrams. On the p - T diagram this two-phase region appears only as a single line because you are looking at the three-dimensional diagram from the side. The p - T diagram shows what we have

Fig. 3.24. p - V - T surface and projections for CO_2 .

so far called the *vapor-pressure curve*, while the associated diagrams show that the "curve" is really a surface on which two phases coexist, each having the properties found at the appropriate bounding line for the surface. A point on the surface shows merely the overall composition of one phase in equilibrium with another, as, for example, at point *A* we have liquid and at point *B* we have vapor.

region is represented in the p - T diagram this way, looking at the schematic

and in between them no single phase exists. If we added the liquid at *A* to the vapor at *B*, we would have a two-phase mixture with the gross properties as shown by point *M*. You will notice that in the p - \hat{V} diagram the lines of constant temperature and pressure become horizontal in the two-phase region, because if you apply the phase rule

$$F = C - \varphi + 2 = 1 - 2 + 2 = 1$$

only one variable can change, the specific volume. In the two-phase region, where condensation or evaporation takes place, the pressure and temperature remain constant. Think back to our discussion of water boiling in this connection.

Other features illustrated on the diagrams are the critical point; the critical isotherm; the triple point, which becomes a triple-point line actually in the p - \hat{V} and in the T - \hat{V} diagrams; and the existence of two solid phases and a liquid phase in equilibrium, such as (Fig. 3.23) solid ice I, solid ice III, and liquid. The temperature at the freezing point for water, i.e., the point where ice, water, air, and water vapor are in equilibrium, is not quite the same temperature as that at the triple point, which is the point where ice, water, and water vapor are in equilibrium. The presence of air lowers the freezing temperature by about 0.001°C so that the triple point is at 0.00602 atm and 0.01°C . The corresponding values for CO_2 are 5 atm and -57°C , respectively. Another triple point for the water system exists at 2200 atm and 20°C between ice III, ice I, and liquid water.

The critical point can be determined from a p - \hat{V} diagram by plotting constant-temperature lines for the experimental data. As you proceed to higher and higher pressures, the horizontal portion of the isothermal line becomes shorter and shorter until finally the isotherm has only an inflection (point of zero slope). Any lines at subsequently higher pressures do not have this inflection. If carefully done, the critical temperature, pressure, and volume can be determined this way. Another way is to use the law of *rectilinear diameter*. Fig. 3.25, which says that the arithmetic average of the densities (or specific volumes) of the pure components in the liquid and the vapor state is a linear function of temperature, if the pairs of measurements are made at the same pressure. This is not an exact relationship but is extremely useful in getting the critical density or critical specific volume, since the linear average density relation can be extrapolated until it crosses the two-phase envelope where experimental data are quite difficult to collect.

3.7.3 Phase Phenomena of Mixtures. Presentation of phase phenomena for mixtures which are completely miscible in the liquid state involves some rather complex reduction of three-, four-, and higher-dimensional diagrams into two dimensions. We shall restrict ourselves to two-component systems because, although the ideas discussed here are applicable to any number of components, the graphical presentation of more complex systems in an elementary text such as this is probably more confusing than helpful. We shall

liquid at A to the gross properties as the lines of constant phase region, because

two-phase region, rate and temperature change in this connection

point; the critical point is actually in the $p-\bar{V}$ plane and a liquid phase and liquid. The temperature, water, air, and pressure as that at the vapor are in equilibrium by $+0.001^\circ\text{C}$ for values point for the water and liquid water. by plotting correspond to higher and becomes shorter point of zero slope). section. If carefully be determined this Fig. 3.25, which says names) of the pure function of temperature. This is not an exact way or critical specific extrapolated until quite difficult to

tion of phase phenomena. liquid state involves n -dimensional dia- two-component sys- tle to any number tems in an ele- h We shall

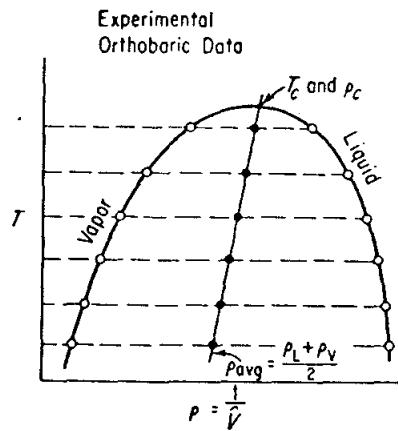


Fig. 3.25. Law of rectilinear diameters used to find critical temperature and density.

use hydrocarbons for most of our examples of two-component systems since a vast amount of experimental work has been reported for these compounds.

It would be convenient if the critical temperature of a mixture were the mole weight average of the critical temperatures of its pure components, and the critical pressure of a mixture were simply a mole weight average of the critical pressures of the pure components (according to Kay's rule), but these maxims simply are not true, as shown in Fig. 3.26. The pseudocritical temperature falls on the dashed line between the critical temperatures of CO_2 and SO_2 , while

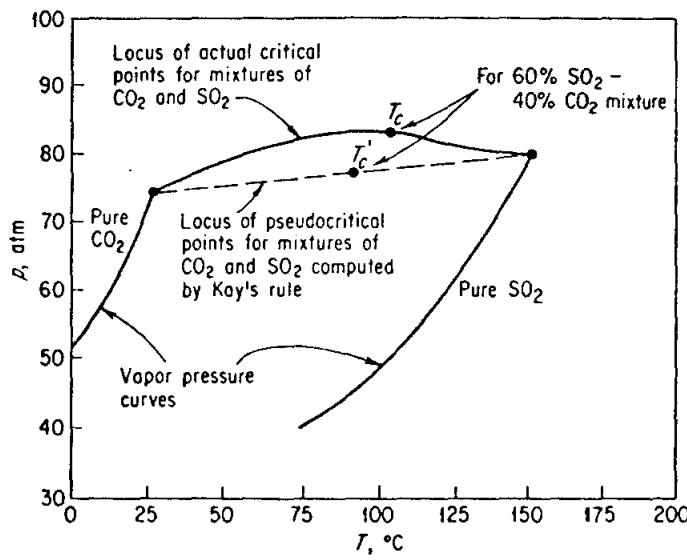


Fig. 3.26. Critical and pseudocritical points for a mixture.

the actual critical point for the mixture lies somewhere else. The dashed line as in Fig. 3.31 illustrates (for another system) the three-dimensional aspects of the locus of the actual critical points.

Figure 3.27 is a p - T diagram for a 25 percent methane-75 percent butane mixture. You can compare this figure with the one for a pure substance, water, as in Fig. 3.12; the p - T curve for pure butane or pure methane would look just

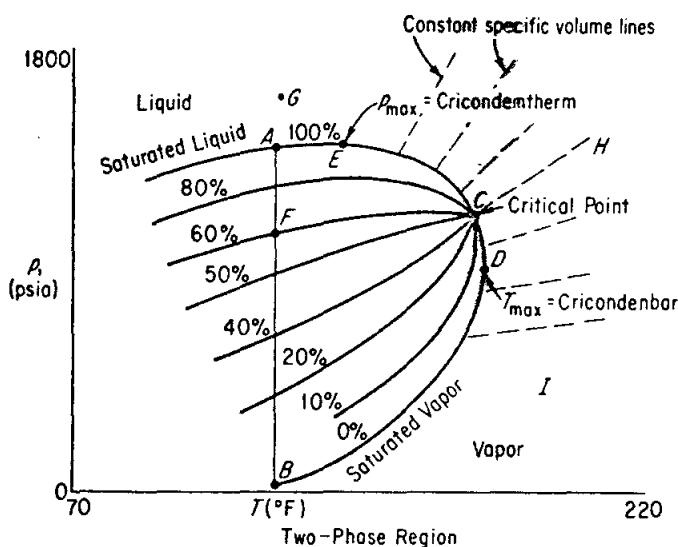


Fig. 3.27. p - T diagram for binary system: 25 percent CH_4 — 75 percent C_4H_{10} .

like the diagram for water (excluding the solid phases). For a mixture of a fixed composition, we have only three variables to consider, p , V , and T . Lines of constant specific volume are shown outside the envelope of the two-phase region. Inside the envelope are shown lines of constant fractions of liquid, starting at the high pressures, where 100 percent liquid exists (zero percent vapor), and ranging down to zero percent liquid and 100 percent vapor at the low pressures. The 100 percent saturated liquid line is the bubble-point line and the 100 percent saturated vapor line is the dew-point line.

The critical point is shown as point C . You will note that this is not the point of maximum temperature at which vapor and liquid can exist in equilibrium; the latter is the maximum cricondentherm, point D . Neither is it the point of maximum pressure at which vapor and liquid can exist in equilibrium because that point is the maximum cricondenbar (point E). The maximum temperature at which liquid and vapor can exist in equilibrium for this mixture is about 30° higher than the critical temperature, and the maximum pressures is 60 or 70 psia greater than the critical pressure. You can clearly see, therefore, that the best definition of the critical point was the one which stated that the

dashed line as in
all aspects of the
5 percent butane
substance, water,
would look just

the lines

tant

condensat

220

75 percent

mixture of a fixed
and T . Lines of
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ns of liquid, start-
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et this is not the
exist in equilib-
Neither is it the
exist in equilibrium
. The maximum
m for this mixture
maximum pressures
arly see, therefore,
ch stated that the

density and other properties of the liquid and vapor become identical at the critical point. This definition holds for single components as well as mixtures.

With the aid of Fig. 3.27 we can indicate some of the phenomena that can take place when you change the pressure on a two-component mixture at constant temperature or change the temperature of a mixture at constant pressure. If you proceed from A in the liquid region to F and then to B in the vapor region by means of an isothermal process of some nature, you can go from 100 percent liquid to 100 percent vapor and notice a phase change. A similar type of analysis could have been applied to the p - T water diagram (Fig. 3.12) and the same conclusion reached, although the fraction of vapor and liquid cannot be found from Fig. 3.12. It is only when you cross the two-phase region that a change of phase will be noticed. If you go from A to G to H to B , the liquid will change from 0 to 100 percent vapor, but there will be no noticeable phase change. Figure 3.28 illustrates this transition for a mixture by a change of shading, and a similar diagram could be drawn for a pure component.

A very interesting phenomenon called *retrograde condensation* (or vaporization) can occur in two-phase systems, a phenomenon which initially appears to be quite contrary to your normal expectations. If you start at point 1 in Fig. 3.29 (an enlarged portion of Fig. 3.27 in the vicinity of the critical region) you

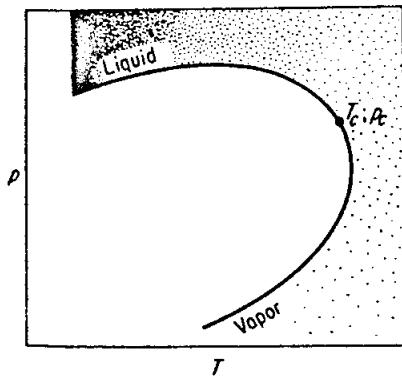


Fig. 3.28. Change in phase characteristics for a mixture of two components.

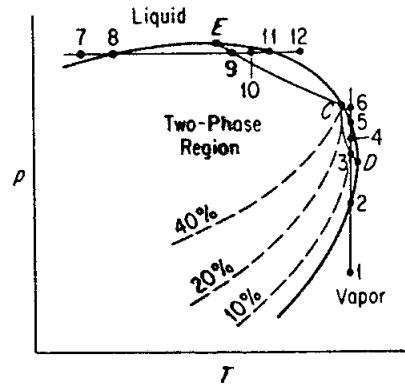


Fig. 3.29. The two types of retrograde condensation.

are in the vapor region. As you proceed to raise the pressure at constant temperature, you will arrive at point 2, where you are on the saturated-vapor line, or the dew point line. Continuing to increase the pressure will, as you might expect, increase the amount of liquid formed. However, soon you will reach a point where a maximum amount of liquid has formed (3), and increasing the pressure still further to points 4 and 5 will reduce the amount of liquid present, and eventually you will wind up back in the vapor region at 6. This phenomenon of retrograde condensation can happen, of course, only if the critical point, C , is located

above and to the left of *D* as shown on the diagram so that there is a "bulge" in the vicinity of *D* for the mixture. The interesting thing about this phenomenon is that you would expect, as the pressure increased at constant temperature, to continually increase the amount of liquid formed, whereas the opposite is actually true after point 3 is reached.

Another type of retrograde phenomenon exists in a few systems when you change the temperature at constant pressure. This would be illustrated by the line 7, 8, 9, 10, 11, and 12, where first, as the temperature increases to point 8 on the bubble-point curve, some liquid starts to vaporize. The liquid continues to vaporize until a maximum of vapor is obtained at 9, and then the quantity of vapor starts to decrease until you reach a point where you have all liquid again at 11. Although the points of maximum percent liquid (or vapor) enveloping the regions of retrograde phenomena are shown in the diagram by solid lines, there are actually no phase boundaries at these points. The solid lines merely represent the locus of the region in which the maximum amount of liquid or vapor can exist (the point of infinite or zero slope on the lines indicating the fraction liquid), exaggerated on the diagram for the purpose of illustration. Formally, retrograde phenomena of these two types are known as (a) isothermal retrograde vaporization (proceeding from 1 to 6) or condensation (proceeding from 6 to 1), or retrograde vaporization or condensation, respectively, of the "first type," and (b) isobaric retrograde vaporization (proceeding from 12 to 7) or condensation (proceeding from 7 to 12), or retrograde vaporization (condensation) of the "second type." Figure 3.30 shows the same phenomena on a *p*- \hat{V} diagram.

Figure 3.30, like Fig. 3.29, is for a mixture of fixed composition. The constant-temperature lines illustrated are T_c , the critical temperature, and T_{\max} , the cricondentherm. The middle line, 6 to 1, shows a process of retrograde condensation of the first kind. The shadowed areas represent the regions in which

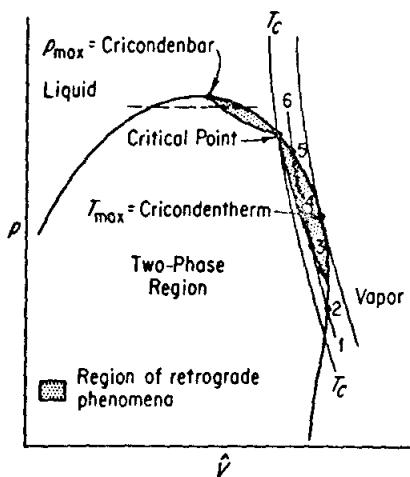


Fig. 3.30. Retrograde condensation on a *p*- \hat{V} diagram.

there is a "bulge" at this phenomenon constant temperature, to has the opposite is

systems when you e illustrated by the increases to point 8 the liquid continues then the quantity of have all liquid again (or) enveloping the by solid lines, there merely represent liquid or vapor can (one fraction liquid), normally, retrograde retrograde vaporiza-

from 1 to 1), or the "bulge," and 7) or condensation condensation) of the $p-T$ diagram. position. The con- currence, and T_{\max} , excess of retrograde the regions in which

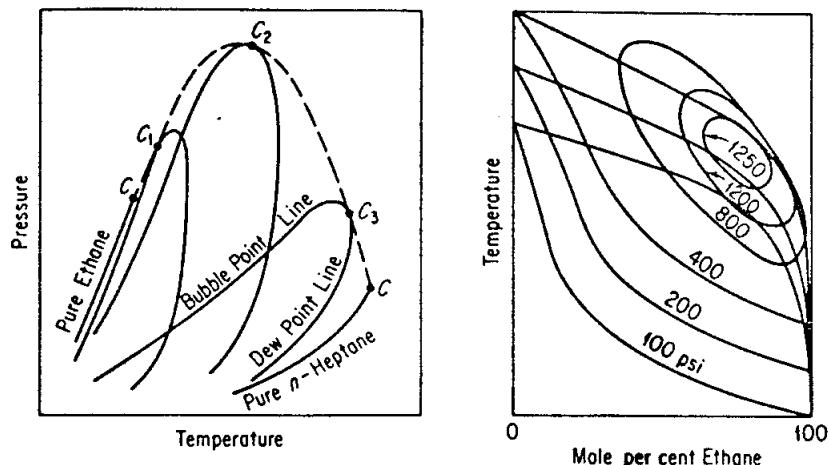


Fig. 3.31. $p-T$ and $T-x$ diagrams for ethane-heptane mixtures of different compositions.

retrograde phenomena take place. A $T-\bar{V}$ diagram is not illustrated since it is not particularly enlightening.

The diagrams shown so far represent two-component systems with a fixed overall composition. You might wonder what a diagram would look like if we were to try to show systems of several compositions on one page. This has been done in Fig. 3.31. Here we have a composite $p-T$ diagram, which is somewhat awkward to visualize, but represents the bubble-point and dew-point curves for various mixtures of ethane and heptane. These curves in essence are intersections of planes in the composition coordinate sliced out of a three-dimensional system and are stacked one in front of the other, although in two dimensions it appears that they overlap one another. The vapor-pressure curves for the two pure components are at the extreme sides of the diagrams as single lines (as you might expect). Each of the loops represents the two-phase area for a system of any specific composition. An infinite number of these slices are possible, of course. The dotted line indicates the envelope of the critical points for each possible composition. Although this line appears to be two-dimensional in Fig. 3.31, it actually is a three-dimensional line of which only the projection is shown in the figure.

Another way to handle and illustrate the phase phenomena for the two-component systems we have been discussing is to use pressure-composition diagrams at constant temperature or, alternatively, to use temperature-composition diagrams at constant pressure. A temperature-composition diagram with pressure as the third parameter is illustrated in Fig. 3.31 for the ethane-heptane system.

Discussion of the phase diagrams for multicomponent systems (ternary and higher) is beyond our scope here.

WHAT YOU SHOULD HAVE LEARNED FROM THIS CHAPTER

1. You should be familiar with the ideal gas laws, know under what circumstances they are applicable, and know how to apply them in problems.
2. You should be able to distinguish under which circumstances a gas acts as an ideal gas and under which circumstances it acts as a real gas, and be able to use, as appropriate, (a) the ideal gas equation, $pV = nRT$; (b) the compressibility factor together with $pV = znRT$; or (c) an equation of state.
3. You should know how to treat ideal and real gas mixtures, and in particular be able to apply Kay's rule.
4. You should be able to use the generalized compressibility chart with ease, and be able to calculate the parameters required for its use.
5. You should know what the following terms mean:

vapor	saturated vapor
gas	bubble point
vapor pressure	dew point
critical point	superheat
critical temperature	subcooled
critical pressure	quality
pseudocritical temperature	saturated air
pseudocritical pressure	relative humidity
condensation	absolute humidity
vaporization	isometric
sublimation	isobaric
equilibrium	isothermal
normal boiling point	retrograde condensation
saturated liquid	

6. You should be able to estimate vapor pressures as a function of temperature.
7. You should know how to solve material balance problems involving vaporization, condensation, saturation, drying, and humidification.
8. You should be able to apply the phase rule to simple systems.
9. You should be familiar with the qualitative phase behavior of pure components and mixtures and also be able to draw typical diagrams illustrating this behavior.

SUPPLEMENTARY REFERENCES

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2. Edmister, Wayne C., *Applied Hydrocarbon Thermodynamics*, Gulf Publications Co., Houston, 1961, Chaps. 1-4.

S CHAPTER

under what circumstances a gas acts as a real gas, and be able to (a) calculate RT ; (b) the compression factor of state. This, and in particular the Henry's law chart with ease, will be of great use.

3. Henley, E. J., and H. Bieber, *Chemical Engineering Calculations*, McGraw-Hill, New York, 1959.
4. Hougen, O. A., K. M. Watson, and R. A. Ragatz, *Chemical Process Principles*, Part I, 2nd ed., Wiley, New York, 1956.
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7. Wexler, A., *Humidity and Moisture*, 4 vols., Van Nostrand Reinhold, New York, 1965.
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1. Ricci, J. E., *The Phase Rule and Heterogeneous Equilibrium*, Van Nostrand Reinhold, New York, 1951.
2. Stanley, H. E., *Introduction to Phase Transitions and Critical Phenomena*, Oxford University Press, London, 1971.

PROBLEMS¹⁸

- 3.1. A given amount of N_2 has a volume of 200 cm^3 at 15.7°C . Find its volume at 0°C , the pressure remaining constant.
- 3.2. A gas measured 300 cm^3 at 27.5°C , and because of a change in temperature, the pressure remaining constant, the volume decreased to 125 cm^3 . What was the new temperature in $^\circ\text{C}$?
- 3.3. Under standard conditions, a gas measures 10.0 liters in volume. What is its volume at 92°F and 29.4 in. Hg?
- 3.4. Since 1917, Goodyear has built over 300 airships, most of them military. One of the newest is the America, which has a bag 192 ft long, is 50 ft in diameter, and holds about $202,000 \text{ ft}^3$ of helium. Her twin 210-hp engines produce a cruising speed of 30–35 mi/hr and a top speed of 50 mi/hr. The 23-ft gondola will hold the pilot and six passengers. Blimps originally were made of rubber-impregnated cotton, but the bag of the America is made of a two-ply fabric of Dacron polyester fiber coated with neoprene. The bag's outer surface is covered with an aluminized coat of Hypalon synthetic rubber. Assuming that the bag size cited is at 1 atm and 25°C , estimate the temperature increase or decrease in the bag at a height of 1000 m (where the pressure is 740 mm Hg) if the bag volume does not change. If the temperature remains 25°C , explain how you might estimate the volume change in the bag.

¹⁸An asterisk designates problems appropriate for computer solution. Also refer to the computer problems after Problem 3.129.

pressure of 150 psia. If you
find the volume of the balloon
is V . How do you solve?

law using the experimental data.
The data taken were:

more Incremental
of vol of balloon, cm³

4.2	4.2
4.9	4.9
5.5	5.5
6.5	6.5
7.0	7.0
9.0	9.0
10.0	10.0
11.5	11.9
13.5	13.5
14.7	14.7

devised at least square
data. What is the
in the balloon?

(see Table 3.1)

a) p^3

of two nonideal gases
in both grams/cm³ of
of \bar{p} and T . Use
 A_0, B_0, C_0, a, b, c

is the mole fraction
been tabulated
v. 46, no. 12. p.
specific volumes in
percent.

Energy Balances

4

How much power will be used in the world 10 years from now?—100 years from now? Forecasts¹ yield a considerable range of disagreement, but one common feature of all the forecasts is that the trend in energy usage is up, and up sharply, as illustrated in Fig. 4.1, for the United States. The combination of growing energy consumption per capita with population growth calls for substantial increases in total energy consumption that dwarfs our current productive facilities. If public expectations make these forecasts come true, the economic allocation of the sources of power and the design of new types of power production facilities will require that engineers continue to play a vital role in our technology.

Another facet of power generation is its relation to our environment. The generation of power by combustion or by nuclear fission by its very nature requires some form of pollution. Fossil- and nuclear-fueled power plants have an impact on land, water, and air resources during the production, processing, utilization, and disposal of the products of the generation of energy. Table 4.1 lists some of these effects. With electrical power usage doubling every 9 years, it is no surprise that the effect on the environment of the generation of energy becomes of considerable concern.

To provide publicly acceptable, effective, and yet economical conversion of energy sources into energy and to properly utilize the energy so generated, you must understand the basic principles underlying the generation, uses, and transformation of energy in its different forms. The answers to questions such as, Is

¹ For example, see *An Energy Model for the United States*, the U.S. Department of the Interior, Government Printing Office, Washington, D.C., 1968.

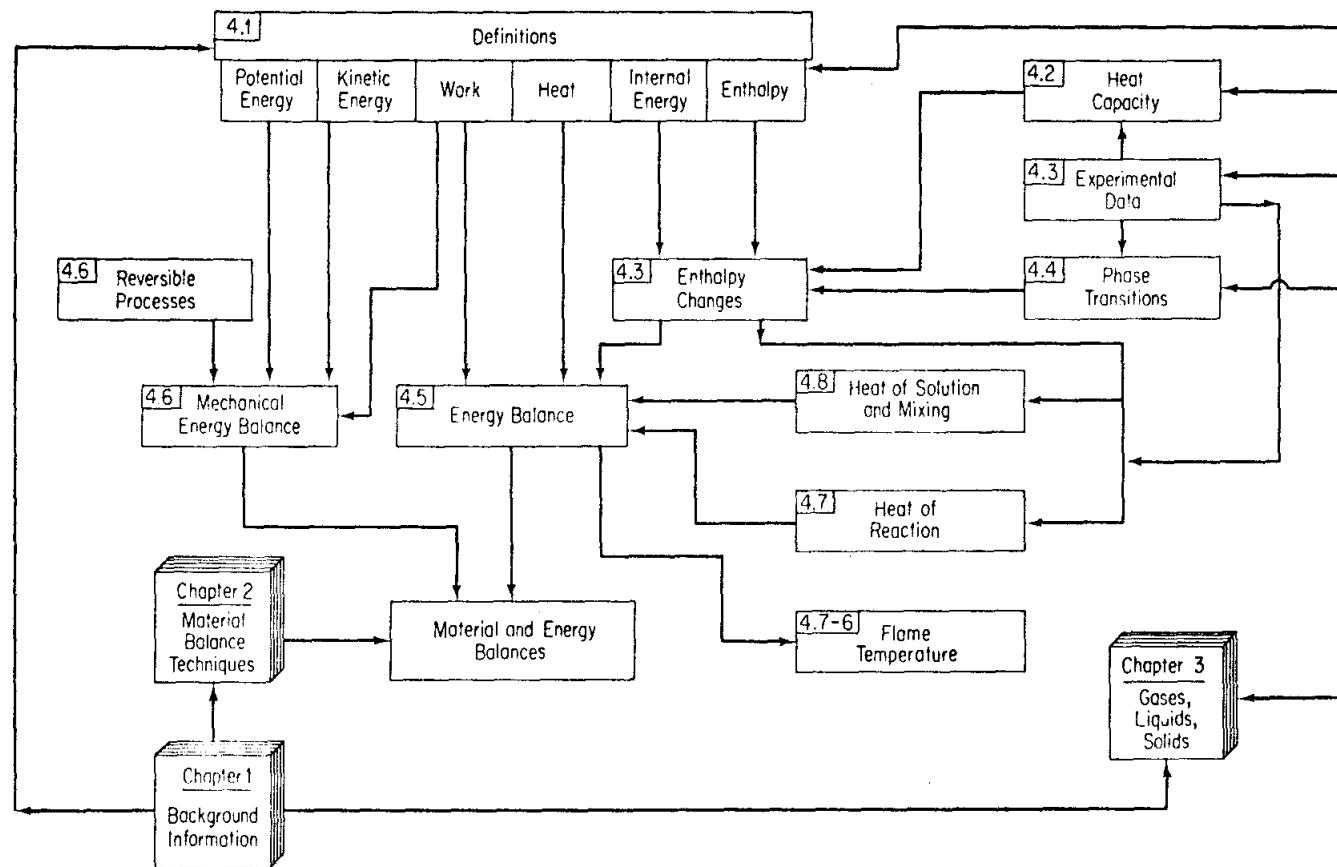


Fig. 4.0. Hierarchy of topics to be studied in this chapter (section numbers are in the upper left-hand corner of the boxes).

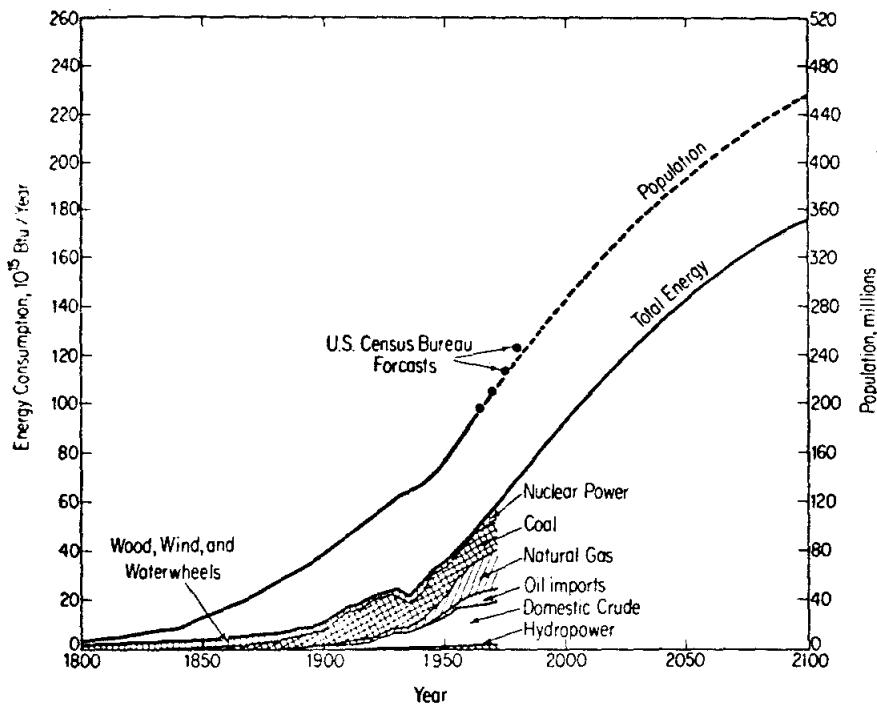


Fig. 4.1. Forecast of future energy consumption.

thermal pollution inherently necessary. What is the most economic source of fuel, What can be done with waste heat, and other related questions can only arise from an understanding of the treatment of energy transfer by natural processes or machines.

In this chapter we shall discuss energy balances together with the accessory background information needed to understand and apply them correctly. Before taking up the energy balance itself, we shall discuss the types of energy that are of major interest to engineers and scientists and some of the methods that are used to measure and evaluate these forms of energy. Our main attention will be devoted to heat, work, enthalpy, and internal energy. Next, the energy balance will be described and applied to practical and hypothetical problems. Finally, we shall discuss the generation of energy through the mechanisms of reaction and how energy generation fits into industrial process calculations. Figure 4.0 shows the relationships among the topics discussed in this chapter and also in previous chapters.

4.1 Concepts and units

When you think about energy, what sort of image comes to mind? Perhaps it is an electric generator whirring at the bottom of a dam, or perhaps a bullet speed-

Fig. 4.0. Hierarchy of topics to be studied in this chapter (section numbers are in the upper left-hand corner of the boxes).

TABLE 4.1 IMPACT OF POWER PLANTS ON THE ENVIRONMENT

Source of Energy	Effect on Land			Effect on Water			Effect on Air		
	Production	Processing	Utilization	Production	Processing	Utilization	Production	Processing	Utilization
Coal	Disturbed land, mine wastes	Solid waste disposal	Ash, slag disposal	Acid mine drainage, silting of streams	Leaching of waste piles	Increased water temps.	Mine fires	Dust	Sulfur oxides, nitrogen oxides, particulate matter
Oil	Pipelines, spills			Oil spills, brines		Increased water temps.			Carbon monoxide, nitrogen oxides, hydrocarbons
Natural gas	Pipelines					Increased water temps.	Waste flaring		
Uranium	Disturbed land		Disposal of radioactive material	Disposal of radioactive material	Increased water temps., accidents			Accidents	

ing through the air. If it is the latter, you instinctively feel that the bullet in motion is different from one at rest. You know a ball of iron in the sun is in a different state than one in the shade. If a gas confined in a cylinder at high pressure is allowed to expand, it can do work against a retarding force, and at the same time the temperature of the gas may fall. However, the same change in the properties of the gas can be brought about in other ways which seem to have very little to do with gas expansion; for example, the temperature of the gas might be reduced by placing the cylinder on a block of ice.

We are able to interpret and explain all these and many other phenomena in terms of the physical quantity *energy*. In Sec. 4.5 we shall relate different types of energy by means of an energy balance. In this section we shall discuss the units used to express energy and shall define several common types of energy. Unfortunately, many of the terms described below are used loosely in our ordinary conversation and writing, whereas others are so fundamental to our thinking that they defy exact definition. You may feel that you understand them from long acquaintance—be sure that you really do.

Table 1.1 lists the units used to express energy in various systems; you can find the conversion factors for these and other units in Appendix A. The calorie is roughly defined as the amount of energy required to raise the temperature of 1 g of water 1°C at a pressure of 1 atm. Similarly, the British thermal unit (Btu) is the amount of energy required to raise 1 lb of water 1°F . However, since the heat capacity of water varies with temperature, it is necessary to be a little more precise in specifying what type of calorie and British thermal unit (Btu) is under consideration (there are four or five common kinds). The type of calorie that forms the basis of the thermochemical properties of substances in this text is the *thermochemical calorie* (equal to 4.184 J). A second type of calorie is the *International Steam Table (I.T.) calorie* (equal to 4.1867 J). The British thermal unit is defined in terms of the calorie:

$$\frac{1 \text{ Btu}}{lb_m} = \frac{1.8 \text{ cal}}{g}$$

You can see that these calories differ by less than one part per thousand, so that for calculations made to slide-rule accuracy (but not for precise measurements) there is hardly any reason for you to consider the differences between them.

Certain terms that have been described in earlier chapters occur repeatedly in this chapter; these terms are summarized below with some elaboration in view of their importance.

(a) *System*. Any arbitrarily specified mass of material or segment of apparatus to which we would like to devote our attention. A system must be defined by surrounding it with a system boundary. A system enclosed by a boundary which prohibits the transfer of mass across the boundary is termed a *closed system*, or *nonflow system*, in distinction to an *open system*, or *flow system*, in which the exchange of mass is permitted. All the mass or apparatus external to

the defined system is termed the *surroundings*. Reexamine some of the example problems in Chap. 2 for illustrations of the location of system boundaries. You should always draw similar boundaries in the solution of your problems, since this will fix clearly the system and surroundings.

(b) *Property*. A characteristic of material which can be measured, such as pressure, volume, or temperature—or calculated, if not directly measured, such as certain types of energy. The properties of a system are dependent on its condition at any given time and not on what has happened to the system in the past.

An *extensive property* (variable, parameter) is one whose value is the sum of the values of each of the subsystems comprising the whole system. For example, a gaseous system can be divided into two subsystems which have volumes or masses different from the original system. Consequently, mass or volume is an extensive property.

An *intensive property* (variable, parameter) is one whose value is not additive and does not vary with the quantity of material in the subsystem. For example, temperature, pressure, density (mass per volume), etc., do not change if the system is sliced in half or if the halves are put together.

Two properties are *independent* of each other if at least one variation of state for the system can be found in which one property varies while the other remains fixed. The set of independent intensive properties necessary and sufficient to fix the state of the system can be ascertained from the phase rule of Sec. 3.7.1.

(c) *State*. Material with a given set of properties at a given time. The state of a system does not depend on the shape or configuration of the system but only on its intensive properties.

Next we shall take up some new concepts, although they may not be entirely new, because you perhaps have encountered some of them before.

(a) *Heat*. In a discussion of *heat* we enter an area in which our everyday use of the term may cause confusion, since we are going to use heat in a very restricted sense when we apply the laws governing energy changes. Heat (Q) is commonly defined as that part of the total energy flow across a system boundary that is caused by a temperature difference between the system and the surroundings. Heat may be exchanged by conduction, convection, or radiation. A more effective general qualitative definition is given by Callen²:

A macroscopic observation [of a system] is a kind of "hazy" observation which discerns gross features but not fine detail. . . . Of the enormous number of atomic coordinates [which can exist], a very few with unique symmetric properties survive the statistical averaging associated with a transition to the macroscopic description [and are macroscopically observable]. Certain of these surviving coordinates are mechanical in

²H. B. Callen, *Thermodynamics*, Wiley, New York, 1960, p. 7.

ine some of the example system boundaries. You of your problems, since

can be measured, such as directly measured, such as are dependent on its related to the system in the

those value is the sum of the system. For example, which have volumes or mass or volume is an

those value is not additive subsystem. For example, do not change if the

last one variation of state while the other remains ary fficient to fix base of Sec. 3.7.1.

a given time. The state of the system but only

they may not be entirely before.

which our everyday use to use heat in a very changes. Heat (Q) is less a system boundary em and the surround- or radiation. A more

“observation the enormous new with unique associated with macroscopically mechanical in

nature [such as volume]. Others are electrical in nature [such as dipole moments]. . . . It is equally possible to transfer energy to the hidden atomic modes of motion [of the atom] as well as to those modes which happen to be macroscopically observable. An energy transfer to the hidden atomic modes is called heat.

To evaluate heat transfer *quantitatively*, unless given *a priori*, you must apply the energy balance that is discussed in Sec. 4.5, and evaluate all the terms except Q . Heat transfer can be *estimated* for engineering purposes by many empirical relations, which can be found in books treating heat transfer or transport processes.

(b) *Work*. Work (W) is commonly defined as energy transferred between the system and its surroundings by means of a vector force acting through a vector displacement on the system boundaries

$$W = \int F dl$$

where F is the direction of dl . However this definition is not exact inasmuch as

- (1) The displacement may not be easy to define.
- (2) The product of $F dl$ does not always result in an equal amount of work.
- (3) Work can be exchanged without a force acting on the system boundaries (such as through magnetic or electric effects).

Since heat and work are by definition mutually exclusive exchanges of energy between the system and the surroundings, we shall qualitatively classify work as energy that can be transferred to or from a mechanical state, or mode, of the system, while heat is the transfer of energy to atomic or molecular states, or modes, which are not macroscopically observable. To measure or evaluate work *quantitatively* by a mechanical device is difficult, so that, unless one of the energy balances in Sec. 4.5 or 4.6 can be applied, in many instances the value of the work done must be given *a priori*.

(c) *Kinetic Energy*. Kinetic energy (K) is the energy a system possesses because of its velocity relative to the surroundings. Kinetic energy may be calculated from the relation

$$K = \frac{1}{2}mv^2 \quad (4.1)$$

or

$$\dot{K} = \frac{1}{2}\dot{m}\dot{v}^2 \quad (4.1a)$$

where the superscript caret (^) refers to the energy per unit mass (or sometimes per mole) and not the total kinetic energy as in Eq. (4.1)

(d) *Potential Energy*. Potential energy (P) is energy the system possesses because of the body force exerted on its mass by a gravitational field with

respect to a reference surface. Potential energy can be calculated from

$$P = mgh \quad (4.2)$$

or

$$\hat{P} = gh \quad (4.2a)$$

where the symbol (\hat{P}) again means potential energy per unit mass (or sometimes per mole).

EXAMPLE 4.1 Energy changes

A 100-lb ball initially on the top of a 15-ft ladder is dropped and hits the ground. See Fig. E4.1. With reference to the ground, determine the following:

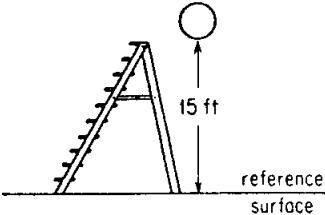


Fig. E4.1.

(a) What is the initial kinetic and potential energy of the ball in $(\text{ft})(\text{lb}_f)$?

$$\text{initial } K = \frac{1}{2}mv^2 = 0$$

$$\text{initial } P = mgh = \frac{100 \text{ lb}_m}{g^f(\text{sec}^2)(\text{lb}_f)} \left| \begin{array}{c} \frac{\text{ft}}{\text{sec}^2} \\ \hline (\text{ft})(\text{lb}_m) \end{array} \right| 15 \text{ ft} = +1500 \text{ (ft)(lb}_f\text{)}$$

(b) What is the final kinetic and potential energy of the ball?

$$\text{final } K = 0$$

$$\text{final } P = 0$$

(c) What is the change in kinetic and potential energy for the process?

$$K_2 - K_1 = \frac{1}{2}m(v_2^2 - v_1^2) = 0$$

$$P_2 - P_1 = mg(h_2 - h_1) = 0 - (+1500) = -1500 \text{ (ft)(lb}_f\text{)}$$

A decrease in potential energy has occurred.

(d) If all the initial potential energy of the ball were somehow converted into heat, how many Btu would this amount to?

$$\frac{1500 \text{ (ft)(lb}_f\text{)}}{778 \text{ (ft)(lb}_f\text{)}} \left| \begin{array}{c} 1 \text{ Btu} \\ \hline 778 \text{ (ft)(lb}_f\text{)} \end{array} \right| = 1.93 \text{ Btu}$$

The system has not been specified in this example. Where would you place the system boundary?

(e) Internal energy
molecular, atomic, microscopic energy exist with which internal energy is macroscopically.

To calculate it can be measured, that it is an exact be described short temperature and s

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By definition of symbol C_v . For that the second subsequently, charac (4.3) as follows

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unit mass (or sometimes

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the following:

the ball in (ft)(lb_f)?

+1500 (ft)(lb_f)

ball?

at the process?

500 (ft)(lb_f)

now converted into heat,

where would you place the

(e) *Internal Energy.* Internal energy (U) is a macroscopic measure of the molecular, atomic, and subatomic energies, all of which follow definite microscopic conservation rules for dynamic systems. Because no instruments exist with which to measure internal energy directly on a macroscopic scale, internal energy is calculated from certain other variables that can be measured macroscopically, such as pressure, volume, temperature, and composition.

To calculate the internal energy per unit mass (\hat{U}) from the variables that can be measured, we make use of a special property of internal energy, namely, that it is an exact differential (because it is a *point* or *state* property, a matter to be described shortly) and, for a pure component, can be expressed in terms of the temperature and specific volume alone. If we say that

$$\hat{U} = \hat{U}(T, \hat{V})$$

by taking the total derivative, we find that

$$d\hat{U} = \left(\frac{\partial \hat{U}}{\partial T}\right)_v dT + \left(\frac{\partial \hat{U}}{\partial \hat{V}}\right)_T d\hat{V} \quad (4.3)$$

By definition $(\partial \hat{U}/\partial T)_v$ is the heat capacity at constant volume, given the special symbol C_v . For most practical purposes in this text the term $(\partial \hat{U}/\partial \hat{V})_T$ is so small that the second term on the right-hand side of Eq. (4.3) can be neglected. Consequently, changes in the internal energy can be computed by integrating Eq. (4.3) as follows:

$$\hat{U}_2 - \hat{U}_1 = \int_{T_1}^{T_2} C_v dT \quad (4.4)$$

Note that you can only calculate *differences* in internal energy, or calculate the internal energy relative to a reference state, but not absolute values of internal energy. Instead of using Eq. (4.4), internal energy changes are usually calculated from enthalpy values, the next topic of discussion.

(f) *Enthalpy.* In applying the energy balance you will encounter a variable which is given the symbol H and the name *enthalpy* (pronounced en'-thal-py). This variable is defined as the combination of two variables which will appear very often in the energy balance

$$H = U + pV \quad (4.5)$$

where p is the pressure and V the volume. [The term enthalpy has replaced the now obsolete terms "heat content" or "total heat," to eliminate any connection whatsoever with heat as defined above in (a).]

To calculate the enthalpy per unit mass, we use the property that the enthalpy is an exact differential. For a pure substance, the enthalpy can be expressed in terms of the temperature and pressure (a more convenient variable for enthalpy than volume). If we let

$$\hat{H} = \hat{H}(T, p)$$

by taking the total derivative of \hat{H} , we can form an expression corresponding to Eq. (4.3):

$$d\hat{H} = \left(\frac{\partial \hat{H}}{\partial T}\right)_p dT + \left(\frac{\partial \hat{H}}{\partial p}\right)_T dp \quad (4.6)$$

By definition $(\partial \hat{H}/\partial T)_p$ is the heat capacity at constant pressure, given the special symbol C_p . For most practical purposes $(\partial \hat{H}/\partial p)_T$ is so small at modest pressures that the second term on the right-hand side of Eq. (4.6) can be neglected. Changes in enthalpy can then be calculated by integration of Eq. (4.6) as follows:

$$\hat{H}_2 - \hat{H}_1 = \int_{T_1}^{T_2} C_p dT \quad (4.7)$$

However, in high-pressure processes the second term on the right-hand side of Eq. (4.6) cannot necessarily be neglected, but must be evaluated from experimental data. One property of ideal gases that should be noted is that their enthalpies and internal energies are functions of temperature only and are not influenced by changes in pressure or volume.

As with internal energy, enthalpy has no absolute value; only changes in enthalpy can be calculated. Often you will use a reference set of conditions (perhaps implicitly) in computing enthalpy changes. For example, the reference conditions used in the steam tables are liquid water at 32°F and its vapor pressure. This does not mean that the enthalpy is actually zero under these conditions but merely that the enthalpy has arbitrarily been assigned a value of zero at these conditions. In computing enthalpy changes, the reference conditions cancel out as can be seen from the following:

<i>initial state of system</i>	<i>final state of system</i>
$\text{enthalpy} = \hat{H}_1 - \hat{H}_{\text{ref}}$	$\text{enthalpy} = \hat{H}_2 - \hat{H}_{\text{ref}}$
<i>Net enthalpy change</i> = $(\hat{H}_2 - \hat{H}_{\text{ref}}) - (\hat{H}_1 - \hat{H}_{\text{ref}}) = \hat{H}_2 - \hat{H}_1$	

(g) *Point, or State, Functions.* The variables enthalpy and internal energy are called *point functions*, or *state variables*, which means that in their differential form they are exact differentials.³ Figure 4.2 illustrates geometrically the concept

³To test if a differential dS is exact, where

$$dS = R dx + Z dy$$

form the partial derivatives $(\partial R/\partial y)_x$ and $(\partial Z/\partial x)_y$, and verify whether

$$\left(\frac{\partial R}{\partial y}\right)_x = \left(\frac{\partial Z}{\partial x}\right)_y$$

If so, dS is exact; if not, dS is not exact. The statement that dS is an exact differential is completely equivalent to saying that S is independent of path. As an example, applying the test to Eq. (4.6) yields

$$\frac{\partial}{\partial p} \left(\frac{\partial \hat{H}}{\partial T} \right)_p = ? \quad \frac{\partial}{\partial T} \left(\frac{\partial \hat{H}}{\partial p} \right)_T$$

or

$$\left(\frac{\partial^2 \hat{H}}{\partial p \partial T} \right) = \left(\frac{\partial^2 \hat{H}}{\partial T \partial p} \right)$$

as expected.

of state variable. In process shown by the wiggly line, ΔH can be calculated by any other route, and still give the same result. This is shown by the wiggly line ΔH between two final states of the system. A passenger flying from New York to Paris, for example, may travel by air, ship, or land, and then at constant temperature. The path taken does not matter as long as the end point is the same. This is analogous to the case of an airplane passenger who flies from New York but is detoured because of bad weather. The gasoline consumed in the two cases is the same. The cost of the trip, however, will depend on the route taken. The gasoline cost, in analogous fashion, depends on the path taken. The properties we deal with, however, are point functions and are independent of path, regardless of path. If the passenger goes from New York to Paris and back, the passenger's enthalpy changes by zero on the return trip, and back to state 1 again. The enthalpy change is zero.

All the intensive properties we have discussed up to now are point functions and are independent of path. This is what we can say, for example, about enthalpy.

Always keep in mind that enthalpy is an exact differential, calculated by taking the partial derivative with respect to initial state, regardless of path.

Before formulating the differential equation of state, let us detail the calculation of enthalpy.

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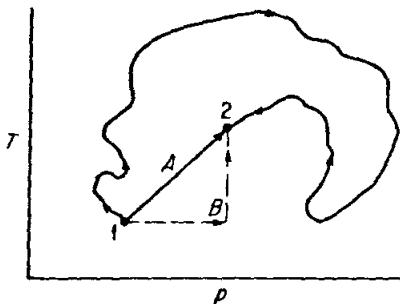


Fig. 4.2. Point function.

of state variable. In proceeding from state 1 to state, 2, the actual process is shown by the wiggly line. However, you may calculate $\Delta\hat{H}$ by route A or B, or any other route, and still obtain the same net enthalpy change as for the route shown by the wiggly line. The change of enthalpy depends only on the initial and final states of the system. A process that proceeds first at constant pressure and then at constant temperature from 1 to 2 will yield exactly the same $\Delta\hat{H}$ as one that takes place first at constant temperature and then at constant pressure as long as the end point is the same. The concept of the point function is the same as that of an airplane passenger who plans to go straight to Chicago from New York but is detoured because of bad weather by way of Cincinnati. His trip costs him the same whatever way he flies, and he eventually arrives at his destination. The gasoline consumption of the plane may vary considerably, and in analogous fashion heat (Q) or work (W), the two "path" functions with which we deal, may vary depending on the specific path chosen, while $\Delta\hat{H}$ is the same regardless of path. If the plane were turned back by bad weather and landed at New York, the passenger might be irate, but at least he could get his money back. Thus $\Delta\hat{H} = 0$ if a cyclical process is involved which goes from state 1 to 2 and back to state 1 again, or

$$\oint d\hat{H} = 0$$

All the intensive properties we shall work with, such as P , T , \hat{U} , p , \hat{H} , etc., are point functions and depend only on the state of the substance of interest, so that we can say, for example, that

$$\oint dT = 0$$

$$\oint d\hat{U} = 0$$

Always keep in mind that the values for a difference in a point function can be calculated by taking the value in the final state and subtracting the value in the initial state, regardless of the actual path.

Before formulating the general energy balance, we shall discuss in some detail the calculation of enthalpy changes and provide some typical examples of

such calculations. The discussion will be initiated with consideration of the heat capacity C_p .

4.2 Heat capacity

The two heat capacities have been defined as

$$(a) \quad C_p = \left(\frac{\partial \hat{H}}{\partial T} \right)_p$$

$$(b) \quad C_v = \left(\frac{\partial \hat{U}}{\partial T} \right)_v$$

To give these two quantities some physical meaning, you can think of them as representing the amount of energy required to increase the temperature of a substance by 1 degree, energy which might be provided by heat transfer in certain specialized processes. To determine from experiment values of C_p (or C_v), the enthalpy (or internal energy) change must first be calculated from the general energy balance, Eq. (4.24), and then the heat capacity evaluated from Eq. (4.7) [or (4.4)] for small enthalpy changes.

We can provide a rough illustration of the calculation of C_p using data from the steam tables. We shall take the enthalpies for water vapor at 1 psia and at 300° and 350°F. Clearly the temperature difference is far too large to precisely approximate a derivative, but it should suffice under the selected conditions to give a C_p valid to two significant figures:

$$\Delta \hat{H} = (1217.3 - 1194.4) = 22.9 \text{ Btu/lb}$$

$$C_p = \left(\frac{\partial \hat{H}}{\partial T} \right)_p \approx \left(\frac{\Delta \hat{H}}{\Delta T} \right)_p = \frac{22.9}{50} = 0.46 \frac{\text{Btu}}{(\text{lb})(\Delta^{\circ}\text{F})}$$

In line with the definition of the calorie or Btu presented in the previous section, we can see that the heat capacity can be expressed in various systems of units and still have the same numerical value; for example, heat capacity may be expressed in the units of

$$\frac{\text{cal}}{(\text{g mole})(^{\circ}\text{C})} = \frac{\text{kcal}}{(\text{kg mole})(^{\circ}\text{C})} = \frac{\text{Btu}}{(\text{lb mole})(^{\circ}\text{F})}$$

Alternatively, heat capacity may be in terms of

$$\frac{\text{cal}}{(\text{g})(^{\circ}\text{C})} = \frac{\text{Btu}}{(\text{lb})(^{\circ}\text{F})} \quad \text{or} \quad \frac{\text{J}}{(\text{kg})(^{\circ}\text{K})}$$

Note that

$$\frac{1 \text{ Btu}}{(\text{lb})(^{\circ}\text{F})} = \frac{4.184 \text{ J}}{(\text{g})(^{\circ}\text{K})}$$

and that the heat capacity of water in the SI system is 4184 J/(kg)(°K). These relations are worth memorizing. Note that in each system of units the heat

capacity consists of a temperature difference.

The heat capacity represented figuratively by the absolute temperature is zero. As the temperature point is reached, the heat capacities shown also on the graph.

Fig. 4.3. Heat capacity.

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capacity consists of energy divided by the product of the mass times the temperature difference.

The heat capacity over a wide temperature range for a pure substance is represented figuratively in Fig. 4.3, where the heat capacity is plotted as a function of the absolute temperature. We see that at zero degrees absolute the heat capacity is zero. As the temperature rises, the heat capacity also increases until a certain point is reached at which a phase transition takes place. The phase transitions are shown also on a related p - T diagram in Fig. 4.4 for water. The phase transi-

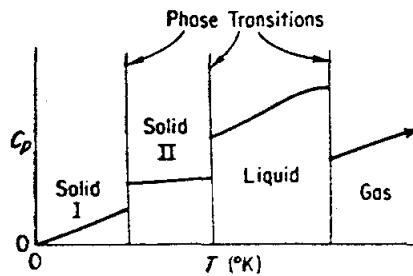


Fig. 4.3. Heat capacity as a function of temperature for a pure substance.

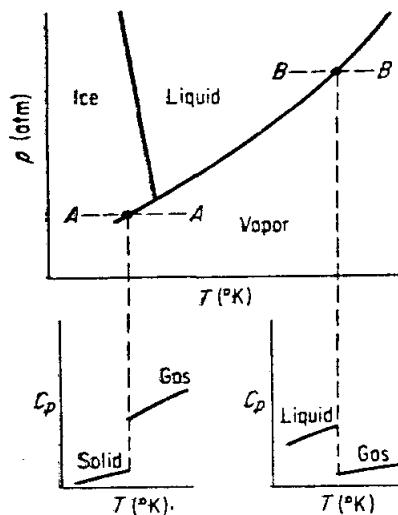


Fig. 4.4. Heat capacity and phase transitions.

tion may take place between two solid states, or between a solid and a liquid state, or between a solid and a gaseous state, or between a liquid and a gaseous state. Figure 4.3 shows first a transition between solid state I and solid state II, then the transition between solid state II and the liquid state, and finally the transition between the liquid and the gaseous state. Note that the heat capacity is a continuous function *only* in the region between the phase transitions; con-

sequently it is not possible to have a heat capacity equation for a substance which will go from absolute zero up to any desired temperature. What the engineer does is to determine experimentally the heat capacity between the temperatures at which the phase transitions occur, fit the data with an equation, and then stop and determine a new heat capacity equation for the next range of temperatures between the succeeding phase transitions.

Experimental evidence indicates that the heat capacity of a substance is not constant with temperature, although at times we may assume that it is constant in order to get approximate results. For the ideal monoatomic gas, of course, the heat capacity at constant pressure is constant even though the temperature varies (see Table 4.2). For typical real gases, see Fig. 4.5; the heat capacities shown are for pure components. For ideal mixtures, the heat capacities of the individual components may be computed separately and each component handled as if it were alone (see Sec. 4.8 for additional details).

TABLE 4.2 HEAT CAPACITIES OF IDEAL GASES

Type Molecule	Approximate Heat Capacity (C_p) High Temperature (Translational, Rotational, and Vibrational Degrees of Freedom)	Room Temperature (Translational and Rotational Degrees of Freedom Only)
Monoatomic	$\frac{3}{2}R$	$\frac{3}{2}R$
Polyatomic, linear	$(3n - \frac{5}{2})R$	$\frac{5}{2}R$
Polyatomic, nonlinear	$(3n - 2)R$	$4R$

n = number of atoms per molecule
R = gas constant defined in Sec. 3.1.

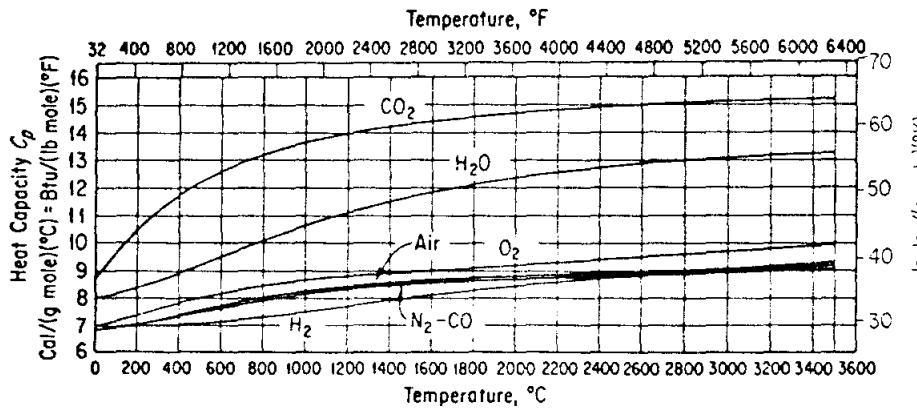


Fig. 4.5. Heat capacity curves for the combustion gases.

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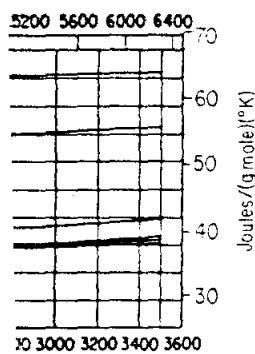
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y of a substance is not assume that it is constant atomic gas, of course, though the temperature ; the heat capacities heat capacities of the and each component (details).

Heat Capacity (C_p) Room Temperature (Translational rotational degrees of Freedom Only)
$\frac{3}{2}R$
$\frac{5}{2}R$
$4R$



gases.

Most of the equations for the heat capacities of solids, liquids, and gases are empirical. We usually express the heat capacity at constant pressure C_p as a function of temperature in a power series, with constants a , b , c , etc.; for example,

$$C_p = a + bT$$

or

$$C_p = a + bT + cT^2$$

where the temperature may be expressed in degrees Centigrade, degrees Fahrenheit, degrees Rankine, or degrees Kelvin. If C_p is expressed in the form of

$$C_p = a + bT + cT^{-1/2}$$

$$C_p = a + bT - cT^{-2}$$

or a form such that we are dividing by T , then it is necessary to use degrees Kelvin or degrees Rankine in the heat capacity equations, because if degrees Centigrade or Fahrenheit were to be used, we might be dividing at some point in the temperature range by zero. Since these heat capacity equations are valid only over moderate temperature ranges, it is possible to have equations of different types represent the experimental heat capacity data with almost equal accuracy. The task of fitting heat capacity equations to heat capacity data is greatly simplified these days by the use of digital computers, which can determine the constants of best fit by means of a standard prepared program and at the same time determine how precise the predicted heat capacities are. Heat capacity information can be found in Appendix E. The change of C_p with pressure at high pressures is beyond the scope of our work here. Details can be found in several of the references listed at the end of the chapter.

Specific heat is a term similar to *specific gravity* in that it is a ratio of the heat capacity of one substance to the heat capacity of a reference substance.⁴ The common reference substance for solids and liquids is water, which is assigned the heat capacity of 1.0 at about 17°C. Since the heat capacity of water is approximately unity in the cgs and American engineering systems, the numerical values of specific heats and heat capacities are about the same although their units are not. For example, the units of the ratio of the heat capacity of substance A to that of water are

$$\frac{C_{p,A}}{C_{p,H_2O}} = \frac{\text{Btu}/(\text{lb}_A)({}^\circ\text{F})}{\text{Btu}/(\text{lb}_{H_2O})({}^\circ\text{F})}$$

EXAMPLE 4.2 Heat capacity equation

The heat capacity equation for CO_2 gas is

$$C_p = 6.393 + 10.100T \times 10^{-3} - 3.405T^2 \times 10^{-6}$$

⁴In some fields of engineering and science, specific heat means heat capacity based on a pound or gram.

with C_p expressed in cal/(g mole)(°K) and T in °K. Convert this equation into a form so that the heat capacity will be expressed over the entire temperature range in

- Cal/(g mole)(°C) with T in °C and ΔT in °C.
- Btu/(lb mole)(°F) with T in °F and ΔT in °F.
- Cal/(g mole)(°K) with T in °F and ΔT in °K.
- J/(kg mole)(°K) with T in °K and ΔT in °K.

Solution:

Changing a heat capacity equation from one set of units to another is merely a problem in the conversion of units. To avoid confusion in the conversion, you must remember to distinguish between the temperature symbols that represent temperature and the temperature symbols that represent temperature difference even though the same symbol often is used for each concept. In the conversions below we shall distinguish between the temperature and the temperature difference for clarity.

- The heat capacity equation with T in °C and ΔT in °C is

$$\begin{aligned} C_p \frac{\text{cal}}{(\text{g mole})(\Delta^\circ\text{C})} &= 6.393 \frac{\text{cal}}{(\text{g mole})(\Delta^\circ\text{K})} \left| \begin{array}{c} 1 \Delta^\circ\text{K} \\ 1 \Delta^\circ\text{C} \end{array} \right. \\ &\quad + 10.100 \times 10^{-3} \frac{\text{cal}}{(\text{g mole})(\Delta^\circ\text{K})(^\circ\text{K})} \left| \begin{array}{c} 1 \Delta^\circ\text{K} \\ 1 \Delta^\circ\text{C} \end{array} \right| (T_c + 273)^\circ\text{K} \\ &\quad - 3.405 \times 10^{-6} \frac{\text{cal}}{(\text{g mole})(\Delta^\circ\text{K})(^\circ\text{K})^2} \left| \begin{array}{c} 1 \Delta^\circ\text{K} \\ 1 \Delta^\circ\text{C} \end{array} \right| (T_c + 273)^2 \text{K}^2 \\ &= 6.393 + 10.100 \times 10^{-3} T_c + 2.757 - 3.405 \times 10^{-6} T_c^2 \\ &\quad - 1.860 \times 10^{-3} T_c - 0.254 \\ &= 8.896 + 8.240 \times 10^{-3} T_c - 3.405 \times 10^{-6} T_c^2 \end{aligned}$$

(b)

$$\begin{aligned} C_p \frac{\text{Btu}}{(\text{lb mole})(\Delta^\circ\text{F})} &= 6.393 \frac{\text{cal}}{(\text{g mole})(\Delta^\circ\text{K})} \left| \begin{array}{c} 454 \text{ g moles} \\ 1 \text{ lb mole} \end{array} \right| \left| \begin{array}{c} 1 \text{ Btu} \\ 252 \text{ cal} \end{array} \right| \left| \begin{array}{c} 1 \Delta^\circ\text{K} \\ 1.8 \Delta^\circ\text{F} \end{array} \right. \\ &\quad + 10.100 \times 10^{-3} \frac{\text{cal}}{(\text{g mole})(\Delta^\circ\text{K})(^\circ\text{K})} \left| \begin{array}{c} 454 \text{ g moles} \\ 1 \text{ lb mole} \end{array} \right| \left| \begin{array}{c} 1 \text{ Btu} \\ 252 \text{ cal} \end{array} \right| \left| \begin{array}{c} 1 \Delta^\circ\text{K} \\ 1.8 \Delta^\circ\text{F} \end{array} \right| \left[273 + \frac{T_f - 32}{1.8} \right]^\circ\text{K} \\ &\quad - 3.405 \times 10^{-6} \frac{\text{cal}}{(\text{g mole})(\Delta^\circ\text{K})(^\circ\text{K})^2} \left| \begin{array}{c} 454 \text{ g moles} \\ 1 \text{ lb mole} \end{array} \right| \left| \begin{array}{c} 1 \text{ Btu} \\ 252 \text{ cal} \end{array} \right| \left| \begin{array}{c} 1 \Delta^\circ\text{K} \\ 1.8 \Delta^\circ\text{F} \end{array} \right| \left[273 + \frac{T_f - 32}{1.8} \right]^2 \text{K}^2 \\ &= 6.393 + 10.100 \times 10^{-3} [273 + (T_f - 32)/1.8] \\ &\quad - 3.405 \times 10^{-6} [273 + (T_f - 32)/1.8]^2 \\ &= 6.393 + 2.575 + 5.61 \times 10^{-3} T_f - 0.222 \\ &\quad - 0.964 \times 10^{-3} T_f^2 - 1.05 \times 10^{-6} T_f^2 \\ &= 8.746 + 4.646 \times 10^{-3} T_f - 1.05 \times 10^{-6} T_f^2 \end{aligned}$$

Note: In Sec. 1.4 we have developed and made use of the expression

$$T_{\text{K}} = 273 + \frac{T_f - 32}{1.8}$$

If the equation for part (a) were available, the solution to part (b) would be simplified by employing it. For example, we use

$$C_p \frac{\text{cal}}{(\text{g mole})(\Delta^\circ\text{C})} = 8.896 + 8.240 \times 10^{-3} T_c - 3.405 \times 10^{-6} T_c^2$$

and convert it into

$$\begin{aligned} C_p \frac{\text{Btu}}{(\text{lb mole})(\Delta^\circ\text{F})} &= 8.240 \times 10^{-3} T_c + 8.896 \\ &\quad - 3.405 \times 10^{-6} T_c^2 \end{aligned}$$

(c) Since

the equation deve

(d)

$$C_p \frac{\text{J}}{(\text{kg mole})(\Delta^\circ\text{K})} =$$

EXAMPLE 4.3

Show that C_p

Solution:

The heat cap

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For the ideal gas,

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is

$$(T_C + 273)^\circ K$$

$$T_C = -73^\circ K^2$$

$$\times 10^{-3} T_C$$

$$\times 10^{-3} T_C - 0.254$$

$$\frac{\Delta^\circ K}{\Delta^\circ F}$$

$$-73 + \frac{T_F - 32}{1.8}^\circ K^2$$

$$-32/1.8]^\circ K^2$$

$$0^{-6} T_F^2$$

expression

(b) would be sim-

$$10^{-1}$$

and convert it into

$$\begin{aligned} C_p & \frac{\text{Btu}}{(\text{lb mole})(\Delta^\circ F)} = \frac{8.896 \text{ cal}}{(\text{g mole})(\Delta^\circ C)} \left| \frac{454 \text{ g moles}}{1 \text{ lb mole}} \right| \frac{1 \text{ Btu}}{252 \text{ cal}} \left| \frac{1 \Delta^\circ C}{1.8 \Delta^\circ F} \right| \\ & = 8.240 \times 10^{-3} \frac{\text{cal}}{(\text{g mole})(\Delta^\circ C)(^\circ C)} \left| \frac{454 \text{ g moles}}{1 \text{ lb mole}} \right| \frac{1 \text{ Btu}}{252 \text{ cal}} \left| \frac{1 \Delta^\circ C}{1.8 \Delta^\circ F} \right| \left[(T_F - 32) / 1.8 \right]^\circ C \\ & = 3.405 \times 10^{-6} \frac{\text{cal}}{(\text{g mole})(\Delta^\circ C)(^\circ C^2)} \left| \frac{454 \text{ g moles}}{1 \text{ lb mole}} \right| \frac{1 \text{ Btu}}{252 \text{ cal}} \left| \frac{1 \Delta^\circ C}{1.8 \Delta^\circ F} \right| \left[(T_F - 32) / 1.8 \right]^\circ C^2 \\ & = 8.746 + 4.646 \times 10^{-3} T_F - 1.05 \times 10^{-6} T_F^2 \end{aligned}$$

(c) Since

$$\frac{\text{Btu}}{(\text{lb mole})(\Delta^\circ F)} = \frac{\text{cal}}{(\text{g mole})(\Delta^\circ K)}$$

the equation developed in part (b) gives the heat capacity in the desired units.

(d)

$$\begin{aligned} C_p & \frac{\text{J}}{(\text{kg mole})(\Delta^\circ K)} = 6.93 \frac{\text{cal}}{(\text{g mole})(\Delta^\circ K)} \left| \frac{4.184 \text{ J}}{1 \text{ cal}} \right| \frac{1000 \text{ g}}{1 \text{ kg}} \\ & + 10.1000 \times 10^{-3} \frac{\text{cal}}{(\text{g mole})(\Delta^\circ K)(^\circ K)} \left| \frac{4.184 \text{ J}}{1 \text{ cal}} \right| \frac{1000 \text{ g}}{1 \text{ kg}} \left| T_K \right| \\ & - 3.405 \times 10^{-6} \frac{\text{cal}}{(\text{g mole})(^\circ K)^2 (\Delta^\circ K)} \left| \frac{4.184 \text{ J}}{1 \text{ cal}} \right| \frac{1000 \text{ g}}{1 \text{ kg}} \left| T_K^2 \right| \\ & = 2.90 \times 10^4 + 42.27 T_K - 1.425 \times 10^{-2} T_K^2 \end{aligned}$$

EXAMPLE 4.3 Heat capacity of the ideal gas

Show that $C_p = C_v + \hat{R}$ for the ideal monoatomic gas.

Solution:

The heat capacity at constant volume is defined as

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v \quad (a)$$

For any gas,

$$\begin{aligned} C_p & = \left(\frac{\partial \hat{H}}{\partial T} \right)_p = \left[\frac{\partial U + p\hat{V}}{\partial T} \right]_p = \left[\frac{\partial U + p\partial \hat{V}}{\partial T} \right]_p \\ & = \left(\frac{\partial U}{\partial T} \right)_p + p \left(\frac{\partial \hat{V}}{\partial T} \right)_p \end{aligned} \quad (b)$$

For the *ideal gas*, since \hat{U} is a function of temperature only,

$$\left(\frac{\partial U}{\partial T} \right)_p = \left(\frac{\partial \hat{U}}{\partial T} \right)_p = C_v \quad (c)$$

and from $p\hat{V} = \hat{R}T$ we can calculate

$$\left(\frac{\partial \hat{V}}{\partial T} \right)_p = \frac{\hat{R}}{p} \quad (d)$$

so that

$$C_p = C_v + \hat{R}$$

4.2.1 Estimation of Heat Capacities. We now mention a few ways by which to estimate heat capacities of solids, liquids and gases. For the most accurate results, you should employ actual experimental heat capacity data or equations derived from such data in your calculations. However, if experimental data are not available, there are a number of equations that you may use which give estimates of values for the heat capacities.

(a) *Solids.* Only very rough approximations of solid heat capacities can be made. Kopp's rule (1864) should only be used as a last resort when experimental data cannot be located or new experiments carried out. Kopp's rule states that at room temperature the sum of the heat capacities of the individual elements is approximately equal to the heat capacity of a solid compound. For elements below potassium, numbers have been assigned from experimental data for the heat capacity for each element as shown in Table 4.3. For liquids Kopp's rule can be applied with a modified series of values for the various elements, as shown in Table 4.3

TABLE 4.3 VALUES FOR MODIFIED KOPP'S RULE

Atomic Heat Capacity at 20°C in cal/(g atom)(°C)		
Element	Solids	Liquids
C	1.8	2.8
H	2.3	4.3
B	2.7	4.7
Si	3.8	5.8
O	4.0	6.0
F	5.0	7.0
P or S	5.4	7.4
All others	6.2	8.0

EXAMPLE 4.4 Use of Kopp's rule

Determine the heat capacity at room temperature of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$.

Basis: 1 g mole $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$

$$\text{Na} \quad 2 \times 6.2 = 12.4 \text{ cal}/(\text{g atom})(\text{°C})$$

$$\text{S} \quad 1 \times 5.4 = 5.4$$

$$\text{O} \quad 14 \times 4.0 = 56.0$$

$$\text{H} \quad 20 \times 2.3 = 46.0$$

$$119.8 \text{ cal}/(\text{g mole})(\text{°C})$$

The experimental value is about 141 cal/(g mole)(°C), so you can see that Kopp's rule does not yield very accurate estimates.

mention a few ways by which heat capacities of gases can be estimated when experimental data or Kopp's rule states that at 25°C the heat capacity of individual elements is zero. For elements for which experimental data for the liquids Kopp's rule can be used, as shown in

heat capacities can be estimated when experimental data or Kopp's rule states that at 25°C the heat capacity of individual elements is zero. For elements for which experimental data for the liquids Kopp's rule can be used, as shown in

(b) Liquids

(1) *Aqueous solutions.* For the special but very important case of aqueous solutions, a rough rule in the absence of experimental data is to use the heat capacity of the water only. For example, a 21.6 percent solution of NaCl is assumed to have a heat capacity of 0.784 cal/(g)(°C); the experimental value at 25°C is 0.806 cal/(g)(°C).

(2) *Hydrocarbons.* An equation for the heat capacity of liquid hydrocarbons and petroleum products recommended by Fallon and Watson⁵ is

$$C_p = [(0.355 + 0.128 \times 10^{-2} \text{ }^{\circ}\text{API}) + (0.503 + 0.117 \times 10^{-2} \text{ }^{\circ}\text{API}) \times 10^{-3}t][0.05K + 0.41]$$

where ${}^{\circ}\text{API} = \frac{141.5}{\text{sp gr } (60^{\circ}\text{F}/60^{\circ}\text{F})} - 131.5$ and is a measure of specific gravity.
 $t = {}^{\circ}\text{F}$

K = The Universal Oil Products characterization factor which has been related to six easily applied laboratory tests. This factor is not a fundamental characteristic but is easy to determine experimentally. Values of K range from 10.1 to 13.0 and are discussed in Appendix K.

$$C_p = \text{Btu/(lb)}({}^{\circ}\text{F})$$

(3) *Organic liquids.* A simple and reasonably accurate relation between C_p and molecular weight is

$$C_p = kM^a$$

where M is the molecular weight and k and a are constants. Pachaiyappan et al.⁶ give a number of values of the set (k, a). For example,

compounds	k	a
Alcohols	0.85	-0.1
Acids	0.91	-0.152
Ketones	0.587	-0.0135
Esters	0.60	-0.0573
Hydrocarbons, aliphatic	0.873	-0.113

Gold⁷ reviews a number of estimation methods for liquids and indicates their precision.

(c) Gases and Vapors

(1) *Petroleum vapors.* The heat capacity of petroleum vapors can be estimated from⁸

$$C_p = \frac{(4.0 - s)(T + 670)}{6450}$$

⁵J. F. Fallon and K. M. Watson, *Natl. Petrol. News, Tech. Sec.* (June 7, 1944).

⁶V. Pachaiyappan, S. H. Ibrahim, and N. R. Kuloor, *Chem. Eng.*, p. 241 (Oct 9, 1967).

⁷P. I., Gold, *Chem. Eng.*, p. 130 (April 7, 1969).

⁸Bahlke and Kay, *Ind. Eng. Chem.*, v. 21, p. 942 (1929).

where C_p is in Btu/(lb)(°F), T is in °F, and s is the sp gr at 60°F/60°F, with air as the reference gas.

(2) Kothari and Doraiswamy⁹ recommend plotting

$$C_p = a + b \log_{10} T,$$

Given two values of C_p at known temperatures, values of C_p can be predicted at other temperatures with good precision. The most accurate methods of estimating heat capacities of vapors are those of Dobratz¹⁰ based on spectroscopic data and generalized correlations based on reduced properties¹¹.

Additional methods of estimating solid and liquid heat capacities may be found in Reid and Sherwood,¹¹ who compare various techniques we do not have the space to discuss and make recommendations as to their use.

4.3 Calculation of enthalpy changes without change of phase

Now that we have examined sources for heat capacity values, we can turn to the details of the calculation of enthalpy changes. If we omit for the moment consideration of phase changes and examine solely the problem of how to calculate enthalpy changes from heat capacity data, we can see that in general if we use Eq. (4.7), $\Delta\hat{H}$ is the area under the curve in Fig. 4.6:

$$\int_{T_1}^{T_2} d\hat{H} = \Delta\hat{H} = \int_{T_1}^{T_2} C_p dT$$

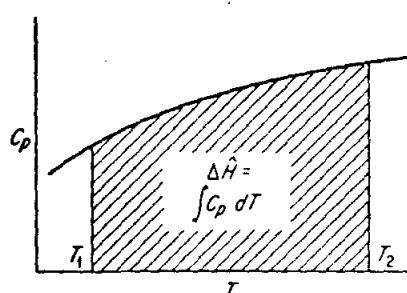


Fig. 4.6. Calculation of enthalpy change.

⁹M. S. Kothari and L. K. Doraiswamy, *Hydrocarbon Processing and Petroleum Refiner*, v. 43, no. 3, p. 133 (1964).

¹⁰C. J. Dobratz, *Ind. Eng. Chem.*, v. 33, p. 759 (1941).

¹¹R. C. Reid and T. K. Sherwood, *The Properties of Gases and Liquids*, 2nd ed., McGraw-Hill, New York, 1966.

-0°F, with air as

be predicted at
methods of esti-
on spectroscopic
11.

capacities may be
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(The technique of graphical integration is illustrated in Example 6.6.) If our heat capacity is expressed in the form $C_p = a + bT + cT^2$, then

$$\Delta \hat{H} = \int_{T_1}^{T_2} (a + bT + cT^2) dT = a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) + \frac{c}{3}(T_2^3 - T_1^3) \quad (4.8)$$

If a different functional form of the heat capacity is available, the integration can still be handled readily.

It is also possible to define a mean heat capacity, which, if known, provides a quick and convenient way of calculating enthalpy changes. The *mean heat capacity*, C_{p_m} , is defined as the enthalpy change divided by the temperature difference for this change, or

$$C_{p_m} = \frac{\hat{H}_2 - \hat{H}_1}{T_2 - T_1} \quad (4.9)$$

Then it is possible to compute an enthalpy change, if C_{p_m} is available, as

$$\Delta \hat{H} = C_{p_m} \Delta T = C_{p_m}(T_2 - T_1) \quad (4.10)$$

where C_{p_m} is between T_1 and T_2 .

TABLE 4.4a MEAN HEAT CAPACITIES OF COMBUSTION GASES
[cal/(g mole)(°C)]

(To convert to J/(kg mole)(°K), multiply by 4184.)

Reference Temperature: 0°C; Pressure: 1 atm

°C	N ₂	O ₂	Air	H ₂	CO	CO ₂	H ₂ O
0	6.959	6.989	6.946	6.838	6.960	8.595	8.001
18	6.960	6.998	6.949	6.858	6.961	8.706	8.009
25	6.960	7.002	6.949	6.864	6.962	8.716	8.012
100	6.965	7.057	6.965	6.926	6.973	9.122	8.061
200	6.985	7.154	7.001	6.955	7.050	9.590	8.150
300	7.023	7.275	7.054	6.967	7.057	10.003	8.256
400	7.075	7.380	7.118	6.983	7.120	10.360	8.377
500	7.138	7.489	7.190	6.998	7.196	10.680	8.507
600	7.207	7.591	7.266	7.015	7.273	10.965	8.644
700	7.277	7.684	7.340	7.036	7.351	11.221	8.785
800	7.350	7.768	7.414	7.062	7.428	11.451	8.928
900	7.420	7.845	7.485	7.093	7.501	11.68	9.070
1000	7.482	7.916	7.549	7.128	7.570	11.85	9.210
1100	7.551	7.980	7.616	7.165	7.635	12.02	9.348
1200	7.610	8.039	7.674	7.205	7.688	12.17	9.482
1300	7.665	8.094	7.729	7.227	7.752	12.32	9.613
1400	7.718	8.146	7.781	7.260	7.805	12.44	9.740
1500	7.769	8.192	7.830	7.296	7.855	12.56	9.86

SOURCE: Page 30 of Reference 12 in Table 4.6.

If the heat capacity can be expressed as a power series, $C_p = a + bT + cT^2$, then $C_{\bar{p}_m}$ is

$$\begin{aligned} C_{\bar{p}_m} &= \frac{\int_{T_1}^{T_2} C_p dT}{\int_{T_1}^{T_2} dT} = \frac{\int_{T_1}^{T_2} (a + bT + cT^2) dT}{T_2 - T_1} \\ &= \frac{a(T_2 - T_1) + (b/2)(T_2^2 - T_1^2) + (c/3)(T_2^3 - T_1^3)}{T_2 - T_1} \end{aligned} \quad (4.11)$$

By choosing 0°F or 0°C as the reference temperature for $C_{\bar{p}_m}$, you can simplify the expression for $C_{\bar{p}_m}$. Tables 4.4a and 4.4b lists mean heat capacities for combustion gases based on the same reference point (0°C) for two different temperature scales.

TABLE 4.4b MEAN HEAT CAPACITIES OF COMBUSTION GASES
[Btu/(lb mole)(°F)]
Reference Temperature: 32°F; Pressure: 1 atm

°F	N ₂	O ₂	Air	H ₂	CO	CO ₂	H ₂ O
32	6.959	6.989	6.946	6.838	6.960	8.595	8.001
60	6.960	6.996	6.948	6.855	6.961	8.682	8.008
77	6.960	7.002	6.949	6.864	6.962	8.715	8.012
100	6.961	7.010	6.952	6.876	6.964	8.793	8.019
200	6.964	7.052	6.963	6.921	6.972	9.091	8.055
300	6.970	7.102	6.978	6.936	6.987	9.362	8.101
400	6.984	7.159	7.001	6.942	7.007	9.612	8.154
500	7.002	7.220	7.028	6.961	7.033	9.844	8.210
600	7.026	7.283	7.060	6.964	7.065	10.060	8.274
700	7.055	7.347	7.096	6.978	7.101	10.262	8.341
800	7.087	7.409	7.134	6.981	7.140	10.450	8.411
900	7.122	7.470	7.174	6.984	7.182	10.626	8.484
1000	7.158	7.529	7.214	6.989	7.224	10.792	8.558
1100	7.197	7.584	7.256	6.993	7.268	10.948	8.634
1200	7.236	7.637	7.298	7.004	7.312	11.094	8.712
1300	7.277	7.688	7.341	7.013	7.355	11.232	8.790
1400	7.317	7.736	7.382	7.032	7.398	11.362	8.870
1500	7.356	7.781	7.422	7.054	7.439	11.484	8.950
1600	7.395	7.824	7.461	7.061	7.480	11.60	9.029
1700	7.433	7.865	7.500	7.073	7.519	11.71	9.107
1800	7.471	7.904	7.537	7.081	7.558	11.81	9.185
1900	7.507	7.941	7.573	7.093	7.595	11.91	9.263
2000	7.542	7.976	7.608	7.114	7.631	12.01	9.339

SOURCE: Page 31 of Reference 12 in Table 4.6.

EXAMPLE 4.5 Calculation of $\Delta\hat{H}$ using mean heat capacity

Calculate the enthalpy change for 1 lb mole of nitrogen (N₂) which is heated at constant pressure (1 atm) from 60°F to 2000°F.

$$C_p = a + bT + cT^2,$$

(4.11)

$$\underline{T_2^3 - T_1^3}$$

C_p , you can simplify
heat capacities for com-
two different tempera-

ON GASES

cm

CO ₂	H ₂ O
8.001	
8.008	
8.012	
8.019	
8.023	
8.055	
8.101	
8.154	
8.210	
8.274	
8.341	
8.411	
8.484	
8.558	
8.634	
8.712	
8.790	
8.870	
8.950	
9.029	
9.107	
9.185	
9.263	
9.339	

) which is heated at

Solution:

The enthalpy data can be taken from Table 4.4b; reference conditions, 32°F:

$$C_{pm} = 7.542 \text{ Btu}/(\text{lb mole})(^{\circ}\text{F}) \quad \text{at } 2000^{\circ}\text{F}$$

$$C_{pm} = 6.960 \text{ Btu}/(\text{lb mole})(^{\circ}\text{F}) \quad \text{at } 60^{\circ}\text{F}$$

Basis: 1 lb mole of N₂

$$\begin{aligned} \Delta\hat{H}_{2000-60} &= \Delta\hat{H}_{2000} - \Delta\hat{H}_{60} \\ &= \frac{7.542 \text{ Btu}}{(\text{lb mole})(^{\circ}\text{F})} | (2000 - 32^{\circ}\text{F}) - \frac{6.960 \text{ Btu}}{(\text{lb mole})(^{\circ}\text{F})} | (60 - 32^{\circ}\text{F}) \\ &= 14,740 \text{ Btu/lb mole} \end{aligned}$$

As shown above, if the reference conditions are not zero (0°K, 0°F etc.), the $\Delta\hat{H}_{2000-60}$ is

$$C_{pm_{2000}}(T_{2000} - T_{ref}) - C_{pm_{60}}(T_{60} - T_{ref})$$

and not $C_{pm_{2000}}T_{2000} - C_{pm_{60}}T_{60}$.EXAMPLE 4.6 Calculation of $\Delta\hat{H}$ using heat capacity equations

The conversion of solid wastes to innocuous gases can be accomplished in incinerators in an environmentally acceptable fashion. However, the hot exhaust gases must be cooled or diluted with air. An economic feasibility study indicates that solid municipal waste can be burned to a gas of the following composition (on a dry basis):

CO ₂	9.2
CO	1.5
O ₂	7.3
N ₂	82.0
	100.0

What is the enthalpy difference for this gas between the bottom and the top of the stack if the temperature at the bottom of the stack is 550°F and the temperature at the top is 200°F? Ignore the water vapor in the gas. Because these are ideal gases, you can neglect any energy effects resulting from the mixing of the gaseous components.

Solution:

Heat capacity equations from Table E.1 in Appendix E (T in °F; C_p = Btu/(lb mole)(°F)) are

$$\text{N}_2: \quad C_p = 6.895 + 0.7624 \times 10^{-3}T - 0.7009 \times 10^{-7}T^2$$

$$\text{O}_2: \quad C_p = 7.104 + 0.7851 \times 10^{-3}T - 0.5528 \times 10^{-7}T^2$$

$$\text{CO}_2: \quad C_p = 8.448 + 5.757 \times 10^{-3}T - 21.59 \times 10^{-7}T^2 + 3.049 \times 10^{-10}T^3$$

$$\text{CO:} \quad C_p = 6.865 + 0.8024 \times 10^{-3}T - 0.7367 \times 10^{-7}T^2$$

Basis: 1.00 lb mole gas

By multiplying these equations by the respective mole fraction of each component, and then adding them together, you can save time in the integration.

$$\text{N}_2: \quad 0.82(6.895 + 0.7624 \times 10^{-3}T - 0.7009 \times 10^{-7}T^2)$$

$$\text{O}_2: \quad 0.073(7.104 + 0.7851 \times 10^{-3}T - 0.5528 \times 10^{-7}T^2)$$

$$\begin{aligned}
 \text{CO}_2: & 0.092(8.448 + 5.757 \times 10^{-3}T - 21.59 \times 10^{-7}T^2 + 3.059 \times 10^{-10}T^3) \\
 \text{CO:} & 0.015(6.865 + 0.8024 \times 10^{-3}T - 0.7367 \times 10^{-7}T^2) \\
 C_p_{\text{net}} &= 7.049 + 1.2243 \times 10^{-3}T - 2.6164 \times 10^{-7}T^2 + 0.2815 \times 10^{-10}T^3 \\
 \Delta\hat{H} &= \int_{550}^{200} C_p dT = \int_{550}^{200} (7.049 + 1.2243 \times 10^{-3}T - 2.6164 \times 10^{-7}T^2 \\
 &\quad + 0.2815 \times 10^{-10}T^3) dT \\
 &= 7.049[(200) - (550)] + \frac{1.2243 \times 10^{-3}}{2} [(200)^2 - (550)^2] \\
 &\quad - \frac{2.6164 \times 10^{-7}}{3} [(200)^3 - (550)^3] \\
 &\quad + \frac{0.2815 \times 10^{-10}}{4} [(200)^4 - (550)^4] \\
 &= -2465 - 160.6 + 13.8 - 0.633 \\
 &= -2612 \text{ Btu/lb mole gas}
 \end{aligned}$$

We shall now briefly discuss the use of enthalpy tables and charts to calculate enthalpy changes. The simplest and quickest method of computing enthalpy

TABLE 4.5a ENTHALPIES OF COMBUSTION GASES
(Btu/lb mole)
Pressure: 1 atm

°R	N ₂	O ₂	Air	H ₂	CO	CO ₂	H ₂ O
492	0.0	0.0	0.0	0.0	0.0	0.0	0.0
500	55.67	55.93	55.57	57.74	55.68	68.95	64.02
520	194.9	195.9	194.6	191.9	194.9	243.1	224.2
537	313.2	315.1	312.7	308.9	313.3	392.2	360.5
600	751.9	758.8	751.2	744.4	752.4	963	867.5
700	1450	1471	1450	1433	1451	1914	1679
800	2150	2194	2153	2122	2154	2915	2501
900	2852	2931	2861	2825	2863	3961	3336
1000	3565	3680	3579	3511	3580	5046	4184
1100	4285	443	4306	4210	4304	6167	5047
1200	5005	5219	5035	4917	5038	7320	5925
1300	5741	6007	5780	5630	5783	8502	6819
1400	6495	6804	6540	6369	6536	9710	7730
1500	7231	6712	7289	7069	7299	10942	8657
1600	8004	8427	8068	7789	8072	12200	9602
1700	8774	9251	8847	8499	8853	13470	10562
1800	9539	10081	9623	9219	9643	14760	11540
1900	10335	10918	10425	9942	10440	16070	12530
2000	11127	11760	11224	10689	11243	17390	13550
2100	11927	12610	12030	11615	12050	18730	14570
2200	12730	13460	12840	12160	12870	20070	15610
2300	13540	14320	13660	12890	13690	21430	16660
2400	14350	15180	14480	13650	14520	22800	17730
2500	15170	16040	15300	14400	15350	24180	18810

SOURCE: Page 30 of Reference 12 in Table 4.6.

$$+ 3.059 \times 10^{-10} T^3)$$

$T^2)$

$$- 2815 \times 10^{-10} T^2$$

$$+ 64 \times 10^{-7} T^2$$

$$- 315 \times 10^{-10} T^3) dT$$

$T^2)$

$T^3)$

$50)^4]$

and charts to calculate computing enthalpy

changes is to use tabulated enthalpy data available in the literature or in reference books. Thus, rather than using integrated heat capacity equations or mean heat capacity data, you should first look to see if you can find enthalpy data listed in tables as a function of temperature. Tables 4.5a and 4.5b list typical enthalpy data for the combustion gases. Some sources of enthalpy data are listed in Table 4.6. The most common source of enthalpy data for water is the steam tables; see Appendix C.¹² The reference by Kobe and associates (Table 4.6, 12) lists heat capacity equation, enthalpy values, and many other thermodynamic functions for over 100 compounds of commercial importance. Some of this information can be found in the Appendix. Computer tapes can be purchased providing information on the physical properties of large numbers of compounds as described in Reference 13 in Table 4.6, or from the Institution of Chemical Engineers, London.

Remembering that enthalpy values are all relative to some reference state, you can make enthalpy difference calculations merely by subtracting the final enthalpy from the initial enthalpy for any two sets of conditions. Of course, if

TABLE 4.5b ENTHALPIES OF COMBUSTION GASES
(cal./g mole)

CO ₂	H ₂ O	K	N ₂	O ₂	Air	H ₂	CO	CO ₂	H ₂ O
0.0	0.0	273	0.0	0.0	0.0	0.0	0.0	0.0	0.0
68.95	64.02	291	125.3	126.0	125.1	123.4	125.5	156.7	144.2
243.1	224.2	298	174.0	175.0	173.7	171.6	174.1	217.9	200.3
392.2	360.5	300	187.9	189.0	187.6	182.5	188.0	235.7	216.4
963	867.5	400	883.2	896.9	883.6	873.6	884.2	1172	1024
1914	1679	500	1588	1628	1592	1575	1590	2200	1853
2915	2501	600	2301	2383	2312	2275	2310	3300	2707
3961	3336	700	3024	3161	3044	2978	3047	4459	3589
5046	4184	800	3766	3959	3795	3684	3800	5667	4499
6167	5047	900	4532	4773	4569	4394	4571	6916	5440
7320	5925	1000	5299	5601	5346	5112	5357	8200	6411
8502	6819	1100	6088	6439	6142	5838	6157	9513	7412
9710	7730	1200	6888	7288	6950	6575	6968	10852	8440
10942	8657	1300	7700	8145	7768	7320	7790	12211	9494
12200	9602	1400	8518	9009	8593	8076	8621	13590	10573
13470	10562	1500	9356	9880	9434	8842	9459	14980	11675
14760	11540	1750	11458	12083	11550	10821	11582	18510	14520
16070	12530	2000	13600	14320	13700	12830	13740	22100	17480
17390	13550	2200	15770	16600	15880	14900	15910	25750	20520
18730	14570	2400	17940	18910	18080	17020	18110	29440	23630
20070	15610	2700	20140	21250	20300	19190	20320	33150	26790
21430	16660	3000	22350	23620	22530	21380	22530	36890	30000
		3500	26800	28450	27040	25820	27000	44430	36520
		4000	31280	33380	31590	30480	31500	52050	43120
		17730							
		18810							

¹²See R. W. Haywood, *Thermodynamic Tables in SI (Metric) Units*, Cambridge University Press, London, 1968, for steam tables in metric units.

the enthalpy data are not available, you will have to rely on calculations involving heat capacities or mean heat capacities.

If a pure material exists in solid, liquid, and gaseous form, a chart or diagram can be prepared showing its properties if sufficient reliable experimental information is available. Examples of such charts are shown in Fig. 4.7 and in Appendix J; sources of such charts are listed in Table 4.7. Many forms of charts

TABLE 4.6 SOURCES OF ENTHALPY DATA

1. American Petroleum Institute, Division of Refining, *Technical Data Book—Petroleum Refining*, 2nd ed., API, Washington D.C., 1970.
2. American Petroleum Institute, Research Project 44, *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*, API, Washington, D.C., 1953.
3. Chermin, H. A. G., *Hydrocarbon Processing & Petroleum Refining*, Parts 26–32, 1961. (Continuation of Kobe compendium for gases; see item 12 below.)
4. Egloff, G., *Physical Constants of Hydrocarbons*, 5 vols., Van Nostrand Reinhold, New York, 1939–1953.
5. Hamblin, F. D., *Abridged Thermodynamic and Thermochemical Tables (S.I. Units)*, Pergamon Press, Elmsford, N.Y. (paperback edition available), 1972.
6. Hilsenrath, J., and others, "Tables of Thermal Properties of Gases," *National Bureau of Standards (U.S.), Circ. 564*, 1955. (Additional single sheets issued as NBS-NACA sponsored tables.)
7. International Atomic Energy Agency, *Thermodynamics of Nuclear Materials*, Vienna, Austria, 1962.
8. *Journal of Physical and Chemical Reference Data*, American Chemical Society, 1972 and following.
9. Keenan, J. H., and F. G. Keyes, *Thermodynamic Properties of Steam*, Wiley, New York, 1936.
10. Keenan, J. H., and J. Kay, *Gas Tables*, Wiley, New York, 1948.
11. Kelley, K. K., various *U.S. Bureau of Mines Bulletins* on the Thermodynamic Properties of Substances, particularly minerals; 1935–1962.
12. Kobe, K. A., et al. "Thermochemistry of Petrochemicals," Reprint no. 44 from the *Petroleum Refiner*. A collection of a series of 24 articles covering 105 different substances that appeared in the *Petroleum Refiner*.
13. Meadows, E. L., "Estimating Physical Properties," *Chem. Eng. Progr.*, v. 61, p. 93 (1965). (A.I.Ch.E. Machine Computation Committee report on the preparation of thermodynamic tables on tapes.)
14. Perry, J. H., *Chemical Engineers' Handbook*, 4th ed., McGraw-Hill, New York, 1964.
15. Ross, L. W., *Chem. Eng.*, p. 205 (Oct. 10, 1966).
16. Rossini, F. K., and others. "Tables of Selected Values of Chemical Thermodynamic Properties," *National Bureau of Standards (U.S.), Circ. 500*, 1952. (Revisions are being issued periodically under the Technical Note 270 series by other authors).
17. Sage, B. H., and W. N. Lacey, *Some Properties of the Lighter Hydrocarbons, Hydrogen Sulfide, and Carbon Dioxide*, American Petroleum Institute, New York, 1955.
18. Stull, D. R., and H. Prophet, *JANAF Thermochemical Tables*, 2nd ed., Government Printing Office No. 0303-0872, C13, 48: 37 (AD-732 043), 1971. (Data for over 1000 compounds.)
19. Zeise, H., *Thermodynamik*, Band III I Taballen, S. Hirzel Verlag, Leipzig, 1954. (Tables of heat capacities, enthalpies, entropies, free energies, and equilibrium constants.)

Chap. 4

calculations involve-

in, a chart or dia-
table experimental
in Fig. 4.7 and in
any forms of charts

Data Book—Petroleum
of Physical and Ther-
API, Washington, D.C.,

Parts 26–32, 1961.

strand Reinhold, New
ables (S.I. Units), Per-

ases," National Bureau
issu BS-NACA

ear Materials, Vienna,

ical Society, 1972 and

Wiley, New York,

odynamic Properties

int no. 44 from the
55 different substances

, v. 61, p. 93 (1965).
on of thermodynamic

, New York, 1964.

ical Thermodynamic
(Revisions are being
authors).

carbons, Hydrogen
York, 1955.

Government Print-
for over 1000 com-

Leipzig, 1954. (Tables
um constants.)

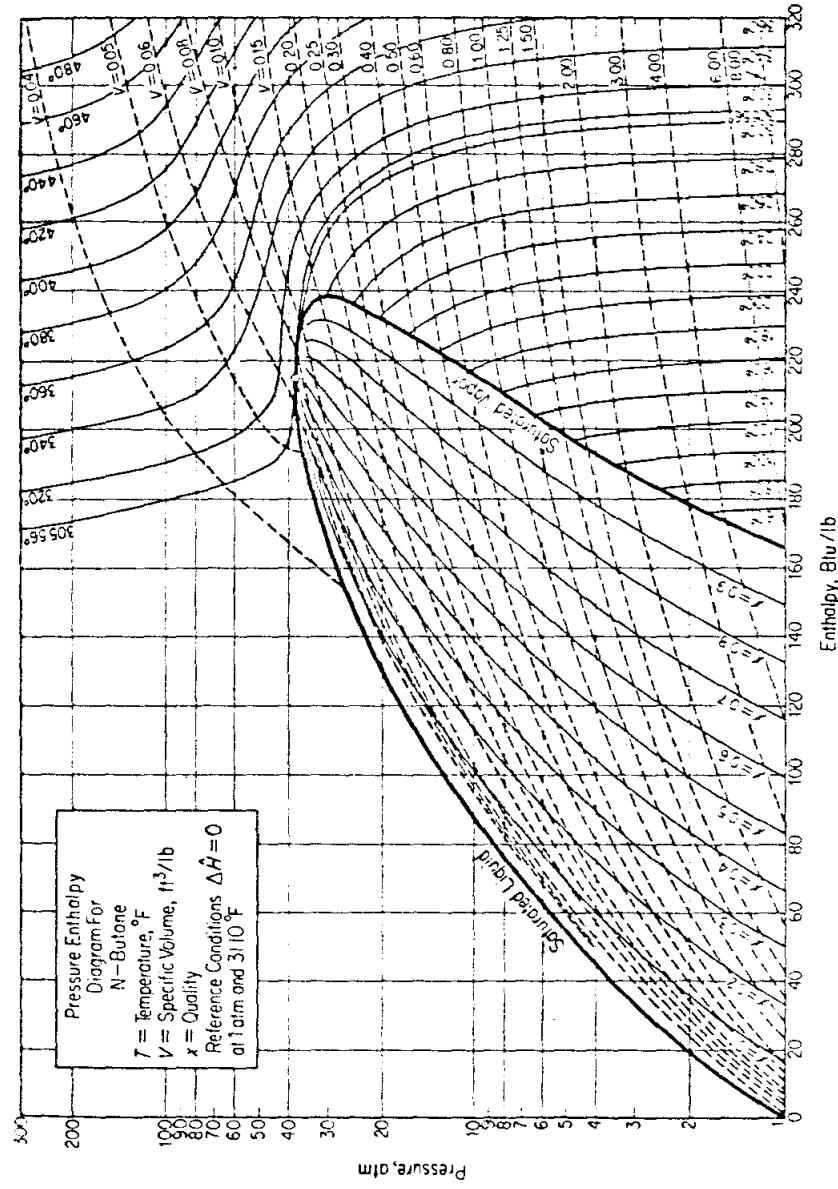


TABLE 4.7 THERMODYNAMIC CHARTS SHOWING ENTHALPY DATA FOR PURE COMPOUNDS
[For mixtures, see V. F. Lesavage et al. *Ind. Eng. Chem.*, v. 59, no. 11, p. 35 (1967).]

Compound	Reference
Acetone	2
Acetylene	1
Air	V. C. Williams, <i>Am. Inst. Chem. Engrs. Trans.</i> , v. 39, p. 93 (1943); <i>A.I.Ch.E. J.</i> , v. 1, p. 302 (1955).
Benzene	1
1, 3-Butadiene	C. H. Meyers, <i>J. Res. Natl. Bur. Std., A.</i> , v. 39, p. 507 (1947).
i-Butane	1, 3
n-Butane	1, 3, 4
n-Butanol	L. W. Shemilt, in <i>Proceedings of the Conference on Thermodynamic Transport Properties of Fluids</i> , London, 1957, Institute of Mechanical Engineers London (1958).
Butanol, <i>tert.</i>	F. Maslan, <i>A.I.Ch.E. J.</i> , v. 7, p. 172 (1961).
n-Butene	1
Chlorine	R. E. Hulme and A. B. Tilman, <i>Chem. Eng.</i> (Jan. 1949).
Ethane	1, 3, 4
Ethanol	R. C. Reid and J. M. Smith, <i>Chem. Eng. Progr.</i> , v. 47, p. 415 (1951).
Ethyl ether	2
Ethylene	1, 3
Ethylene oxide	J. E. Mock and J. M. Smith, <i>Ind. Eng. Chem.</i> , v. 42, p. 2125 (1950).
n-Heptane	E. B. Stuart, et al., <i>Chem. Eng. Progr.</i> , v. 46, p. 311 (1950).
n-Hexane	1
Hydrogen sulfide	J. R. West, <i>Chem. Eng. Progr.</i> , v. 44, p. 287 (1948).
Isopropyl ether	2
Mercury	General Electric Co. Report GET-1879A, 1949.
Methane	1, 3, 4
Methanol	J. M. Smith, <i>Chem. Eng. Progr.</i> , v. 44, p. 52 (1948).
Methyl ethyl ketone	2
Monomethyl hydrazine	F. Bizjak, and D. F. Stai, <i>A.I.A.A. J.</i> , v. 2, p. 954 (1964).
Neon	Cryogenic Data Center, National Bureau of Standards, Boulder, Colo.
Nitrogen	G. S. Lin, <i>Chem. Eng. Progr.</i> , v. 59, no. 11, p. 69 (1963).
n-Pentane	1, 3, 4
Propane	1, 3, 4
n-Propanol	L. W. Shemilt, (see ref. for butanol).
Propylene	1, 3
Refrigerant 245	R. L. Shank, <i>J. Chem. Eng. Data</i> , v. 12, p. 474 (1967).
Sulfur dioxide	J. R. West, and G. P. Giusti, <i>J. Phys. Colloid Chem.</i> , v. 54, p. 601 (1950).
Combustion gases	H. C. Hottel, G. C. Williams, and C. N. Satterfield, <i>Thermodynamic Charts for Combustion Processes</i> (I) Text, (II) Charts, Wiley, New York, 1949.
Hydrocarbons	3

1. L. N. Cajar, et al., *Thermodynamic Properties and Reduced Correlations for Gases*, Gulf Publishing Co., Houston, Texas, 1967. (Series of articles which appeared in the magazine *Hydrocarbon Processing* from 1962 to 1965.)
2. P. T. Eubank and J. M. Smith, *J. Chem. Eng. Data*, v. 7, p. 75 (1962).
3. W. C. Edmister, *Applied Hydrocarbon Thermodynamics*, Gulf Publishing Co., Houston, Texas, 1961.
4. K. E. Starling et al., *Hydrocarbon Processing*, 1971 and following; to be published as a book. Charts available from Gulf Publishing Co., Houston, Texas, separately.

Since a chart can be plotted at any temperature, for example, the enthalpy axis can be drawn.

You should learn to specify two points to fix the state of a substance that specifies properties will be the same ones usually specified (pressure); the internal energy of any two in equilibrium can be seen to be the same.

Although there are among the substances listed, you will find it best to want.

Enthalpy is calculated method of contributions.

EXAMPLE 4.2

Recalculate the solution.

For the solution at 20°C at 1 atm.

at 100°C at 1 atm.

PURE COMPOUNDS
p. 35 (1967).]

39, p. 93 (1943); A.I.

507 (1947).

ce on Thermodynamic
Institute of Mechanical

1949).

. 47, p. 415 (1951).

42, p. 118 (1950).
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1.

- (1964).

zards, Boulder, Colo.
(1963).

967).
m., v. 54, p. 601 (1950).
terfield, *Thermodynamic
charts*, Wiley, New York.

relations for Gases. Guilt
which appeared in the

7 (1962).
ublishing Co., Houston.

with published as
. The separately.

are available. Some types that may occur to you would have as coordinate axes

$$p \text{ vs. } \hat{H}$$

$$p \text{ vs. } \hat{V}$$

$$p \text{ vs. } T$$

$$\hat{H} \text{ vs. } \hat{S}^{13}$$

Since a chart has only two dimensions, the other parameters of interest have to be plotted as lines of constant value across the face of the chart. Recall, for example, that in the $p\hat{V}$ diagram for CO_2 , Figs. 3.2 and 3.24, lines of constant temperature were shown as parameters. Similarly, on a chart with pressure and enthalpy as the axes, lines of constant volume and/or temperature might be drawn.

You should have noted for pure gases in the illustrated problems that we had to specify two physical properties such as temperature and pressure to definitely fix the state of the gas. Since we know from our previous discussion in Chap. 3 that specifying two properties for a pure gas will ensure that all the other properties will have definite values, any two properties can be chosen at will. The ones usually selected are the ones easiest to measure (such as temperature and pressure); then the others (specific volume, density, specific enthalpy, specific internal energy, etc.) are fixed. Since a particular state for a gas can be defined by any two independent properties, a two-dimensional thermodynamic chart can be seen to be a handy way to present combinations of physical properties.

Although diagrams and charts are helpful in that they portray the relations among the phases and give approximate values for the physical properties of a substance, to get more precise data (unless the chart is quite large), usually you will find it best to see if tables are available which list the physical properties you want.

Enthalpies and other thermodynamic properties can be estimated by generalized methods based on the theory of corresponding states or additive bond contributions.^{14,15,16}

EXAMPLE 4.7 Calculation of enthalpy change using tabulated enthalpy values

Recalculate Example 4.5 using data from enthalpy tables.

Solution:

For the same change as in Example 4.5, the data from Table 4.5a are

$$\begin{aligned} \text{at } 2000^{\circ}\text{F} \Leftrightarrow 2460^{\circ}\text{R}: & \quad \Delta\hat{H} = 14,880 \text{ Btu/lb mole} \\ \text{at } 60^{\circ}\text{F} \Leftrightarrow 520^{\circ}\text{R}: & \quad \Delta\hat{H} = 194.9 \text{ Btu/lb mole} \end{aligned} \quad \left. \begin{array}{l} \text{ref. temp.} = 32^{\circ}\text{F} \\ \text{Basis: 1 lb mole N}_2 \end{array} \right\}$$

$$\Delta\hat{H} = 14,880 - 194.9 = 14,685 \text{ Btu/lb mole}$$

¹³ S is entropy—this diagram is called a Mollier diagram.

¹⁴Lyderson, Greenkorn, and Hougen, *op. cit.*

¹⁵T. J. Janz, *Estimation of Thermodynamic Properties of Organic Compounds*, Academic Press, New York, 1967.

¹⁶F. K. Landis, M. T. Cannon, and L. N. Canjar, *Hydrocarbon Processing*, v. 44, p. 154 (1965).

EXAMPLE 4.8 Use of the steam tables

What is the enthalpy change in British thermal units when 1 gal of water is heated from 60° to 1150°F and 240 psig?

Solution:

Basis: 1 lb H₂O at 60°F

From steam tables (ref. temp. = 32°F),

$$\hat{H} = 28.07 \text{ Btu/lb} \quad \text{at } 60^\circ\text{F}$$

$$\hat{H} = 1604.5 \text{ Btu/lb} \quad \text{at } 1150^\circ\text{F and 240 psig (254.7 psia)}$$

$$\Delta\hat{H} = (1604.5 - 28.07) = 1576.4 \text{ Btu/lb}$$

$$\Delta H = 1576(8.345) = 13,150 \text{ Btu/gal}$$

Note: The enthalpy values which have been used for liquid water as taken from the steam tables are for the saturated liquid under its own vapor pressure. Since the enthalpy of liquid water changes negligibly with pressure, no loss of accuracy is encountered for engineering purposes if the initial pressure on the water is not stated.

4.4 Enthalpy changes for transitions

In making enthalpy calculations, we noted in Fig. 4.3 that the heat capacity data are discontinuous at the points of a phase transition. The name usually given to the enthalpy changes for these phase transitions is *latent heat* changes, latent meaning "hidden" in the sense that the substance (for example, water) can absorb a large amount of heat without any noticeable increase in temperature. Unfortunately, the word *heat* is still associated with these enthalpy changes for historical reasons, although they have nothing directly to do with heat as defined in Sec. 4.1. Ice at 0°C can absorb energy amounting to 80 cal/g without undergoing a temperature rise or a pressure change. The enthalpy change from a solid to a liquid is called the *heat of fusion*, and the enthalpy change for the phase transition between solid and liquid water is thus 80 cal/g. The *heat of vaporization* is the enthalpy change for the phase transition between liquid and vapor, and we also have the *heat of sublimation*, which is the enthalpy change for the transition directly from solid to vapor. Dry ice at room temperature and pressure sublimes. The $\Delta\hat{H}$ for the phase change from gas to liquid is called the *heat of condensation*. You can find experimental values of latent heats in the references in Table 4.6, and a brief tabulation is shown in Appendix D. The symbols used for latent heat changes vary, but you usually find one or more of the following employed: $\Delta\hat{H}$, L , λ , Λ .

To calculate the enthalpy change for the vaporization of water using steam table data, the liquid or gaseous water should be heated or cooled to the dew point and vaporized at the dew point. Keep in mind that the enthalpy changes

for vaporization given in the steam tables are for water under its vapor pressure at the indicated temperature. National Bureau of Standards Circular 500 provides the data at 25°C that we can use to compare the heat of vaporization of water at its vapor pressure and at 1 atm:

°C	mm Hg	kcal/g mole	Btu/lb mole
25	23.75	10.514	18,925
25	760.	10.520	18,936

You can see that the effect of pressure is quite small and may be neglected for ordinary engineering calculations.

In the absence of experimental values for the latent heats of transition, the following approximate methods will provide a rough estimate of the molar latent heats. Reid and Sherwood, *The Properties of Gases and Liquids*, give more sophisticated methods.¹⁷

4.4.1 Heat of Fusion. The heat of fusion for many elements and compounds can be expressed as

$$\frac{\Delta\hat{H}_f}{T_f} = \text{constant} = \begin{cases} 2-3 & \text{for elements} \\ 5-7 & \text{for inorganic compounds} \\ 9-11 & \text{for organic compounds} \end{cases} \quad (4.12)$$

where $\Delta\hat{H}_f$ = molar heat of fusion in cal/g mole

T_f = melting point in °K

4.4.2 Heat of Vaporization. (a) Kistyakowsky's equation. Kistyakowsky¹⁸ developed Eq. (4.13) for nonpolar liquids, and it provides quite accurate values of the molar heat of vaporization for these liquids:

$$\frac{\Delta\hat{H}_v}{T_b} = 8.75 + 4.517 \log_{10} T_b \quad (4.13)$$

where $\Delta\hat{H}_v$ = molar heat of vaporization at T_b in cal/g mole

T_b = normal boiling point in °K

(b) Clausius-Clapeyron Equation. The Clapeyron equation itself is an exact thermodynamic relationship between the slope of the vapor-pressure curve and the molar heat of vaporization and the other variables listed below:

$$\frac{dp^*}{dT} = \frac{\Delta\hat{H}_v}{T(\bar{V}_g - \bar{V}_l)} \quad (4.14)$$

where p^* = the vapor pressure

T = absolute temperature

$\Delta\hat{H}_v$ = molar heat of vaporization at T

\bar{V}_g = molar volume of gas or liquid as indicated by the subscript g or l

¹⁷Also see S. H. Fishtine, *Hydrocarbon Processing*, v. 45, no. 4, p. 173 (1965).

¹⁸W. Kistyakowsky, *Z. Physik u. Chem.*, v. 107, p. 65 (1923).

Any consistent set of units may be used. If we assume that

- (1) \hat{V}_v is negligible in comparison with \hat{V}_s ,
- (2) The ideal gas law is applicable for the vapor:

$$\hat{V}_v = RT/p^*$$

$$\frac{dp^*}{p^*} = \frac{\Delta\hat{H}_v}{RT^2} dT$$

Rearranging the form,

$$\frac{d \ln p^*}{d(1/T)} = 2.303 \frac{d \log_{10} p^*}{d(1/T)} = -\frac{\Delta\hat{H}_v}{R} \quad (4.15)$$

You can plot the $\log_{10} p^*$ vs. $1/T$ and obtain the slope $-(\Delta\hat{H}_v/2.303R)$.

(3) $\Delta\hat{H}_v$ is constant over the temperature range of interest, integration of Eq. (4.15) yields an indefinite integral

$$\log_{10} p^* = -\frac{\Delta\hat{H}_v}{2.3RT} + B \quad (4.16)$$

or a definite one

$$\log_{10} \frac{p_1^*}{p_2^*} = \frac{\Delta\hat{H}_v}{2.3R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (4.17)$$

Either of these equations can be used graphically or analytically to obtain $\Delta\hat{H}_v$ for a short temperature interval.

EXAMPLE 4.9 Heat of vaporization from the Clausius-Clapeyron equation

Estimate the heat of vaporization of isobutyric acid at 200°C.

Solution:

The vapor-pressure data for isobutyric acid (from Perry) are

pressure (mm)	temp. (°C)	pressure (atm)	temp. (°C)
100	98.0	1	154.5
200	115.8	2	179.8
400	134.5	5	217.0
760	154.5	10	250.0

Basis: 1 g mole isobutyric acid

Since $\Delta\hat{H}_v$ remains essentially constant for short temperature intervals, the heat of vaporization can be estimated from Eq. (4.17) and the vapor-pressure data at 179.8°C and 217.0°C.

$$179.8^\circ\text{C} \approx 452.8^\circ\text{K}; \quad 217^\circ\text{C} \approx 490^\circ\text{K}$$

$$\log_{10} \frac{2}{5} = \frac{\Delta\hat{H}_v}{(2.303)(1.987)} \left[\frac{1}{490} - \frac{1}{452.8} \right]$$

$$\Delta\hat{H}_v = 10,700 \text{ cal/g mole} = 19,500 \text{ Btu/lb mole}$$

A reduced $\log_{10} p^*$ vs. $1/T$ plot can be made for several of the substances.

(c) Reference data: estimate the heat of vaporization at its boiling point for a known liquid substance.

(1) Duhring plot: against the temperature. For example, if a pure substance (water) are plotted against temperatures of 100°C, approximately a straight line is obtained.

To indicate the composition of components.

If the vapor pressure is plotted against the temperature of Eq. (4.18),

or in terms of the vapor pressure ratio,

Given the slope of the line, it can be used to calculate $\Delta\hat{H}_v$.

(2) Othmer plot: Duhring plot except that the curves for each other at equal temperatures are plotted against $\log_{10}(P/P_0)$ for a very wide temperature range.

¹⁹D. F. Othmer, "A New Technique and a Critical Survey of the Clausius-Clapeyron Equation," *J. Am. Chem. Soc.*, 56, 1459 (1934); S. Yu, *Ind. Eng. Chem., Res.*, 1, 100 (1962); *Ind. Eng. Chem.,* v. 60, no. 10, 1968.

A reduced form of the Clapeyron equation, i.e., an equation in terms of the reduced pressure and temperature which gives good results is described in several of the references at the end of this chapter.

(c) *Reference substance plots.* Several methods have been developed to estimate the molal heat of vaporization of a liquid at any temperature (not just at its boiling point) by comparing the $\Delta\hat{H}_v$ for the unknown liquid with that of a known liquid such as water.

(1) *Duhring plot.* The temperature of the wanted compound A is plotted against the temperature of the known (reference) liquid at *equal vapor pressure*. For example, if the temperatures of A (isobutyric acid) and the reference substance (water) are determined at 760, 400, and 200 mm pressure, then a plot of the temperatures of A vs. the temperatures of the reference substance will be approximately a straight line over a wide temperature range.

To indicate how to apply the Duhring plot to estimate the heat of vaporization of compound A , we apply the Clapeyron equation to each substance:

$$\frac{d(\ln p_A^*)}{d(\ln p_{ref}^*)} = \frac{-\Delta\hat{H}_{v,A}}{R d(1/T_A)} = \frac{-\Delta\hat{H}_{v,ref}}{R d(1/T_{ref})} \quad (4.18)$$

If the vapor pressures of A and the reference substance are the same, rearrangement of Eq. (4.18) gives

$$\frac{d\left(\frac{1}{T_{ref}}\right)}{dT_A} = \frac{\frac{dT_{ref}}{dT_A}}{\frac{T_{ref}^2}{T_A^2}} = \frac{\Delta\hat{H}_{v,A}}{\Delta\hat{H}_{v,ref}}$$

or in terms of the slope of the Duhring plot,

$$\frac{dT_{ref}}{dT_A} = \frac{\Delta\hat{H}_{v,A}}{\Delta\hat{H}_{v,ref}} \frac{T_{ref}^2}{T_A^2} \quad (4.19)$$

Given the slope of the Duhring plot, $\Delta\hat{H}_{v,ref}$, and T_{ref} and T_A , Eq. (4.19) can be used to calculate $\Delta\hat{H}_{v,A}$.

(2) *Othmer plot.* The Othmer plot¹⁹ is based on the same concepts as the Duhring plot except that the *logarithms* of vapor pressures are plotted against each other at *equal temperature*. As illustrated in Fig. 4.8, a plot of the $\log_{10}(p_A^*)$ against $\log_{10}(p_{ref}^*)$ chosen at the same temperature yields a straight line over a very wide temperature range. By choosing values of vapor pressure at equal

¹⁹D. F. Othmer, *Ind. Eng. Chem.*, v. 32, p. 841 (1940). For a complete review of the technique and a comparative statistical analysis among various predictive methods, refer to D. F. Othmer and H. N. Huang, *Ind. Eng. Chem.*, v. 57, p. 40 (1965); D. F. Othmer and E. S. Yu, *Ind. Eng. Chem.*, v. 60, no. 1, p. 22 (1968); and D. F. Othmer and H. T. Chem., *Ind. Eng. Chem.*, v. 60, no. 4, p. 39 (1968).

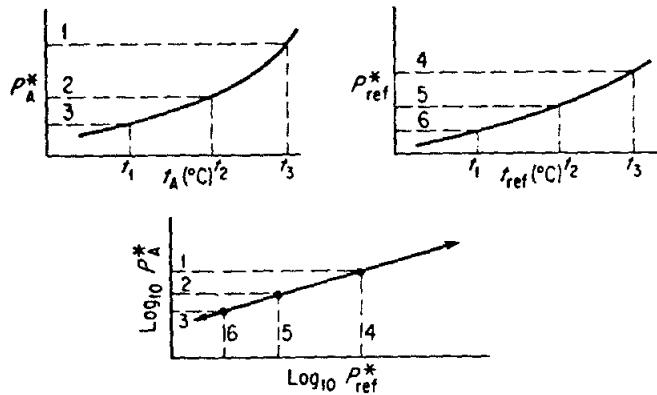


Fig. 4.8. Othmer plot and vapor-pressure curves.

temperature ($T_A = T_{ref}$) in Eq. (4.18), we obtain

$$\frac{(d \ln p_A^*)}{(d \ln p_{ref}^*)} = \frac{\Delta \hat{H}_{v,A}}{\Delta \hat{H}_{v,ref}} = m = \text{slope of Othmer plot as in Fig. 4.8.} \quad (4.20)$$

The Othmer plot works well because the errors inherent in the assumptions made in deriving Eq. (4.20) cancel out to a considerable extent. At very high pressures the Othmer plot is not too effective. Incidentally, this type of plot has been applied to a wide variety of thermodynamic and transport relations, such as equilibrium constants, diffusion coefficients, solubility relations, ionization and dissociation constants, etc., with considerable success.

Othmer recommended another type of relationship that can be used to estimate the heats of vaporization:

$$\ln p_{r,A}^* = \frac{\Delta \hat{H}_{v,A}}{\Delta \hat{H}_{v,ref}} \frac{T_{c,ref}}{T_{c,A}} \ln p_{r,ref}^* \quad (4.21)$$

where p_r^* is the reduced vapor pressure. Equation (4.21) is effective and gives a straight line through the point $p_{r,A}^* = 1$ and $T_{c,A} = 1$. The Gordon method plots the log of the vapor pressure of A versus that of the reference substance at equal reduced temperature.

EXAMPLE 4.10 Use of Othmer plot

Repeat the calculation for the heat of vaporization of isobutyric acid at 200°C using an Othmer plot.

Solution:

Data are as follows:

temp. (°C)	p_{iso}^* (atm)	$\log p^*$	$p_{H_2O}^*$ (atm)	$\log p^*$
154.5	1	0	5.28	0.723
179.8	2	0.3010	9.87	0.994
217.0	5	0.698	21.6	1.334
250.0	10	1.00	39.1	1.592

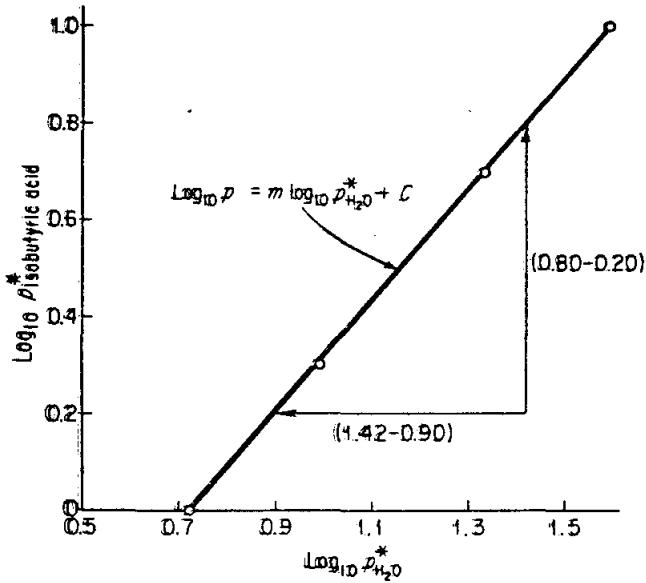


Fig. E4.10.

From Othmer plot, Fig. E4.10

$$\text{slope} = \frac{\Delta \hat{H}_{v,iso}}{\Delta \hat{H}_{v,H_2O}} = \frac{0.80 - 0.20}{1.42 - 0.90} = 1.15$$

At 200°C (392°F), from the steam tables,

$$\Delta \hat{H}_{v,H_2O} = 15,000 \text{ Btu/lb mole} \quad (833.8 \text{ Btu/lb})$$

Then

$$\Delta \hat{H}_{v,iso} = (15,000)(1.15) = 17,250 \text{ Btu/lb mole}$$

The answer in this case is lower than that in Example 4.9. Without the experimental value, it is difficult to say what the proper answer is. However, at the normal boiling point (154°C), $\Delta \hat{H}_{v,iso}$ is known to be 17,700 Btu/lb mole, and $\Delta \hat{H}_{v,iso}$ should be lower at 200°C so that 17,250 Btu/lb mole seems to be the more satisfactory value.

(d) *Empirical relation of Watson.*²⁰ Watson found empirically that

$$\frac{\Delta \hat{H}_{v_2}}{\Delta \hat{H}_{v_1}} = \left(\frac{1 - T_2}{1 - T_1} \right)^{0.38}$$

where $\Delta \hat{H}_{v_2}$ = heat of vaporization of a pure liquid at T_2

$\Delta \hat{H}_{v_1}$ = heat of vaporization of the same liquid at T_1

Gold²¹ summarizes numerous estimation methods and delineates their ranges of application.

²⁰K. M. Watson, *Ind. Eng. Chem.*, v. 23, p. 360 (1931); v. 35, p. 398 (1943).

²¹P. I. Gold, *Chem. Eng.*, p. 109, (Feb. 24, 1969).

4.5 The general energy balance

Scientists did not begin to write energy balances for physical systems prior to the latter half of the nineteenth century. Before 1850 they were not sure what energy was or even if it was important. But in the 1850s the concepts of energy and the energy balance became clearly formulated. We do not have the space here to outline the historical development of the energy balance and of special cases of it, but it truly makes a most interesting story and can be found elsewhere.^{22,23,24,25,26} Today we consider the energy balance to be so fundamental a physical principle that we invent new kinds of energy to make sure that the equation indeed does balance. Equation (4.22) as written below is a generalization of the results of numerous experiments on relatively simple special cases. We universally believe the equation is valid because we cannot find exceptions to it in practice, taking into account the precision of the measurements.

It is necessary to keep in mind two important points as you read what follows. First, we shall examine only systems that are homogeneous, not charged, and without surface effects, in order to make the energy balance as simple as possible. Second, the energy balance will be developed and applied from the macroscopic viewpoint (overall about the system) rather than from a microscopic viewpoint, i.e., an elemental volume within the system.

The concept of the macroscopic energy balance is similar to the concept of the macroscopic material balance, namely,

$$\left\{ \begin{array}{l} \text{Accumulation of} \\ \text{energy within the} \\ \text{system} \end{array} \right\} = \left\{ \begin{array}{l} \text{transfer of energy} \\ \text{into system through} \\ \text{system boundary} \end{array} \right\} - \left\{ \begin{array}{l} \text{transfer of energy out} \\ \text{of system through} \\ \text{system boundary} \end{array} \right\} + \left\{ \begin{array}{l} \text{energy genera-} \\ \text{tion within} \\ \text{system} \end{array} \right\} - \left\{ \begin{array}{l} \text{energy con-} \\ \text{sumption} \\ \text{within system} \end{array} \right\} \quad (4.22)$$

While the formulation of the energy balance in words as outlined in Eq. (4.22) is easily understood and rigorous, you will discover in later courses that to express each term of (4.22) in mathematical notation may require certain simplifications to be introduced, a discussion of which is beyond our scope here, but which have a quite minor influence on our final balance. We shall split the energy (E) associated with mass, mass either in the system or transported across the system boundaries, into three categories: internal energy (U), kinetic energy (K), and potential energy (P). In addition to the energy transported across the

²²A. W. Porter, *Thermodynamics*, 4th ed., Methuen, London, 1951.

²³D. Roller, *The Early Development of the Concepts of Temperature and Heat*, Harvard University Press, Cambridge, Mass., 1950.

²⁴T. M. Brown, *Am. J. Physics*, v. 33, no. 10, p. 1 (1965).

²⁵J. Zernike, *Chem. Weekblad*, v. 61, pp. 270-274, 277-279 (1965).

²⁶L. K. Nash, *J. Chem. Educ.*, v. 42, p. 64 (1965) (a resource paper).

systems prior to were not sure what concepts of energy not have the space and of special can be found elsewhere so fundamental to make sure that written below is a relatively simple because we cannot measure

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system boundaries associated with mass flow into and out of the system, energy can be transferred by heat (Q) and work (W). For most of the purposes of this text, energy generation or loss will be zero. However, energy transferred to the system by an external electric or magnetic field, or by the slowing down of neutrons, energy transfer not conveniently included in Q or W , may be included conceptually in the energy balance as a generation term. Similarly, radioactive decay can be viewed as a generation term.

Figure 4.9 shows the various types of energy to be accounted for in Eq. (4.22), while Table 4.8 lists the specific individual terms which are to be employed in Eq. (4.22). As to the notation, the subscripts t_1 and t_2 refer to the initial and final time periods over which the accumulation is to be evaluated, with $t_2 > t_1$. The superscript caret (^) means that the symbol stands for energy per unit mass; without the caret, the symbol means energy of the total mass present. Other notation is evident from Figs. 4.9 and 4.10 and can be found in the notation list at the end of the book. Fig. 4.11 shows the energy balance for the earth.

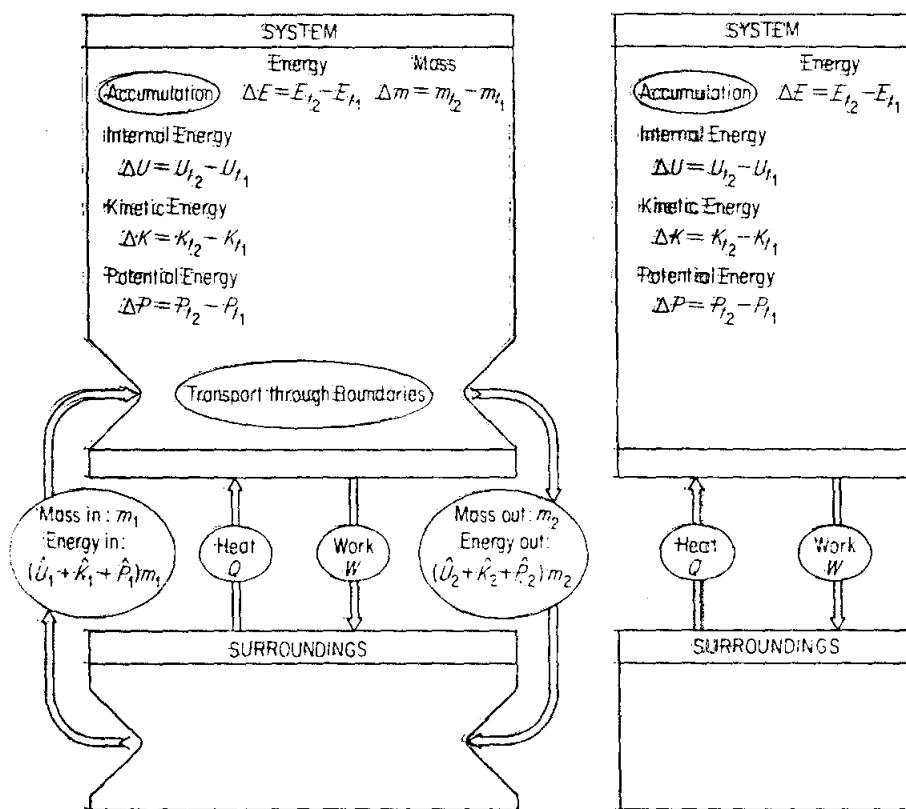


Fig. 4.9. Energy balance over a time period for flow and nonflow systems.

With the aid of the symbols from Table 4.8, the general energy balance, Eq. (4.22), can be written as follows. (An alternative formulation of the balance in terms of differentials is given in Chap. 6, where emphasis is placed on the instantaneous rate of change of energy of a system rather than just the initial and final states of the system; the formulation in this chapter can be considered to be the result of integrating the balance in Chap. 6.):

$$m_{i_1}(\hat{U} + \hat{K} + \hat{P})_{i_1} - m_{i_1}(\hat{U} + \hat{K} + \hat{P})_{i_1} = (\hat{U}_1 + \hat{K}_1 + \hat{P}_1)m_1 - (\hat{U}_2 + \hat{K}_2 + \hat{P})m_2 + Q - W + p_1\hat{V}_1m_1 - p_2\hat{V}_2m_2 \quad (4.23)$$

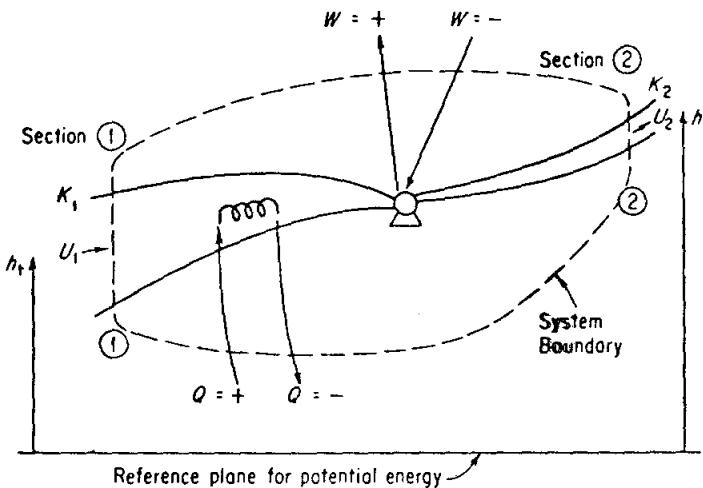


Fig. 4.10. General process showing the system boundary and energy transport across the boundary.

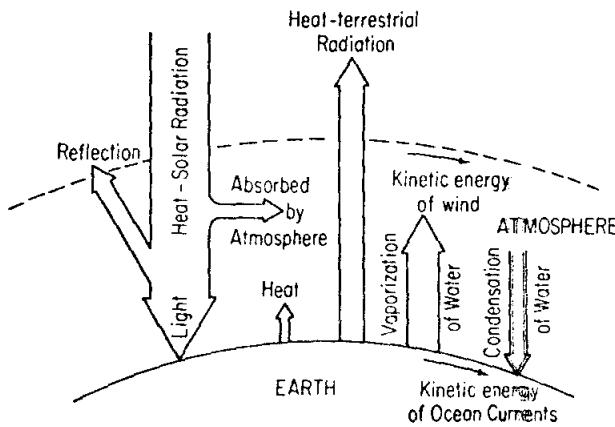


Fig. 4.11. Energy balance on the earth and its atmosphere. The thickness of the arrows are roughly proportional to the magnitude of the energy transfers.

TABLE 4.8 LIST OF SYMBOLS USED IN THE GENERAL ENERGY BALANCE

Accumulation term			
Type of energy		At time t_1	At time t_2
Internal		U_{t_1}	U_{t_2}
Kinetic		K_{t_1}	K_{t_2}
Potential		P_{t_1}	P_{t_2}
Mass		m_{t_1}	m_{t_2}
Energy accompanying mass transport			
Type of energy		Transport in	Transport out
Internal		U_1	U_2
Kinetic		K_1	K_2
Potential		P_1	P_2
Mass		m_1	m_2
Net heat input to system			Q
Net work done by system on surroundings			W
Mechanical work or work by moving parts:			
Work to introduce material into system, less work recovered on removing material from system:			$(p_2 \hat{V}_2)m_2 - (p_1 \hat{V}_1)m_1$

or in simpler form, which is easier to memorize,

$$\Delta E = E_{t_2} - E_{t_1} = -\Delta[\hat{H} + \hat{K} + \hat{P}]m + Q - W \quad (4.24)$$

where Δ = difference operator signifying *out* minus *in*, *exit* minus *entrance*, or *final* minus *initial* in time

$$\hat{E} = \hat{U} + \hat{K} + \hat{P}$$

$$\hat{H} = \hat{U} + p\hat{V}$$

Q = heat absorbed by the system *from* the surroundings (Q is positive for heat entering the system)

W = mechanical work done *by* the system *on* the surroundings (W is positive for work going from the system to the surroundings)

Note that the expression $\Delta\hat{U} + \Delta p\hat{V} = \Delta\hat{H}$ has been employed in consolidating Eq. (4.23) into (4.24), so that the significance of the enthalpy term in the energy balance manifests itself. A more rigorous derivation of Eq. (4.24) from a microscopic balance may be found in a paper by Bird.²⁷

Keep in mind that a system may do work, or have work done on it, without some obvious mechanical device such as a turbine, pump, shaft, etc., being present. Often the nature of the work is implied rather than explicitly stated. For example, a cylinder filled with gas enclosed by a movable piston implies that the surrounding atmosphere can do work on the piston or the reverse; a batch fuel cell does no mechanical work, unless it produces bubbles, but does deliver a current at a potential difference; and so forth.

²⁷R. B. Bird, Reprint no. 293, *Univ. Wis. Eng. Expt. Sta. Rept.*, 1957.

Now for a word of warning: Be certain you use *consistent units* for all terms; the use of foot-pound, for example, and Btu in different places in Eq. (4.24) is a common error for the beginner.

The terms $p_1\hat{V}_1$ and $p_2\hat{V}_2$ in Eq. (4.23) and Table 4.7 represent the so-called "pV work," or "pressure energy" or "flow work," or "flow energy" i.e., the work done by the surroundings to put a unit mass of matter into the system at 1 in Fig. 4.10 and the work done by the system on the surroundings as a unit mass leaves the system at 2. If work is defined as

$$W = \int_0^l F dl$$

then, since the pressures at the entrance and exit to the system are constant for differential displacements of mass, the work done by the surroundings on the system adds energy to the system at 1:

$$W_1 = \int_0^{l_1} F_1 dl = \int_0^{\hat{V}_1} p_1 d\hat{V} = p_1(\hat{V}_1 - 0) = p_1\hat{V}_1$$

where \hat{V} is the volume per unit mass. Similarly, the work done by the fluid on the surroundings as the fluid leaves the system is $W_2 = p_2\hat{V}_2$, a term that has to be subtracted from the right hand side of Eq. (4.23).

In most problems you do not have to use all of the terms of the general energy balance equation because certain terms may be zero or may be so small that they can be neglected in comparison with the other terms. Several special cases can be deduced from the general energy balance of considerable industrial importance by introducing certain simplifying assumptions:

- (a) No mass transfer (*closed* or *batch* system) ($m_1 = m_2 = 0$)

$$\Delta E = Q - W \quad (4.25)$$

Equation (4.25) is known as the *first law of thermodynamics* for a closed system.

- (b) No accumulation ($\Delta E = 0$), no mass transfer ($m_1 = m_2 = 0$):

$$Q = W \quad (4.26)$$

- (c) No accumulation ($\Delta E = 0$), but with mass flow:

$$Q - W = \Delta[(\hat{H} + \hat{K} + \hat{P})m] \quad (4.27)$$

- (d) No accumulation, $Q = 0$, $W = 0$, $\hat{K} = 0$, $\hat{P} = 0$,

$$\Delta\hat{H} = 0 \quad (4.28)$$

Equation (4.28) is the so-called "enthalpy balance."

- (e) No accumulation ($\Delta E = 0$), no mass transfer ($m_1 = m_2 = 0$):

$$Q = W \quad (4.29)$$

Take, for example, the flow system shown in Fig. 4.12. Overall, between sections 1 and 5, we would find that $\Delta P = 0$. In fact, the **only** portion of the

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$$m_1 = m_2 = 0 \quad (4.26)$$

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4.12. Overall, between the only portion of the

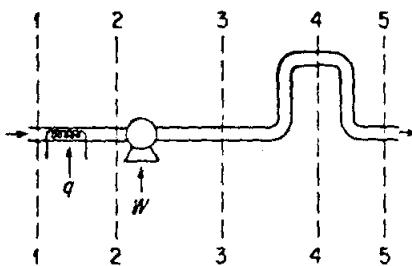


Fig. 4.12. Flow system.

system where ΔP would be of concern would be between section 4 and some other section. Between 3 and 4, ΔP may be consequential, but between 2 and 4 it may be negligible in comparison with the work introduced by the pump. Between section 3 and any further downstream point both Q and W are zero. After reading the problem statements in the examples below but before continuing to read to solution, you should try to apply Eq. (4.24) yourself to test your ability to simplify the energy balance for particular cases.

Some special process names associated with energy balance problems are worth remembering:

- (a) *Isothermal* ($dT = 0$)—constant-temperature process.
- (b) *Adiabatic* ($Q = 0$)—no heat interchange, i.e., an insulated system. If we inquire as to the circumstances under which a process can be called adiabatic, one of the following is most likely:
 - (1) The system is insulated.
 - (2) Q is very small in relation to the other terms in the energy equation and may be neglected.
 - (3) The process takes place so fast that there is no time for heat to be transferred.
- (c) *Isobaric* ($dp = 0$)—constant-pressure process.
- (d) *Isometric or isochoric* ($dV = 0$)—constant-volume process.

Occasionally in a problem you will encounter a special term called *sensible heat*. Sensible heat is the enthalpy difference (normally for a gas) between some reference temperature and the temperature of the material under consideration, excluding any enthalpy differences for phase changes that we have previously termed latent heats.

One further remark that we should make is that the energy balance we have presented has included only the most commonly used energy terms. If a change in surface energy, rotational energy, or some other form of energy is important, these more obscure energy terms can be incorporated in an appropriate energy expression by separating the energy of special interest from the term in which it presently is incorporated in Eq. (4.23). As an example, kinetic energy might be split into linear kinetic energy (translation) and angular kinetic energy (rotation).

We turn now to some examples of the application of the general energy balance.

EXAMPLE 4.11 Application of the energy balance

Changes in the heat input that spacecraft encounter constitute a threat both to the occupants and to the payload of instruments. If a satellite passes into the earth's shadow the heat flux that it receives may be as little as 10 percent of that in direct sunlight. Consider the case in which a satellite leaves the earth's shadow and heats up. For simplicity we shall select just the air in the spacecraft as the system. It holds 4.00 kg of air at 20°C (the air has an internal energy of 8.00×10^5 J/kg with reference to fixed datum conditions). Energy from the sun's radiation enters the air as heat until the internal energy is 10.04×10^5 J/kg. (a) How much heat has been transferred to the air? (b) If by some machinery in the spacecraft 0.110×10^5 J of work were done on the air over the same interval, how would your answer to part (a) change?

Solution:

(a) The air is chosen as the system, and the process is clearly a closed or batch system. Everything outside the air is the surroundings. See Fig. E4.11. Using Eq. (4.24)

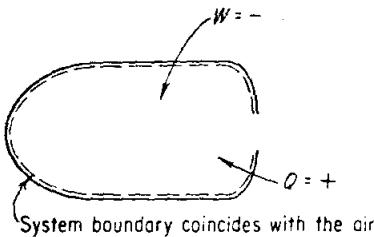


Fig. E4.11.

with the absence of K and P in the accumulation term inside the tank, and with no mass flow from the system to the surroundings or the reverse, we have (for $W = 0$)

$$\Delta U = U_{t_2} - U_{t_1} = Q - W$$

Basis: 1 kg air

$$U_{t_2} - U_{t_1} = (10.04 \times 10^5) - (8.00 \times 10^5) = 2.04 \times 10^5 \text{ J/kg}$$

so that $\hat{Q} = 2.04 \times 10^5 \text{ J/kg}$. Note that the sign of Q is positive, indicating that heat has been added to the system.

Basis: 4.00 kg of air

$$Q = \frac{2.04 \times 10^5 \text{ J}}{\text{kg}} \times 4.00 \text{ kg} = 8.16 \times 10^5 \text{ J}$$

(b) If work is done on the air (by compression or otherwise), then the work term is not zero but

$$W = -0.110 \times 10^5 \text{ J}$$

Note that the sign on the work is negative since work is done on the gas. In this second case,

$$Q = \Delta U + W = (8.16 \times 10^5) - (0.11 \times 10^5) = 8.05 \times 10^5 \text{ J}$$

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EXAMPLE 4.12

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4.11. Using Eq. (4.24)

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 $5 \times 10^4 \text{ J}$

Less heat is required than before to reach the same value for the internal energy because some work has been done on the gas.

EXAMPLE 4.12 Application of the energy balance

Air is being compressed from 1 atm and 460°R (where it has an enthalpy of 210.5 Btu/lb) to 10 atm and 500°R (where it has an enthalpy of 219.0 Btu/lb). The exit velocity of the air from the compressor is 200 ft/sec. What is the horsepower required for the compressor if the load is 200 lb/hr of air?

Solution:

This is clearly a flow process or open system as shown in Fig. E4.12. Equation (4.24) can be used with the assumptions that there is no accumulation of air in the com-

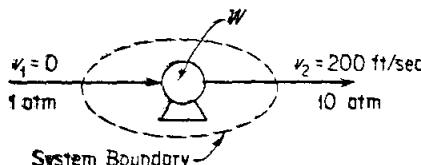


Fig. E4.12.

pressor ($\Delta E = 0$ and $m_1 = m_2$), $Q = 0$ (no heat exchange), and no potential energy terms are of importance. Then

Basis: 1 lb_m air

$$\dot{W} = -\Delta(\hat{H} + \frac{v^2}{2})$$

$$\Delta\hat{H} = 219 - 210.5 = 8.5 \text{ Btu/lb}_m$$

Next, we shall assume that the entering velocity of the air is zero, so that

$$\begin{aligned} \frac{\Delta v^2}{2} &= \frac{(200 \text{ ft})^2}{\text{sec}^2} \left| \frac{32.2 (\text{ft})(\text{lb}_m)}{(\text{sec}^2)(\text{lb}_f)} \right| \frac{1 \text{ Btu}}{778 (\text{ft})(\text{lb}_f)} \Big| \frac{1}{2} \\ &= 0.80 \text{ Btu/lb}_m \end{aligned}$$

$$\dot{W} = -(8.5 + 0.8) = -9.3 \text{ Btu/lb}_m$$

(Note: The minus sign indicates work is done on the air.) To convert to power (work/time),

Basis: 200 lb air/hr

$$\text{hp} = \frac{9.3 \text{ Btu}}{\text{lb}} \left| \frac{200 \text{ lb}}{\text{hr}} \right| \frac{1 \text{ hp}}{2545 \frac{\text{Btu}}{\text{hr}}} = 0.73 \text{ hp}$$

EXAMPLE 4.13 Application of the energy balance

A steel ball weighing 100 lb is dropped 100 ft to the ground. What are the values of Q and W and the change in U , K , and P for this process? What is the change in the total energy of the universe (system plus surroundings)?

Solution:

See Fig. E4.13.

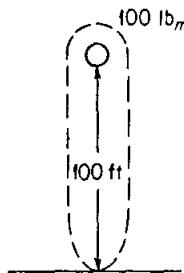


Fig. E4.13.

Let the system be the ball and the surroundings be everything else. This is a batch (nonflow) process. The general energy balance reduces to

$$[(\hat{U}_{t_2} + \hat{K}_{t_2} + \hat{P}_{t_2}) - (\hat{U}_{t_1} + \hat{K}_{t_1} + \hat{P}_{t_1})]m = Q - W$$

After the ball hits the ground and is at rest, we know that its velocity is zero, so that $\Delta K = 0$. We can let the ground be the reference plane for potential energy. Consequently,

$$\begin{aligned} m(\hat{P}_{t_2} - \hat{P}_{t_1}) &= m(g/g_c)(h_2 - h_1) \\ &= (100 \text{ lb}_m)(g/g_c)(-100 \text{ ft}) = -10,000 \text{ (ft)(lb}_f\text{)} \end{aligned}$$

If Q and W are zero, then $U_{t_2} - U_{t_1}$ may be calculated. If Q and W are not zero, then $U_{t_2} - U_{t_1}$ is dependent on the values of Q and W , which are not specifically stated in the problem. If $U_{t_2} - U_{t_1}$ were known, then $Q - W$ could be determined. Without more information or without making a series of assumptions concerning Q , W , and $U_{t_2} - U_{t_1}$, it is not possible to complete the requested calculations.

The change in the total energy of the universe is zero.

EXAMPLE 4.14 Application of the energy balance

Water is being pumped from the bottom of a well 150 ft deep at the rate of 200 gal/hr into a vented storage tank 30 ft above the ground. To prevent freezing in the winter a small heater puts 30,000 Btu/hr into the water during its transfer from the well to the storage tank. Heat is lost from the whole system at the constant rate of 25,000 Btu/hr. What is the rise or fall in the temperature of the water as it enters the storage tank, assuming the well water is at 35°F? A 2-hp pump is being used to pump the water. About 55 percent of the rated horsepower goes into the work of pumping and the rest is dissipated as heat to the atmosphere.

Solution:

Let the system consist of the well inlet, the piping, and the outlet at the storage tank. It is a flow process since material is continually entering and leaving the system. See Fig. E4.14.

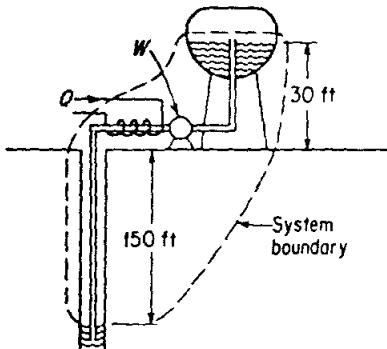


Fig. E4.14.

The general energy equation reduces to

$$Q - W = \Delta[\hat{H} + \hat{K} + \hat{P}]m \quad (a)$$

The term ΔE is zero because no accumulation of energy takes place in the pipe.

Basis: 1 hr operation

The total amount of water pumped is

$$\frac{200 \text{ gal}}{\text{hr}} \left| \frac{1 \text{ hr}}{1 \text{ gal}} \right| \frac{8.33 \text{ lb}}{1 \text{ gal}} = 1666 \text{ lb/hr}$$

The water initially has a velocity of zero at the well inlet. The problem does not specify the size of pipe through which the water is being pumped so it is impossible to calculate the increase in kinetic energy experienced by the water as it leaves the pipe at the storage tank. Unless the pipe is exceptionally small, however, the kinetic energy term may be considered negligible in comparison with the other energy terms in the equation. Thus

$$\hat{K}_1 = \hat{K}_2 \approx 0$$

The potential energy change is

$$m \Delta \hat{P} = mg \Delta h = \frac{1666 \text{ lb}_m}{\text{hr}} \left| \frac{32.2 \text{ ft}}{\text{sec}^2} \right| \left| \frac{180 \text{ ft}}{\frac{32.2 (\text{ft})(\text{lb}_m)}{(\text{sec}^2)(\text{lb}_f)}} \right| = 300,000 \text{ (ft)(lb}_f\text{)/hr}$$

or

$$\frac{300,000 \text{ (ft)(lb}_f\text{)/hr}}{778 \text{ (ft)(lb}_f\text{) Btu}} = 386 \text{ Btu/hr}$$

The heat lost by the system is 25,000 Btu/hr while the heater puts 30,000 Btu/hr into the system. The net heat exchange is

$$Q = 30,000 - 25,000 = 5000 \text{ Btu/hr}$$

The rate of work being done on the water by the pump is

$$W = -\frac{2 \text{ hp}}{(min)(hp)} \left| 0.55 \right| \frac{33,000 \text{ (ft-lb)(lb)}}{Btu} \left| \frac{60 \text{ min}}{\text{hr}} \right| \frac{Btu}{778 \text{ (ft)(lb}_f\text{)}} \\ = -2800 \text{ Btu/hr}$$

ΔH can be calculated from Eq. (a):

$$5000 - (-2800) = \Delta H + 0 + 386$$

$$\Delta H = 7414 \text{ Btu/hr}$$

We know from Eq. (4.7) that, for an incompressible fluid such as water,

$$\Delta \hat{H} = \int_{T_1}^{T_2} C_p dT$$

Because the temperature range considered is small, the heat capacity of liquid water may be assumed to be constant and equal to 1.0 Btu/(lb)(°F) for the problem. Thus

$$\Delta \hat{H} = C_p \Delta T = (1.0)(\Delta T)$$

Basis: 1 lb H₂O

Now

$$\Delta \hat{H} = \frac{7414 \text{ Btu}}{\text{hr}} \left| \frac{1666 \text{ lb}}{\text{hr}} \right. = 6.36 \text{ Btu/lb}$$

$$= (1.0)(\Delta T)$$

$$\Delta T \approx 6.4^\circ\text{F} \text{ temperature rise}$$

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(b) The enthal

The ΔH ,

(c) The enthal

EXAMPLE 4.15 Energy balance

Steam that is used to heat a batch reaction vessel enters the steam chest, which is segregated from the reactants, at 250°C saturated and is completely condensed. The reaction absorbs 1000 Btu/lb of material in the reactor. Heat loss from the steam chest to the surroundings is 5000 Btu/hr. The reactants are placed in the vessel at 70°F and at the end of the reaction the material is at 212°F. If the charge consists of 325 lb of material and both products and reactants have an average heat capacity of $C_p = 0.78 \text{ Btu}/(\text{lb})(^\circ\text{F})$, how many pounds of steam are needed per pound of charge? The charge remains in the reaction vessel for 1 hr.

Solution:

Analysis of the process reveals that no potential energy, kinetic energy, or work terms are significant in the energy balance. The steam flows in and out, while the reacting material stays within the system. Thus there is an accumulation of energy for the material being processed but no accumulation of mass or energy associated with the steam. See Fig. E4.15(a).

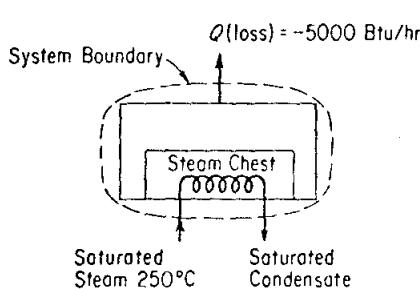


Fig. E4.15(a).

Note that
enthalpy of
products is

ΔH_{prod}

(d) In addition
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Basis: 1 hr of operation

System: Reaction vessel, including steam chest

The energy balance reduces to

$$(U_{t_1} - U_t)_{\text{material}} = -\Delta H_{\text{steam}} + Q \quad (\text{a})$$

However, since enthalpy is more convenient to work with than internal energy, we let $\hat{U} = \hat{H} - p\hat{V}$,

$$[(\hat{H}_{t_1} - \hat{H}_t) - (p_{t_1}\hat{V}_{t_1} - p_t\hat{V}_t)]m = Q - \Delta H_{\text{steam}}$$

Since no information is available concerning the $p\hat{V}$ difference, and it would no doubt be negligible if we could calculate it, it will be neglected, and then

$$(\hat{H}_{t_1} - \hat{H}_t)m = -\Delta H_{\text{steam}} + Q \quad (\text{b})$$

(a) The heat loss is given as $Q = -5000 \text{ Btu/hr}$.

(b) The enthalpy change for the steam can be determined from the steam tables.

The ΔH_{vap} of saturated steam at 250°C is 732.2 Btu/lb, so that

$$\Delta H_{\text{steam}} = -732.2 \text{ Btu/lb}$$

(c) The enthalpy of the initial reactants, with reference to zero enthalpy at 70°F, is

$$\Delta H_{t_1} = m(\Delta \hat{H}) = m \int_{70}^{70} C_p dT = 0$$

Note that the selection of zero enthalpy at 70°F makes the calculation of the enthalpy of the reactants at the start quite easy. The enthalpy of the final products relative to zero enthalpy at 70°F is

$$\begin{aligned} \Delta H_{t_1} &= m \int_{70}^{212} C_p dT = mC_p(212 - 70) \\ &= \frac{325 \text{ lb}}{\text{hr}} \left| \frac{0.78 \text{ Btu}}{(\text{lb})(^{\circ}\text{F})} \right| (212 - 70)^{\circ}\text{F} = 36,000 \text{ Btu/hr} \end{aligned}$$

$$\Delta H_{\text{material}} = 36,000 \text{ Btu/hr}$$

(d) In addition to the changes in enthalpy occurring in the material entering and leaving the system, the reaction absorbs 1000 Btu/lb. This quantity of energy can be conveniently thought of as an energy loss term, or alternately as an adjustment to the enthalpy of the reactants.

$$\Delta H = \frac{-1000 \text{ Btu}}{\text{lb}} \left| \frac{325 \text{ lb}}{\text{hr}} \right| = -325,000 \text{ Btu/hr}$$

Introducing these numbers into Eq. (b), we find that

$$\begin{aligned} 36,000 \frac{\text{Btu}}{\text{hr}} &= \left(737.2 \frac{\text{Btu}}{\text{lb steam}} \right) \left(S \frac{\text{lb steam}}{\text{hr}} \right) \\ &\quad - 5000 \frac{\text{Btu}}{\text{hr}} - 325,000 \frac{\text{Btu}}{\text{hr}} \end{aligned} \quad (\text{c})$$

from which the pounds of steam per hour, S , can be calculated as

$$S = \frac{366,000 \text{ Btu}}{\text{hr}} \left| \frac{1 \text{ lb steam}}{737.2 \text{ Btu}} \right| = 496 \frac{\text{lb steam}}{\text{hr}}$$

or

$$\frac{366,000 \text{ Btu}}{\text{hr}} \left| \frac{1 \text{ lb steam}}{737.2 \text{ Btu}} \right| \left| \frac{1 \text{ hr}}{325 \text{ lb charge}} \right| = 1.53 \frac{\text{lb steam}}{\text{lb charge}}$$

If the system is chosen to be everything but the steam coils and lines, then we would have a situation as shown in Fig. E4.15(b). Under these circumstances we could talk about the heat transferred into the reactor from the steam chest. From a balance on the steam chest (no accumulation),

$$Q = \Delta H_{\text{steam}}$$

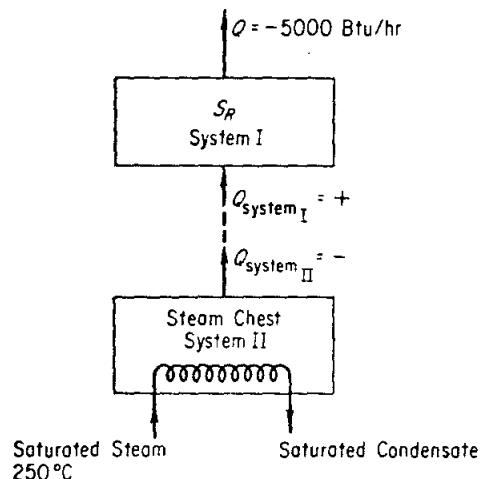


Fig. E4.15(b)

Both have negative values, but remember that

$$Q_{\text{system I}} = -Q_{\text{system II}}$$

so that the value of $Q_{\text{system I}}$ is plus.

The energy balance on system I reduces to

$$(\hat{H}_{t_i} - \hat{H}_{t_f})m = Q \quad (d)$$

where $Q = Q_{\text{system chest}} + (-5000 \text{ Btu})$. The steam used can be calculated from Eq. (d); the numbers will be identical to the calculation made for the original system.

EXAMPLE 4.16 Energy balance

Ten pounds of water at 35°F, 4.00 lb ice at 32°F, and 6.00 lb steam at 250°F and 20 psia are mixed together. What is the final temperature of the mixture? How much steam condenses?

Solution:

We shall assume that the overall batch process takes place adiabatically. See Fig. E4.16. The system is 20 lb of H_2O in various phases. The energy balance reduces to (superscripts are s = steam, w = water, i = ice)

$$20\hat{U}_{t_f} - (60\hat{U}_{t_i}^s + 10\hat{U}_{t_i}^w + 4\hat{U}_{t_i}^i) = 0 \quad (a)$$

on coils and lines, then we
these circumstances we could
steam chest. From a balance

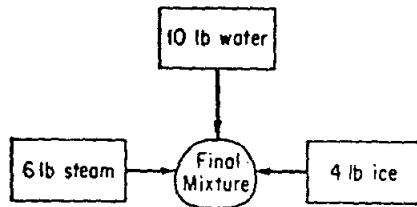


Fig. E4.16.

If U is replaced with $\hat{H} - p\hat{V}$ for convenience in the calculations, we get

$$\begin{aligned} 20\hat{H}_{t_1} - (6\hat{H}_{t_1}^i + 10\hat{H}_{t_1}^w + 4\hat{H}_{t_1}^f) \\ = 20(p\hat{V})_{t_1} - 6(p\hat{V})_{t_1}^i - 10(p\hat{V})_{t_1}^w - 4(p\hat{V})_{t_1}^f \end{aligned} \quad (\text{b})$$

The last two terms on the right-hand side of Eq. (b) cannot be more than 1 Btu at the very most and can safely be neglected.

Because of the phase changes that take place as well as the nonlinearity of the heat capacities as a function of temperature, it is not possible to replace the enthalpies in Eq. (b) with functions of temperature and get a linear algebraic equation that is easy to solve. The simplest way to solve the problem is to assume the final conditions of temperature and pressure and check the assumption by Eq. (c)

$$20\hat{H}_{t_1} - 20(p\hat{V})_{t_1} = (6\hat{H}_{t_1}^i + 10\hat{H}_{t_1}^w + 4\hat{H}_{t_1}^f) - 6(p\hat{V})_{t_1}^i \quad (\text{c})$$

If the assumption proves wrong, a new assumption can be made, leading to a solution to the problem by a series of iterative calculations:

$$\text{Basis: } \begin{cases} 4 \text{ lb ice at } 32^\circ\text{F} \\ 10 \text{ lb H}_2\text{O at } 35^\circ\text{F} \\ 6 \text{ lb steam at } 250^\circ\text{F and 20 psia} \end{cases}$$

Since the enthalpy change corresponding to the heat of condensation of the steam is quite large, we might expect that the final temperature of the mixture would be near or at the saturation temperature of the 20 psia steam. Let us assume that $T_{\text{final}} = 228^\circ\text{F}$ (the saturated temperature of 20 psia of steam). We shall also assume that all the steam condenses as a first guess.

Using the steam tables (ref.: zero enthalpy at 32°F , saturated liquid), we can calculate the following quantities to test our assumption:

	<i>Btu</i>
$6 \Delta\hat{H}_{t_1}^i = \frac{6 \text{ lb}}{\text{lb}} \mid \frac{1168.0 \text{ Btu}}{\text{lb}}$	$= 7008.0$
$10 \Delta\hat{H}_{t_1}^w = \frac{10 \text{ lb}}{\text{lb}} \mid \frac{3.02 \text{ Btu}}{\text{lb}}$	$= 30.2$

The heat of fusion of ice is 143.6 Btu/lb:

$4 \Delta\hat{H}_{t_1}^f = \frac{4 \text{ lb}}{\text{lb}} \mid \frac{143.6 \text{ Btu}}{\text{lb}}$	$= -574.4$
$-6(p\hat{V})_{t_1}^i = -\frac{6 \text{ lb}_m}{\text{in.}^2} \mid \frac{20 \text{ lb}_f}{1 \text{ ft}^2} \mid \frac{(12 \text{ in.})^2}{1 \text{ ft}^2} \mid \frac{20.81 \text{ ft}^3}{\text{lb}_m} \mid \frac{1 \text{ Btu}}{778 (\text{ft})(\text{lb}_f)}$	$= -453.2$
total right-hand side of Eq. (c)	$= 6010.6$

(d)

can be calculated from
the original system.

nd 6.00 lb steam at 250°F
ture of the mixture? How

ace adiabatically. See Fig.
e energy balance reduces

$= 0$

(a)

The left-hand side of Eq. (c) is

$$20 \Delta \hat{H}_{t_i} = \frac{20 \text{ lb}}{\text{lb}} \left| \frac{196.2 \text{ Btu}}{\text{lb}} \right| = 3924.0$$

$$-20(p\hat{V})_{t_i} = -\frac{20 \text{ lb}_m}{\text{in.}^2} \left| \frac{19.7 \text{ lb}_f}{\text{in.}^2} \right| \left| \frac{(12 \text{ in.})^2}{1 \text{ ft}} \right| \left| \frac{0.0168 \text{ ft}^3}{\text{in.}^3} \right| \left| \frac{1 \text{ Btu}}{778 (\text{ft})(\text{lb}_f)} \right| = -1.2$$

liquid

total left-hand side of Eq. (c) = 3922.8

Evidently our assumption that all the steam condenses is wrong, since the value of the left-hand side of Eq. (c) is too small. With this initial calculation we can foresee that the final temperature of the mixture will be 228°F and that a saturated steam-liquid water mixture will finally exist in the vessel. The next question is, How much steam condenses?

Let S = the amount of steam at 228°F:

$$S[\hat{H}_{t_i} - p\hat{V}]_{\text{vapor}} + (20 - S)[\hat{H}_{t_i} - p\hat{V}]_{\text{liquid}} = 6010.6$$

$$(\Delta \hat{H}_{t_i})_{\text{vapor}} = 1156.1 \text{ Btu/lb}$$

$$(\Delta \hat{H}_{t_i})_{\text{liquid}} = 196.2 \text{ Btu/lb}$$

$$(p\hat{V})_{\text{vapor}} = (19.7)(12)^2(20.08)/(778) = 73.2 \text{ Btu/lb}$$

$$(p\hat{V})_{\text{liquid}} \approx 0.0$$

$$S(1156.1 - 73.2) + (20 - S)(196.2) = 6010.6$$

$$S = 2.35 \text{ lb}$$

In effect, $6.00 - 2.35 = 3.65$ lb of steam can be said to condense.

If there had been only 1 lb of steam instead of 6 lb to start with, then on the first calculation the right-hand side of Eq. (c) would have been

$$1168.0 + 30.2 - 574.4 - (1/6)(453.2) = 548.3 \text{ Btu}$$

Hence lower temperatures would have been chosen until the left-hand side of Eq. (c) was small enough. Only liquid water would be present.

EXAMPLE 4.17 Application of the energy balance

The peaks of Mount Everest, Mount Fujiyama, Mount Washington, and other mountains are usually covered with clouds even when the surrounding area has nice weather. It is clear that water condenses because the temperature is lower, but why doesn't water condense elsewhere at the same altitude? Is the cloud cap stuck by some force? See Fig. E4.17.

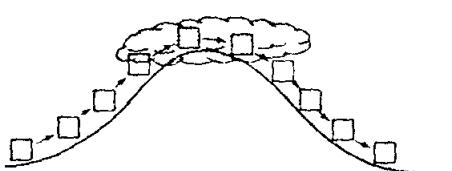


Fig. E4.17.

Solution:

The formation balance. As a unit mass with only modest heating air ($Q = 0$), net $= 0$. Both kinetic energy reduces to

Now

and

Assume that an ideal gas follows pressure change with a constant error the change in temperature is roughly 3° to 4°F/1000 ft. In the mountain, the clouds are to be for a cloud to form at the bottom of the peak or at the top, humidity can be for a cloud to form (altitude 6388 ft), the relative humidity is 40 percent.

A more complicated problem is the formation of clouds.

4.6 Reversible processes and mechanical energy

The energy balance of a system is energy without inquiry. Experience with machines and transformations are no longer available. They cannot be transferred to the reverse direction. Mechanical work. To state the second law of thermodynamics.

As applied to a system, the second law of thermodynamics states that "quality" can be envisaged.

- (a) The so-called potential energy

$$= 3924.0$$

$$\frac{1 \text{ Btu}}{78 \text{ (ft)(lb)}_f} = -1.2$$

$$= 3922.8$$

ing, since the value of the
on we can foresee that the
erated steam-liquid water
w much steam condenses?

$$= 6010.6$$

$$1 \text{ Btu/lb}$$

5

hence.
art with, then on the first

$$3.3 \text{ Btu}$$

left-hand side of Eq. (c)

Washington, and other
surrounding area has nice
ature is lower, but why
cloud cap stuck by some

Solution:

The formation of cloud caps can be predicted with the aid of the general energy balance. As a unit mass of warm moist air, our system, moves up the side of a mountain with only modest breezes, it cannot exchange energy by way of heat with the surrounding air ($Q = 0$), nor does it exchange a significant amount of water vapor ($m_1 = m_2 = 0$). Both kinetic and potential energy effects can be neglected, so that Eq. (4.24) reduces to

$$\Delta U = -W$$

Now

$$\Delta U = \int_{T_1}^{T_2} \hat{C}_v dT \cong \hat{C}_v(T_2 - T_1)$$

and

$$W = \int_{V_1}^{V_2} p d\hat{V}$$

Assume that an ideal gas expands so that $p\hat{V} = \hat{R}T$. Then, from information as to the pressure change with altitude plus the fact that $C_v = 0.25 \text{ cal/(g mole)(}^{\circ}\text{K)}$, by trial and error the change in temperature can be determined as the air rises. The cooling is roughly 3° to $4^{\circ}\text{F}/1000 \text{ ft}$ of elevation. During the descent of the air on the other side of the mountain, the cloud will evaporate. You can also calculate how high a peak has to be for a cloud to form for a given relative humidity and temperature of air at the bottom of the peak or, alternatively, given the peak height, what the highest relative humidity can be for a cloud not to form. As an example of the latter, for Mt. Washington (altitude 6388 ft), the maximum percent relative humidity of 70°F air at sea level is 40 percent.

A more complicated but related problem that we do not have the space to go into is the formation of contrails by supersonic aircraft.

4.6 Reversible processes and the mechanical energy balance

The energy balance of the previous section is concerned with various classes of energy without inquiring into how "useful" each form of energy is to man. Our experience with machines and thermal processes indicates that all types of energy transformation are not equally possible. For example, it is well known that heat cannot be transferred from a low temperature to a high temperature, but only in the reverse direction, nor can internal energy be completely converted into mechanical work. To account for these limitations on energy utilization, the second law of thermodynamics was eventually developed as a general principle.

As applied to fluid dynamic problems, one of the consequences of the second law of thermodynamics is that two categories of energy of different "quality" can be envisioned:

- (a) The so-called *mechanical* forms of energy, such as kinetic energy, potential energy, and work, which are *completely* convertible by an *ideal*

(frictionless, reversible) engine from one form to another within the class.

- (b) Other forms of energy, such as internal energy and heat, which are not so freely convertible.

Of course, in any real process with friction, viscous effects, mixing of components, and other dissipative phenomena taking place which prevent the complete conversion of one form of mechanical energy to another, allowances will have to be made in making a balance on mechanical energy for these "losses" in quality.

To describe the loss or transfer of energy of the freely convertible kind to energy of lesser quality, a concept termed *irreversibility* has been coined. A process which operates without the degradation of the convertible types of energy is termed a *reversible* process; one which does not is an irreversible process. A reversible process proceeds under conditions of differentially balanced forces. Only an infinitesimal change is required to reverse the process, a concept which leads to the name reversible.

Take, for example, the piston shown in Fig. 4.13. During the expansion process the piston moves the distance x and the volume of gas confined in the

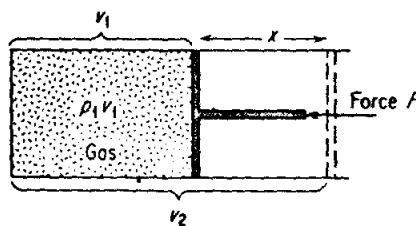


Fig. 4.13. Gas expansion.

piston increases from V_1 to V_2 . Two forces act on the reversible (frictionless) piston; one is the force exerted by the gas, equal to the pressure times the area of the piston, and the other is the force on the piston shaft. If the force exerted by the gas equals the force F , nothing happens. If F is greater than the force of the gas, the gas will be compressed, while if F is less than the force of the gas, the gas will expand.

In the latter case, the work done by the expanding gas and the piston will be $W = \int F dx$. The work of the gas would be $W = \int p dV$ if the process were reversible, i.e., if the force F divided by the piston area were differentially less at all times than the pressure of the gas, and if the piston were frictionless; but in a real process some of the work done by the gas is dissipated by viscous effects, and the piston will not be frictionless so that the work as measured by $\int F dx$ will be less than $\int p dV$. For these two integrals to be equal, none of the available energy of the system can be degenerated to heat or internal energy. To achieve such a situation we shall have to ensure that the movement of the piston is

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Equation (4)
reversibl-
applied to
the work of
systems. As

EXAMPLE

Given:

Required:

Solution:

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mixing of components prevent the conversion; allowances will be made for these "losses" in

convertible kind to have been coined. A convertible type of it is an irreversible differentially balanced process, a concept

using the expansion gas confined in the

versible (frictionless) are times the area of the force exerted by than the force of the of the gas, the gas

the piston will be the process were differentially less at frictionless; but in a by viscous effects, measured by $\int F dx$ one of the available energy. To achieve of the piston is

frictionless and that the motion of the piston proceeds under only a differential imbalance of forces so no shock or turbulence is present. Naturally such a process would take a long time to complete.

No real process which involves friction, shock, finite temperature differences, unrestricted expansion, viscous dissipation, or mixing can be reversible, and so we see that the dropping of a weight from a tower, the operation of a heat exchanger, and the combustion of gases in a furnace are all irreversible processes. Since practically all real processes are irreversible you may wonder why we bother paying attention to the theoretical reversible process. The reason is that it represents the best that can be done, the ideal case, and gives us a measure of our maximum accomplishment. In a real process we cannot do as well and so are less effective. A goal is provided by which to measure our effectiveness. And then, many processes are not too irreversible, so that there is not a big discrepancy between the practical and the ideal process.

A balance on mechanical energy can be written on a microscopic basis for an elemental volume by taking the scalar product of the local velocity and the equation of motion.²⁸ After integration over the entire volume of the system the steady-state mechanical energy balance (for a system with mass interchange with the surroundings) becomes, on a per unit mass basis,

$$\Delta(\hat{K} + \hat{P}) + \int_{p_1}^{p_2} \hat{V} dp + \hat{W} + \hat{E}_v = 0 \quad (4.30)$$

where E_v represents the loss of mechanical energy, i.e., the irreversible conversion by the flowing fluid of mechanical energy to internal energy, a term which must in each individual process be evaluated by experiment (or, as occurs in practice, by use of already existing experimental results for a similar process). Equation (4.30) is sometimes called the Bernoulli equation, especially for the reversible process for which $\hat{E}_v = 0$. The mechanical energy balance is best applied in fluid-flow calculations when the kinetic and potential energy terms and the work are of importance, and the friction losses can be evaluated from handbooks with the aid of friction factors or orifice coefficients.

EXAMPLE 4.18 Application of the mechanical energy balance

Calculate the work per minute required to pump 1 lb of water per minute from 100 psia and 80°F to 1000 psia and 100°F.

Solution:

If the process is assumed to be reversible so that $E_v = 0$, if the pump is 100 percent efficient, and if no kinetic or potential energy terms are involved in the process, Eq. (4.30) reduces to

$$\hat{W} = - \int_{p_1}^{p_2} \hat{V} dp$$

²⁸R. B. Bird, *op. cit.*

From the steam tables, the specific volume of liquid water is $0.01608 \text{ ft}^3/\text{lb}_m$ at 80°F and $0.01613 \text{ ft}^3/\text{lb}_m$ at 100°F . For all practical purposes the water is incompressible, and the specific volume can be taken to be $0.0161 \text{ ft}^3/\text{lb}_m$. Then,

Basis: 1 min

$$\begin{aligned} W &= -\frac{1 \text{ lb}_m}{\text{min}} \int_{100}^{1000} 0.0161 \, dp \\ &= -\frac{1 \text{ lb}_m}{\text{min}} \left| \frac{0.0161 \text{ ft}^3}{\text{lb}_m} \right| \left| \frac{(1000 - 100) \text{ lb}_f}{\text{in.}^2} \right| \left| \left(\frac{12 \text{ in.}}{1 \text{ ft}} \right)^2 \right| \left| \frac{1 \text{ Btu}}{778 (\text{ft})(\text{lb}_f)} \right| \\ &= -2.68 \frac{\text{Btu}}{\text{min}} \end{aligned}$$

About the same value can be calculated using Eq. (4.24) if $\hat{Q} = \hat{K} = \hat{P} = 0$, because the enthalpy change²⁹ for a reversible process for 1 lb of water going from 100 psia and 100°F to 1000 psia is 2.70 Btu. However, usually the enthalpy data for liquids other than water are missing, or not of sufficient accuracy to be of much value, which forces the engineer to turn to the mechanical energy balance.

One might now well inquire for the purpose of purchasing a pump-motor, say, as to what the work would be for a real process, instead of the fictitious reversible process assumed above. First, you would need to know the efficiency of the combined pump and motor so that the actual input from the surroundings (the electric connection) to the system would be known. Second, the friction losses in the pipe, valves, and fittings must be estimated so that the term \hat{E}_v could be reintroduced into Eq. (4.30). Suppose, for the purposes of illustration, that \hat{E}_v was estimated to be, from an appropriate handbook, $320 (\text{ft})(\text{lb}_f)/\text{lb}_m$ and the motor-pump efficiency was 60 percent (based on 100 percent efficiency for a reversible pump-motor). Then,

$$\begin{aligned} E_v &= \frac{320 (\text{ft})(\text{lb}_f)}{1 \text{ lb}_m} \left| \frac{1 \text{ Btu}}{778 (\text{ft})(\text{lb}_f)} \right| \left| \frac{1 \text{ lb}_m}{\text{min}} \right| = 0.41 \text{ Btu/min} \\ W &= -(2.68 + 0.41) = -3.09 \text{ Btu/min} \end{aligned}$$

Remember that the minus sign indicates work is done on the system. The pump motor must have the capacity

$$\frac{3.09 \text{ Btu}}{1 \text{ min}} \left| \frac{1}{0.60} \right| \left| \frac{1 \text{ min}}{60 \text{ sec}} \right| \left| \frac{1.415 \text{ hp}}{1 \text{ Btu/sec}} \right| = 0.122 \text{ hp}$$

EXAMPLE 4.19 Calculation of work for a batch process

One pound mole of N_2 is in a horizontal cylinder at 100 psia and 70°F . A 1-in.² piston of 5-lb weight seals the cylinder and is fixed by a pin. The pin is released and the N_2 volume is doubled, at which time the piston is stopped again. What is the work done by the gas in this process?

Solution:

- (a) Draw a picture. See Fig. E4.19.
- (b) Is the process a flow or nonflow process? Since no material leaves or enters the cylinder, let us analyze the process as a nonflow system.

²⁹From J. H. Keenan and F. G. Keyes, *Thermodynamic Properties of Steam*, Table 3, Wiley, New York, 1936.

$0.01608 \text{ ft}^3/\text{lb}_m$ at 80°F
is incompressible, and

$$\frac{1 \text{ Btu}}{778 (\text{ft})(\text{lb}_f)}$$

if $\hat{Q} = \hat{K} = \hat{P} = 0$,
of water going from 100°
the enthalpy data for
may to be of much value.
balance.

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in the pipe, valves, and
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Btu/min

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2 hp

psia and 70°F. A 1-in.²
pin is released and the
chain. What is the work

material leaves or enters
system.

Properties of Steam, Table 3.

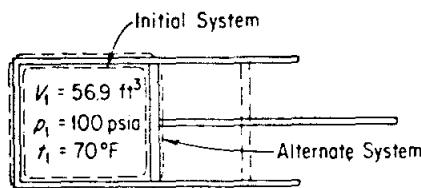


Fig. E4.19.

- (c) This process is definitely irreversible because of friction between the piston (and the gas) and the walls of the cylinder, turbulence in the gas, the large pressure drops, etc.
- (d) In selecting a system to work with, we can choose either the gas itself or the gas plus the piston. Let us initially select the N₂ gas as the system, with the surroundings being everything else including the piston and the cylinder.
- (e) Since the gas expansion is a nonflow process, Eq. (4.30) does not apply. Even if you had an expression for the unsteady-state mechanical energy balance (which we have not discussed since it involves the concept of entropy), it would not be possible to calculate the work done by the gas because the process is irreversible and the E_s term would not be known. As might be expected, a direct application of $W = \int F dl$ fails for this problem because the pressure of the gas does not necessarily equal the force per unit area applied by the piston to the gas, i.e., the work cannot be obtained from $W = \int p dV$.
- (f) Let us change our system to include the gas, the piston, and the cylinder. With this choice, the system expansion is still irreversible, but the pressure in the surroundings can be assumed to be atmospheric pressure and is constant. The work done in pushing back the atmosphere probably is done almost reversibly from the viewpoint of the surroundings and can be closely estimated by calculating the work done on the surroundings:

$$W = \int_{V_1}^{V_2} F dl = \int_{V_1}^{V_2} p dV = p \Delta V$$

$$p = \frac{14.7 \text{ lb}_f}{\text{in.}} \left| \frac{144 \text{ in.}^2}{1 \text{ ft}^2} \right| = \frac{2120 \text{ lb}_f}{\text{ft}^2}$$

Assuming that $z = 0.995$ and is constant, the initial volume of gas is

$$V_1 = \frac{359 \text{ ft}^3}{1 \text{ lb mole}} \left| \frac{530^\circ\text{R}}{492^\circ\text{R}} \right| \left| \frac{14.7}{100} \right| = 56.9 \text{ ft}^3/\text{lb mole}$$

and ΔV of the gas is $2V_1 - V_1 = V_1 = 56.9 \text{ ft}^3/\text{lb mole}$ so that the volume change of the surroundings is -56.9 ft^3 . Then the work done on the surroundings is

$$W = \frac{2120 \text{ lb}_f}{\text{ft}^2} \left| \frac{-56.9 \text{ ft}^3}{1 \text{ lb mole}} \right| \left| \frac{1 \text{ lb mole}}{1 \text{ lb}} \right|$$

$$= -120,000 (\text{ft})(\text{lb}_f)$$

The minus sign indicates that work is done on the surroundings. From this we know that the work done by the alternative system is

$$W_{\text{system}} = -W_{\text{surroundings}} = -(-120,000) = 120,000 (\text{ft})(\text{lb}_f)$$

- (g) This still does not answer the question of what work was done by ... gas, because our system now includes both the piston and the cylinder as well as the gas. You may wonder what happens to the energy transferred from the gas to the piston itself. Some of it goes into work against the atmosphere, which we have just calculated; where does the rest of it go? This energy can go into raising the temperature of the piston or the cylinder or the gas. With time, part of it can be transferred to the surroundings to raise the temperature of the surroundings. From our macroscopic viewpoint we cannot say specifically what happens to this "lost" energy.
- (h) You should also note that if the surroundings were a vacuum instead of air, then no work would be done by the system, consisting of the piston plus the cylinder plus the gas, although the gas itself probably still would do some work.

4.7 Heat of reaction

So far we have not discussed how to treat energy changes caused by chemical reactions, a topic that is frequently called *thermochemistry*. The energy change that appears directly as a result of a reaction is termed the *heat of reaction*, ΔH_{rxn} , a term which is a legacy of the days of the caloric theory. ("Heat of reaction" in terms of modern concepts is best thought of as the energy released or absorbed because of the reaction that may be transferred as heat in certain types of experiments which are delineated below but may also end up as internal energy or as another form of energy.) The energy released or absorbed during a reaction comes from the rearrangement of the bonds holding together the atoms of the reacting molecules. For an exothermic reaction, the energy required to hold the products of the reaction together is less than that required to hold the reactants together and the surplus energy is released.

To take account of possible energy changes caused by a reaction, in the energy balance we incorporate in the enthalpy of each individual constituent an additional quantity termed the standard heat (really enthalpy) of formation, $\Delta \hat{H}_f^\circ$, a quantity that is discussed in detail below. Thus, for the case of a single species *A* without any pressure effect on the enthalpy and omitting phase changes,

$$\Delta \hat{H}_A = \Delta \hat{H}_{fA}^\circ + \int_{T_{ref}}^T C_{pA} dT \quad (4.31)$$

For several species in which there is no energy change on mixing we would have

$$\Delta H_{mixture} = \sum_{i=1}^s n_i \Delta \hat{H}_{fi}^\circ + \sum_{i=1}^s \int_{T_{ref}}^T n_i C_{pi} dT \quad (4.32)$$

where *i* designates each species, n_i is the number of moles of species *i*, and *s* is the total number of species.

If a mixture enters and leaves a system without a reaction taking place, we would find that the same species entered and left so that the enthalpy change in

either the flow or the ferment with the modif because the terms tha would cancel. For ex output enthalpy woul

$$\Delta H_{output} = n$$

and the input enthalpy

$$\Delta H_{input} = n$$

We observe that ΔH_{input} terms that we have de

However, if a re differ, and the terms example, suppose that 4 leave. Then

$$\Delta H_{out} - \Delta H_{in} = (n_i + \int_{T_{ref}}^{T_{out}} (n_i$$

To determine the the experimenter usual energy, potential energ process (a bomb calor process in an experimenter of Eq. (4.33) are zero term) version of Eq. (4.33)

and

$$\Delta H_{out} - \Delta H_{in} = 0$$

In other words, the enthalpy change that appears as heat to the system is observed is termed the heat of reaction. If $W = 0$, and the temperature of the streams, can also be used. The left side of Eq. (4.33) is zero for a calorimeter of constant volume.

The calculations are simple, although the effect of pressure under most conditions, make the necessary corrections.

There are certain

work was done by the gas, and the cylinder as well as energy transferred from the system against the atmosphere, if it goes? This energy can come from the cylinder or the gas. With no work to raise the temperature we cannot say specifically.

In a vacuum instead of air, nothing of the piston plus the cylinder would do some work.

processes caused by chemical reactions. The energy change is called the *heat of reaction*, or *exergy*. ("Heat of reaction" is energy released or absorbed as heat in certain processes; it also ends up as internal energy or absorbed during a reaction, the atoms being together the atoms and the energy required to hold them required to hold the

caused by a reaction, in the individual constituent amounts (enthalpy) of formation, for the case of a single phase and omitting phase

$$(4.31)$$

in mixing we would have dT

$$(4.32)$$

values of species i , and s is the reaction taking place, we have the enthalpy change in

either the flow or the accumulation terms in Eq. (4.24) would not be any different with the modification described above than what we have used before, because the terms that account for the heat of reaction in the energy balance would cancel. For example, for the case of two species in a flow system, the output enthalpy would be

$$\Delta H_{\text{output}} = n_1 \Delta \hat{H}_{f1}^{\circ} + n_2 \Delta \hat{H}_{f2}^{\circ} + \int_{T_{\text{ref}}}^{T_{\text{out}}} (n_1 C_{p1} + n_2 C_{p2}) dT$$

and the input enthalpy would be

$$\Delta H_{\text{input}} = n_1 \Delta \hat{H}_{f1}^{\circ} + n_2 \Delta \hat{H}_{f2}^{\circ} + \int_{T_{\text{ref}}}^{T_{\text{in}}} (n_1 C_{p1} + n_2 C_{p2}) dT$$

We observe that $\Delta H_{\text{output}} - \Delta H_{\text{input}}$ would only involve the "sensible heat" terms that we have described before.

However, if a reaction takes place, the species that enter and leave will differ, and the terms involving the heat of formation will not cancel. For example, suppose that species 1 and 2 enter the system, react, and species 3 and 4 leave. Then

$$\begin{aligned} \Delta H_{\text{out}} - \Delta H_{\text{in}} &= (n_1 \Delta \hat{H}_{f3}^{\circ} + n_2 \Delta \hat{H}_{f4}^{\circ}) - (n_1 \Delta \hat{H}_{f1}^{\circ} + n_2 \Delta \hat{H}_{f2}^{\circ}) \\ &\quad + \int_{T_{\text{ref}}}^{T_{\text{out}}} (n_3 C_{p3} + n_4 C_{p4}) dT - \int_{T_{\text{ref}}}^{T_{\text{in}}} (n_1 C_{p1} + n_2 C_{p2}) dT \end{aligned} \quad (4.33)$$

To determine the values of the standard heats (enthalpies) of formation, the experimenter usually selects either a simple flow process without kinetic energy, potential energy, or work effects (a flow calorimeter), or a simple batch process (a bomb calorimeter), in which to conduct the reaction. For the flow process in an experiment in which the sensible heat terms on the right-hand side of Eq. (4.33) are zero and no work is done, the steady-state (no accumulation term) version of Eq. (4.24) reduces to

$$Q = \Delta[\hat{H}_m] = \Delta H_{\text{rxn}}$$

and

$$\Delta H_{\text{rxn}}^{\circ} = (\sum_{\text{products}} n_i \Delta \hat{H}_{f_i}^{\circ} - \sum_{\text{reactants}} n_i \Delta \hat{H}_{f_i}^{\circ}) \quad (4.34)$$

In other words, the energy change caused by the reaction in such an experiment appears as heat transferred to or from the system, and the value of Q that is observed is termed the heat of reaction. A flow calorimeter in which $Q = 0$, $H' = 0$, and the temperature change is measured between the input and output streams, can also be used to compute the heat of reaction, because the left-hand side of Eq. (4.33) is zero. Refer to Sec. 4.7-3 for an analysis of the batch bomb calorimeter of constant volume.

The calculations that we shall make here will all be for low pressures, and, although the effect of pressure upon heats of reaction is relatively negligible under most conditions, if exceedingly high pressures are encountered, you should make the necessary corrections as explained in most texts on thermochemistry.

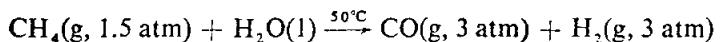
There are certain conventions and symbols which you should always keep in

mind concerning thermochemical calculations if you are to avoid difficulty later on. These conventions can be summarized as follows:

- (a) The reactants are shown on the left-hand side of the equation, and the products are shown on the right—for example,



- (b) The conditions of phase, temperature, and pressure must be specified unless the last two are the standard conditions, as presumed in the example above, when only the phase is required. This is particularly important for compounds such as H_2O , which can exist as more than one phase under common conditions. If the reaction takes place at other than standard conditions, you might write



- (c) Unless otherwise specified, the heats of reaction, the enthalpy changes, and all the constituents are at the standard state of 25°C (77°F) and 1 atm total pressure. The heat of reaction under these conditions is called the *standard heat of reaction*, and is distinguished by the superscript $^\circ$ symbol.
- (d) Unless the amounts of material reacting are stated, it is assumed that the quantities reacting are the stoichiometric amounts shown in the chemical equation.

Data to compute the standard heat of reaction are reported and tabulated in two different but essentially equivalent forms:

- (a) Standard heats of formation
- (b) Standard heats of combustion

We shall first describe the standard heat of formation ($\Delta\hat{H}_f^\circ$) and afterward the standard heat of combustion ($\Delta\hat{H}_c^\circ$). (The superscript $^\circ$ denotes *standard state*.) The units of both quantities are usually tabulated as energy per mole, such as kilocalories per gram mole. The "per mole" refers to the specified reference substance in the related stoichiometric equation.

4.7.1 Standard Heat of Formation. This is a special type of heat of reaction, one for the formation of a compound from the elements. The initial reactants and final products must be stable and at 25°C and 1 atm. The reaction does not necessarily represent a real reaction that would proceed at constant temperature but can be a fictitious process for the formation of a compound from the elements. By defining the heat of formation as zero in the standard state for each *element*, it is possible to design a system to express the heats of formation

for all *compounds*. Then the *theoretical* experience a standard heat of reaction $\Delta\hat{H}_f^\circ$.

A formal form 1 mole of reaction $\Delta\hat{H}_f^\circ$ (molar) standard heat of reaction $\Delta\hat{H}_c^\circ$.

EXAMPLE 4.1

What is the

Solution:

In the reac-

Tabulated data

both $\text{H}_2(\text{g})$ and Appendix E (for this compound above). The value of $\Delta\hat{H}_f^\circ$ for the reaction or by some other method.

EXAMPLE 4.2

Suppose we have the following experimental data. Calculate $\Delta\hat{H}_c^\circ$ for the combustion of C_2H_6 (ethane).

A:	C_2H_6
B:	CO_2
C:	H_2O
D:	N_2

The energy released in the combustion of C_2H_6 is

to avoid difficulty later
in the equation, and the

$\Delta H_2(g)$

must be specified
as presumed in the
This is particularly
exist as more than
takes place at other

$+ H_2(g, 3 \text{ atm})$

the enthalpy changes
of 25°C (77°F) and
these conditions is
this is the super-

it is assumed that
amounts shown in the

reported and tabulated

(ΔH_f°) and afterward the
notes standard state.)
say per mole, such as
the specified reference

special type of heat of
elements. The initial
1 atm. The reaction
proceed at constant
of a compound from
the standard state for
heats of formation

for all compounds at 25°C and 1 atm. If you use the conventions discussed above, then the thermochemical calculations will all be consistent, and you should not experience any confusion as to signs. Consequently, with the use of well-defined standard heats of formation, it is not necessary to record the experimental heats of reaction for every reaction that can take place.

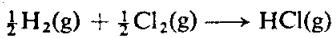
A formation reaction is understood by convention to be a reaction which forms 1 mole of compound from the elements which make it up. Standard heats of reaction for any reaction can be calculated from the tabulated (or experimental) standard heats of formation values by using Eq. (4.34), because the standard heat of formation is a state (point) function.

EXAMPLE 4.20 Heats of formation

What is the standard heat of formation of $\text{HCl}(g)$?

Solution:

In the reaction at 25°C and 1 atm,



Tabulated data: $\Delta\hat{H}_f^{\circ}\left(\frac{\text{cal}}{\text{g mole}}\right) \quad 0 \quad 0 \quad -22,063$

both $\text{H}_2(g)$ and $\text{Cl}_2(g)$ would be assigned $\Delta\hat{H}_f^{\circ}$ values of 0, and the value shown in Appendix F for $\text{HCl}(g)$ of $-22,063 \text{ cal/g mole}$ is the standard heat of formation for this compound (as well as the standard heat of reaction for the reaction as written above). The value tabulated in Appendix F might actually be determined by carrying out the reaction shown for $\text{HCl}(g)$ and measuring the energy liberated in a calorimeter, or by some other more convenient method.

EXAMPLE 4.21 Indirect determination of heats of formation

Suppose that you want to find the standard heat of formation of CO from experimental data. Can you prepare pure CO from C and O_2 and measure the energy liberated? This would be far too difficult. It would be easier experimentally to find the energy liberated for the two reactions shown below and add them as follows:

Basis: 1 g mole CO

$\Delta\hat{H}_{rxn}^{\circ}(\text{experimental})$

$A: \text{C}(\beta) + \text{O}_2(g) \longrightarrow \text{CO}_2(g) \quad -94.052 \text{ kcal/g mole}$

$B: \text{CO}(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{CO}_2(g) \quad -67.636 \text{ kcal/g mole}$

$C: \text{B: } \text{C}(\beta) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{CO}(g)$

$$\Delta\hat{H}_{rxn}^{\circ} A-B = (-94.052) - (-67.636) = \Delta\hat{H}_f^{\circ} = -26.416 \text{ kcal/g mole}$$

The energy change for the overall reaction scheme is the desired heat of formation per mole of $\text{CO}(g)$. See Fig. E4.21.

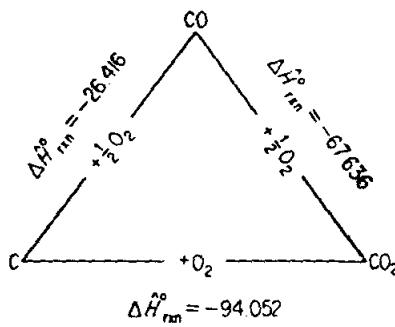
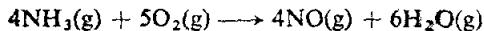


Fig. E4.21.

EXAMPLE 4.22 Calculation of the heat of reaction

Calculate $\Delta\hat{H}_{rxn}^\circ$ for the following reaction of 5 moles of NH₃:



Solution:

Basis: 4 g mole NH₃

tabulated data	NH ₃ (g)	O ₂ (g)	NO(g)	HO ₂ (g)
$\Delta\hat{H}_f^\circ$ per mole at 25°C and 1 atm (kcal/g mole)	-11.04	0	+21.60	-57.80

We shall use Eq. (4.34) to calculate $\Delta\hat{H}_{rxn}^\circ$ for 5 g moles of NH₃:

$$\begin{aligned}\Delta\hat{H}_{rxn}^\circ &= [4(21.60) + 6(-57.80)] - [5(0) + 4(-11.04)] \\ &= -216.24 \text{ kcal/g mole} \quad \text{or} \quad \Delta\hat{H}_{rxn}^\circ = -54.0 \text{ kcal/g mole NH}_3 \\ \Delta\hat{H}_{rxn}^\circ &= \frac{(-54.0) \text{ kcal}}{\text{g mole NH}_3} \times 5 \text{ g mole NH}_3 = -270.0 \text{ kcal}\end{aligned}$$

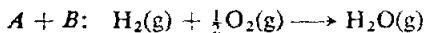
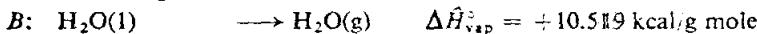
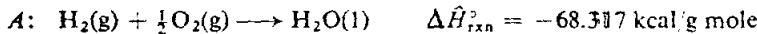
EXAMPLE 4.23 Heat of formation with a phase change

If the standard heat of formation for H₂O(l) is -68,317 cal/g mole and the heat of evaporation is +10,519 cal/g mole at 25°C and 1 atm, what is the standard heat of formation of H₂O(g)?

Solution:

Basis: 1 g mole H₂O

We shall proceed as in Example 4.21 to add the known chemical equations to yield the desired chemical equation and carry out the same operations on the heats of reaction. For reaction A, $\Delta\hat{H}_{rxn}^\circ = \sum \Delta\hat{H}_f^\circ_{\text{products}} - \sum \hat{H}_f^\circ_{\text{reactants}}$:



$$\Delta\hat{H}_{rxn,A}^\circ + \Delta\hat{H}_{vap}^\circ = \Delta\hat{H}_{rxn,\text{H}_2\text{O}(\text{g})}^\circ = \Delta\hat{H}_f^\circ_{\text{H}_2\text{O}(\text{g})} = -57.798 \text{ kcal/g mole}$$

You can use algebraic rules of subtraction to calculate

To solve at 25°C and as H₂O(g), into account

Practically, 1 cal/g mole w

There are 500, and its heats of form heat of form chemical liter and Doraisw Remember for exotherm

4.7.2 S

are the second chemical cal standard sta with the sta

(a) Th pro

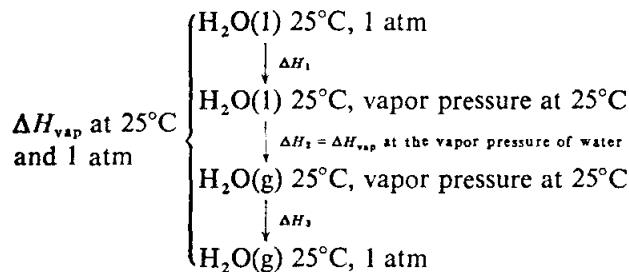
(b) Th

(c) Ze for

20 K. K.
(1965).
HCl(aq)

You can see that any number of chemical equations can be treated by algebraic methods, and the corresponding heats of reaction can be added or subtracted in the same fashion as are the equations. By carefully following these rules of procedure, you will avoid most of the common errors in thermochemical calculations.

To simplify matters, the value cited for ΔH_{vap} of water in Example 4.23 was at 25°C and 1 atm. To calculate this value, if the final state for water is specified as $\text{H}_2\text{O}(\text{g})$ at 25°C and 1 atm, the following enthalpy changes should be taken into account if you start with $\text{H}_2\text{O}(\text{l})$ at 25°C and 1 atm:



Practically, the value of ΔH_{vap} at 25°C and the vapor pressure of water of 10,495 cal/g mole will be adequate for engineering calculations.

There are many sources of tabulated values for the standard heats of formation. A good source of extensive data is the *National Bureau of Standards Bulletin* 500, and its supplements, by F. K. Rossini. A condensed set of values for the heats of formation may be found in Appendix F. If you cannot find a standard heat of formation for a particular compound in reference books or in the chemical literature, $\Delta \hat{H}_f^\circ$, may be estimated by the methods described in Verma and Doraiswamy³⁰ or by some of the authors listed as references in their article. Remember that the values for the standard heats of formation are negative for exothermic reactions.

4.7.2 Standard Heat of Combustion. Standard heats of combustion are the second method of expressing thermochemical data useful for thermochemical calculations. The standard heats of combustion do not have the same standard states as the standard heats of formation. The conventions used with the standard heats of combustion are

- The compound is oxidized with oxygen or some other substance to the products $\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\text{l})$, $\text{HCl}(\text{aq})$,³¹ etc.
- The reference conditions are still 25°C and 1 atm.
- Zero values of $\Delta \hat{H}_c^\circ$ are assigned to certain of the oxidation products as, for example, $\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\text{l})$, and $\text{HCl}(\text{aq})$.

³⁰K. K. Verma and L. K. Doraiswamy, *Ind. Eng. Chem. Fundamentals*, v. 4, p. 389 (1965).

³¹ $\text{HCl}(\text{aq})$ represents an infinitely dilute solution of HCl (see Sec. 4.8).

- (d) If other oxidizing substances are present, such as S or N₂, or if Cl₂ is present, it is necessary to make sure that states of the products are carefully specified and are identical to (or can be transformed into) the final conditions which determine the standard state as shown in Appendix F.

The standard heat of combustion can never be positive but is always negative. A positive value would mean that the substance would not burn or oxidize.

In the search for better high-energy fuels, the heat of combustion of each element in terms of energy per unit mass is of interest. You can see from Fig. 4.14 that the best fuels will use H, Be or B as building blocks. With everything

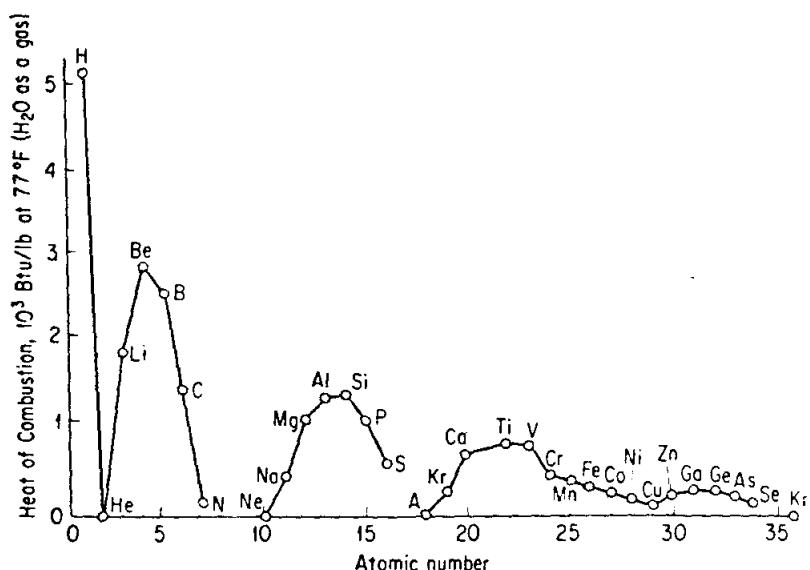


Fig. 4.14.

else held constant, the greater the heat of combustion per unit mass, the longer the range of an airplane or missile.

For a fuel such as coal or oil, the standard heat of combustion is known as the *heating value* of the fuel. To determine the heating value, a weighed sample is burned in oxygen in a calorimeter bomb, and the energy given off is detected by measuring the temperature increase of the bomb and surrounding apparatus.

Because the water produced in the calorimeter is in the vicinity of room temperature (although the gas within the bomb is saturated with water vapor at this temperature), essentially all the water formed in the combustion process is condensed into liquid water. This is not like a real combustion process in a furnace where the water remains as a vapor and passes up the stack. Consequently we have two heating values for fuels containing hydrogen: (a) the gross, or higher, heating value, in which all the water formed is condensed into li-

such as S or N_2 , or if Cl_2 is present, the states of the products are to be transformed into the standard state as shown in

Table 4.1. The heat of combustion of each element is positive but is always negative. It could not burn or oxidize. The heat of combustion of each element is positive. You can see from Fig. 4.1 that the heat of combustion of each element is positive. With everything

in liquid state, and (b) the net, or lower, heating value, in which all the water formed remains in the vapor state. The value you determine in the calorimeter is the gross heating value; this is the one reported along with the fuel analysis and should be presumed unless the data state specifically that the net heating value is being reported.

You can estimate the heating value of a coal within about 3 percent from the Dulong formula³²:

The higher heating value (HHV) in British thermal units per pound

$$= 14,544C + 62,028\left(H - \frac{O}{8}\right) + 4050S$$

where C = weight fraction carbon

S = weight fraction net sulfur

$H - \frac{O}{8}$ = weight fraction net hydrogen

= total weight fraction hydrogen - $\frac{1}{8}$ weight fraction oxygen

The values of C , H , S , and O can be taken from the fuel or flue-gas analysis. If the heating value of a fuel is known and the C and S are known, the approximate value of the net H can be determined from the Dulong formula.

EXAMPLE 4.24 Heating value of coal

Coal gasification consists of the chemical transformation of solid coal into gas. The heating values of coal differ, but the higher the heating value, the higher the value of the gas produced (essentially methane, carbon monoxide, hydrogen, etc.). The following coal has a reported heating value of 12,810 Btu/lb as received. Assuming that this is the gross heating value, calculate the net heating value.

comp.	%
C	71.0
H_2	5.6
N_2	1.6
Net S	2.7
Ash	6.1
O_2	13.0
	100.0

Solution:

The corrected ultimate analysis shows 5.6 percent hydrogen on the as-received basis.

Basis: 100 lb coal as received

The water formed on combustion is

$$\frac{5.6 \text{ lb } H_2}{2.02 \text{ lb } H_2} \mid \frac{1 \text{ lb mole } H_2}{1 \text{ lb mole } H_2} \mid \frac{1 \text{ lb mole } H_2O}{1 \text{ lb mole } H_2} \mid \frac{18 \text{ lb } H_2O}{1 \text{ lb mole } H_2O} = 50 \text{ lb } H_2O$$

³²H. H. Lowry, ed., *Chemistry of Coal Utilization*, Wiley, New York, 1945, Chap. 4.

The energy required to evaporate the water is

$$\frac{50 \text{ lb H}_2\text{O}}{100 \text{ lb coal}} \mid \frac{1020 \text{ Btu}}{1 \text{ lb H}_2\text{O}} = \frac{510 \text{ Btu}}{1 \text{ lb coal}}$$

The net heating value is

$$12,810 - 510 = 12,300 \text{ Btu/lb}$$

The value 1020 Btu/lb is not the latent heat of vaporization of water at 77°F (1050 Btu/lb) but includes the effect of a change from a heating value at constant volume to one at constant pressure (-30 Btu/lb) as described in a later section of this chapter.

A general relation between the gross heating value and the net heating value is

$$\text{net Btu/lb coal} = \text{gross Btu/lb coal} - 91(\% \text{ total H by weight})$$

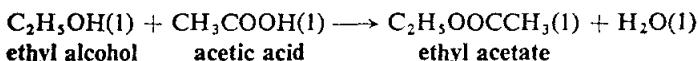
Standard heats of reaction can be calculated from standard heats of combustion by an equation analogous to Eq. (4.34):

$$\begin{aligned}\Delta H_{rxn}^{\circ} &= -[\sum \Delta H_c^{\circ} \text{ products} - \sum H_c^{\circ} \text{ reactants}] \\ &= -[\sum n_{prod} \Delta \hat{H}_c^{\circ} \text{ prod} - \sum n_{react} \Delta \hat{H}_c^{\circ} \text{ react}]\end{aligned}\quad (4.35)$$

Note: The minus sign in front of the summation expression occurs because the choice of reference states is zero for the right-hand side of the standard equations.

EXAMPLE 4.25 Calculation of heat of reaction from heat of combustion data

What is the heat of reaction of the following reaction:



Solution:

Basis: 1 g mole C₂H₅OH

Tabulated data	C ₂ H ₅ OH(l)	CH ₃ COOH(l)	C ₂ H ₅ OOCCH ₃ (l)	H ₂ O(l)
Δ̂H _c [°] per mole at 25°C and 1 atm (kcal/g mole)	-326.70	-208.34	-538.75	0

We use Eq. (4.35):

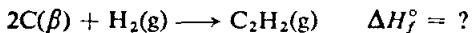
$$\Delta H_{rxn}^{\circ} = -[-538.75 - (-326.70 - 208.34)] = +3.72 \text{ kcal/g mole}$$

EXAMPLE 4.26 Calculation of heat of formation from heats of combustion

Calculate the standard heat of formation of C₂H₂(g) (acetylene) from the standard heat of combustion data.

Solution:

The standard heat of formation for C₂H₂(g) would be expressed in the following manner (basis: 1 g mole C₂H₂):



How can data? The pro of combustion equations (B a The details are

A: C₂
B: C(/
C: H₂
-A + 2B
2C

$$\Delta H_{net}^{\circ} = \Delta H$$

EXAMPLE 4.27

The follow below at 25°C

1. C₃H₈(g)
2. C₃H₈(g)
3. H₂(g)
4. H₂O(l)
5. C (diamond)
6. C (graphite)

Calculate the fo

- (a) The sta
- (b) The sta
- (c) The n
- Hg sat

Solution:
(a) Refer to values.

- (1) C₃H₈
- (2) C₃H₈
- (3) -471
- (6) -50
- (7) -61

How can we obtain this equation using known standard heat of combustion data? The procedure is to take the chemical equation which gives the standard heat of combustion of $C_2H_2(g)$ (Eq. A below) and add or subtract other known combustion equations (B and C) so that the desired equation is finally obtained algebraically. The details are shown below:

	$\Delta\hat{H}_c^\circ$ (kcal/g mole)
A: $C_2H_2(g) + 2\frac{1}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$	-310.615
B: $C(\beta) + O_2(g) \rightarrow CO_2(g)$	-94.052
C: $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$	-68.312
-A + 2B + C:	
$2C(\beta) + H_2(g) \rightarrow C_2H_2(g)$	
$\Delta H_{net}^\circ = \Delta H_f^\circ = -(-310.615) + 2(-94.052) + (-68.317) = +54.194 \frac{\text{kcal}}{\text{g mole}}$	

EXAMPLE 4.27 Combination of heats of reaction at 25°C

The following heats of reaction are known from experiments for the reactions below at 25°C in the standard thermochemical state:

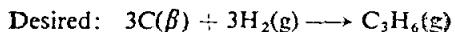
rxn	$\Delta\hat{H}_{rxn}^\circ$ kcal/g mole
1. $C_3H_6(g) + H_2(g) \rightarrow C_3H_8(g)$	-29.6
2. $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$	-530.6
3. $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$	-68.3
4. $H_2O(l) \rightarrow H_2O(g)$	+10.5 ($\Delta\hat{H}_{vap}^\circ$)
5. $C(\text{diamond}) + O_2(g) \rightarrow CO_2(g)$	-94.50
6. $C(\text{graphite}) + O_2(g) \rightarrow CO_2(g)$	-94.05

Calculate the following:

- The standard heat of formation of propylene (C_3H_6 gas).
- The standard heat of combustion of propylene (C_3H_8 gas).
- The net heating value of propylene in Btu/ft³ measured at 60°F and 30 in. Hg saturated with water vapor.

Solution:

(a) Reference state: 25°C, 1 atm; $C(\beta)$ (graphite) and $H_2(g)$ are assigned zero values.



$$\Delta H_f^\circ = ?$$

kcal/g mole

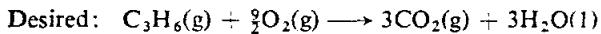
(1) $C_3H_6(g) + H_2(g) \rightarrow C_3H_8(g)$	$\Delta H_1 = -29.6$
(2) $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$	$\Delta H_2 = -530.6$
(3) $-4[H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)]$	$-4\Delta H_3 = +273.2$
(6) $-3[C(\beta) + O_2(g) \rightarrow CO_2(g)]$	$-3\Delta H_6 = +282.2$

$$(7) = (1) + (2) + (3) + (6):$$

$$C_3H_6(g) \rightarrow 3C(\beta) + 3H_2(g) \quad \Delta H_{rxn}^\circ = -4.8$$

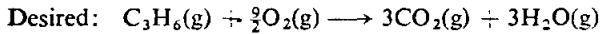
$$\Delta H_f^\circ_{C_3H_6(g)} = +4.8 \text{ kcal/g mole}$$

(b) Reference state: 25°C, 1 atm; CO₂(g) and H₂O(l) have zero values.



	kcal/g mole
(1) C ₃ H ₆ (g) + H ₂ (g) → C ₃ H ₈ (g)	$\Delta H_1 = -29.6$
(2) C ₃ H ₈ (g) + 5O ₂ (g) → 3CO ₂ (g) + 4H ₂ O(l)	$\Delta H_2 = -530.6$
(3) [H ₂ (g) + ½O ₂ (g) → H ₂ O(l)]	$-\Delta H_3 = +68.3$
(8) = (1) + (2) + (3):	
C ₃ H ₆ (g) + ½O ₂ (g) → 3CO ₂ (g) + 3H ₂ O(l)	$\Delta H_{rxn}^{\circ} = -491.9$
	$\Delta H_{c, C_3H_6(g)}^{\circ} = -491.9 \text{ kcal/g mole}$

(c) Net heating value.



	kcal/g mole
(8) C ₃ H ₆ (g) + ½O ₂ (g) → 3CO ₂ (g) + 3H ₂ O(l)	$\Delta H_8 = -491.9$
(4) 3H ₂ O(l) → 3H ₂ O(g)	$3\Delta H_4 = +31.5$
(9) = (8) + (4):	
C ₃ H ₆ (g) + ½O ₂ (g) → 3 CO ₂ (g) + 3H ₂ O(g)	$\Delta H_{rxn} = -460.4$
	$\Delta H'_c = -460,400 \text{ cal/g mole}$

$$\Delta H_c = (-460,400)(1.8) = -829,000 \text{ Btu/lb mole}$$

At 60°F, 30 in. Hg, saturated with water vapor,

vapor pressure of H₂O at 60°F = 13.3 mm Hg

$$\begin{aligned} \text{pressure on gas} &= (760) \left(\frac{30.00}{29.92} \right) - 13.3 \\ &= 763 - 13.3 = 749.7 \approx 750 \text{ mm Hg} \end{aligned}$$

$$\text{molal volume} = \frac{359 + 760 + (460 + 60)}{750 + (460 + 32)} = 384 \text{ ft}^3/\text{lb mole}$$

$$\text{heating value} = \frac{829,000}{384} = 2160 \text{ Btu/ft}^3 \text{ measured at } 60^\circ\text{F and 30 in. Hg satd.}$$

At 60°F, 30 in. Hg, dry,

$$\text{molal volume} = 379 \text{ ft}^3/\text{lb mole}$$

$$\text{net heating value} = \frac{829,000}{379} = 2185 \text{ Btu/ft}^3$$

One of the common errors made in these thermochemical calculations is to forget that the standard state for heat of combustion calculations is liquid water, and that if gaseous water is present, a phase change (the heat of vaporization or heat of condensation) must be included in the calculations. If the final product in Example 4.25 had been H₂O(g) rather than H₂O(l), we would have incorporated

: have zero values:



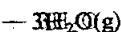
kcal/g mole

$$\Delta H_1 = -29.6$$

$$\Delta H_2 = -530.6$$

$$-\Delta H_3 = +68.3$$

$$\Delta H_{\text{rxn}}^{\circ} = -491.9$$



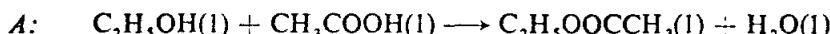
Kcal/g mole

$$\Delta H_8 = -491.9$$

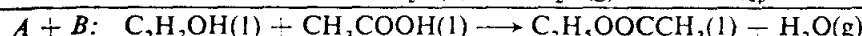
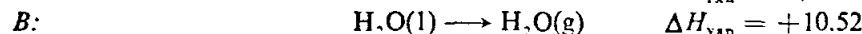
$$-\Delta H_4 = +31.5$$

$$\Delta H_{\text{rxn}}^{\circ} = -460.4$$

the phase transition for water as follows:



$$\Delta H_{\text{rxn}}^{\circ} = +3.72$$



$$\Delta H_{\text{rxn}}^{\circ} = (+3.72) + (10.52) = +14.24 \text{ kcal/g mole}$$

With adequate data available you will find it simpler to use only the heats of combustion or only the heats of formation in the same algebraic calculation for a heat of reaction. Mixing these two sources of enthalpy change data, unless you take care, will only lead to error and confusion. Of course, when called upon, you should be able to calculate the heat of formation from the heat of combustion, or the reverse, being careful to remember and take into account the fact that the standard states for these two types of calculations are different. Since the heat of combustion values are so large, calculations made by subtracting these large values from each other can be a source of considerable error. To avoid other major errors, carefully check all signs and make sure all equations are not only balanced but are written according to the proper convention.

4.7.3 Heats of Reaction at Constant Pressure or at Constant Volume. Let us first consider the heat of reaction of a substance obtained in a bomb calorimeter, such as in a bomb in which the volume is constant but not the pressure. For such a process (the system is the material in the bomb), the general energy balance, Eq. (4.24), reduces to (with no work, mass flow, nor kinetic or potential energy effects)

$$\Delta U = U_n - U_i = Q_v \quad (4.36)$$

Here Q_v designates the heat transferred from the bomb. Next, let us assume that the heat of reaction is determined in a steady-state flow calorimeter with $W = 0$. Then if the process takes place at constant pressure the general energy balance reduces to:

$$\Delta H = Q_p$$

Here Q_p designates the heat transferred from the flow calorimeter.

If we subtract Q_p from Q_v and introduce $H = U + pV$, we find that

$$Q_p - Q_v = \Delta H - (U_n - U_i) = (U_2 - U_1) - (U_n - U_i) \quad (4.37)$$

$$+ (m_2 p_2 \hat{V}_2 - m_1 p_1 \hat{V}_1)$$

Suppose, furthermore, that the internal energy change per unit mass for the batch, constant volume process is made identical to the internal energy difference between the outlet and inlet in the flow process by a suitable adjustment of the temperature of the water bath surrounding the calorimeter. Then

$$(U_n - U_i) = (U_2 - U_1)$$

and

$$Q_p - Q_v = (m_2 p_2 \hat{V}_2 - m_1 p_1 \hat{V}_1) \quad (4.38)$$

To evaluate the terms on the right-hand side of Eq. (4.38), we can assume for solids and liquids that the $\Delta m \hat{V}$ change is negligible and can be ignored. Therefore, the only change which must be taken into account is for gases present as products and/or reactants. If, for simplicity, the gases are assumed to be ideal, then at constant temperature

$$m p \hat{V} = nRT$$

$$\Delta m p \hat{V} = \Delta n RT$$

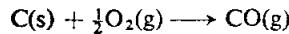
and

$$Q_p - Q_v = \Delta n (RT) \quad (4.39)$$

Equation (4.39) gives the difference between the heat of reaction for the constant pressure experiment and the constant volume experiment.

EXAMPLE 4.28 Difference between heat of reaction at constant pressure and at constant volume

Find the difference between the heat of reaction at constant pressure and at constant volume for the following reaction at 25°C (assuming that it could take place):



Solution:

Basis: 1 mole of C(s)

Examine Fig. E4.28. The system is the bomb; $Q = +$ when heat is absorbed by the bomb.

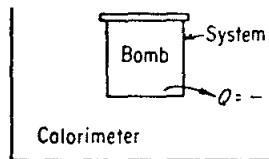


Fig. E4.28.

From Eq. (4.39), $Q_p - Q_v = \Delta n (RT)$.

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

since C is a solid.

$$Q_p - Q_v = \frac{1}{2} RT = 0.5(1.987)(298) = 296 \text{ cal}$$

If the measured heat evolved from the bomb was 26,711 cal,

$$Q_p = Q_v + 296 = -26,711 + 296 = -26,416 \text{ cal}$$

The size of this correction is relatively insignificant compared to either the quantity Q_p or Q_v . In any case, the heat of reaction calculated from the bomb experiment is

$$\Delta \hat{H}_{rxn.} = \frac{Q_v}{n} = \frac{-26,711}{1} = -26,711 \text{ cal/g mole}$$

Since reported value of $-26,7$

4.7.4 Inc should calculate actually formed the portion of the absorb some en of the reaction. include it in the tants or produc or not, you mus 4.7.5).

EXAMPLE 4.29

An iron pyri dirt, rock, etc.) is ing to the reaction

in order to produc product (cinder) which per kilogram of e

Solution:
The material b standard heat of r

Required O₂:

Entering O₂:

Entering N₂:

The solid waste pute the amount of

(4.38), we can assume
ole and can be ignored.
ount is for gases present
ases are assumed to be

(4.39)

reaction for the constant
ent.

at constant pressure and at

constant pressure and at
ing that it could take place:

then heat is absorbed by the

= 296 cal

cal,

-26,416 cal

mpared to either the quantity
from the bomb experiment is

$\frac{211 \text{ cal}}{\text{g}}$

Since reported heats of reaction are normally for constant pressure processes, the value of -26,711 would not be reported, but instead you would report that

$$\Delta\hat{H}_{rxn} = \frac{Q_p}{n} = \frac{-26,416}{1} = -26,416 \text{ cal/g mole}$$

4.7.4 Incomplete Reactions. If an incomplete reaction occurs, you should calculate the standard heat of reaction only for the products which are actually formed from the reactants which actually react. In other words, only the portion of the reactants which actually undergo some change and liberate or absorb some energy are to be considered in calculating the overall standard heat of the reaction. If some material passes through unchanged, then you should not include it in the *standard heat of reaction* calculations (however, when the reactants or products are at conditions *other* than 25°C and 1 atm. whether they react or not, you must include them in the enthalpy calculations as explained in Sec. 4.7.5).

EXAMPLE 4.29 Incomplete reactions

An iron pyrites ore containing 85.0 percent FeS₂ and 15.0 percent gangue (inert dirt, rock, etc.) is roasted with an amount of air equal to 200 percent excess air according to the reaction



in order to produce SO₂. All the gangue plus the Fe₂O₃ end up in the solid waste product (cinder) which analyzes 4.0 percent FeS₂. Determine the standard heat of reaction per kilogram of ore.

Solution:

The material balance for the problem must be worked out prior to determining the standard heat of reaction.

Basis: 100 kg ore

Ore			
Comp.	kg = %	mol. wt	kg moles
FeS ₂	85.0	120	0.708
Gangue	15.0		
<hr/>			100.0

$$\text{Required O}_2: \frac{0.708 \text{ kg mole FeS}_2}{4 \text{ kg moles FeS}_2} \times 11 \text{ kg moles O}_2 = 1.94 \text{ kg moles O}_2$$

$$\text{Entering O}_2: (1 + 2)(1.94) = 5.82 \text{ kg moles O}_2$$

$$\text{Entering N}_2: 5.82 \left(\frac{79}{21} \right) = 21.9 \text{ kg moles N}_2$$

The solid waste comprises Fe₂O₃, gangue, and unburned FeS₂. We need to compute the amount of unburned FeS₂ on the basis of 100 kg of ore. Let x = kg FeS₂.

that does not burn. Then the cinder comprises

<i>component</i>	<i>kg</i>
FeS ₂	<i>x</i>
Gangue	15

$$\text{Fe}_2\text{O}_3 \quad \frac{(85 - x) \text{ kg FeS}_2 \text{ burned}}{120 \frac{\text{kg FeS}_2}{\text{kg mole FeS}_2}} \quad \left| \begin{array}{l} 2 \text{ moles Fe}_2\text{O}_3 \\ 4 \text{ moles FeS}_2 \end{array} \right| \frac{160 \text{ kg Fe}_2\text{O}_3}{\text{kg mole Fe}_2\text{O}_3} = \left(\frac{2}{3} \right)(85 - x)$$

Thus

$$0.040 = \frac{x}{x + 15 + (2/3)(85 - x)}$$

$$x = 2.90 \text{ kg FeS}_2$$

$$(2/3)(85 - x) = 54.7 \text{ kg Fe}_2\text{O}_3$$

The composition of the solid waste is

<i>Solid waste</i>			
<i>comp.</i>	<i>kg</i>	<i>mol. wt</i>	<i>kg moles</i>
FeS ₂	2.90	120	0.0242
Fe ₂ O ₃	54.7	160	0.342
Gangue	15		

Finally, the FeS₂ that is oxidized is

$$\frac{(85 - 2.90) \text{ kg FeS}_2}{120 \text{ kg FeS}_2} \quad \left| \begin{array}{l} 1 \text{ kg mole FeS}_2 \\ 4 \text{ kg moles FeS}_2 \end{array} \right| = 0.685 \text{ kg mole FeS}_2$$

Corresponding to 0.685 kg mole of FeS₂ oxidized:

$$\frac{0.685 \text{ kg mole FeS}_2}{4 \text{ kg moles FeS}_2} \quad \left| \begin{array}{l} 8 \text{ kg moles SO}_2 \\ 4 \text{ kg moles FeS}_2 \end{array} \right| = 1.37 \text{ kg moles SO}_2 \text{ produced}$$

$$\frac{0.685 \text{ kg mole FeS}_2}{4 \text{ kg moles FeS}_2} \quad \left| \begin{array}{l} 11 \text{ kg moles O}_2 \\ 4 \text{ kg moles FeS}_2 \end{array} \right| = 1.88 \text{ kg moles O}_2 \text{ used}$$

Tabulated heats of formation in kilocalories per gram mole are

Comp.:	FeS ₂ (c)	O ₂ (g)	Fe ₂ O ₃ (c)	SO ₂ (g)
$\Delta\hat{H}_f^\circ$:	-42.520	0	-196.500	-70.960

$$\Delta H_{rxn}^\circ = (1.37)(-70.960) + (0.342)(-196.500) - (0.685)(-42.520) \\ = -135.292 \text{ kcal}$$

$$\Delta\hat{H}_{rxn}^\circ = 1.353 \text{ kcal/kg ore}$$

Note that only the moles reacting and produced are used in computing the heat of reaction. The unoxidized FeS₂ is not included, nor is the N₂. The O₂ used contributes a value of zero to the ΔH_{rxn}° because the ΔH_f° of the O₂ is zero.

4.7.5 The Energy Balance when the Products and Reactants Are Not at 25°C. You no doubt realize that the standard state of 25°C for the heats of formation is only by accident the temperature at which the products enter and the reactants leave a process. In most instances the temperatures of the

materials
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(4.24) top
process b

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(b) V
(c) V
(d) I
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(c) A

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materials entering and leaving will be higher or lower than 25°C. However, since enthalpies (and hence heats of reaction) are point functions, you can use Eq. (4.24) together with Eq. (4.34), or Eq. (4.35), to answer questions about the process being analyzed. Typical questions might be

- What is the heat of reaction at a temperature other than 25°C, but still at 1 atm?
- What is the temperature of an incoming or exit stream?
- What is the temperature of the reaction?
- How much material must be introduced to provide a specified amount of heat transfer?

Consider the process illustrated in Fig. 4.15, for which the reaction is

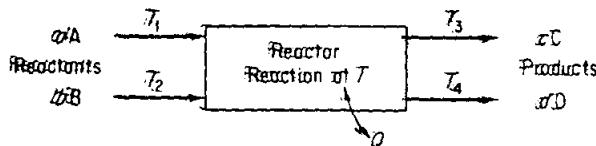
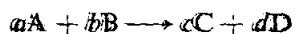


Fig. 4.15. Process with reaction.

In employing Eqs. (4.24) and (4.34), you should always first choose a reference state at which the heat of reaction is known. This usually turns out to be 25°C and 1 atm. Then the next step is to calculate the enthalpy changes for each stream entering and leaving *relative to this reference state*. Finally, the enthalpy changes are summed up, including the heat of reaction calculated in the standard state by Eq. (4.34), and the other terms in Eq. (4.24) introduced if pertinent. Usually it proves convenient in calculating the enthalpy change to compute the "sensible heat" changes and the heat of reaction separately. Methods you can use to determine the "sensible heat" ΔH values for the individual streams are

- Obtain the enthalpy values from a set of published tables, e.g., the steam tables or tables such as in Appendix D,
- Use $\Delta H = C_{p,n}(T_2 - T_{ref}) - C_{p,n}(T_1 - T_{ref})$, as previously discussed in Sec. 4.2,
- Analytically, graphically, or numerically, find

$$\Delta H = \int_{T_1}^{T_2} C_p dT$$

for each component individually, using the respective heat capacity equations.

Any phase changes taking place among the reactants or products not accounted for in the chemical equation must also be taken into account in the calculations.

$\mu g/mole$
0.0242
0.342
 x
 x
 x
 x

x kg FeS_2
notes SO_2 produced
uses O_2 used
1 mole are
 $SO_3(g)$
 ~ 70.960
 $(0.685)(-42.520)$

in computing the heat of
The O_2 used contributes
zero.

ts and Reactants Are
at state of 25°C for the
at which the products
the temperatures of the

Let us first demonstrate how to calculate the heat of reaction at a temperature other than 25°C. By this we mean that the reactants enter and the products leave at the same temperature—a temperature different from the standard state of 25°C. Figure 4.16 illustrates the information flow for the calculations assuming a steady-state process ($\Delta E = 0$), no kinetic or potential energy changes, and $W = 0$. The general energy balance, Eq. (4.24), reduces to

$$Q = \Delta H$$

or

$$Q = (\Delta H_p - \Delta H_r) + (\Delta \hat{H}_{rxn,T}) \quad (4.40)$$

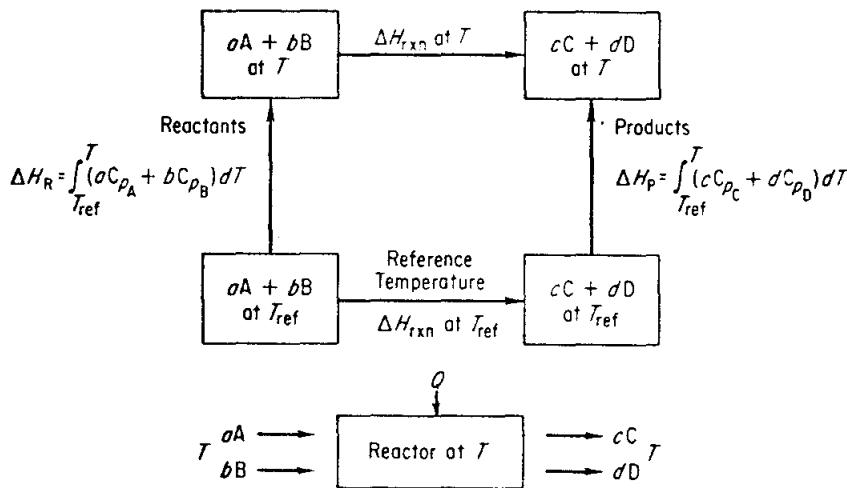


Fig. 4.16. Heat of reaction at a temperature other than standard conditions.

in terms of the notation in Fig. 4.16. By definition, Q , as calculated by Eq. (4.40), is equal to the "heat of reaction at the temperature T " so that

$$\Delta H_{rxn,T} = \Delta H_{rxn,T_{ref}} + \Delta H_p - \Delta H_r \quad (4.41)$$

To indicate a simplified way to calculate $\Delta H_p - \Delta H_r$, suppose that the heat capacity equations are expressed as

$$C_p = \alpha + \beta T + \gamma T^2 \quad (4.42)$$

Then, to obtain $\Delta H_p - \Delta H_r$, we add up the enthalpy changes for the products and subtract those for the reactants. Rather than integrate separately, let us consolidate like terms as follows. Each heat capacity equation is multiplied by the proper number of moles:

$$aC_{pA} = a[\alpha_A + \beta_A T + \gamma_A T^2] \quad (4.43a)$$

$$bC_{pB} = b[\alpha_B + \beta_B T + \gamma_B T^2] \quad (4.43b)$$

$$cC_{pC} = c[\alpha_C + \beta_C T + \gamma_C T^2] \quad (4.43c)$$

$$dC_{pD} = d[\alpha_D + \beta_D T + \gamma_D T^2] \quad (4.43d)$$

of reaction at a temperature enter and the products from the standard state for the calculations assume enthalpy changes, and this to

$$(4.40)$$

$$-\frac{dD}{T}$$

Products

$$\Delta H_p = \int_{T_{ref}}^T (cC_{pC} + dC_{pD}) dT$$

$$-\frac{dL}{T_{ref}}$$

$$-\frac{cC}{T}$$

standard conditions.

as calculated by Eq. (4.40), so that

$$\Delta H_R \quad (4.41)$$

ΔH_R , suppose that the heat

$$(4.42)$$

changes for the products integrate separately, let us equation is multiplied by

$$(4.43a)$$

$$(4.43b)$$

$$(4.43c)$$

$$(4.43d)$$

Sec. 4.7

Then we define a new term ΔC_p , which is equal to

original expression	equivalent new term
$cC_{pC} + dC_{pD} - (aC_{pA} + bC_{pB})$	ΔC_p

and

$$[(c\alpha_C + d\alpha_D) - (a\alpha_A + b\alpha_B)] = \Delta\alpha \quad (4.44)$$

$$T[c\beta_C + d\beta_D] - (a\beta_A + b\beta_B) = T\Delta\beta$$

$$T^2[c\gamma_C + d\gamma_D] - (a\gamma_A + b\gamma_B) = T^2\Delta\gamma$$

Simplified, ΔC_p can be expressed as

$$\Delta C_p = \Delta\alpha + \Delta\beta T + \Delta\gamma T^2 \quad (4.45)$$

Furthermore,

$$\begin{aligned} (\Delta H_p - \Delta H_R) &= \int_{T_R}^T \Delta C_p dT = \int_{T_R}^T (\Delta\alpha + \Delta\beta T + \Delta\gamma T^2) dT \\ &= \Delta\alpha(T - T_R) + \frac{\Delta\beta}{2}(T^2 - T_R^2) + \frac{\Delta\gamma}{3}(T^3 - T_R^3) \end{aligned} \quad (4.46)$$

where we let $T_R = T_{ref}$ for simplicity.

If the integration is carried out without definite limits,

$$(\Delta H_p - \Delta H_R) = \int (\Delta C_p) dT = \Delta\alpha T + \frac{\Delta\beta}{2}T^2 + \frac{\Delta\gamma}{3}T^3 + C \quad (4.47)$$

where C is the integration constant.

Finally ΔH_{rxn} at the new temperature T is

$$\Delta H_{rxn_T} = \Delta H_{rxn_{T_R}} + \Delta\alpha(T - T_R) + \frac{\Delta\beta}{2}(T^2 - T_R^2) + \frac{\Delta\gamma}{3}(T^3 - T_R^3) \quad (4.48a)$$

or

$$\Delta H_{rxn_T} = \Delta H_{rxn_{T_R}} + \Delta\alpha T + \frac{\Delta\beta}{2}T^2 + \frac{\Delta\gamma}{3}T^3 + C \quad (4.48b)$$

as the case may be. Using Eq. (4.48a) and knowing ΔH_{rxn} at the reference temperature T_R , you can easily calculate ΔH_{rxn} at any other temperature.

Equation (4.48b) can be consolidated into

$$\Delta H_{rxn_T} = \Delta H_0 + \Delta\alpha T + \frac{\Delta\beta}{2}T^2 + \frac{\Delta\gamma}{3}T^3 \quad (4.49)$$

where

$$\Delta H_0 = (\Delta H_{rxn_{T_R}} + C)$$

Now, if ΔH_{rxn} is known at any temperature T , you can calculate ΔH_0 as follows:

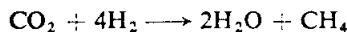
$$\Delta H_0 = \Delta H_{rxn_T} - \Delta\alpha(T) - \frac{\Delta\beta}{2}(T^2) - \frac{\Delta\gamma}{3}T^3 \quad (4.50)$$

Then you can use this value of ΔH_0 to assist in the calculation of ΔH_{rxn} at any other temperature. Probably the easiest way to compute the necessary enthalpy changes is to use enthalpy data obtained directly from published tables. Do not

forget to take into account phase changes, if they take place, in the enthalpy calculations.

EXAMPLE 4.30 Calculation of heat of reaction at a temperature different from standard conditions

An inventor thinks he has developed a new catalyst which can make the gas phase reaction



proceed with 100 percent conversion. Estimate the heat which must be provided or removed if the gases enter and leave at 500°C.

Solution:

In effect we need to calculate heat of reaction at 500°C from Eq. (4.41) or Q in Eq. (4.40). For illustrative purposes we first use the technique based on Eqs. (4.49) and (4.50).

Basis: 1 g mole CO₂(g)



$-\Delta\hat{H}_f^\circ \left(\frac{\text{kcal}}{\text{kg mole}} \right)$	94,052	0	57,798	17,889
--	--------	---	--------	--------

$$\begin{aligned}\Delta\hat{H}_{rxn,ss,^{\circ}\text{K}} &= [-17,889 - (2)(57,798)] - [(4)(0) - 94,052] \\ &= -39,433 \text{ cal/g mole CO}_2\end{aligned}$$

First we shall calculate ΔC_p :

$$C_{p,\text{CO}_2} = 6.393 + 10.100 \times 10^{-3}T - 3.405 \times 10^{-6}T^2 \quad T \text{ in } ^\circ\text{K}$$

$$C_{p,\text{H}_2} = 6.424 + 1.039 \times 10^{-3}T - 0.078 \times 10^{-6}T^2 \quad T \text{ in } ^\circ\text{K}$$

$$C_{p,\text{H}_2\text{O}} = 6.970 + 3.464 \times 10^{-3}T - 0.483 \times 10^{-6}T^2 \quad T \text{ in } ^\circ\text{K}$$

$$C_{p,\text{CH}_4} = 3.204 + 18.41 \times 10^{-3}T - 4.48 \times 10^{-6}T^2 \quad T \text{ in } ^\circ\text{K}$$

$$\begin{aligned}\Delta\alpha &= [(1)(3.204) + (2)(6.970)] - [(1)(6.393) + (4)(6.424)] \\ &= -14.945\end{aligned}$$

$$\begin{aligned}\Delta\beta &= [(1)(18.41) + (2)(3.464)](10^{-3}) - [(1)(10.100) + (4)(1.039)](10^{-3}) \\ &= 11.087 \times 10^{-3}\end{aligned}$$

$$\begin{aligned}\Delta\gamma &= [(1)(-4.48) + (2)(-0.483)](10^{-6}) - [(1)(-3.405) + (4)(-0.078)](10^{-6}) \\ &= -1.729 \times 10^{-6}\end{aligned}$$

$$\Delta C_p = -14.945 + 11.082 \times 10^{-3}T - 1.729 \times 10^{-6}T^2$$

Next we find ΔH_0 , using as a reference temperature 298°K.

$$\begin{aligned}\Delta H_0 &= \Delta H_{rxn,ss} - \Delta\alpha T - \frac{\Delta\beta}{2}T^2 - \frac{\Delta\gamma}{3}T^3 \\ &= -39,443 - (-14.945)(298) - \frac{11.082 \times 10^{-3}}{2}(298)^2 \\ &\quad - \frac{(-1.729 \times 10^{-6})(298)^3}{3} \\ &= -39,443 + 4450 - 493 + 15 = -35,431 \text{ cal}\end{aligned}$$

Then, with

EXAMPLE
standard con

Repeat
Table 4.5b

Solution:
The hea

From Eq. (4

Note that the reference temperatures in this example, however, are not as those in the standard conditions.

EXAMPLE

Carbon
excess air
ber at 500°F
British thermal

they take place, in the enthalpy

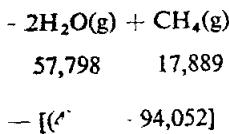
at a temperature different from

that which can make the gas phase



heat which must be provided

at 500°C from Eq. (4.41) or Q
a technique based on Eqs. (4.49)



$$\begin{aligned} & \times 10^{-6}T^2 \quad T \text{ in } ^\circ\text{K} \\ & 10^{-6}T^2 \quad T \text{ in } ^\circ\text{K} \\ & 10^{-6}T^2 \quad T \text{ in } ^\circ\text{K} \\ & 10^{-6}T^2 \quad T \text{ in } ^\circ\text{K} \\ & (6.424) \end{aligned}$$

$$+ (4)(1.039)(10^{-3})$$

$$3.405 + (4)(-0.078)(10^{-6})$$

$$1.729 \times 10^{-6}T^2$$

298°K.

$$\frac{1.729 \times 10^{-6}}{2}(298)^2$$

$$-35,431 \text{ cal}$$

Then, with ΔH_0 known, the ΔH_{rxn} at 773°K can be determined.

$$\begin{aligned} \Delta H_{rxn,773\text{K}} &= \Delta H_0 + \Delta\alpha T + \frac{\Delta\beta}{2}T^2 + \frac{\Delta\gamma}{3}T^3 \\ &= -35,431 - 14.945(773) + \frac{11.082 \times 10^{-3}}{2}(773)^2 \\ &\quad - \frac{1.729 \times 10^{-6}}{3}(773)^3 \\ &= -43,925 \text{ cal} \end{aligned}$$

or 43,925 kcal/kg mole CO_2 must be removed.

EXAMPLE 4.31 Calculation of heat of reaction at a temperature different from standard conditions

Repeat the calculation of the previous example using enthalpy values from Table 4.5b and Appendix D.

Solution:

The heat of reaction at 25°C and 1 atm from the previous example is

$$\hat{\Delta H}_{rxn,25^\circ\text{C}} = -39,433 \frac{\text{kcal}}{\text{kg mole}}$$

$\hat{\Delta H}$ (kcal/kg mole); reference is 0°C

temperature	CO_2	H_2	H_2O	CH_4
25°C	218	172	200	210
500°C	5340	3499	4254	5730

From Eq. (4.41),

$$\begin{aligned} \Delta H_{rxn,500^\circ\text{C}} &= \Delta H_{rxn,25^\circ\text{C}} + \Delta H_{\text{products}} - \Delta H_{\text{reactants}} \\ &= -39,433 + [(1)(5730 - 210) + 2(4254 - 200)] \\ &\quad - [(1)(5340 - 218) + 4(3499 - 172)] \\ &= 44,235 \frac{\text{kcal}}{\text{kg mole CO}_2} \end{aligned}$$

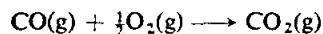
Note that the enthalpies of the products and of the reactants are both based on the reference temperature of 25°C. The answer is not quite the same as in the previous example, because the heat capacity data used in Example 4.30 were not quite the same as those used in calculating the ΔH values in the tables.

EXAMPLE 4.32 Application of the energy balance to a reaction

Carbon monoxide at 50°F is completely burned at 2 atm pressure with 50 percent excess air which is at 1000°F. The products of combustion leave the combustion chamber at 800°F. Calculate the heat evolved from the combustion chamber expressed as British thermal units per pound of CO entering.

Solution:

Basis: 1 lb mole of CO



Material balance:

Amount of air entering:

$$\begin{array}{l} \text{1 lb mole CO} \quad | \quad 0.5 \text{ lb mole O}_2 \quad | \quad 1.5 \text{ lb mole O}_2 \text{ used} \quad | \quad \text{1 lb mole air} \\ \hline & | \quad 1 \text{ lb mole CO} \quad | \quad 1.0 \text{ lb O}_2 \text{ mole needed} \quad | \quad 0.21 \text{ lb mole O}_2 \\ = & 3.57 \text{ lb mole air} \end{array}$$

Amount of O₂ leaving, unreacted:

$$(0.21)(3.57) - 0.5 = 0.25 \text{ lb mole O}_2$$

Amount of N_2 leaving:

$$(0.79)(3.57) = 2.82 \text{ lb mole N}_2$$

Enthalpy data have been taken from Table 4.5a and Appendix D. The heat of reaction at 25°C (77°F) and 1 atm from Example 4.21 is -67,636 cal/g mole of CO or -121,745 Btu/lb mole of CO. We can assume that the slightly higher pressure of 2 atm has no effect on the heat of reaction or the enthalpy values. See Fig. E4.32.

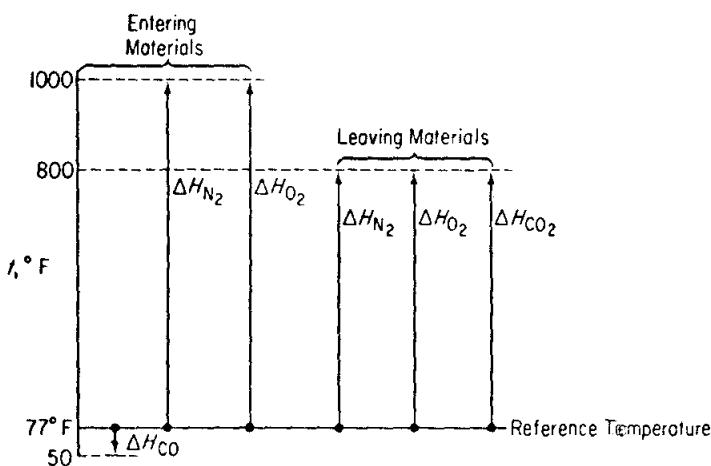


Fig. E4.32.

ΔH (Btu/lb mole); reference is 32°F

<i>temperature</i>	CO	air	O ₂	N ₂	CO ₂
50°F	125.2	—	—	—	—
77°F	313.3	312.7	315.1	312.2	392.2
800°F	—	—	5690	5443	8026
1000°F	—	6984	—	—	—

$$Q = \Delta H_{\text{rxn, E}} + \Delta H_{\text{products}} - \Delta H_{\text{reactants}}$$

$$\Delta \hat{H}_{rxn_{77,F}} = -121,745 \text{ Btu/lb mole}$$

(a)

$$\begin{aligned}
 \text{(b)} \quad \Delta H_{\text{products}} &= \Delta H_{800\text{ F}} - \Delta H_{77\text{ F}} \\
 &\quad \text{CO}_2 \qquad \qquad \qquad \text{N}_2 \\
 &= (1)(8026 - 392.2) + (2.82)(5443 - 312.2) \\
 &\quad \text{O}_2 \\
 &\quad + (0.25)(5690 - 315.1) \\
 &= 7633.8 + 14,480 + 1343 \\
 &= 23,457 \text{ Btu/lb mole} \\
 \text{(c)} \quad \Delta H_{\text{reactants}} &= \Delta H_{1000\text{ F}} - \Delta H_{77\text{ F}} + \Delta H_{50\text{ F}} - \Delta H_{77\text{ F}} \\
 &= (3.57)(6984 - 312.7) + (1)(125.2 - 313.3) \\
 &= 23,800 - 188.1 = 23,612 \text{ Btu/lb mole} \\
 \text{(d)} \quad Q &= -121,745 + 23,457 - 23,612 \\
 &= -121,900 \text{ Btu/lb mole} \\
 -121,900 \text{ Btu} &\quad \frac{1 \text{ lb mole CO}}{\text{lb mole CO}} = -4360 \text{ Btu/lb CO}
 \end{aligned}$$

and Appendix D. The heat of combustion of carbon is $-67,636 \text{ cal/g}$ mole of carbon at the slightly higher pressure of 1 atm. See Fig. E4.32.

4.7.6 Temperature of a Reaction. We are now equipped to determine what is called the *adiabatic reaction temperature*. This is the temperature obtained inside the process when (a) the reaction is carried out under adiabatic conditions, i.e., there is no heat interchange between the container in which the reaction is taking place and the surroundings, and (b) when there are no other effects present, such as electrical effects, work, ionization, free radical formation, etc. In calculations of flame temperatures for combustion reactions, the adiabatic reaction temperature assumes complete combustion. Equilibrium considerations may dictate less than complete combustion for an actual case. For example, the adiabatic flame temperature for the combustion of CH_4 with theoretical air has been calculated to be 2010°C ; allowing for incomplete combustion, it would be 1920°C . The actual temperature when measured is 1885°C .

The adiabatic reaction temperature tells us the temperature ceiling of a process. We can do no better, but of course the actual temperature may be less. The adiabatic reaction temperature helps us select the types of materials that must be specified for the container in which the reaction is taking place. Chemical combustion with air produces gases at a maximum temperature of 2500°K which can be increased to 3000°K with the use of oxygen and more exotic oxidants, and even this value can be exceeded although handling and safety problems are severe. Applications of such hot gases lie in the preparation of new materials, micromachining, welding using laser beams, and the direct generation of electricity using ionized gases as the driving fluid.

To calculate the adiabatic reaction temperature, you assume that all the energy liberated from the reaction at some base temperature plus that brought in by the entering stream (relative to the same base temperature) is available to raise the temperature of the products. We assume that the products leave at the

1 lb mole air
0.21 lb mole O_2

and Appendix D. The heat of combustion of carbon is $-67,636 \text{ cal/g}$ mole of carbon at the slightly higher pressure of 1 atm. See Fig. E4.32.

T_{CO_2}

Reference Temperature

T

	CO_2
77	—
8026	392.2

constants

temperature of the reaction, and thus if you know the temperature of the products, you automatically know the temperature of the reaction. In effect, for this adiabatic process we can apply Eq. (4.40).

Since no heat escapes and the energy liberated is allowed only to increase the enthalpy of the products of the reaction, we have

$$\Delta H_{\text{products}} = \boxed{\Delta H_{\text{reactants}} + \Delta H_{\text{rxn}}^{\circ}}$$

"energy pool"

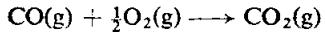
(4.51)

Any phase changes that take place and are not accounted for by the chemical equation must be incorporated into the "energy pool." Because of the character of the information available, the determination of the adiabatic reaction temperature or flame temperature may involve a trial-and-error solution; hence the iterative solution of adiabatic flame temperature problems is often carried out on the computer.

EXAMPLE 4.33 Adiabatic flame temperature

Calculate the theoretical flame temperature for CO burned at constant pressure with 100 percent excess air, when the reactants enter at 200°F.

Solution:



Basis: 1 g mole CO(g); ref. temp. 25°C (77°F)

(200°F ≈ 93.3°C)

Material balance:

entering reactants		exit products	
comp.	moles	comp.	moles
CO(g)	1.00	CO ₂ (g)	1.00
O ₂ (req.)	0.50	O ₂ (g)	0.50
O ₂ (xs)	0.50	N ₂ (g)	3.76
O ₂ (total)	1.00		
N ₂	3.76		
Air	4.76		

$$\Delta H_{\text{rxn}} \text{ at } 25^\circ\text{C} = -67,636 \text{ cal}$$

Note: For the purposes of illustration, in this example the mean heat capacities have a reference temperature of 25°C rather than 0°C.

Then, for Eq. (4.51), $\Delta H_{\text{reactants}}$:

<i>reactants</i>				
comp.	moles	ΔT	C_{p_m}	ΔH
CO(g)	1.00	68.3	6.981	476
Air	4.76	68.3	6.993	2270
				$\sum \Delta H_{\text{R}} = 2746 \text{ cal}$

$$\Delta H_{\text{products}} = 2746 + 67,636 = 70,382 \text{ cal}$$

w the temperature of the pro
the reaction. In effect, for this

led is allowed only to increase
have

$$\Delta H_{rxn}^{\circ} \quad (4.51)$$

accounted for by the chemical
sol." Because of the character
of the adiabatic reaction tem-
and-error solution; hence the
problems is often carried out on

CO burned at constant pressure
at 200°F.

(g)

25°

products	moles
CO ₂	1.00
O ₂	0.50
N ₂	3.76

cal

sample the mean heat capacities

$$\begin{aligned}\Delta H & \\ 476 & \\ 2270 & \\ \hline & = 2746 \text{ cal} \\ & \\ 0.382 \text{ cal} &\end{aligned}$$

To find the temperature which yields a $\Delta H_{products}$ of 70,382 cal, the simplest procedure is to assume various values of the exit temperature of the products until the $\sum \Delta H_p = 70,382$.

Assume TFT (theoretical flame temperature) = 1800°C:

$$\Delta T = 1800 - 25 = 1775^\circ\text{C}$$

comp.	moles	C_p	ΔH
CO ₂	1.00	12.94	23,000
O ₂	0.50	8.349	7,400
N ₂	3.76	7.924	52,900
$\sum \Delta H_p = 83,300 \text{ cal}$			

Assume TFT = 1500°C:

$$\Delta T = 1500 - 25 = 1475^\circ\text{C}$$

comp.	moles	C_p	ΔH
CO ₂	1.00	12.70	18,740
O ₂	0.50	8.305	6,120
N ₂	3.76	7.879	43,600
$\sum \Delta H_p = 68,460 \text{ cal}$			

Make a linear interpolation:

$$\text{TFT} = 1500 + \frac{70,382 - 68,460}{83,300 - 68,460}(300) = 1500 + 39$$

$$\text{TFT} = 1539^\circ\text{C} \approx 2798^\circ\text{F}$$

4.8 Heats of solution and mixing

So far in our energy calculations, we have been considering each substance to be a completely pure and separate material. The physical properties of an ideal solution or mixture may be computed from the sum of the properties in question for the individual components. For gases, mole fractions can be used as weighting values, or, alternatively, each component can be considered to be independent of the others. In most instances so far in this book we have used the latter procedure. Using the former technique, as we did in a few instances, we could write down, for the heat capacity of an ideal mixture,

$$C_p \text{ mixture} = x_A C_{pA} + x_B C_{pB} + x_C C_{pC} + \dots \quad (4.52)$$

or, for the enthalpy,

$$\Delta \hat{H}_{\text{mixture}} = x_A \Delta \hat{H}_A + x_B \Delta \hat{H}_B + x_C \Delta \hat{H}_C + \dots \quad (4.53)$$

These equations are applicable to ideal mixtures only.

When two or more pure substances are mixed to form a gas or liquid solution, we frequently find energy is absorbed or evolved upon mixing. Such a solution would be called a "real" solution. The total heat of mixing (ΔH_{mixing}) has to be determined experimentally, but can be retrieved from tabulated experimental (smoothed) results, once such data are available. This type of

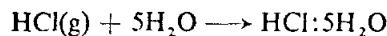
energy change has been given the formal name *heat of solution* when one substance dissolves in another; and there is also the negative of the heat of solution, the *heat of dissolution*, for a substance which separates from a solution. Tabulated data for heats of solution appear in Table 4.9 in terms of energy per mole for consecutively added quantities of solvent to solute; the gram mole refers to the gram mole of solute. Heats of solution are somewhat similar to heats of reaction in that an energy change takes place because of differences in the forces of attraction of the solvent and solute molecules. Of course, these energy changes are much smaller than those we find accompanying the breaking and combining of chemical bonds. Heats of solution are conveniently accommodated in exactly the same way as are the heats of reaction in the energy balance.

TABLE 4.9 HEAT OF SOLUTION OF HCl
(at 25°C and 1 atm)

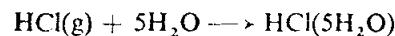
Composition	Total Moles H ₂ O Added to 1 mole HCl	-ΔH° for Each Incremental Step (cal/g mole)	Integral Heat of Solution: The Cumulative -ΔH° (cal/g mole)
HCl(g)	0		
HCl·1H ₂ O	1	6268	6,268
HCl·2H ₂ O	2	5400	11,668
HCl·3H ₂ O	3	1920	13,588
HCl·4H ₂ O	4	1040	14,628
HCl·5H ₂ O	5	680	15,308
HCl·8H ₂ O	8	1000	16,308
HCl·10H ₂ O	10	300	16,608
HCl·15H ₂ O	15	359	16,967
HCl·25H ₂ O	25	305	17,272
HCl·50H ₂ O	50	242	17,514
HCl·100H ₂ O	100	136	17,650
HCl·200H ₂ O	200	85	17,735
HCl·500H ₂ O	500	76	17,811
HCl·1000H ₂ O	1,000	39	17,850
HCl·5000H ₂ O	5,000	59	17,909
HCl·50,000H ₂ O	50,000	35	17,944
HCl·∞H ₂ O		16	17,960

SOURCE: National Bureau of Standards Circular 500 (Reference 15 in Table 4.6).

The solution process can be represented by an equation such as the following:



or



$$\Delta\hat{H}_{\text{soln}}^{\circ} = -15,308 \text{ cal/g mole HCl}(g)$$

The expe
5 moles of
of HCl. T
moles of w

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increments
tion (the i
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products h
just the ne
Fig. 4.17, a

becomes m
standard int
HCl. In th
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EXAMPLE

Calcula

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It is im

solution when one subtracts the heat of solution of a solution. Tabulated values of energy per mole for 1 molmole refers to the changes in the forces of breaking and combining accommodated in exactly balance.

**Integral Heat of Solution:
The Cumulative
 $\Delta\hat{H}_f^\circ$ (cal/g mole)**

6,268
11,668
13,588
14,628
15,308
16,308
16,608
16,967
17,272
17,514
17,650
17,735
17,811
17,850
17,909
17,944
17,960

in Table 4.6).

uation such as the fol-

g)

The expression $\text{HCl}(5\text{H}_2\text{O})$ means that 1 mole of HCl has been dissolved in 5 moles of water, and the enthalpy change for the process is $-15,308 \text{ cal/g mole}$ of HCl. Table 4.9 shows the heat of solution for various cumulative numbers of moles of water added to 1 mole of HCl.

The *standard integral heat of solution* is the cumulative $\Delta\hat{H}_{\text{soln}}^\circ$ as shown in the last column for the indicated number of molecules of water. As successive increments of water are added to the mole of HCl, the cumulative heat of solution (the integral heat of solution) increases, but the incremental enthalpy change decreases as shown in Table 4.9. Note that both the reactants and products have to be at standard conditions. The heat of dissolution would be just the negative of these values. The integral heat of the solution is plotted in Fig. 4.17, and you can see that an asymptotic value is approached as the solution

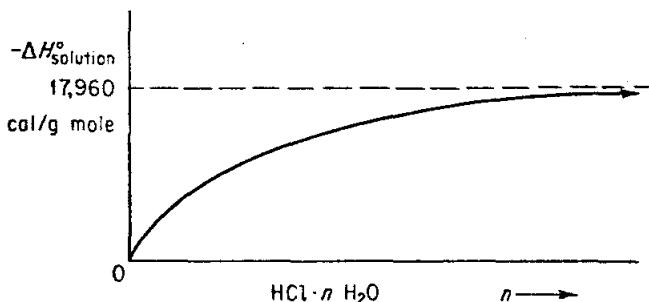


Fig. 4.17. Integral heat of solution of HCl in water.

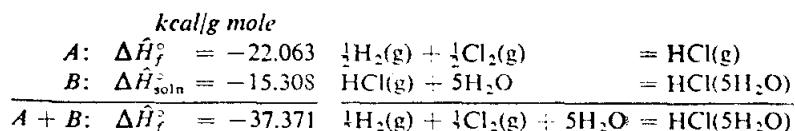
becomes more and more dilute. At infinite dilution this value is called the *standard integral heat of solution at infinite dilution* and is $-17,960 \text{ cal/g mole}$ of HCl. In the Appendix are other tables presenting standard integral heat of solution data. Since the energy changes for heats of solution are point functions, you can easily look up any two concentrations of HCl and find the energy change caused by adding or subtracting water.

EXAMPLE 4.34 Heat of solution

Calculate the standard heat of formation of HCl in 5 g moles of water.

Solution:

We treat the solution process in an identical fashion to a chemical reaction:



It is important to remember that the heat of formation of H_2O itself does not

enter into the calculation. The heat of formation of HCl in an infinitely dilute solution is

$$\Delta\hat{H}_f^\circ = -22.063 - 17.960 = -40.023 \text{ kcal/g mole}$$

Another type of heat of solution which is occasionally encountered is the partial molal heat of solution. Information about this thermodynamic property can be found in most standard thermodynamic texts or in books on thermochemistry, but we do not have the space to discuss it here.

One point of special importance concerns the formation of water in a chemical reaction. When water participates in a chemical reaction in solution as a reactant or product of the reaction, you must include the heat of formation of the water as well as the heat of solution in the energy balance. Thus, if HCl reacts with sodium hydroxide to form water and the reaction is carried out in only 2 moles of water to start with, it is apparent that you will have 3 moles of water at the end of the process. Not only do you have to take into account the heat of reaction when the water is formed, but there is also a heat of solution contribution. If gaseous HCl reacts with crystalline sodium hydroxide and the product is 1 mole of gaseous water vapor, then you could employ the energy balance without worrying about the heat of solution effect.

If an enthalpy-concentration diagram is available for the system in which you are interested, then the enthalpy changes can be obtained directly from the diagram by convenient graphical methods. See Chap. 5 for illustrations of this technique.

EXAMPLE 4.35 Application of heat of solution data

An ammonium hydroxide solution is to be prepared at 77°F by dissolving gaseous NH₃ in water. Prepare charts showing

- (a) The amount of cooling needed in Btu to prepare a solution containing 1 lb mole of NH₃ at any concentration desired.
- (b) The amount of cooling needed in Btu to prepare 100 gal of a solution of any concentration up to 35 percent NH₃.
- (c) If a 10.5 percent NH₃ solution is made up without cooling, at what temperature will the solution end up?

Solution:

Heat of solution data have been taken from *NBS Circular 500*.

(a) Basis: 17 lb NH₃ = 1 lb mole NH₃

Reference temperature = 77°F ≈ 25°C

To convert from kilocalories per gram mole to British thermal units per pound mole, multiply by 1800.

an infinitely dilute solution
per mole

usually encountered is the thermodynamic property in books on thermodynamics. Formation of water in a chemical reaction in solution as a heat of formation of balance. Thus, if HCl reaction is carried out in water will have 3 moles of to take into account the also a heat of solution sum oxide and the liquid by the energy of.

or the system in which defined directly from the illustrations of this

F by dissolving gaseous solution containing 1 lb gal of a solution of any strong, at what temperature or 500.

one units per pound

description	state	$-\Delta\hat{H}_f^\circ$ kcal/g mole	$-\Delta\hat{H}_f^\circ$ Btu/lb mole	$-\Delta\hat{H}_{soln}^\circ$ Btu/lb mole	weight %NH ₃
1H ₂ O	g	11.04	19,900	0	100
1H ₂ O	aq	18.1	32,600	12,700	48.5
2H ₂ O	aq	18.7	33,600	13,700	32.0
3H ₂ O	aq	18.87	34,000	14,100	23.9
4H ₂ O	aq	18.99	34,200	14,300	19.1
5H ₂ O	aq	19.07	34,350	14,450	15.9
10H ₂ O	aq	19.23	34,600	14,700	8.63
20H ₂ O	aq	19.27	34,700	14,800	4.51
30H ₂ O	aq	19.28	34,700	14,800	3.05
40H ₂ O	aq	19.28	34,700	14,800	2.30
50H ₂ O	aq	19.29	34,750	14,850	1.85
100H ₂ O	aq	19.30	34,750	14,850	0.94
200H ₂ O	aq	19.32	34,800	14,900	0.47
∞ H ₂ O	aq	19.32	34,800	14,900	0.0

Standard heats of solution have been calculated from the cumulative data as follows:

$$\Delta\hat{H}_{soln}^\circ = \Delta\hat{H}_f^\circ - \Delta\hat{H}_{f,gas}^\circ$$

For example,

$$\begin{aligned}\Delta\hat{H}_{soln}^\circ &= [-32,600 - (-19,900)] \\ &= -12,700 \text{ Btu/lb mole NH}_3\end{aligned}$$

Weight percents have been computed as follows:

$$\text{wt \%NH}_3 = \frac{\text{lb NH}_3(100)}{\text{lb H}_2\text{O} + \text{lb NH}_3}$$

$$\% \text{NH}_3 \text{ for } 1 \text{ H}_2\text{O} = \frac{17(100)}{18(1) + 17} = 48.5\%$$

The heat of solution values shown in Fig. E4.35(a) are equivalent to the cooling duty required.

(b) Part (b) of the problem requires that a new basis be selected, 100 gal of solution. Additional data concerning densities of NH₄OH are shown in Table E4.35.

Sample calculations are as follows:

$$\text{density, lb/100 gal} = \frac{(\text{sp gr soln})(62.4 \text{ lb/ft}^3)(1.003)(100)}{(7.48 \text{ gal/ft}^3)}$$

Note: 1.003 is the specific gravity of water at 77°F.

$$\text{density @ 32.0\%NH}_3 = \frac{(0.889)(62.4)(1.003)(100)}{7.48} = 741 \text{ lb/100 gal}$$

$$\left. \text{cooling req'd} \right\} = \left(\frac{\text{lb moles NH}_3}{100 \text{ gal}} \right) \left(-\Delta\hat{H}_{soln}^\circ \frac{\text{Btu}}{\text{lb mole NH}_3} \right)$$

$$\left. \text{cooling req'd for 100 gal} \right\} = (13.94)(13,700) = 191,000 \text{ Btu/100 gal soln}$$

These data are portrayed in Fig. E4.35(b).

Basis: 100 gal of solution at concentrations and densities shown

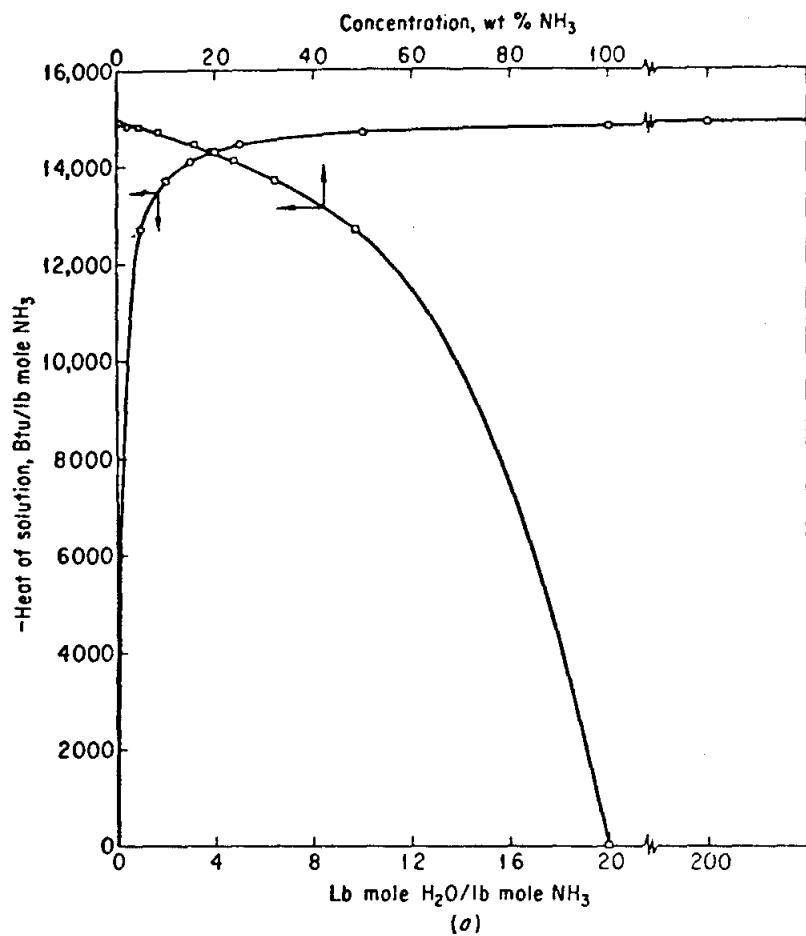


Fig. E4.35(a).

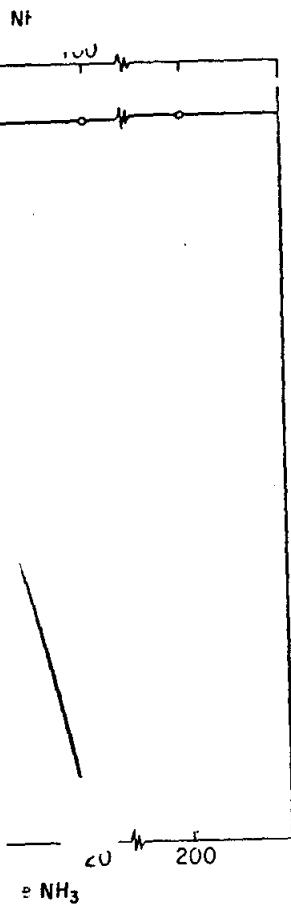
TABLE E4.35

%NH ₃	sp gr* (@4°C)	density, lb/100 gal	lb NH ₃ 100 gal	lb moles NH ₃ 100 gal	$-\Delta\bar{H}_{\text{soln}}^{\circ}$ Btu lb mole NH ₃	cooling req'd per 100 gal. Btu
32.0	0.889	741	237	13.94	13,700	191,000
23.9	0.914	761	182	10.70	14,100	151,000
19.1	0.929	774	148	8.70	14,300	124,000
15.9	0.940	784	124.7	7.32	14,450	106,000
8.63	0.965	805	69.4	4.08	14,700	60,000
4.51	0.981	819	37.0	2.18	14,800	32,200
3.05	0.986					
2.30	0.990	826	19.0	1.12	14,800	16,600
1.85	0.992					
0.94	0.995	830	7.8	0.46	14,850	6,800
0.47	0.998					
0.0	1.000	834	0	0	14,900	0

*SOURCE: N. A. Lange, *Handbook of Chemistry*, 8th ed., Handbook Publishers Inc., Sandusky, Ohio, 1958.

WHAT YOU

1. You should be able to solve the equation. This means you should be able to know what terms can be omitted.



Chap. 4

What You Should Have Learned from This Chapter 337

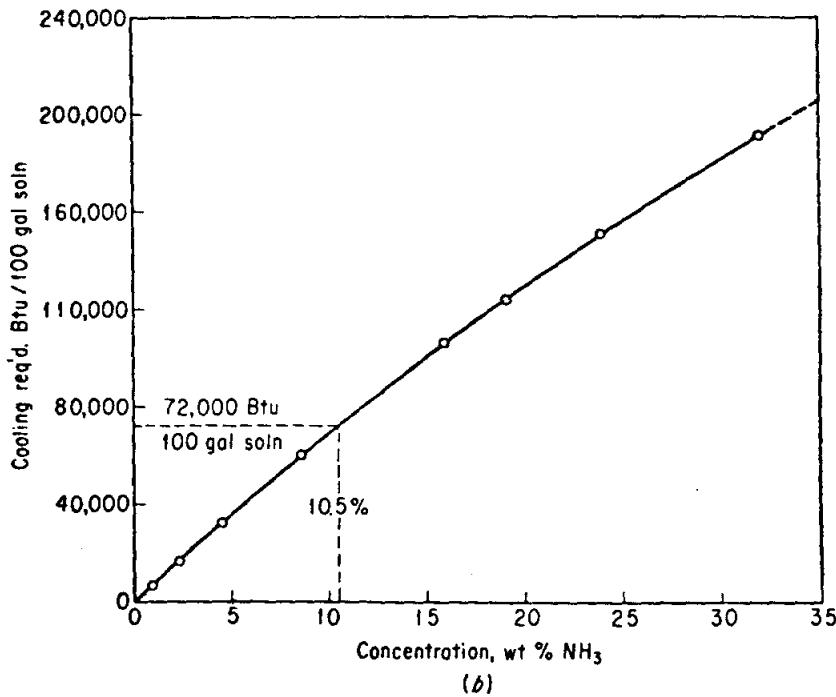


Fig. E4.35(b).

(c)

Basis: 100 gal soln at 10.5% NH₃

$$\Delta E \cong \Delta H = mC_p\Delta T = 72,000 \text{ Btu}/100 \text{ gal} \quad [\text{cf. Fig. E4.35(b)}]$$

$$\text{sp gr soln} = 0.955$$

$$m = \frac{(0.955)(62.4)(1.003)(100)}{7.48} = 800 \text{ lb}$$

$$C_p \text{ 10.5% NH}_3 \text{ soln} = 4.261 \text{ J/(g)(}^\circ\text{C)}$$

$$= 1.02 \text{ Btu/(lb)(}^\circ\text{F)}$$

$$\Delta T = \frac{\Delta H}{mC_p} = \frac{72,000}{(800)(1.02)} = 88^\circ\text{F}$$

$$T_{\text{final}} = 77 + 88 = 165^\circ\text{F}$$

WHAT YOU SHOULD HAVE LEARNED FROM THIS CHAPTER

1. You should know what the energy balance is in words and as a mathematical equation. You should be able to explain what each term in the equation means and be able to apply the equation to practical or simulated problems, i.e., be able to state what each term is in light of the conditions in the problem, know what assumptions can and cannot be made, and know what terms can be omitted.

You should be able to set up flow and nonflow problems to be considered to be

energy and heat and

locate enthalpy or heat if such data are not available.

and how it differs from a

chemistry, and especially the heats of reaction with various temperatures, and heats of combustion from

the heats of solution or type.

temperature for simple or not and whether or proportions.

Gulf Publishing Co.,

Calculations, McGraw-Hill.

Chemical Process Principles.

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Bonding States Principle."

ained, Dover, New York.

Engineering Thermodynamics

8. Yesavage, V. F., et al., "Enthalpies of Fluids at Elevated Pressures and Low Temperatures," *Ind. Eng. Chem.*, v. 59, no. 11, p. 35 (1967).
9. Zermansky, M. W., and H. C. Van Ness, *Basic Engineering Thermodynamics*, McGraw-Hill, New York, 1966.

PROBLEMS³²

- 4.1. Explain specifically what the system is for each of the following processes; indicate the portions of the energy transfer which are heat and work by the symbols Q and W , respectively:
 - (a) A liquid inside a metal can, well insulated on the outside of the can, is shaken very rapidly in a vibrating shaker.
 - (b) Hydrogen is exploded in a calorimetric bomb and the water layer outside the bomb rises in temperature by 1°C .
 - (c) A motor boat is driven by an outboard-motor propeller.
 - (d) Water flows through a pipe at 10 ft/min , and the temperature of the water and the air surrounding the pipe are the same.
- 4.2. Draw a simple sketch of each of the following processes, and, in each, label the system boundary, the system, the surroundings, and the streams of material and energy which cross the system boundary:
 - (a) Water enters a boiler, is vaporized, and leaves as steam. The energy for vaporization is obtained by combustion of a fuel gas with air outside the boiler surface.
 - (b) The steam enters a rotary steam turbine and turns a shaft connected to an electric generator. The steam is exhausted at a low pressure from the turbine.
 - (c) A battery is charged by connecting it to a source of current.
 - (d) A tree obtains water and minerals through its roots and gives off carbon dioxide from its leaves. The tree, of course, gives off oxygen at night.
- 4.3. Draw a simple sketch of the following processes; indicate the system boundary; and classify the system as open or closed:

(a) Automobile engine.	(e) A river.
(b) Water wheel.	(f) The earth and its atmosphere.
(c) Pressure cooker.	(g) An air compressor.
(d) Man himself.	(h) A coffee pot.
- 4.4. Are the following variables intensive or extensive variables? Explain for each.
 - (a) Pressure.
 - (b) Volume.
 - (c) Specific volume.
 - (d) Refractive index.
 - (e) Surface tension.

³²An asterisk designates problems appropriate for computer solution. Also refer to the computer problems after Problem 4.111.

Combined Material and Energy Balances

5

Now that you have accumulated some experience in making energy balances and in the principles of thermochemistry, it is time to apply this knowledge to situations and problems involving both material and energy balances. You have already encountered some simple examples of combined material and energy balances, as, for example, in the calculation of the adiabatic reaction temperature, where a material balance provides the groundwork for the writing of an energy balance. In fact, in all energy balance problems, however trifling they may seem, you must know the amount of material entering and leaving the process if you are to apply successfully the appropriate energy balance equation(s).

In this chapter we shall consider both those problems which require you to make a preliminary material balance prior to making an energy balance and also problems which require you to solve simultaneous material and energy balances. In line with this discussion we shall take up two special types of charts, enthalpy-concentration charts and humidity charts, which are prepared by combining material and energy balances and which are useful in a wide variety of practical problems. Figure 5.0 shows the relationships among the topics to be discussed in this chapter and the relationships with topics in previous chapters.

Material and Balances

5

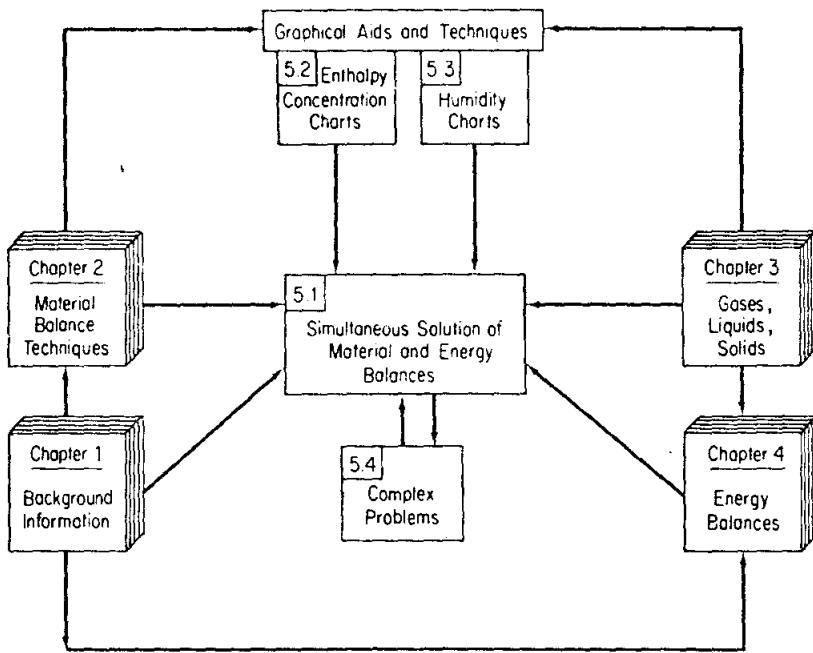


Fig. 5.0. Hierarchy of topics to be studied in this chapter (section numbers are in the upper left-hand corner of the boxes).

5.1 Simultaneous use of material and energy balances for the steady state

For any specified system or piece of equipment you can write

- A total material balance.
- A material balance for each chemical component (or each atomic species, if preferred).

You can use the energy balance to add one additional independent overall equation to your arsenal, but you cannot make energy balances for each individual chemical component in a mixture or solution. As we mentioned previously, you need one independent equation for each unknown in a given problem. The energy balance often provides the extra piece of information to help you resolve an apparently insuperable calculation composed solely of material balances.

We can illustrate any given system or piece of equipment *in the steady state* by drawing a diagram such as Fig. 5.1. Figure 5.1 could represent a boiler, a distillation column, a drier, a human being, or a city, and takes into account processes involving a chemical reaction.

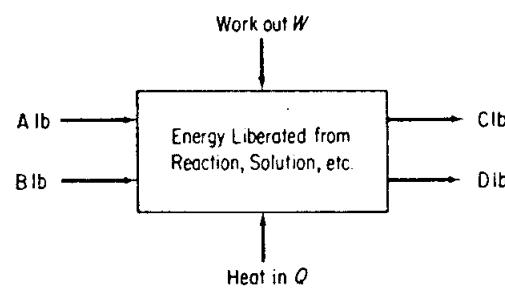


Fig. 5.1. Sketch of generalized flow process with chemical reaction.

Let x_i = weight fraction of any component

\hat{H}_i = enthalpy per unit mass of any component with respect to some reference temperature

If the subscript numbers 1, 2, 3, etc., represent the components in each stream, you can write the following material balances in algebraic form:

$$\begin{array}{lll}
 \text{balance} & \text{in} & = \text{out} \\
 \text{Total:} & A + B & = C + D \\
 \text{Component 1:} & Ax_{A_1} + Bx_{B_1} & = Cx_{C_1} + Dx_{D_1} \\
 \text{Component 2:} & Ax_{A_2} + Bx_{B_2} & = Cx_{C_2} + Dx_{D_2} \\
 & \text{etc.} &
 \end{array}$$

As previously discussed, the number of independent equations is one less than the total number of equations.

In addition, an overall energy balance can be written as (ignoring kinetic and potential energy changes)

$$Q - W = (C\hat{H}_c + D\hat{H}_d) - (A\hat{H}_A + B\hat{H}_B)$$

For a more complex situation, examine the interrelated pieces of equipment in Fig. 5.2.

Again the streams are labeled, and the components are 1, 2, 3, etc. How should you attack a problem of this nature? From an overall viewpoint, the problem reduces to that shown in Fig. 5.1. In addition, a series of material balances and an energy balance can be made around each piece of equipment I, II, and III. Naturally, all these equations are not independent, because, if you add up the total material balances around boxes I, II, and III, you simply have the grand overall material balance around the whole process. Similarly, if you add up the component balances for each box, you have a grand component balance for the entire process, and the sum of the energy balances around boxes I, II, and III gives the overall energy balance. Following Fig. 5.2 (on p. 365) is a list of the material and energy balances that you can write for it.

Bo
ind
bo

Bou
over

En

Pr

Pr

Pr

Note the
these bal

EXAMPLE

A dist
chloroben
column is 5
1 percent b

→ Clb
→ Dilb

chemical reaction.

at with respect to some

ponents in each stream, stoic form:

$$\begin{aligned} \text{out} \\ + \\ + Dx_{D_1} \\ + Dx_{D_2} \end{aligned}$$

equations is one less than

then as (ignoring kinetic

$$B\hat{H}_B)$$

pieces of equipment in

1, 2, 3, etc. How should viewpoint, the problem of material balances and equipment I, II, and III. use, if you add up the simply have the grand early, if you add up the component balance for the end boxes I, II, and III (p. 365) is a list of the

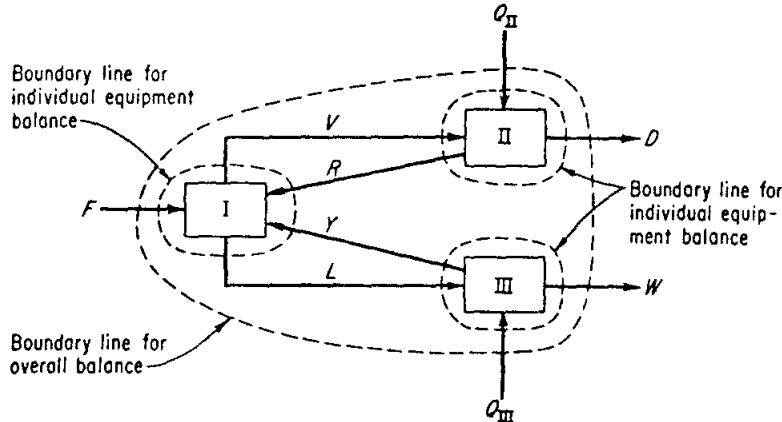


Fig. 5.2. Sketch for interrelated processes and streams.

	balance	in	out
<i>Entire process:</i>			
Total		$F = D + W$	
Component		$Fx_{P_i} = Dx_{D_i} + Wx_{W_i}$	
Energy		$Q_{II} + Q_{III} + F\Delta\hat{H}_F = D\Delta\hat{H}_D + W\Delta\hat{H}_W$	
<i>Process I:</i>			
Total		$F + R + Y = V + L$	
Component		$Fx_{P_i} + Rx_{R_i} + Yx_{Y_i} = Vx_{V_i} + Lx_{L_i}$	
Energy		$F\Delta\hat{H}_F + R\Delta\hat{H}_R + Y\Delta\hat{H}_Y = V\Delta\hat{H}_V + L\Delta\hat{H}_L$	
<i>Process II:</i>			
Total		$V = R + D$	
Component		$Vx_{V_i} = Rx_{R_i} + Dx_{D_i}$	
Energy		$Q_{II} + V\Delta\hat{H}_V = R\Delta\hat{H}_R + D\Delta\hat{H}_D$	
<i>Process III:</i>			
Total		$L = Y + W$	
Component		$Lx_{L_i} = Yx_{Y_i} + Wx_{W_i}$	
Energy		$Q_{III} + L\Delta\hat{H}_L = Y\Delta\hat{H}_Y + W\Delta\hat{H}_W$	

Note the symmetry among these equations. The methods of writing and applying these balances are now illustrated by an example.

EXAMPLE 5.1 Simultaneous material and energy balances

A distillation column separates 10,000 lb/hr of a 40 percent benzene, 60 percent chlorobenzene liquid solution which is at 70°F. The liquid product from the top of the column is 99.5 percent benzene, while the bottoms (stream from the reboiler) contains 1 percent benzene. The condenser uses water which enters at 60°F and leaves at 140°F,

while the reboiler uses saturated steam at 280°F. The reflux ratio (the ratio of the liquid overhead returned to the column to the liquid overhead product removed) is 6 to 1. Assume that both the condenser and reboiler operate at 1 atm pressure, that the temperature calculated for the condenser is 178°F and for the reboiler 268°F, and that the calculated fraction benzene in the vapor from the reboiler is 3.9 weight percent (5.5 mole percent). Calculate the following:

- The pounds of overhead product (distillate) and bottoms per hour.
- The pounds of reflux per hour.
- The pounds of liquid entering the reboiler and the reboiler vapor per hour.
- The pounds of steam and cooling water used per hour.

Solution:

(a) Figure E5.1 will help visualize the process and assist in pointing out what additional data have to be determined.

First we have to get some pertinent enthalpy or heat capacity data. Then we can make our material and energy balances. (The exit streams have the same composition as the solutions in the condenser or reboiler.)

(b) Convert the reboiler analysis into mole fractions.

Basis: 100 lb B

comp.	lb	mol. wt	lb moles	mole fr.
Bz	1	78.1	0.0128	0.014
Cl	99	112.6	0.88	0.986
			0.8928	1.000

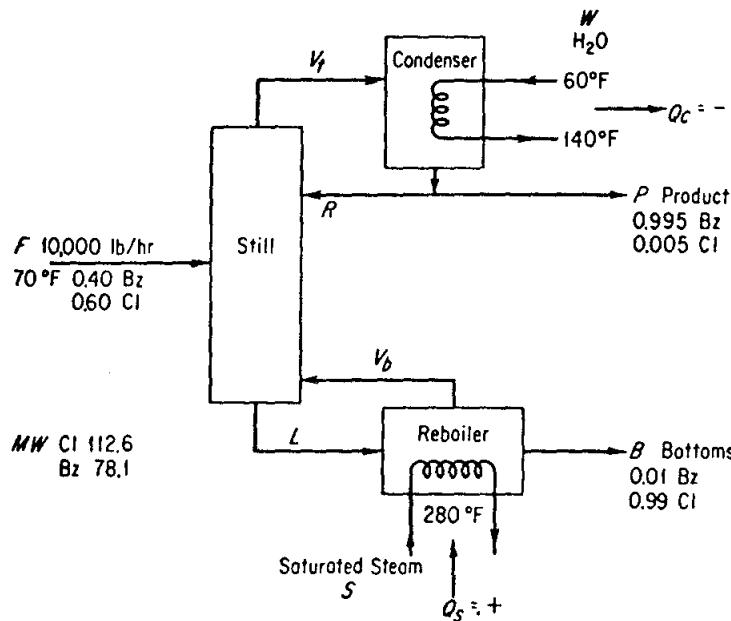


Fig. E5.1.

ratio (the ratio of the liquid product removed) is 6 to 1. At atm pressure, that the reboiler 268°F, and that water is 3.9 weight percent

atoms per hour.

reboiler vapor per hour.

list in pointing out what

capacity data. Then we can have the same com-

maize fr.

Layout

20

°F

$Q_c = -$

Product
0.995 Bz
0.005 Cl

Bottoms
0.01 Bz
0.99 Cl

(c) The heat capacity data for liquid benzene and chlorobenzene will be assumed to be as follows¹ (no enthalpy tables are available):

Temp. (°F)	$C_p, \text{Btu}/(\text{lb})(^{\circ}\text{F})$		$\Delta\hat{H}_{\text{vaporization}}, \text{Btu}/\text{lb}$	
	Cl	Bz	Cl	Bz
70	0.31	0.405		
90	0.32	0.415		
120	0.335	0.43		
150	0.345	0.45		
180	0.36	0.47	140	170
210	0.375	0.485	135	166
240	0.39	0.50	130	160
270	0.40	0.52	126	154

Basis: 10,000 lb feed/hr

(d) Overall material balances:

Overall total material balance:

$$F = P + B$$

$$10,000 = P + B$$

Overall benzene balance:

$$Fx_P = Px_P + Bx_B$$

$$10,000(0.40) = P(0.995) + B(0.01)$$

$$10,000(0.40) = P(0.995) + (10,000 - P)(0.01)$$

$$P = 3960 \text{ lb/hr} \quad \text{--- (a)}$$

$$B = 6040 \text{ lb/hr} \quad \text{--- (b)}$$

(e) Material balances around the condenser:

$$\frac{R}{P} = 6 \quad \text{or} \quad R = 6P = 6(3960) = 23,760 \text{ lb/hr} \quad \text{--- (b)}$$

$$V_t = R + P = 23,760 + 3960 = 27,720 \text{ lb/hr}$$

(f) Material balances around the reboiler:

Total:

$$L = B + V_b$$

Benzene:

$$Lx_L = Bx_B + V_b x_{V_b}$$

$$L = 6040 + V_b$$

$$Lx_L = 6040(0.01) + V_b(0.039)$$

We have three unknowns and only two independent equations. We can write additional equations around the still, but these will not resolve the problem since we would still be left with one unknown more than the number of independent equations. This is the stage at which energy balances can be used effectively.

¹Data estimated from tabulations in the Appendix of *Process Heat Transfer* by D. Q. Kern, McGraw-Hill, New York, 1950.

(g) Overall energy balance: Let the reference temperature be 70°F; this will eliminate the feed from the enthalpy calculations. Assume that the solutions are ideal so that the thermodynamic properties (enthalpies and heat capacities) are additive. No work or potential or kinetic energy is involved in this problem. Thus

$$Q_{\text{steam}} + Q_{\text{condenser}} = \underbrace{P \int_{70}^{178} C_{p_P} dt}_{\Delta \hat{H}_P} + \underbrace{B \int_{70}^{268} C_{p_B} dt}_{\Delta \hat{H}_B} - \underbrace{F \int_{70}^{70} C_{p_F} dt}_{\Delta \hat{H}_F} = 0$$

We know all the terms except Q_{steam} and $Q_{\text{condenser}}$ and still need more equations.

(h) Energy balance on the condenser: This time we shall let the reference temperature equal 178°F; this choice simplifies the calculation, because then neither the R nor P streams have to be included. Assume that the product leaves at the saturation temperature in the condenser of 178°F. With the condenser as the system and the water as the surroundings we have

system (condenser)	surroundings (water)
$\Delta H_{\text{condenser}} = Q_{\text{condenser}}$	$\Delta H_{\text{water}} = Q_{\text{water}}$

and, since $Q_{\text{system}} = -Q_{\text{surroundings}}$, $\Delta H_{\text{condenser}} = -\Delta H_{\text{water}}$

$$V_r(-\Delta \hat{H}_{\text{vaporization}}) = -W C_{p_{H_2O}}(t_2 - t_1)$$

$$27,720[170(0.995) + 140(0.005)] = W(1)(140 - 60) = Q_{\text{water}} = -Q_{\text{condenser}}$$

Solving, $Q_C = -4.71 \times 10^6 \text{ Btu/hr}$ (heat evolved), and the cooling water used is

$$W = 5.89 \times 10^4 \text{ lb H}_2\text{O/hr} \leftarrow \textcircled{d}_1$$

(i) Amount of steam used: We shall use the overall energy balance from step (g).

$$Q_{\text{steam}} = 3960 \frac{\text{lb}}{\text{hr}} \left(46.9 \frac{\text{Btu}}{\text{lb}} \right) + 6040 \frac{\text{lb}}{\text{hr}} \left(68.3 \frac{\text{Btu}}{\text{lb}} \right) + 4.71 \times 10^6 \frac{\text{Btu}}{\text{hr}}$$

In the preceding equation the $\int C_p dt$ was determined by first graphically integrating $\int C_p dt$ to get $\Delta \hat{H}$ for each component and then weighting the $\Delta \hat{H}$ values by their respective weight fractions:

$$\Delta \hat{H}_P = \int_{70}^{178} C_{p_P} dt \quad \text{Btu/lb} \quad \Delta \hat{H}_B = \int_{70}^{268} C_{p_B} dt \quad \text{Btu/lb}$$

Bz	Cl	Avg	Bz	Cl	Avg
47.0	36.2	46.9	88.1	68.0	68.3

An assumption that the P stream was pure benzene and the B stream was pure chlorobenzene would be quite satisfactory since the value of Q_C is one order of magnitude larger than the "sensible heat" terms

$$Q_{\text{steam}} = 5.31 \times 10^6 \text{ Btu/hr}$$

From the steam tables, $\Delta \hat{H}_{\text{vap}}$ at 280°F is 923 Btu/lb. Assume that the steam leaves at its saturation temperature and is not subcooled. Then

$$\text{lb steam used/hr} = \frac{5.31 \times 10^6 \text{ Btu/hr}}{923 \text{ Btu/lb}} = 5760 \text{ lb/hr} \leftarrow \textcircled{d}_2$$

(j) Energy balance around the reboiler:

$$Q_{\text{steam}} + L(\Delta \hat{H}_L) + V_b(\Delta \hat{H}_{V_b}) + B(\Delta \hat{H}_B)$$

ture be 70°F ; this will let the solutions are ideal capacities) are additive. problem. Thus

$$-\frac{F \int_{T_0}^{T_0} C_{p_F} dt}{\Delta \hat{H}_F} = 0$$

need more equations. let the reference temperature then neither the R leaves at the saturation temperature system and the water

water)

water

 $-t_1$) $\Delta_{\text{water}} = -Q_{\text{condenser}}$

cooling water used is

balance from step (g).

$$4.71 \times 10^6 \frac{\text{Btu}}{\text{hr}}$$

graphically integrating the $\Delta \hat{H}$ values by their dt Btu/lb

Avg

0 68.3

stream was pure chloro-
one order of magnitude

that the steam leaves

at $\leftarrow (d_2)$

We know that $Q_{\text{steam}} = 5.31 \times 10^6 \text{ Btu/hr}$. We do not know L or the value of $\Delta \hat{H}_L$. However, even if $\Delta \hat{H}_L$ is not known, the temperature of stream L entering the reboiler would not be more than 20°F lower than 268°F at the very most, and the heat capacity would be about that of chlorobenzene. We shall assume a difference of 20°F , but you can note in the calculations below that the effect of including $\Delta \hat{H}_L$, as opposed to ignoring it, is minor.

The value of V_b is still unknown, but all the other values ($\Delta \hat{H}_V$, B , $\Delta \hat{H}_B$) are known or can be calculated. Thus, if we combine the energy balance around the reboiler with the overall material balance around the reboiler, we can find both L and V_b .

Reference temperature: 268°F

Energy balance:

$$5.31 \times 10^6 \frac{\text{Btu}}{\text{hr}} + (L \text{ lb}) \left(0.39 \frac{\text{Btu}}{(\text{lb})(^{\circ}\text{F})} \right) (-20^{\circ}\text{F}) = V_b [(0.99)(126) + (0.01)(154)] + B(0)$$

Material balance:

$$L = 6040 + V_b$$

$$5.31 \times 10^6 - (6040 + V_b)(7.8) = 126.3 V_b$$

$$5.31 \times 10^6 - 0.047 \times 10^6 = 126.3 V_b + 7.8 V_b$$

$$V_b = \frac{5.26 \times 10^6}{134} = 39,300 \text{ lb/hr} \quad \text{--- (c}_1\text{)}$$

$$L = V_b + B = 39,300 + 6040 = 45,340 \text{ lb/hr} \quad \text{--- (c}_2\text{)}$$

If we had ignored the enthalpy of the L stream, then V_b would have been

$$V_b = \frac{5.31 \times 10^6}{126.3} = 42,100 \text{ lb/hr}$$

a difference of about 7.1 percent.

In practice, the solution of steady-state material and energy balances is quite tedious, a situation which has led engineers to the use of digital and hybrid computer routines. Certain special problems are encountered in the solution of large-scale sets of equations, problems of sufficient complexity to be beyond our scope here.

An important aspect of combined material and energy balance problems is how to ensure that the process equations are determinate, i.e., have at least one solution. We can use the phase rule (discussed in Sec. 3.7-1) plus some common sense to provide a guide as to the number of variables that must be specified and the number of variables that can be unknown in any problem. The phase rule gives the relationship between the number of degrees of freedom and the intensive variables such as temperature, pressure, specific volume, and composition that are associated with each stream. According to Eq. (3.57), the number of degrees of freedom for a single phase at equilibrium is

$$F = C - 1 + 2 = C + 1$$

However, to completely specify a stream, we need to know how much material is flowing, so that in addition to the $C + 1$ intensive variables, one extensive variable must be given, for a total of

$$N_t = C + 2$$

where N_t is the total number of variables to be specified for a single stream.

Each *independent* material and energy balance that is written reduces the degrees of freedom in a problem by one. Consequently, in any problem you can add up the total number of variables and subtract the number of equality constraints and specified input conditions to get the difference, which is the number of variables that have to be specified if the problem is to be determinate. If a chemical reaction takes place, the number of independent material balances that can be made is equal to the number of atomic species, not C , the number of components.

We shall now illustrate the application of the above concept to several simple cases.

EXAMPLE 5.2 Determining the degrees of freedom in a process

We shall consider five typical processes, as depicted by the respective figures below, and for each ask the question, How many variables have to be specified, i.e., what are the degrees of freedom (d.f.) to make the problem of solving the combined material and energy balances determinate. All the processes will be steady-state ones.

(a) *Simple stream junction, single phase* [Fig. E5.2(a)]. We assume that $Q = 0$ and $W = 0$, and that the pressure and temperature of P_1 and P_2 are the same as that

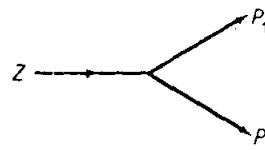


Fig. E5.2(a).

of Z , the input stream. The statement of the total number of variables, constraints, and degrees of freedom can be summarized as follows.

Total number of variables (3 streams): $3(C + 2)$

Number of independent equality constraints:

Material balances:	C
--------------------	-----

Energy balance:	1
-----------------	---

$T_{P_1} = T_Z; T_{P_2} = T_Z;$	2
---------------------------------	---

$P_{P_1} = P_Z; P_{P_2} = P_Z;$	2
---------------------------------	---

Input conditions in Z specified:	$C + 2$
------------------------------------	---------

Total no. d.f. = $3(C + 2) - 2C - 7 = C - 1$

Note that a
ponents and
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We can
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 $= 2 - 1 =$
Material ba

Energy bala

Definitions:

If Z, x_Z, T_Z ,
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balance can
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If the in
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Consequently

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(b) Mi

know how much material variables, one extensive

for a single stream, is written reduces the in any problem you can number of equality constraints, which is the number to be determinate. If a set of material balances that is, not C , the number of

above concept to several

process

by the respective figures have to be specified, i.e., of ; the combined will. steady-state ones. We assume that $Q = 0$ and P_Z are the same as that

of variables, constraints,

$$3(C + 2)$$

$$\begin{matrix} C \\ 1 \\ 2 \\ 2 \\ C + 2 \\ - 1 \end{matrix}$$

Note that although $C + 1$ material balances can be written corresponding to C components and one total balance, only C of the balances are independent and included in the tally above.

We can illustrate the relation between the count for the degrees of freedom above and the constraints by considering a two-component system for which d.f. = $C - 1 = 2 - 1 = 1$:

Material balances:

$$\begin{aligned} Z &= P_1 + P_2 \\ Zx_Z &= P_1 x_{P_1} + P_2 x_{P_2} \\ Zy_Z &= P_1 y_{P_1} + P_2 y_{P_2} \end{aligned}$$

Energy balance:

$$P_1 \hat{H}_{P_1} + P_2 \hat{H}_{P_2} - Z \hat{H}_Z = 0$$

Definitions:

$$\begin{aligned} x_{P_1} + y_{P_1} &= 1 \\ x_{P_2} + y_{P_2} &= 1 \\ x_Z + y_Z &= 1 \end{aligned}$$

If Z , x_Z , T_Z , and p_Z are specified in the input, then \hat{H}_Z is known because H is a function only of T , p , and x . We have as given $T_{P_1} = T_Z = T_{P_2}$ and $p_{P_1} = p_Z = p_{P_2}$, so that \hat{H}_{P_1} and \hat{H}_{P_2} depend only on x_{P_1} and x_{P_2} , respectively. You can see by inspection that if P_1 is specified, representing the 1 degree of freedom available, the total material balance can be solved for P_2 , and then the (nonlinear) energy balance and one-component material balance can be solved simultaneously for x_{P_1} and x_{P_2} .

If the initial assumption had been that the compositions of P_1 and P_2 were the same as Z and we reduced the total d.f. by an additional factor of $2(C - 1)$, there being $C - 1$ compositions to be specified, we would be making an error because the number of independent equations would not be $C + 1$ anymore but would simply be 1. The component material balances and energy balance would all be the same. Consequently the number of degrees of freedom would be

$$3(C + 2) - 1 - 2 - 2 - (C + 2) - 2(C - 1) = 1$$

the same as before.

(b) Mixer [Fig. E5.2(b)]. For this process we assume that $W = 0$.

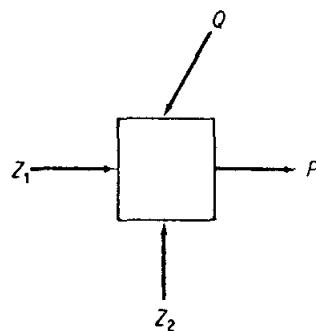


Fig. E5.2(b).

Total number of variables (3 streams + Q): $3(C + 2) + 1$

Number of independent equality constraints:

Material balances: C

Energy balance: 1

$$\text{Total no. d.f.} = 3(C + 2) + 1 - C - 1 = 2C + 6$$

(c) *Heat exchanger* [Fig. E5.2(c)]. For this process we assume that $W = 0$.

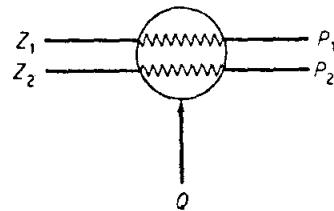


Fig. E5.2(c).

Total number of variables (4 streams + Q): $4(C + 2) + 1$

Number of independent equality constraints:

Material balances (2 separate lines): $2C$

Energy balance: 1

$$\text{Total no. d.f.} = 4(C + 2) + 1 - 2C - 1 = 2C + 8$$

(d) *Pump* [Fig. E5.2(d)]. Here $Q = 0$.

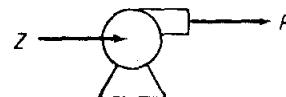


Fig. E5.2(d)

Total number of variables (2 streams + W): $2(C + 2) + 1$

Number of independent equality constraints:

Material balances: C

Energy balance: 1

$$\text{Total no. d.f.} = 2(C + 2) + 1 - C - 1 = C + 4$$

(e) *Two-phase well-mixed tank (stage) at equilibrium* [Fig. E5.2(e)] (L , liquid phase; V , vapor phase). Here $W = 0$. Although two phases exist at equilibrium inside

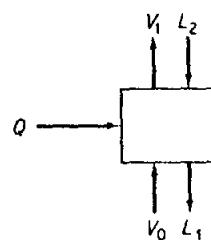


Fig. E5.2(e).

the system, we mean that is known component.

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Other choices

You can different simple freedom. In double count interconnection.

EXAMPLE 5

Consider we could consider as a sector, an equilibrium the total d.f. redundant co

The net d.f. you can see

We can Z is actually

$$: \quad 3(C + 2) + 1$$

$$\text{ts:} \quad \begin{array}{r} C \\ 1 \\ - 1 = 2C + 6 \end{array}$$

ss we assume that $W = 0$.

$$\begin{array}{l} - P_1 \\ - P_2 \end{array}$$

$$: \quad 4(C + 2) + 1$$

$$\text{ts:} \quad \begin{array}{r} 2C \\ 1 \\ - 1 = 2C + 8 \end{array}$$

P

$$: \quad 2(C + 2) + 1$$

$$\begin{array}{r} C \\ 1 \\ - 1 = C + 4 \end{array}$$

rium [Fig. E5.2(e)] (L , liquid phases exist at equilibrium inside

the system, the streams entering and leaving are single-phase streams. By equilibrium we mean that both phases are at the same temperature and pressure and that an equation is known that relates the composition in one phase to that in the other for each component.

$$\text{Total number of variables (4 streams + } Q\text{):} \quad 4(C + 2) + 1$$

Number of independent equality constraints:

Material balances:	C
Energy balance:	1
Composition relations at equilibrium:	C
Temperatures in the two phases equal:	1
Pressures in the two phases equal:	1

$$\text{Total no. d.f.} = 4(C + 2) + 1 - 2C - 3 = 2C + 6$$

In general you might specify the following variables to make the problem determinate:

Input stream L_2 :	$C + 2$
Input stream V_0 :	$C + 2$
Pressure:	1
Q :	1
Total:	$\underline{\underline{2C + 6}}$

Other choices are of course possible.

You can compute the degrees of freedom for combinations of like or different simple processes by proper combination of their individual degrees of freedom. In adding the degrees of freedom for units, you must eliminate any double counting either for variables or constraints and take proper account of interconnecting streams whose characteristics are often fixed only by implication.

EXAMPLE 5.3 Degrees of freedom in combined units

Consider the mixer-separator shown in Fig. E5.3. Superficially it would seem that we could carry out an analysis as follows to combine the units. For the mixer considered as a separate unit, from the previous example, d.f. = $2C + 6$. For the separator, an equilibrium unit, we find from the previous example that d.f. = $C + 4$. Hence the total d.f. = $2C + 6 + C + 4 = 3C + 10$. However, we have to eliminate certain redundant counts of variables and constraints for the combination:

Eliminate variable Z :	$C + 2$
Eliminate Q_s :	1
Total:	$\underline{\underline{C + 3}}$
Eliminate one energy balance:	1
Net change:	$\underline{\underline{C + 2}}$

The net d.f. for the entire unit would be $2C + 8$, but this count is incorrect because you can see from the previous example that the correct number of d.f. = $2C + 6$.

We can locate the source of this discrepancy if we note for the mixer that stream Z is actually a *two-phase stream*; hence $N_t = C + 1$, not $C + 2$. The proper analysis

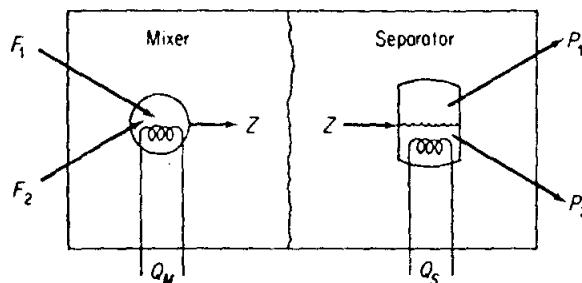


Fig. E5.3. Degrees of freedom in combined units.

is as follows:

For the mixer:

	single-phase streams	two-phase stream	Q_M
--	----------------------	------------------	-------

$$\begin{array}{l} \text{Total no. variables: } 2(C+2) + 1(C+1) + 1 = 3C + 6 \\ \text{Constraints (as before): } C+1 \\ \hline \text{Net: } 2C + 5 \end{array}$$

For the separator:

$$\begin{array}{l} \text{Total no. variables: } 2(C+2) + 1(C+1) + 1 = 3C + 6 \\ \text{Constraints (as before): } 2C + 3 \\ \hline \text{Net: } C + 3 \end{array}$$

Eliminate redundant counting:

$$\begin{array}{ll} \text{Drop } Q_S: & 1 \\ \text{Eliminate } Z: & \underline{C+1} \\ \text{Together:} & \underline{C+2} \end{array}$$

Consequently the total degrees of freedom are

$$(2C + 5) + (C + 3) - (C + 2) = 2C + 6$$

as in Example 5.2.

We do not have the space to illustrate additional combinations of simple units to form more complex units, but Kwauk² prepared several excellent tables summarizing the variables and degrees of freedom for distillation columns, absorbers, heat exchangers, and the like.

5.2 Enthalpy-concentration charts

An enthalpy-concentration chart is a convenient graphical method of representing enthalpy data for a binary mixture. If available,³ such charts are useful

²M. Kwauk, *A.I.Ch.E. J.*, v. 2, p. 240 (1956).

³For a literature survey as of 1957 see Robert Lemlich, Chad Gottschlich, and Ronald Hoke, *Chem. Eng. Data Series*, v. 2, p. 32 (1957). Additional references: for CCl_4 , see M. M.

in making combined material and energy balances calculations in distillation, crystallization, and all sorts of mixing and separation problems. You will find a few examples of enthalpy-concentration charts in Appendix I.

At some time in your career you may find you have to make numerous repetitive material and energy balance calculations on a given binary system and would like to use an enthalpy-concentration chart for the system, but you cannot find one in the literature or in your files. How do you go about constructing such a chart?

5.2-1 Construction of an Enthalpy-Concentration Chart. As usual, the first thing to do is choose a basis—some given amount of the mixture, usually 1 lb or 1 lb mole. Then choose a reference temperature ($H_0 = 0$ at T_0) for the enthalpy calculations. Assuming 1 lb is the basis, you then write an energy balance for solutions of various compositions at various temperatures:

$$\Delta\hat{H}_{\text{mixture}} = x_A \Delta\hat{H}_A + x_B \Delta\hat{H}_B + \Delta\hat{H}_{\text{mixing}} \quad (5.1)$$

where $\Delta\hat{H}_{\text{mixture}}$ = the enthalpy of 1 lb of the mixture

$\Delta\hat{H}_A$, $\Delta\hat{H}_B$ = the enthalpies of the pure components per lb relative to the reference temperature (the reference temperature does not have to be the same for A as for B)

$\Delta\hat{H}_{\text{mixing}}$ = the heat of mixing (solution) per lb at the temperature of the given calculation

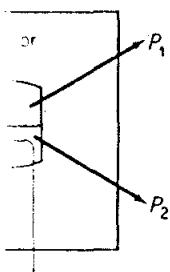
In the common case where the $\Delta\hat{H}_{\text{mixing}}$ is known only at one temperature (usually 77°F), a modified procedure as discussed below would have to be followed to calculate the enthalpy of the mixture.

The choice of the reference temperatures for A and B locates the zero enthalpy datum on each side of the diagram (see Fig. 5.3). From enthalpy tables such as the steam tables, or by finding

$$(\hat{H}_A - \hat{H}_{A0}) = \int_{T_0}^{T=77^\circ\text{F}} C_{p_A} dt$$

you can find $\Delta\hat{H}_A$ at 77°F and similarly obtain $\Delta\hat{H}_B$ at 77°F. Now you have located points A and B. If one of the components is water, it is advisable to choose 32°F as T_0 because then you can use the steam tables as a source of data. If both components have the same reference temperature, the temperature isotherm will intersect on both sides of the diagram at 0, but there is no particular advantage in this.

Krishnaiah et al., *J. Chem. Eng. Data*, v. 10, p. 117 (1965); for EtOH-EtAc, see Robert Lemlich, Chad Gottschlich, and Ronald Hoke, *Brit. Chem. Eng.*, v. 10, p. 703 (1965); for methanol-toluene, see C. A. Plank and D. E. Burke, *Hydrocarbon Processing*, v. 45, no. 8, p. 167 (1966); for acetone-isopropanol, see S. N. Balasubramanian, *Brit. Chem. Eng.*, v. 11, p. 1540 (1966); for alcohol-aromatic systems, see C. C. Reddy and P. S. Murti, *Brit. Chem. Eng.*, v. 12, p. 1231 (1967); for acetonitrile-water-ethanol, see Reddy and Murti, *ibid.*, v. 13, p. 1443 (1968); and for alcohol-aliphatics, see Reddy and Murti, *ibid.*, v. 16, p. 1036 (1971).



defined units.

$$\begin{aligned} \text{sum } Q_M \\ - 1) + 1 &= 3C + 6 \\ &\frac{C + 1}{2C + 5} \end{aligned}$$

$$\begin{aligned} - 1) + 1 &= 3C + 6 \\ &\frac{2C + 3}{C + 3} \end{aligned}$$

$$\begin{aligned} 1 \\ - 1 \\ \hline C + 2 \\ 2C + 6 \end{aligned}$$

final combinations of simple
mared several excellent tables
for distillation columns.

graphical method of repre-
sible,³ such charts are useful

Chad Gottschlich, and Ronald
references: for CCl_4 , see M. M.

a plot of enthalpy vs. tem-

7 psia

and pure C_7 (358°F). Fix the by plotting the temperature-enthalpy of the pure C_4 at 146°F mole. These are marked in

of liquid between A and B experimental measurements are component per mole by the

$x_{C_7}x_{C_4}$

med. In this way the bubble-

RATED¹ = 100 PSIA

Btu/lb mole

	$\Delta\hat{H}_L =$ $\Delta\hat{H}_{C_7}x_{C_7} + \Delta\hat{H}_{C_4}x_{C_4}$	
0	19,250	19,250
.254	18,250	18,504
.490	17,280	17,770
.710	16,300	17,010
.100	14,600	15,700
.515	12,650	14,165
.870	11,000	12,870
.420	8,300	10,720
.800	6,240	9,040
.100	4,700	7,800
.360	3,480	6,840
.500	2,440	5,940
.600	1,540	5,140
.740	740	4,480
.800	366	4,166
.970	0	3,970

Step 3: Plot the enthalpy values for the saturated pure vapor (dew point), points C and D . A supplementary graph again is required to assist in interpolating enthalpy values.

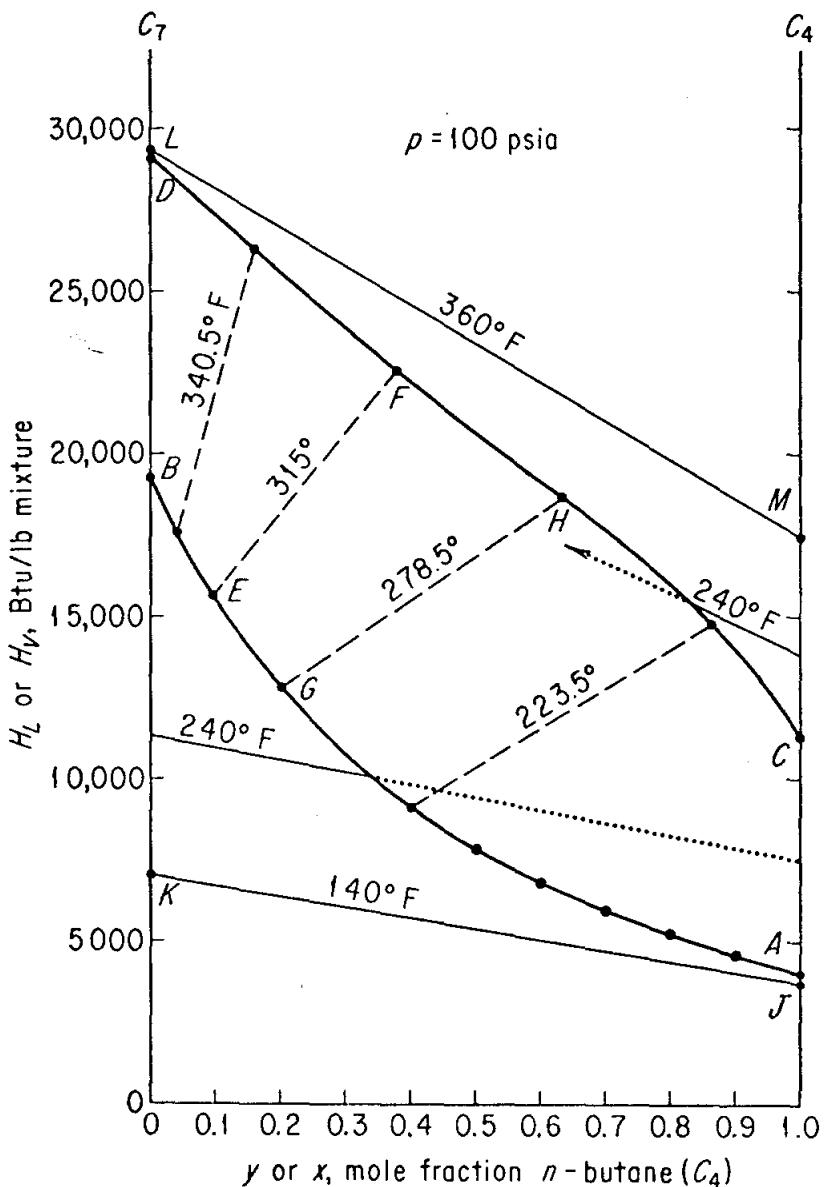


Fig. E5.4.

Step 4: Fill in the saturated-vapor curve between C and D by the following calculations:

$$\Delta\hat{H}_V = \Delta\hat{H}_{C_7}y_{C_7} + \Delta\hat{H}_{C_4}y_{C_4}$$

Intermediate values of enthalpy were interpolated from a plot of enthalpy vs. temperature prepared from the data given on p. 377.

Step 3: P
points C and
enthalpy value

Basis: 1 lb mole mixture

Reference conditions: 32°F and 14.7 psia

Step 1: Plot the boiling points of pure C_4 (146°F) and pure C_7 (358°F). Fix the enthalpy scale from 0 to 30,000 Btu/lb mole mixture. By plotting the temperature-enthalpy data on separate graphs you can find that the enthalpy of the pure C_4 at 146°F is 3970 Btu/lb mole and that of C_7 at 358°F is 19,250 Btu/lb mole. These are marked in Fig. E5.4 as points A and B, respectively.

Step 2: Now choose various other compositions of liquid between A and B (the corresponding temperatures determined from experimental measurements are shown in the table), and multiply the enthalpy of the pure component per mole by the mole fraction present:

$$\Delta\hat{H}_{\text{liquid mixture}} = \Delta\hat{H}_{C_4}x_{C_4} + \Delta\hat{H}_{C_7}x_{C_7}$$

No heat of mixing is present since ideality was assumed. In this way the bubble-point line between A and B can be established.

H-x CALCULATIONS FOR C_4 - C_7 , LIQUID (SATURATED) AT 100 PSIA

Enthalpy, Btu/lb mole

Temp., °F	Mole fr.		$\Delta\hat{H}_L = \frac{\Delta\hat{H}_{C_4}x_{C_4}}{\Delta\hat{H}_{C_4}x_{C_4} + \Delta\hat{H}_{C_7}x_{C_7}}$				
	x_{C_4}	x_{C_7}	$\Delta\hat{H}_{C_4}$	$\Delta\hat{H}_{C_7}$	$\Delta\hat{H}_{C_4}x_{C_7}$	$\Delta\hat{H}_{C_7}x_{C_4}$	$\Delta\hat{H}_L$
358	0	1.0	13,200	19,250	0	19,250	19,250
349	0.02	0.98	12,700	18,650	254	18,250	18,504
340.5	0.04	0.96	12,220	18,000	490	17,280	17,770
331.5	0.06	0.94	11,750	17,380	710	16,300	17,010
315	0.10	0.90	11,000	16,200	1,100	14,600	15,700
296	0.15	0.85	10,100	14,900	1,515	12,650	14,165
278.5	0.20	0.80	9,350	13,750	1,870	11,000	12,870
248	0.30	0.70	8,050	11,850	2,420	8,300	10,720
223.5	0.40	0.60	7,000	10,400	2,800	6,240	9,040
204	0.50	0.50	6,200	9,400	3,100	4,700	7,800
188	0.60	0.40	5,600	8,700	3,360	3,480	6,840
173.8	0.70	0.30	5,000	8,120	3,500	2,440	5,940
160.5	0.80	0.20	4,500	7,700	3,600	1,540	5,140
151.0	0.90	0.10	4,150	7,400	3,740	740	4,480
147.8	0.95	0.05	4,000	7,310	3,800	366	4,166
146.0	1.0	0	3,970	7,280	3,970	0	3,970

H_L or H_P, Btu/lb mixture

Step 4: F
calculations:

Enthalpy, Btu/lb mole

Temp., °F	Mole fr.	$\Delta\hat{H}_v = \Delta\hat{H}_{C_4}y_{C_4} + \Delta\hat{H}_{C_7}y_{C_7}$				
		$\Delta\hat{H}_{C_4}$	$\Delta\hat{H}_{C_7}$	$\Delta\hat{H}_{C_4}y_{C_4}$	$\Delta\hat{H}_{C_7}y_{C_7}$	$\Delta\hat{H}_v$
358	0	17,500	29,250	0	29,250	29,250
349	0.084	17,150	28,700	1,440	26,200	27,640
340.5	0.160	16,850	28,100	2,700	23,600	26,300
331.5	0.241	16,500	27,550	3,970	20,860	24,830
315	0.378	16,050	26,700	6,060	16,600	22,660
296	0.518	15,800	25,800	8,050	12,420	20,470
278.5	0.630	14,980	24,900	9,425	9,210	18,635
248	0.776	14,100	23,600	10,950	5,290	16,240
223.5	0.857	13,420	22,550	11,500	3,220	14,720
204	0.907	12,950	21,700	11,750	2,020	13,770
188	0.942	12,500	21,100	11,780	1,225	13,005
173.8	0.968	12,100	20,600	11,700	659	12,359
160.5	0.986	11,800	26,100	11,620	282	11,902
151.0	0.996	11,500	19,720	11,450	79	11,529
147.8	0.999	11,450	19,600	11,430	20	11,450
146.0	1.000	11,400	19,540	11,400	0	11,400

Step 5: Draw tie lines (the dashed lines) between the bubble-point and dew-point lines (lines *E-F*, *G-H*, etc.). These lines of constant temperature show the equilibrium concentrations in the vapor and liquid phases. The experimental data were selected so that identical temperatures could be used in the above calculations for each phase; if such data were not available, you would have to prepare additional graphs or tables to use in interpolating the isobaric data (data at 100 psia) with respect to the mole fraction *y* or *x*. If you wanted to draw the lines at even temperature intervals, such as 140, 160, 180°F, etc., you would also have to interpolate.

Step 6: Draw isothermal lines at 140, 160°F, etc., in the liquid and vapor regions. Presumably these will be straight lines since there is no heat of mixing. Since:

$$x_{C_7} + x_{C_4} = 1 \quad (a)$$

$$\begin{aligned} \Delta\hat{H}_L &= \Delta\hat{H}_{\text{mixture}} = x_{C_4}\Delta\hat{H}_{C_4} + x_{C_7}\Delta\hat{H}_{C_7} = x_{C_4}\Delta\hat{H}_{C_4} + (1 - x_{C_4})\Delta\hat{H}_{C_7}, \\ &= (\Delta\hat{H}_{C_4} - \Delta\hat{H}_{C_7})x_{C_4} + \Delta\hat{H}_{C_7}, \end{aligned} \quad (b)$$

Because $\Delta\hat{H}_{C_4}$ and $\Delta\hat{H}_{C_7}$ are constant at any given temperature, $\Delta\hat{H}_{C_4} - \Delta\hat{H}_{C_7}$ is constant, and Eq. (b) is the equation of a straight line on a plot of $\Delta\hat{H}_{\text{mixture}}$ vs. x_{C_4} .

The 140°F isotherm is fixed by the points *J* and *K* in the liquid region, and the 360°F isotherm is fixed by points *L* and *M* in the vapor region:

	140°F, liquid $\Delta\hat{H}_L$ (Btu/mole)	360°F, vapor $\Delta\hat{H}_v$ (Btu/mole)
<i>J(C₄)</i>	3800	(C ₄) 17,550
<i>K(C₇)</i>	7100	(C ₇) 29,300

The 240°F isotherm up to the saturated-in the vapor region

EXAMPLE 5.5 A

One hundred pounds of water at 32°F are required to give a 10 percent excess of steam at 32°F.

Use the steam table I as your source of steam at 32°F for liquid NaOH pure caustic having

Solution:
The data required:
From
NaOH
conc. 73
10

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The tie element in total H₂O added to

100 lb
10 lb

Next we make an

To differentiate be

lb mole

$$\Delta \hat{H}_v = \Delta \hat{H}_{c,y_c} + \Delta \hat{H}_{c,y_c}$$

29,250	29,250
26,200	27,640
23,600	26,300
20,860	24,830
16,600	22,660
12,420	20,470
9,210	18,635
5,290	16,240
3,220	14,720
2,020	13,770
1,225	13,005
659	12,359
282	11,902
79	11,529
20	11,450
0	11,400

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eratu
the equilib-
experimental data were
e calculations for each
repare additional graphs
sia) with respect to the
temperature intervals,
rate.
liquid and vapor regions.
f mixing. Since:

(a)

$$-(1 - x_{C_v})\Delta \hat{H}_{C_v}$$

(b)

Mixture, $\Delta \hat{H}_{C_v} - \Delta \hat{H}_{C_l}$, is
of $\Delta \hat{H}_{mixture}$ vs. x_{C_v} .
liquid region, and the

360°F, vapor
 $\Delta \hat{H}_v$ (Btu/mole)

$$\begin{array}{l} 17,550 \\ 29,300 \end{array}$$

The 240°F isotherm (and others higher than 140°F) in the liquid region is real only up to the saturated-liquid line—the dotted portion is fictitious. Portions of isotherms in the vapor region lower than 360°F would also be fictitious, as, for example, at 240°F.

EXAMPLE 5.5 Application of the enthalpy-concentration chart

One hundred pounds of a 73 percent NaOH solution at 350°F are to be diluted to give a 10 percent solution at 80°F. How many pounds of water at 80°F and ice at 32°F are required if there is no external source of cooling available? See Fig. E5.5.

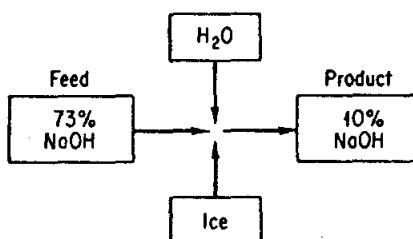


Fig. E5.5.

Use the steam tables and the NaOH-H₂O enthalpy-concentration chart in Appendix I as your source of data. (The reference conditions for the latter chart are $H = 0$ at 32°F for liquid water and $H = 0$ for an infinitely dilute solution of NaOH, with pure caustic having an enthalpy at 68°F of 455 Btu/lb above this datum.)

Solution:

The data required to make a material and an energy balance are as follows:

From Appendix I			From the steam tables	
NaOH	conc.	temp., °F	$\Delta \hat{H}$, Btu/lb	$\Delta \hat{H}$ of liquid H ₂ O
	73	350	468	= 48 Btu/lb
	10	80	42	$\Delta \hat{H}$ of ice = -143 Btu/lb (or minus the heat of fusion)

We can make a material balance first.

Basis: 100 lb 73 percent at 350°F

The tie element in the material balance is the NaOH, and using it we can find the total H₂O added (ice plus H₂O):

$$\frac{100 \text{ lb product}}{10 \text{ lb NaOH}} \left| \frac{73 \text{ lb NaOH}}{100 \text{ lb feed}} \right. = 730 \text{ lb product/100 lb feed}$$

$$\text{less } \frac{100 \text{ lb feed}}{\text{gives } \underline{\underline{630 \text{ lb H}_2\text{O added/100 lb feed}}}}$$

Next we make an energy (enthalpy) balance,

$$\Delta H_{\text{overall}} = 0 \quad \text{or} \quad \Delta H_{\text{in}} = \Delta H_{\text{out}}$$

To differentiate between the ice and the liquid water added, let us designate the ice

as x lb and then the H_2O becomes $(630 - x)$ lb:

in		out	
73% NaOH solution	H_2O	ice	10% NaOH solution
100 lb	468 Btu	$(630 - x)$ lb	730 lb
lb	lb	lb	lb
$46,800 + 30,240 - 191x = 30,660$			
$x = 243$ lb ice at $32^\circ F$			
liquid H_2O at $80^\circ F = 387$ lb			

EXAMPLE 5.6 Application of the enthalpy-concentration chart

Six hundred pounds of 10 percent NaOH at $200^\circ F$ are added to 400 lb of 50 percent NaOH at the boiling point. Calculate the following:

- (a) The final temperature of the solution.
- (b) The final concentration of the solution.
- (c) The pounds of water evaporated during the mixing process.

Solution:

Basis: 1000 lb final solution

Use the same NaOH- H_2O enthalpy-concentration chart as in the previous problem to obtain the enthalpy data. We can write the following material balance:

comp.	10% solution	+ 50% solution	= final solution	wt %
NaOH	60	200	260	26
H_2O	540	200	740	74
total	600	400	1000	100

Next, the energy (enthalpy) balance (in Btu) is

$$\begin{array}{ccc} 10\% \text{ solution} & 50\% \text{ solution} & \text{final solution} \\ 600(152) & + & 400(290) = \Delta H \\ 91,200 & + & 116,000 = 207,200 \end{array}$$

Note that the enthalpy of the 50 percent solution at its boiling point is taken from the bubble-point curve at $x = 0.50$. The enthalpy per pound is

$$\frac{207,200 \text{ Btu}}{1000 \text{ lb}} = 207 \text{ Btu/lb}$$

On the enthalpy-concentration chart for NaOH- H_2O , for a 26 percent NaOH solution with an enthalpy of 207 Btu/lb, you would find that only a two-phase mixture of (a) saturated H_2O vapor and (b) NaOH- H_2O solution at the boiling point could exist. To get the fraction H_2O vapor, we have to make an additional energy (enthalpy) balance. By interpolation, draw the tie line through the point $x = 0.26$, $H = 207$ (make it parallel to the 220° and $250^\circ F$ tie lines). The final temperature appears from Fig. E5.6 to be $232^\circ F$; the enthalpy of the liquid at the bubble point is about 175 Btu/lb. The enthalpy of the saturated water vapor (no NaOH is in the vapor phase) from the steam tables at $232^\circ F$ is 1158 Btu/lb. Let $x = 1$ lb H_2O evaporated.

5.2
One of the problems can be solved by this technique; charts at

Any problem with the B, and C

out	
10% NaOH solution	
.3 Btu	730 lb 42 Btu
.0	lb

360

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are added to 400 lb of 50 per-

ing process.

Let us in the previous problem
material balance:

solution	wt %
260	26
740	74
1000	100

solution

 $H = 200$ Boiling point is taken from
and is

26 percent NaOH solution
a two-phase mixture of (a)
boiling point could exist
tional energy (enthalpy)
point $x = 0.26$, $H = 207$
temperature appears from
bubble point is about 175
OH is in the vapor phase
 H_2O is saturated.

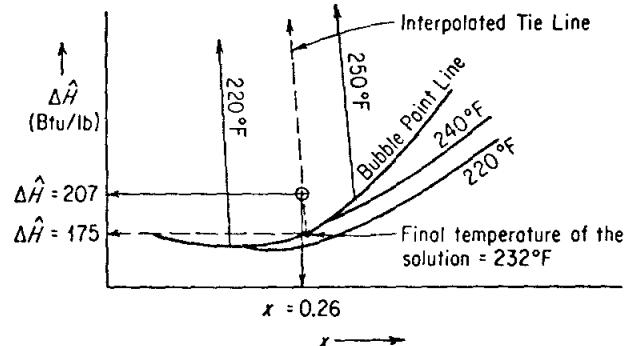


Fig. E5.6.

Basis: 1000 lb final solution

$$x(1158) + (1000 - x) 175 = 1000(207)$$

$$983x = 32,000$$

$$x = 32.6 \text{ lb } H_2O \text{ evaporated}$$

5.2-2 Graphical Solutions on an Enthalpy-Concentration Chart. One of the major advantages of an enthalpy-concentration chart is that the same problems we have just used as examples, and a wide variety of other problems, can be solved graphically directly on the chart. We shall just indicate the scope of this technique, which in its complete form is usually called the Ponchon-Savaritt method; you can refer to some of the references for enthalpy-concentration charts at the end of this chapter for additional details.

Any steady-state process with three streams and a net heat interchange Q with the surroundings can be represented by a simple diagram as in Fig. 5.4. A , B , and C are in pounds or moles. An overall material balance gives us

$$A + B = C \quad (5.3)$$

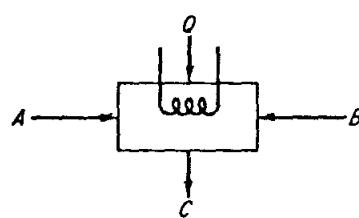


Fig. 5.4. A typical process with mass and heat interchange.

and a component material balance gives

$$Ax_A + Bx_B = Cx_C \quad (5.4)$$

An energy balance for a flow process (neglecting the work and the kinetic and potential energy effects) gives us⁴

$$Q = \Delta H$$

or

$$Q + AH_A + BH_B = CH_C \quad (5.5)$$

First we must choose some basis for carrying out the calculations, and then Q is dependent on this basis. Thus, if A is chosen as the basis, Q_A will be Q per unit amount of A , or

$$Q_A = \frac{Q}{A} \quad (5.6)$$

Similarly, if B is the basis,

$$Q_B = \frac{Q}{B} \quad (5.7)$$

Thus

$$Q = A Q_A = B Q_B = C Q_C \quad (5.8)$$

Let us choose A as the basis for working the problem, and then Eq. (5.5) becomes

$$AQ_A + AH_A + BH_B = CH_C \quad (5.9)$$

or

$$A(H_A + Q_A) + BH_B = CH_C \quad (5.10)$$

Similar equations can be written if B or C is chosen as the basis.

(a) *Adiabatic processes*. As a special case, consider the adiabatic process ($Q = 0$). Then (with A as the basis) the energy balance becomes

$$AH_A + BH_B = CH_C = (A + B)H_C = AH_C + BH_C$$

or

$$A(H_A - H_C) = B(H_C - H_B)$$

or

$$\frac{A}{B} = \frac{H_C - H_B}{H_A - H_C} \quad (5.11)$$

Combining material balances,

$$Ax_A + Bx_B = Cx_C = (A + B)x_C = Ax_C + Bx_C$$

or

$$A(x_A - x_C) = B(x_C - x_B)$$

or

$$\frac{A}{B} = \frac{x_C - x_B}{x_A - x_C} \quad (5.12)$$

⁴In what follows H is always the enthalpy relative to some reference value, and we suppress the caret (^) and the symbol Δ to make the notation more compact.

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the basis, Q_A will be Q per

(5.6)

(5.7)

(5.8)

and then Eq. (5.5) becomes

(5.9)

(5.10)

as the basis.
Under the adiabatic process
case becomes $AH_C + BH_C$

(5.11)

 $x_c + Bx_c$

(5.12)

some reference value, and we
more compact.

Obviously then,

$$\frac{A}{B} = \frac{x_c - x_B}{x_A - x_c} = \frac{H_C - H_B}{H_A - H_C} \quad (5.13)$$

Similarly, solving the energy and material balances for A and C instead of A and B , we can get

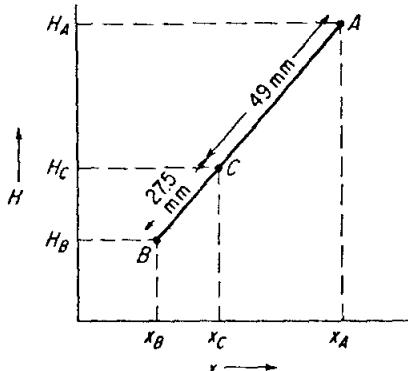
$$\frac{A}{C} = \frac{x_c - x_B}{x_A - x_B} = \frac{H_C - H_B}{H_A - H_C} \quad (5.14)$$

and in terms of B and C we could get a like relation. Rearranging the two right-hand members of Eq. (5.13), we can find that

$$\frac{H_C - H_B}{x_c - x_B} = \frac{H_A - H_C}{x_A - x_c} \quad (5.13a)$$

Also, from Eq. (5.14),

$$\frac{H_C - H_B}{x_c - x_B} = \frac{H_A - H_B}{x_A - x_B} \quad (5.14a)$$

On an enthalpy-concentration diagram (an H - x plot) the distances $H_C - H_B$, $H_A - H_B$, and $H_A - H_C$ are projections on the H axis of a curve, while the distances $x_c - x_B$, $x_A - x_B$, $x_A - x_C$ are the corresponding projections on the x axis (see Fig. 5.5). The form of Eqs. (5.13a) and (5.14a) is such that they tell us that they areFig. 5.5. Projections of the line BCA on the H and x axes.each equations of a straight line on an H - x plot and that these lines pass through the points A , B , and C which are represented on an H - x diagram by the coordinates $A(H_A, x_A)$, $B(H_B, x_B)$, and $C(H_C, x_C)$, respectively.Since Eqs. (5.13a) and (5.14a) both pass through point C , a common point, and have the same slope $(H_C - H_B)/(x_c - x_B)$, mathematical logic tells us they must be equations of the same line, i.e., the lines are actually a single line passing through B , C , and A , as shown in Fig. 5.5. The symmetry of this type of arrangement leads to use of the *lever arm* rule.

If $A + B = C$, then point C lies on a line between A and B , and nearer to the quantity present in the *largest* amount. If more B is added, C will lie nearer to B . When two streams are subtracted, the resulting stream will lie *outside* the region of a line between the two subtracted streams, and *nearer* the one present in the larger amount. Thus if $C - B = A$, and C is larger than A , then A will lie on a straight line through C and B nearer to C than B . Look at Fig. 5.5 and imagine that B is removed from C . A represents what is left after B is taken from C .

The *inverse lever arm principle* tells us how far to go along the line through A and B to find C if $A + B = C$, or how far to go along the line through C and B if $C - B = A$. In the case of $A + B = C$, we saw that the weight (or mole) ratio of A to B was given by Eq. (5.13). From the symmetry of Fig. 5.5, you can see that if the ratio of A to B is equal to the ratio of the projections of line segments BC and AC on the H or x axes, then the amount of $A + B$ should be proportional to the sum of the line segments $(x_c - x_b) + (x_a - x_c)$, or $(H_c - H_b) + (H_a - H_c)$. Furthermore, the amount of A should be proportional to the measured distance \overline{BC} and the amount of B proportional to the distance \overline{AC} . Also the ratio of A to B should be

$$\frac{A}{B} = \frac{\text{distance } \overline{BC}}{\text{distance } \overline{AC}} \quad (5.15)$$

This relation is the *inverse lever arm rule*. The distances \overline{BC} , \overline{AC} , and \overline{AB} can be measured with a ruler.

As an example of the application of Eq. (5.15), if A were 100 lb and the measured distances were

$$\overline{BC} = 27.5 \text{ mm}$$

$$\overline{AC} = 49.0 \text{ mm}$$

$$\overline{AB} = 76.5 \text{ mm}$$

then

$$\frac{A}{B} = \frac{100}{B} = \frac{\overline{BC}}{\overline{AC}} = \frac{27.5 \text{ mm}}{49.0 \text{ mm}} = 0.561$$

and

$$B = \frac{100}{0.561} = 178 \text{ lb}$$

The sum of $A + B = C$ is $100 + 178 = 278$ lb. Alternatively,

$$\frac{A}{C} = \frac{\overline{BC}}{\overline{AB}} = \frac{27.5 \text{ mm}}{76.5 \text{ mm}} = 0.360$$

$$C = \frac{A}{0.360} = \frac{100}{0.360} = 278 \text{ lb}$$

(b) *Nonadiabatic processes*. Let us now consider the circumstances under which Q is not equal to zero in Eq. (5.5). This time, for variety, let us take C as

a basis again,

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and B , and nearer to C will lie nearer to A . If C will lie outside the line through A and B the one present closer than A , then $A + B$. Look at Fig. 5.5 if left after B is taken

along the line through A and B line through C and the weight (or mole) of Fig. 5.5, you can projections of line of $A + B$ should be $(x_B + x_A)$, or should be proportional to the

$$(5.15)$$

\overline{AC} , \overline{B} can be

were 100 lb and the

a basis so that $Q = CQ_C$. Then we have two pairs of equations to work with again,

$$AH_A + BH_B = C(H_C - Q_C) \quad (5.16)$$

$$Ax_A + Bx_B = Cx_C \quad (5.4)$$

Briefly, Eqs. (5.16) and (5.4) tell us that on an H - x diagram points A , B , and C lie on a straight line if the coordinates of the points are $A(H_A, x_A)$, $B(H_B, x_B)$, and $C[(H_C - Q_C), x_C]$, respectively,⁵ as illustrated in Fig. 5.6. Since the coordi-

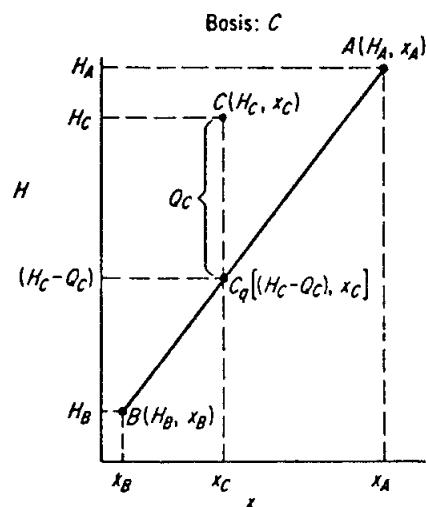


Fig. 5.6. Inverse lever arm rule applied to a nonadiabatic process.

⁵Proof of these relations is analogous to the previous development.

Material balances:

$$Ax_A + Bx_B = Cx_C = (A + B)x_C = Ax_C + Bx_C \quad (a)$$

$$A(x_A - x_C) = B(x_C - x_B) \quad (b)$$

Energy balance:

$$\begin{aligned} AH_A + BH_B &= C(H_C - Q_C) = (A + B)(H_C - Q_C) \\ &= A(H_C - Q_C) + B(H_C - Q_C) \end{aligned} \quad (c)$$

$$A[H_A - (H_C - Q_C)] = B(H_C - Q_C) - H_B \quad (d)$$

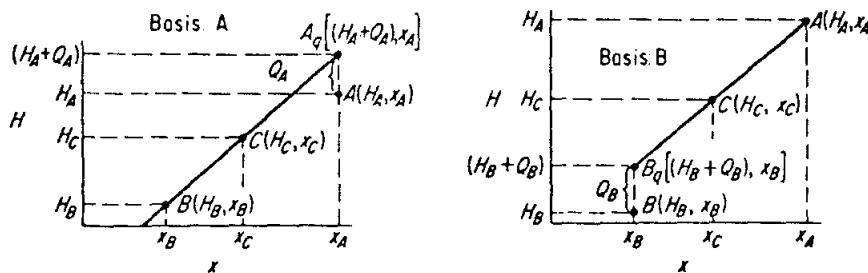
Thus

$$\frac{A}{B} = \frac{x_C - x_B}{x_A - x_C} = \frac{(H_C - Q_C) - H_B}{H_A - (H_C - Q_C)} \quad (e)$$

and, rearranging,

$$\frac{H_A - (H_C - Q_C)}{x_A - x_C} = \frac{(H_C - Q_C) - H_B}{x_C - x_B} \quad (f)$$

A similar equation can be obtained for the ratio A/C .



Figs. 5.7 and 5.8. Inverse lever arm principle for different bases.

nates of *C* are really fictitious coordinates and the enthalpy projection of *C* is $(H_c - Q_c)$, we shall designate the point through which the line passes $[(H_c - Q_c), x_c]$ by the more appropriate notation C_q . If *A* or *B* had been chosen as the basis, we would have set up diagrams such as Figs. 5.7 and 5.8.

A different series of figures could be drawn for other typical problems, as, for example, *C* being split up into two streams with heat being absorbed or evolved. Additional details related to more complex problems will be found in the references on enthalpy-concentration charts at the end of the chapter.

To obtain
as in Fig. I.

EXAMPLE 5.7 Graphical use of enthalpy-concentration charts

Do Example 5.5 again by graphical means.

Solution:

Plot the known points *A* and *C* on the *H*-*x* diagram for NaOH. The known points are as follows (with the given coordinates or data):

solution	<i>x</i>	<i>H</i> , Btu/lb	<i>T</i> , °F
Initial (A)	0.73	468	350
Final (C)	0.10		80
Added (D)	0.00		80
(E)	0.00		32 (ice)

What we shall do is remove solution *A* from the final solution *C* to obtain solution *B*, i.e., subtract *C* - *A* to get *B* as in Fig. E5.7a. This is the reverse of adding *A* to *B* to get *C*.

Draw a line through *A* and *C* until it intersects the *x* = 0 axis (for pure water). The measured (with a ruler) ratio of the lines *BC* to *AC* is the ratio of 73 percent NaOH solution to pure water.

Basis: 100 lb 73 percent NaOH solution at 350°F (*A*)

$$\frac{100 \text{ lb } (A)}{\text{lb } H_2O (B)} = \frac{\overline{BC}}{\overline{AC}} = \frac{2.85 \text{ units}}{17.95 \text{ units}} = 0.159$$

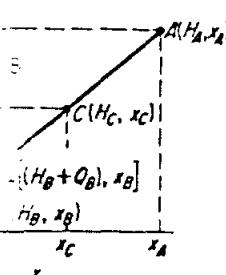
$$\frac{100}{0.159} = 1 \text{ lb } H_2O = 630 \text{ lb ice plus liquid water } (B)$$

EXAMPLE

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Solution

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Copy projection of C such the line passes or B had been chosen 5.7 and 5.8

typical problems, as, being absorbed or ems will be found in of t chapter.

NaOH. The known

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(ice)

to obtain solution use of adding A to B

axis (for pure water). of 73 percent NaOH

(A)

3)

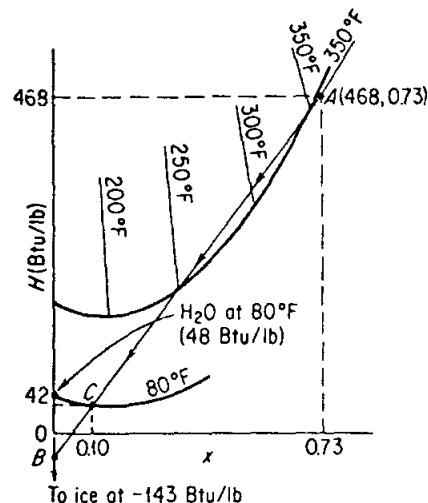


Fig. E5.7(a).

To obtain the proportions of ice and water, we want to subtract D from B to get E as in Fig. E5.7(b).

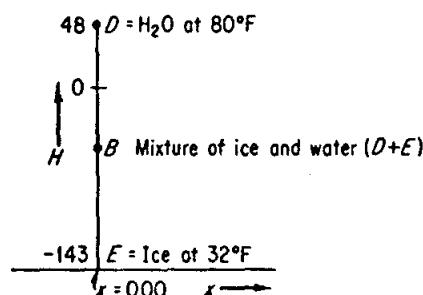


Fig. E5.7(b).

We measure the distances \overline{DE} and \overline{BE} . Then,

$$\frac{\text{lb H}_2\text{O (D)}}{\text{lb total (B)}} = \frac{\overline{BE}}{\overline{DE}} = \frac{3.65 \text{ units}}{5.95 \text{ units}} = 0.613$$

$$\text{lb H}_2\text{O (D)} = 630(0.613) = 386 \text{ lb}$$

$$\text{lb ice (E)} = 630 - 386 = 244 \text{ lb}$$

EXAMPLE 5.8 Graphical use of enthalpy-concentration charts

Do Example 5.6 again by graphical means.

Solution:

See Fig. E5.8.

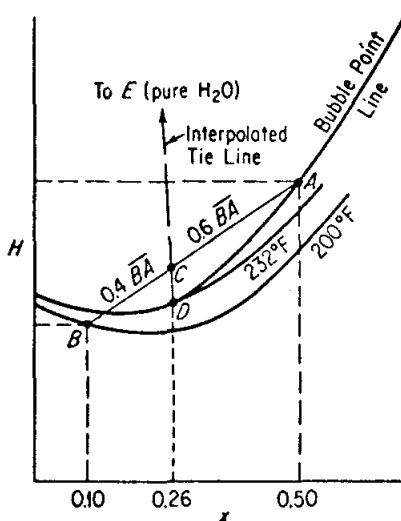


Fig. E5.8. Graphical use of enthalpy charts.

Basis: 1000 lb of total solution

Again plot the known data on an H - x chart. Point C , the sum of solutions A and B , is found graphically by noting by the inverse lever arm rule that

$$\frac{\text{distance } \overline{BC}}{\text{distance } \overline{BA}} = \frac{\text{lb } A}{\text{lb } A + B} = \frac{400}{1000} = 0.4$$

Now measure \overline{BA} on Fig. E5.8 and plot \overline{BC} as $0.4(\overline{BA})$. This fixes point C .

Since C is in the two-phase region, draw a tie line through C (parallel to the nearby tie lines) and measure the distances \overline{CD} and \overline{ED} . They will give the H_2O evaporated as follows:

$$\frac{\overline{CD}}{\overline{ED}} = \frac{\text{lb H}_2\text{O evaporated}}{1000 \text{ lb mixture}}$$

$$\text{lb H}_2\text{O evaporated} \approx 33 \text{ lb}$$

The final concentration of the solution and the temperature of the solution can be read off the H - x chart as before as

$$T = 232^\circ\text{F}, \quad x = 26\%$$

EXAMPLE 5.9 Graphical use of enthalpy-concentration charts with processes involving heat transfer

An acetic acid-water mixture is being concentrated as shown in Fig. E5.9(a). How much heat is added or removed?

Solution:

First we have to prepare an enthalpy concentration chart by plotting the data for the acetic acid-water system from Appendix I.

The coordinates of all the points, A , B , and C , are known. These points can be plotted on the H - x chart, and then some basis chosen, A , B , or C .

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is added and i

or

Connect point
(see Fig. E5.9)

$H = (H_A - Q_A)$
To reach A_Q ha
plus value ha

If point A_Q ha
and Q_A would
If we con

or

Basis: 1 lb mole A

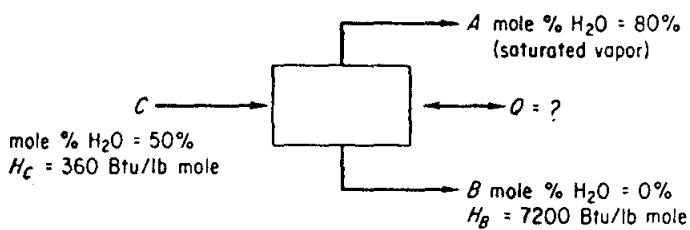


Fig. E5.9(a). Graphical use of enthalpy-concentration charts with processes involving heat transfer.

The governing material and energy balances in this case are (assuming that Q is added and is plus)

$$Cx_C = Ax_A + Bx_B$$

$$Q + CH_C = AH_A + BH_B = AQ_A + CH_C$$

or

$$A(H_A - Q_A) + BH_B = CH_C$$

Connect points B and C with a line, and extend the line toward the right-hand axis (see Fig. E5.9(b)). What we are looking for is the point A_Q located at the coordinates

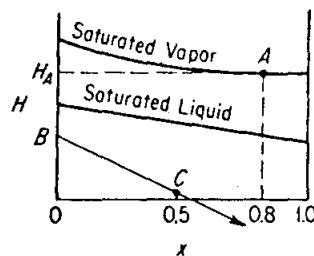


Fig. E5.9(b)

$H = (H_A - Q_A)$ and $x = 0.80$ on the extension of the line \overline{BC} through B and C. To reach A_Q from A, we must subtract Q_A ; by measuring on Fig. E5.9(c), we find a plus value has to be subtracted from H_A , or

$$Q_A = +24,000 \text{ Btu/lb mole A} \quad (\text{heat added})$$

If point A_Q had fallen above A, then heat would have been removed from the system and Q_A would have been negative.

If we convert our answer to the basis of 1 lb mole of C, we find that

$$\frac{A}{C} = \frac{\overline{BC}}{\overline{AB}} = \frac{0.5 - 0}{0.8 - 0} = 0.625$$

or

$$C = \frac{1}{0.625} = 1.60 \text{ lb mole}$$

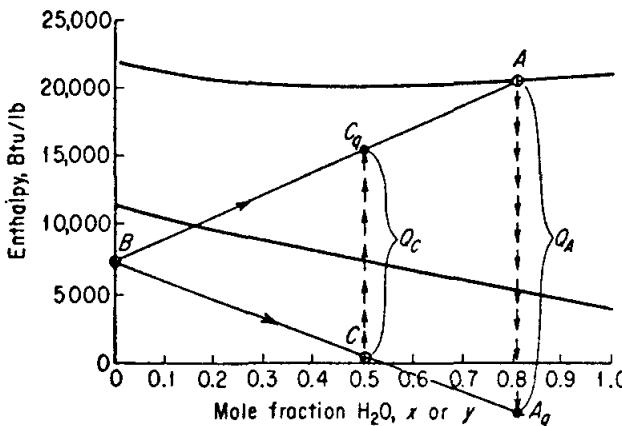


Fig. E5.9(c).

Basis: 1 lb mole C

$$Q_C = \frac{24,000 \text{ Btu}}{1.00 \text{ lb mole } A} \left| \frac{1.00 \text{ lb mole } A}{1.60 \text{ lb mole } C} \right| = 15,000 \text{ Btu/lb mole } C$$

As an alternative solution, we could have selected C as the basis to start with and used the equations

$$Cx_C = Ax_A + Bx_B$$

$$Q + CH_C = AH_A + BH_B = C(H_C + Q_C)$$

In this case, join A and B and find point C_Q at $x = 0.50$ on the line \overline{AB} . Measure $\overline{C_Q C}$; it is 14,900 Btu, which is close enough to the value of 15,000 Btu/lb mole C calculated above.

A similar calculation might have been made with B as the basis, by joining points A and C and extending to the $x = 0$ axis in order to get B_Q . Q_B would be measured from B_Q to B on the $x = 0$ axis.

5.3 Humidity charts and their use

In Chap. 3 we discussed humidity, condensation, and vaporization. In this section we are going to apply simultaneous material and energy balances to humidification, air conditioning, water cooling towers, and the like. Before proceeding further, you should review briefly the sections in Chap. 3 dealing with vapor pressure.

Recall that the *humidity* \mathfrak{H} is the pounds of water vapor per pound of bone-dry air (some texts use moles of water vapor per mole of dry air as the humidity) or, as indicated by Eq. (3.52),

$$\mathfrak{H} = \frac{18p_{H_2O}}{29(p_T - p_{H_2O})} = \frac{18n_{H_2O}}{29(n_T - n_{H_2O})} \quad (5.17)$$

You will also find it indispensable to learn the following special definitions and relations.

- (a) The *humid heat* is the heat capacity of an air-water vapor mixture expressed on the basis of 1 lb of bone-dry air. Thus the humid heat C_s is

$$C_s = C_{\text{air}} + (C_{pH_2O \text{ vapor}})(3C) \quad (5.18)$$

where the heat capacities are all per pound and not per mole. Assuming that the heat capacities of air and water vapor are constant under the narrow range of conditions found for air conditioning and humidification calculations, we can write

$$C_s = 0.240 + 0.45(3C) \quad (5.19)$$

where C_s is in Btu/(°F)(lb dry air).

- (b) The *humid volume* is the volume of 1 lb of dry air plus the water vapor in the air,

$$\begin{aligned} \hat{V} &= \frac{359 \text{ ft}^3}{1 \text{ lb mole}} \left| \frac{1 \text{ lb mole air}}{29 \text{ lb air}} \right| \frac{T_{\text{F}} + 460}{32 + 460} \\ &\quad + \frac{359 \text{ ft}^3}{1 \text{ lb mole}} \left| \frac{1 \text{ lb mole H}_2\text{O}}{18 \text{ lb H}_2\text{O}} \right| \frac{T_{\text{F}} + 460}{32 + 460} \left| \frac{3C \text{ lb H}_2\text{O}}{1 \text{ lb air}} \right| \\ &= (0.730T_{\text{F}} + 336) \left(\frac{1}{29} + \frac{3C}{18} \right) \end{aligned} \quad (5.20)$$

where \hat{V} is in ft^3/lb dry air.

- (c) The *dry-bulb temperature* (T_{DB}) is the ordinary temperature you always have been using for a gas in °F.
(d) The *wet-bulb temperature* (T_{WB}) you may guess, even though you may never have heard of this term before, has something to do with water (or other liquid, if we are concerned not with humidity but with saturation) evaporating from around an ordinary mercury thermometer bulb. Suppose that you put a wick, or porous cotton cloth, on the mercury bulb of a thermometer and wet the wick. Next you either (1) whirl the thermometer in the air as in Fig. 5.9 (this apparatus is called a sling psychrometer when the wet-bulb and dry-bulb thermometers are mounted together), or (2) set up a fan to blow rapidly on the bulb at 1000 ft^3/min or more. What happens to the temperature recorded by the wet-bulb thermometer?

As the water from the wick evaporates, the wick cools down and continues to cool until the rate of energy transferred to the wick by the air blowing on it equals the rate of loss of energy caused by the water evaporating from the wick. We say that the temperature at equilibrium with the wet wick is the wet-bulb temperature. (Of course, if water continues to evaporate, it eventually will all

disappear, and the wick temperature will rise.) The final temperature for the process described above will lie on the 100 percent relative humidity curve (saturated-air curve), while the so-called wet-bulb line showing how the wet-bulb temperature changes on approaching equilibrium is approximately a straight line and has a negative slope, as illustrated in Fig. 5.10.

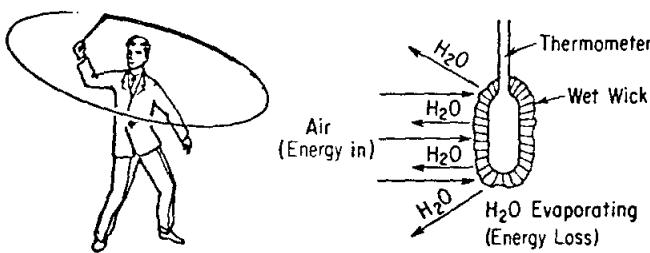


Fig. 5.9. The wet-bulb temperature obtained with a sling psychrometer.

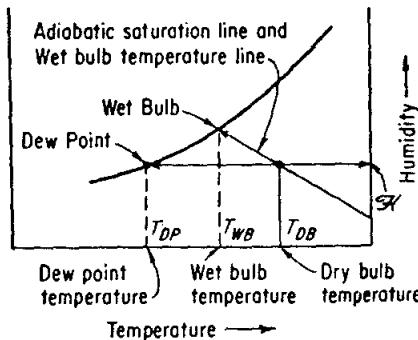


Fig. 5.10. General layout of the humidity chart showing the location of the wet-bulb and dry-bulb temperatures, the dew point and dew-point temperature, and the adiabatic saturation line and wet-bulb line.

Now that we have an idea of what the various features portrayed on the *humidity chart* (psychrometric chart) are, let us look at the chart itself, Fig. 5.11 (a) and 5.11 (b) (inside back cover). It is nothing more than a graphical means of presenting the relationships for and between the material and energy balances in water vapor-air mixtures. Its skeleton consists of a *humidity* (\mathcal{H}) — *temperature* (T_{DB}) set of coordinates together with the additional parameters (lines) of

- (a) Constant relative humidity (10–90 percent).
- (b) Constant moist volume (humid volume).

(c)

(d)

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- (c) Adiabatic cooling lines which are the same (for water vapor only⁶) as the wet-bulb or psychrometric lines.
- (d) The 100 percent relative humidity (identical to the 100 percent absolute humidity) curve or saturated-air curve.

With any two values known, you can pinpoint the air-moisture condition on the chart and determine all the other required values.

Off to the left of the 100 percent relative humidity line you will observe scales showing the enthalpy per pound of dry air of a saturated air-water vapor mixture. Enthalpy corrections for air less than saturated are shown on the chart itself. The enthalpy of the wet air, in Btu/lb dry air, is

$$\Delta\hat{H} = \Delta\hat{H}_{\text{air}} + \Delta\hat{H}_{\text{H}_2\text{O vapor}}(\mathcal{C}) \quad (5.21)$$

We should mention at this point that the reference conditions for the humidity chart are liquid water at 32°F and 1 atm (not the vapor pressure of H₂O) for water, and 0°F and 1 atm for air. The chart is suitable for use only at normal atmospheric conditions and must be modified⁷ if the pressure is significantly different than 1 atm. If you wanted to, you could calculate the enthalpy values shown on the chart directly from tables listing the enthalpies of air and water vapor by the methods described in Chap. 4, or you could, by making use of Eq. (5.21), compute the enthalpies with reasonable accuracy from the following equation for 1 lb of air:

$$\Delta\hat{H} = \underbrace{0.240(T_{\mathcal{F}} - 0)}_{C_p(\Delta T) \text{ for air}} + \underbrace{\mathcal{C}[1075]}_{\text{heat of vaporization of water at } 32} + \underbrace{0.45(T_{\mathcal{F}} - 32)}_{C_p(\Delta T) \text{ for water vapor}} \quad (5.22)$$

Consolidating terms:

$$\Delta\hat{H} = 0.240T_{\mathcal{F}} + \mathcal{C}(1061 + 0.45T_{\mathcal{F}}) \quad (5.23)$$

You will recall that the idea of the wet-bulb temperature is based on the equilibrium between the rates of energy transfer to the bulb and evaporation of water. Rates of processes are a topic that we have not discussed. The fundamental idea is that a large amount of air is brought into contact with a little bit of water and that presumably the evaporation of the water leaves the temperature and humidity of the air unchanged. Only the temperature of the water changes. The equation of the wet-bulb line is

$$h_c(T - T_{\text{WB}}) = k' \Delta\hat{H}_{\text{vap}}(\mathcal{C}_{\text{WB}} - \mathcal{C}) \quad (5.24)$$

⁶For a detailed discussion of the uniqueness of this coincidence, consult any of the references at the end of this chapter.

⁷See G. E. McElroy, *U.S. Bur. Mines Rept. Invest.*, No. 4165, Dec. 1947.

where h_c = heat transfer coefficient for convection to the bulb

k'_s = mass transfer coefficient

$\Delta\hat{H}_{vap}$ = latent heat of vaporization

\mathfrak{C} = humidity of moist air

T = temperature of moist air in °F

The equation for the wet-bulb lines is based on a number of assumptions, a discussion of which is beyond the scope of this book. However, we can form the ratio

$$\frac{(\mathfrak{C}_{WB} - \mathfrak{C})}{(T_{WB} - T)} = - \frac{h_c}{(k'_s)\Delta\hat{H}_{vap}} \quad (5.25)$$

For water only, it so happens that $h_c/k'_s \approx C_s$, i.e., the numerical value is about 0.25, which gives the wet-bulb lines the slope of

$$\frac{(\mathfrak{C}_{WB} - \mathfrak{C})}{(T_{WB} - T)} = - \frac{C_s}{\Delta\hat{H}_{vap}} \quad (5.26)$$

For other substances, the value of h_c/k'_s can be as much as twice that of water.

Another type of process of some importance occurs when an adiabatic cooling or humidification takes place between air and water that is recycled as in Fig. 5.12. In this process the air is both cooled and humidified (its water

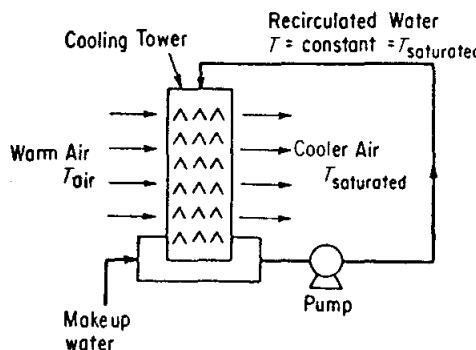


Fig. 5.12. Adiabatic humidification with recycle of water.

content rises) while a little bit of the recirculated water is evaporated. At equilibrium, in the steady state, the temperature of the air is the same as the temperature of the water, and the exit air is saturated at this temperature. By making an overall energy balance around the process ($Q = 0$), we can obtain the equation for the adiabatic cooling of the air. The equation, when plotted on the humidity chart, yields what is known as an adiabatic cooling line. Employing a version of Eq. (5.22) with the equilibrium temperature of the water, T_s , taken as a reference temperature rather than 0 or 32°F, we get, ignoring the small amount of

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makeup water or assuming that it enters at T_s ,

$$\frac{\text{enthalpy of air entering}}{0.240(T_{\text{air}} - T_s) + \mathcal{H}_{\text{air}}[\Delta\hat{H}_{\text{vap H}_2\text{O at }T_s} + 0.45(T_{\text{air}} - T_s)]} = \frac{\text{enthalpy of water vapor in air entering}}{0.240(T_s - T_s) + \mathcal{H}_s[\Delta\hat{H}_{\text{vap H}_2\text{O at }T_s} + 0.45(T_s - T_s)]} \quad (5.27)$$

This can be reduced to

$$T_{\text{air}} = \frac{\Delta\hat{H}_{\text{vap H}_2\text{O at }T_s}(\mathcal{H}_s - \mathcal{H}_{\text{air}})}{0.240 + 0.45\mathcal{H}_{\text{air}}} + T_s \quad (5.28)$$

which is the equation for adiabatic cooling.

Notice that this equation can be written as

$$\frac{(\mathcal{H}_s - \mathcal{H})}{(T_s - T_{\text{air}})} = -\frac{C_s}{\Delta\hat{H}_{\text{vap at }T_s}} \quad (5.29)$$

because $C_s = 0.240 + 0.45\mathcal{H}$ and $T_{\text{WB}} = T_s$. Thus the wet-bulb process equation, for water only, is essentially the same as the adiabatic cooling equation. For other materials these two equations have different slopes.

Only two of the quantities in Eq. (5.28) are variables, if T_s is known, because \mathcal{H}_s is the humidity of saturated air at T_s and $\Delta\hat{H}_{\text{vap H}_2\text{O at }T_s}$ is fixed by T_s . Thus, for any value of T_s , you can make a plot of Eqs. (5.25) and/or (5.29) on the humidity chart in the form of \mathcal{H} vs. T_{air} . These curves, which are essentially linear, will intersect the 100 percent relative humidity curve at \mathcal{H}_s and T_s , as described earlier.

The adiabatic cooling lines are lines of almost constant enthalpy for the entering air-water mixture, and you can use them as such without much error (1 or 2 percent). However, if you want to correct a saturated enthalpy value for the deviation which exists for a less-than-saturated air-water vapor mixture, you can employ the enthalpy deviation lines which appear on the chart and which can be used as illustrated in the examples below. Any process which is not a wet-bulb process or an adiabatic process with recirculated water can be treated by the usual material and energy balances, taking the basic data for the calculation from the humidity charts. If there is any increase or decrease in the moisture content of the air in a psychrometric process, the small enthalpy effect of the moisture added to the air or lost by the air may be included in the energy balance for the process to make it more exact as illustrated in Examples 5.11 and 5.13.

You can find further details regarding the construction of humidity charts in the references at the end of this chapter. Tables are also available listing all the thermodynamic properties (p , \hat{V} , \mathcal{H} , $\Delta\hat{H}$, and S) in great detail.* Although

*Microfilms of Psychrometric Tables, 1953, by Byron Engelbach are available from University Microfilms, Ann Arbor, Mich.

we shall be discussing humidity charts exclusively, charts can be prepared for mixtures of any two substances in the vapor phase, such as CCl_4 and air or acetone and nitrogen, by use of Eqs. (5.17)–(5.28) if all the values of the physical constants for water and air are replaced by those of the desired gas and vapor. The equations themselves can be used for humidity problems if charts are too inaccurate or are not available.

EXAMPLE 5.10 Properties of moist air from the humidity chart

List all the properties you can find on the humidity chart for moist air at a dry-bulb temperature of 90°F and a wet-bulb temperature of 70°F .

Solution:

A diagram will help explain the various properties obtained from the humidity chart. You can find the location of point *A* for 90°F DB (dry bulb) and 70°F WB (wet bulb) by following a vertical line at $T_{DB} = 90^\circ\text{F}$ until it crosses the wet-bulb line for 70°F . This wet-bulb line can be located by searching along the 100 percent humidity line until the saturation temperature of 70°F is reached, or, alternatively, by proceeding up a vertical line at 70°F until it intersects the 100 percent humidity line. From the wet-bulb temperature of 70°F , follow the adiabatic cooling line (which is the same as the wet-bulb temperature line on the humidity chart) to the right until it intersects the 90°F DB line. Now that point *A* has been fixed, you can read the other properties of the moist air from the chart. See Fig. E5.10.

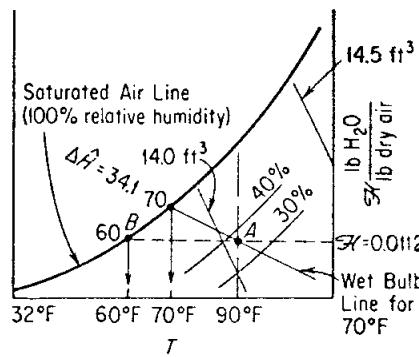


Fig. E5.10.

- (a) *Dew point.* When the air at *A* is cooled at constant pressure (and in effect at constant humidity), as described in Chap. 3, it eventually reaches a temperature at which the moisture begins to condense. This is represented by a horizontal line, a constant-humidity line, on the humidity chart, and the dew point is located at *B*, or about 60°F .
- (b) *Relative humidity.* By interpolating between the 40 percent RH and 30 percent RH lines with a ruler, you can find that point *A* is at about 37 percent RH.

can be prepared for Cl_2 and air or acetones of the physical dried gas and vapor. If charts are too

or moist air at a dry-

ed from the humidity bulb) and 70°F WB crosses the wet-bulb along the 100 percent line, or, alternatively, 100 percent humidity tie cooling line (which part go right until you reach the other

- (c) *Humidity (RH)*. You can read the humidity from the right-hand ordinate as $0.0112 \text{ lb H}_2\text{O/lb air}$.
- (d) *Humid volume*. By interpolation again between the 14.0 - and the $14.5 \text{ ft}^3/\text{lb}$ lines, you can find the humid volume to be $14.097 \text{ ft}^3/\text{lb dry air}$.
- (e) *Enthalpy*. The enthalpy value for saturated air with a wet-bulb temperature of 70°F is $\hat{\Delta H} = 34.1 \text{ Btu/lb dry air}$ (a more accurate value can be obtained from psychrometric tables if needed). The enthalpy deviation for less-than-saturated air is about $-0.2 \text{ Btu/lb dry air}$; consequently the actual enthalpy of air at 37 percent RH is $34.1 - 0.2 = 33.9 \text{ Btu/lb dry air}$.

EXAMPLE 5.11 Heating at constant humidity

Moist air at 50°F and 50 percent RH is heated in your furnace to 100°F . How much heat has to be added per cubic foot of initial moist air, and what is the final dew point of the air?

Solution:

As shown in Fig. E5.11, the process goes from point A to point B on a horizontal line of constant humidity. The initial conditions are fixed at $T_{DB} = 50^\circ\text{F}$ and 50 percent

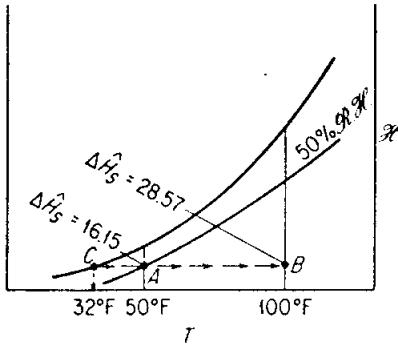


Fig. E5.11.

RH. Point B is fixed by the intersection of the horizontal line from A and the vertical line at 100°F . The dew point is unchanged in this process and is located at C at 32.5°F .

The enthalpy values are as follows (all in Btu/lb dry air):

point	ΔH_{satd}	δH	ΔH_{actual}
A	16.15	-0.02	16.13
B	28.57	-0.26	28.31

Also at A the volume of the moist air is $12.92 \text{ ft}^3/\text{lb dry air}$. Consequently the heat added is ($Q = \Delta H$) $28.31 - 16.13 = 12.18 \text{ Btu/lb dry air}$.

$$\frac{12.18 \text{ Btu}}{1 \text{ lb dry air}} \cdot \frac{1 \text{ lb dry air}}{12.92 \text{ ft}^3} = 0.942 \text{ Btu/ft}^3 \text{ initial moist air}$$

EXAMPLE 5.12 Cooling and humidification

One way of adding moisture to air is by passing it through water sprays or air washers. See Fig. E5.12(a). Normally, the water used is recirculated rather than

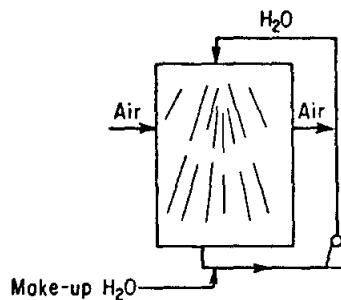


Fig. E5.12(a).

wasted. Then, in the steady state, the water is at the adiabatic saturation temperature which is the same as the wet-bulb temperature. The air passing through the washer is cooled, and if the contact time between the air and the water is long enough, the air will be at the wet-bulb temperature also. However, we shall assume that the washer is small enough so that the air does not reach the wet-bulb temperature; instead the following conditions prevail:

	T_{DB} , °F	T_{WB} , °F
Entering air	100	70
Exit air	80	

Find the moisture added per pound of dry air.

Solution:

The whole process is assumed to be *adiabatic*, and, as shown in Fig. E5.12(b), takes place between points *A* and *B* along the adiabatic cooling line. The wet-bulb temperature remains constant at 70°F.

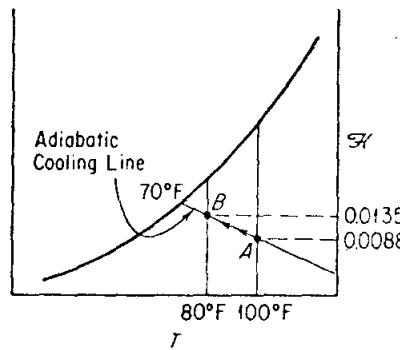


Fig. E5.12(b).

Difference:

EXAMPLE 5

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Solution:
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Look at Fig. E

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Humidity values are

$$\begin{array}{ll} \text{C}, \frac{\text{lb H}_2\text{O}}{\text{lb air}} \\ \text{B} & 0.0135 \\ \text{A} & \underline{0.0088} \end{array}$$

Difference:

$$0.0047 \frac{\text{lb H}_2\text{O}}{\text{lb dry air}} \quad \text{added.}$$

EXAMPLE 5.13 Cooling and dehumidification

A process which takes moisture out of the air by passing the air through water sprays sounds peculiar but is perfectly practical as long as the water temperature is below the dew point of the air. Equipment such as shown in Fig. E5.13(a) would do the

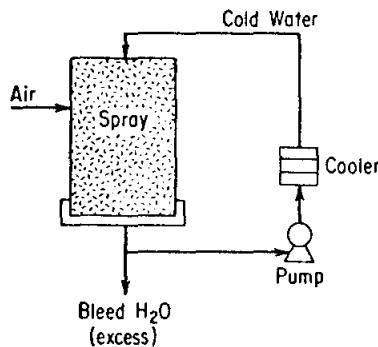


Fig. E5.13(a).

trick. If the entering air has a dew point of 70°F and is at 40 percent RH, how much heat has to be removed by the cooler, and how much water vapor is removed, if the exit air is at 56°F with a dew point of 54°F ?

Solution:

From Fig. 5.11(b) the initial and final values of the enthalpies and humidities are

	A	B
$\text{RH} \left(\frac{\text{grains H}_2\text{O}}{\text{lb dry air}} \right)$	111	62
$\Delta H \left(\frac{\text{Btu}}{\text{lb dry air}} \right)$	$41.3 - 0.2 = 41.1$	$23.0 - 0 = 23.0$

Look at Fig. E5.13(b) to locate A and B. The grains of H_2O removed are

$$111 - 62 = 49 \text{ grains/lb dry air}$$

The cooling duty is approximately

$$41.1 - 23.0 = 18.1 \text{ Btu/lb dry air}$$

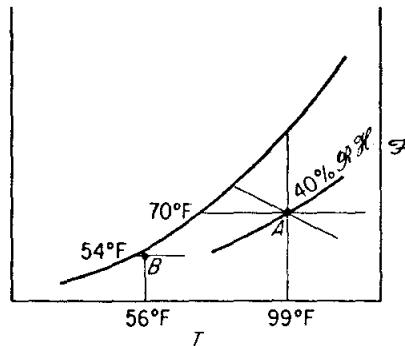


Fig. E5.13(b).

In the upper left of the humidity chart is a little insert which gives the value of the small correction factor for the water condensed from the air which leaves the system. Assuming that the water leaves at the dew point of 54°F, read for 49 grains a correction of -0.15 Btu/lb dry air. You could calculate the same value by taking the enthalpy of liquid water from the steam tables and saying,

$$\frac{22 \text{ Btu}}{\text{lb H}_2\text{O}} \mid \frac{1 \text{ lb H}_2\text{O}}{7000 \text{ grains}} \mid \frac{49 \text{ grains rejected}}{1 \text{ lb dry air}} = 0.154 \text{ Btu/lb dry air}$$

The energy (enthalpy) balance will then give us the cooling load:

$$\begin{array}{r} \text{air in} \quad \text{air out} \quad \text{H}_2\text{O out} \\ 41.1 - 23.0 = 0.15 = 17.9 \text{ Btu/lb dry air} \end{array}$$

EXAMPLE 5.14 Combined material and energy balances for a cooling tower

You have been requested to redesign a water-cooling tower which has a blower with a capacity of $8.30 \times 10^6 \text{ ft}^3/\text{hr}$ of moist air (at 80°F and a wet-bulb temperature of 65°F). The exit air leaves at 95°F and 90°F wet bulb. How much water can be cooled in pounds per hour if the water to be cooled is not recycled, enters the tower at 120°F, and leaves the tower at 90°F?

Solution:

Enthalpy, humidity, and humid volume data taken from the humidity chart are as follows (see Fig. E5.14)

	A	B
$\mathcal{H}\left(\frac{\text{lb H}_2\text{O}}{\text{lb dry air}}\right)$	0.0098	0.0297
$\mathcal{H}\left(\frac{\text{grains H}_2\text{O}}{\text{lb dry air}}\right)$	69	208
$\Delta\hat{H}\left(\frac{\text{Btu}}{\text{lb dry air}}\right)$	$30.05 - 0.12 = 29.93$	$55.93 - 0.10 = 55.83$
$\hat{V}\left(\frac{\text{ft}^3}{\text{lb dry air}}\right)$	13.82	14.65

The cooling process.

The cooling process at 1 atm

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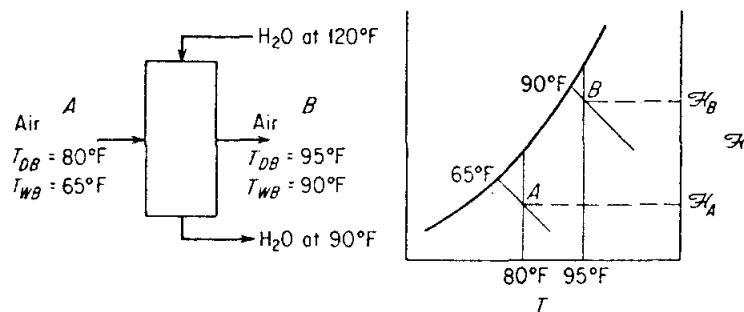


Fig. ES.14.

gives the value of the which leaves the system. **Ex 49** grains a correction by taking the enthalpy

lb dry air

ed:

a cooling tower

ver which has a blower \pm wet-bulb temperature \pm how much water can be cycled, enters the tower

the humidity chart

B

0.0297

208

$0.10 = 55.83$

14.65

The cooling water exit temperature can be obtained from an energy balance around the process.

Basis: $8.30 \times 10^6 \text{ ft}^3/\text{hr}$ moist air

$$\frac{8.30 \times 10^6 \text{ ft}^3}{13.82 \text{ ft}^3} \mid \frac{\text{lb dry air}}{\text{lb dry air}} = 6.00 \times 10^5 \text{ lb dry air/hr}$$

The enthalpy of the entering water stream is (reference temperature is 32°F and 1 atm)

$$\Delta \hat{H} = C_{p_{H_2O}} \Delta T = 1(120 - 32) = 88 \text{ Btu/lb H}_2\text{O}$$

while that of the exit stream is 58 Btu/lb H₂O. [The value from the steam tables at 120°F for liquid water of 87.92 Btu/lb H₂O is slightly different since it represents water at its vapor pressure (1.69 psia) based on reference conditions of 32°F and liquid water at its vapor pressure.] Any other datum could be used instead of 32°F for the liquid water. For example, if you chose 90°F, one water stream would not have to be taken into account because its enthalpy would be zero.

The loss of water to the air is

$$0.0297 - 0.0098 = 0.0199 \text{ lb H}_2\text{O/lb dry air}$$

(a) Material balance for water stream:

Let $W = \text{lb H}_2\text{O entering the tower in the water stream per lb dry air}$

Then $(W - 0.0199) = \text{lb H}_2\text{O leaving tower in the water stream per lb dry air}$

(b) Energy balance (enthalpy balance) around the entire process:

air and water in air entering

$$\frac{29.93 \text{ Btu}}{\text{lb dry air}} \mid \frac{6.00 \times 10^5 \text{ lb dry air}}{\text{lb dry air}}$$

water stream entering

$$+ \frac{88 \text{ Btu}}{\text{lb H}_2\text{O}} \mid \frac{W \text{ lb H}_2\text{O}}{\text{lb dry air}} \mid \frac{6.00 \times 10^5 \text{ lb dry air}}{\text{lb dry air}}$$

air and water in air leaving

$$= \frac{55.83 \text{ Btu}}{\text{lb dry air}} \mid \frac{6.00 \times 10^5 \text{ lb dry air}}{\text{lb dry air}}$$

$$\begin{array}{c}
 \text{water stream leaving} \\
 + \frac{58 \text{ Btu}}{\text{lb H}_2\text{O}} | \frac{(W - 0.0199) \text{ lb H}_2\text{O}}{\text{lb dry air}} | \frac{6.00 \times 10^5 \text{ lb dry air}}{} \\
 29.93 + 88W = 55.83 + 58(W - 0.0199) \\
 W = 0.825 \text{ lb H}_2\text{O/lb dry air} \\
 (W - 0.0199) = 0.805 \text{ lb H}_2\text{O/lb dry air}
 \end{array}$$

The total water leaving the tower is

$$\frac{0.805 \text{ lb H}_2\text{O}}{\text{lb dry air}} | \frac{6.00 \times 10^5 \text{ lb dry air}}{\text{hr}} = 4.83 \times 10^5 \text{ lb/hr}$$

5.4 Complex problems

In this book we have treated only small segments of material and energy balance problems. Put a large number of these segments together and you will have a real industrial process. We do not have the space to describe the details of any specific process, but for such information you can consult the references at the end of this chapter. It is always wise to read about a process and gain as much information as you can about the stoichiometry and energy relations involved before undertaking to make any calculations. Do not be unnerved by the complexity of a large-scale detailed plant. With the techniques you have accumulated while studying this text you will find that you will be able to break down the overall scheme into smaller sections involving a manageable number of streams that can be handled in the same way you have handled the material and energy balances in this text. Perhaps you can find a tie element (or make one up) that will permit you to work from one unit of the process to the next. Example 5.15 briefly outlines, without much descriptive explanation, how you should apply your knowledge of material and energy balances to a not-too-complex alcohol plant.

Problems in which simultaneous material and energy balances appear can often be solved using special-purpose digital computer programs intended for the design and operation of chemical plants. Such computer programs include techniques of solving the material and energy balances for an almost endless combination of pumps, compressors, heat exchangers, distillation columns, reactors, and so forth. To be able to solve the balances for even one of these pieces of equipment, you need to have a bank of data for the stream properties. Most programs furnish the necessary physical data and make provision for you to provide any missing information. Assuming that subprograms have been prepared and are available that simulate the behavior of individual pieces of process equipment and produce numerical outputs for varying inputs and process parameters, as the user your main task is to designate the interconnections between the units and the choice of the subprograms to represent each

5 lb dry air

:99)

air

air

 $\times 10^5 \text{ lb/hr}$

material and energy balances together and you will have to describe the details. You can consult the references, but if you lack access and gain as many energy relations as possible, you will be able to break up the techniques you have learned to handle the material and element (or make one up) to the next. Example 2 illustrates how you should go about it.

Energy balances appear can programs intended for computer programs include codes for an almost endless variety of distillation columns, codes for even one of these or for the stream properties to make provision for you subprograms have been written of individual pieces of code for varying inputs and designate the interconnection programs to represent each

TABLE 5.1

Name	Where Developed	Reference
APACHE	General Electric Co., Bethesda, Md.	
CHEOPS	Shell Development Co., Emeryville, Calif.	R. R. Hughes et al., <i>6th World Petrol. Conf. Proc., Frankfurt, Sec. VII</i> , paper 17, p. 93 (1963)
CHESS	University of Houston	R. L. Motard, H. M. Lee, and R. W. Barkley, <i>CHESS—Chemical Engineering Simulation System</i> , Tech Publishing Co., Houston, 1968
CHIPS	Service Bureau Corp., I.B.M.	
FLOWTRAN	Monsanto Co., St. Louis, Mo.	R. L. Rorschack and R. E. Harris, "Process Simulation Made by Computer," <i>Oil and Gas J.</i> , p. 62 (Aug. 17, 1970)
GEMCS	McMaster University, Hamilton, Ont., Canada	A. J. Johnson, <i>GEMCS Manual</i> , Dept. Chem. Eng., McMaster Univ., Hamilton, Ontario, 1969
NETWORK 67	I.C.I., Ltd., Runcorn, England	S. M. Andrew, "Computer Flowsheeting Using Network 67; an Example," <i>Trans. Inst. Chem. Eng.</i> , v. 46, p. T123 (1967)
PACER	Purdue University and Dartmouth College	C. M. Crowe et al., <i>Chemical Plant Simulation</i> , Prentice-Hall, Englewood Cliffs, N.J., 1971
REMUS	University of Pennsylvania	P. T. Shannon et al., "Computer Simulation of a Sulfuric Acid Plant," <i>Chem. Eng. Progress</i> , v. 62, No. 6, p. 49 (1966)
SWAPSCO	Stone and Webster, Boston, Mass.	P. E. Ham, <i>Users' Manual for Remus (Routine for Executive Multi-Unit Simulation)</i> , School of Chem. Eng., Univ. of Pennsylvania, Philadelphia, 1969
UOS	Bonner and Moore Assoc., Houston, Texas	T. Utsumi, "Computer Package Aids Systems Engineering," <i>Oil and Gas J.</i> , p. 100 (June 8, 1970)

unit. In some instances you can also select the subroutine to be used to solve the large sets of nonlinear equations that must be solved simultaneously. Table 5.1 lists some of the programs available that are user-oriented. Evans et al.⁹ give a very lucid state of the art survey of heat and material balance programs, and additional references can be found at the end of this chapter.

EXAMPLE 5.15 A more complex problem

The Blue Ribbon Sour Mash Company plans to make commercial alcohol by a process shown in Fig. E5.15(a). Grain mash is fed through a heat exchanger where it is heated to 170°F. The alcohol is removed as 60 percent (weight) alcohol from the

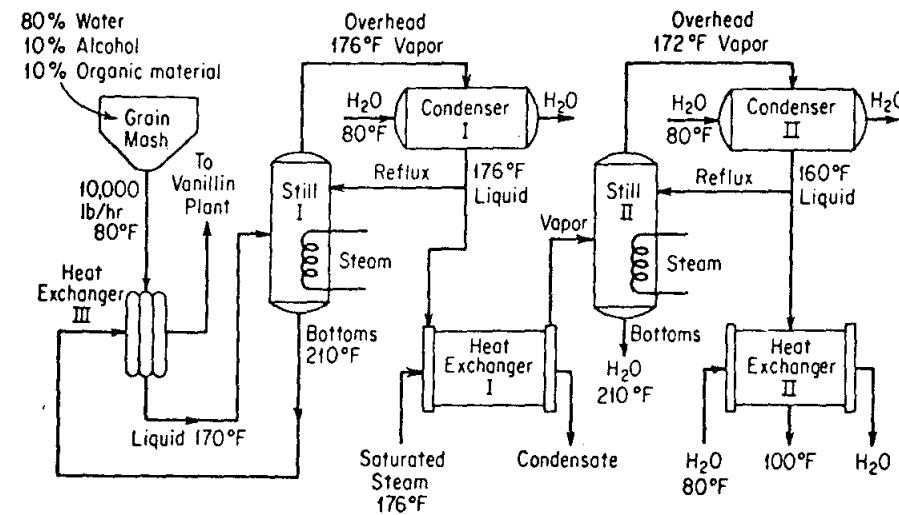


Fig. E5.15(a).

⁹L. B. Evans et al., *Chem. Eng. Progress*, v. 64, no. 4, p. 39 1968).

first fraction further fract column. Botl of the colum and physical venience:

st1

Feed
60%
Bott
95%
Bott

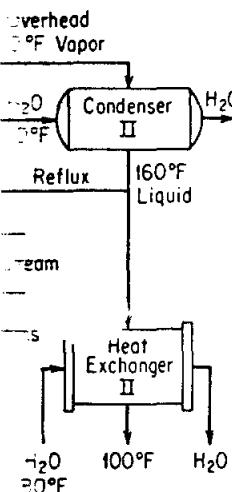
Make a c

- (a) Deter
 - (1) O
 - (2) R
 - (3) B
 - (4) O
 - (5) R
 - (6) B
 - (b) Calcu
 - (c) Deter
 - (d) Calcu
- II in g
130°F

Solution:
Let us cal

to be used to solve the simultaneously. Table 5.1 and Evans et al.⁹ give convenience programs, and later.

commercial alcohol by a heat exchanger where it (right) alcohol from the



first fractionating column; the bottoms contain no alcohol. The 60 percent alcohol is further fractionated to 95 percent alcohol and essentially pure water in the second column. Both stills operate at a 3-to-1 reflux ratio and heat is supplied to the bottom of the columns by steam. Condenser water is obtainable at 80°F. The operating data and physical properties of the streams have been accumulated and are listed for convenience:

operating information and data

stream	state	b.p. (°F)	heat of vaporization	
			$C_p, \text{Btu}/(\text{lb})(\text{°F})$	vapor (Btu/lb)
Feed	Liquid	170	0.96	950
60% alcohol	Liquid or vapor	176	0.85	675
Bottoms (I)	Liquid	212	1.00	970
95% alcohol	Liquid or vapor	172	0.72	650
Bottoms (II)	Liquid	212	1.00	970

Make a complete material balance on the process and

- Determine the weight of the following streams per hour:
 - Overhead product, column (I).
 - Reflux, column (I).
 - Bottoms, column (I).
 - Overhead product, column (II).
 - Reflux, column (II).
 - Bottoms, column (II).
- Calculate the temperature of the bottoms leaving heat exchanger III.
- Determine the total heat input to the system in Btu/hr.
- Calculate the water requirements for each condenser and heat exchanger II in gal/hr if the maximum exit temperature of water from this equipment is 130°F.

Solution:

Let us call the alcohol A for short and the organic matter M.

STEP 1: MATERIAL BALANCES

Basis: 10,000 lb/hr mash

(a) Material balance around column I and condenser:

	<i>In</i>
Feed	$\begin{cases} A & (0.10)(10,000) = 1,000 \text{ lb} \\ H_2O & (0.80)(10,000) = 8,000 \\ M & (0.10)(10,000) = 1,000 \end{cases}$
	$\underline{10,000 \text{ lb}}$

	<i>Out</i>
Product	$\begin{cases} A & = 1,000 \text{ lb} \\ H_2O & \left(\frac{1000}{0.60}\right) - 1000 = 667 \end{cases}$
Bottoms	$\begin{cases} H_2O & (8000 - 667) = 7,333 \\ M & = 1,000 \end{cases}$
	$\underline{10,000 \text{ lb}}$

(b) Material balance around column I only:

Feed	$\begin{cases} A & = 1,000 \text{ lb} \\ H_2O & = 8,000 \\ M & = 1,000 \end{cases}$
Reflux	$\begin{cases} A & (3)(1000) = 3,000 \\ H_2O & (3)(667) = 2,000 \end{cases}$
	$\underline{15,000 \text{ lb}}$

Overhead vapor	$\begin{cases} A & 4(1000) = 4,000 \text{ lb} \\ H_2O & 4(667) = 2,667 \end{cases}$
Bottoms	$\begin{cases} H_2O & = 7,333 \\ M & = 1,000 \end{cases}$

(c) Material balance around column II and condenser:

Feed	$\begin{cases} A & = 1,000 \text{ lb} \\ H_2O & = 667 \end{cases}$
	$\underline{1,667 \text{ lb}}$

(d) Overhead product	$\begin{cases} A & = 1,000 \text{ lb} \\ H_2O & \left(\frac{1000}{0.95} - 1000\right) = 50 \end{cases}$
Bottoms	$\begin{cases} H_2O & (667 - 50) = 617 \end{cases}$

(d) Material balance on column II cutting reflux and overhead vapor:

	<i>In</i>	<i>Out</i>
	$\begin{cases} A & = 1,000 \text{ lb} \\ H_2O & = 667 \end{cases}$	$\begin{cases} A & = 1,000 \text{ lb} \\ H_2O & = 617 \end{cases}$

$$\text{Feed } \left\{ \begin{array}{l} A \\ H_2O \end{array} \right. = \frac{1,000 \text{ lb}}{667} \quad \text{(d) Overhead product} \left\{ \begin{array}{l} A \\ H_2O \end{array} \right. \frac{\left(\frac{1000}{0.95} - 1000 \right)}{(667 - 50)} = \frac{50}{617} \\ \underline{1,667 \text{ lb}} \quad \underline{1,667 \text{ lb}}$$

(d) Material balance on column II cutting reflux and overhead vapor:

	<i>In</i>		<i>Out</i>
Feed	$\left\{ \begin{array}{l} A \\ H_2O \end{array} \right.$	= 1,000 lb	Vapor $\left\{ \begin{array}{l} A \\ H_2O \end{array} \right.$
		= 667	(4)(1000) = 4,000 lb
(e)	$\left\{ \begin{array}{l} A \\ H_2O \end{array} \right.$	= 3(1000)	Bottoms $\left\{ \begin{array}{l} A \\ H_2O \end{array} \right.$
Reflux	$\left\{ \begin{array}{l} A \\ H_2O \end{array} \right.$	= 3(50)	(4)(50) = 200
		= 150	Bottoms $\left\{ \begin{array}{l} A \\ H_2O \end{array} \right.$
		$\underline{4,817 \text{ lb}}$	(667 - 50) = 617
			$\underline{4,817 \text{ lb}}$

STEP 2: ENERGY BALANCES

(a) Energy balance on heat exchanger III [Fig. E5.15(b)]:

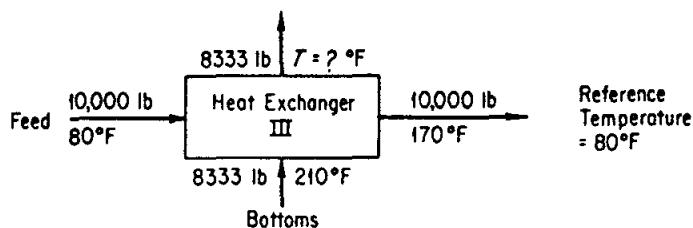


Fig. E5.15(b).

$$\begin{array}{lll} \text{In} & & \text{Out} \\ \text{Feed} \quad (10,000)(0.96)(80 - 80) = & 0 \text{ Btu} & \text{Feed} \quad (10,000)(0.96)(170 - 80) \\ \text{Bottoms} \quad (8333)(1.0)(210 - 80) = 1,084,000 \text{ Btu} & & = (8333)(1.0)(T - 80) \\ & 1,084,000 = 8333T - 666,000 + 864,000 \\ & 886,000 = 8333T \\ & T = 106.5^{\circ}\text{F} \xrightarrow{\text{⑥}} \end{array}$$

(b) Energy balance around heat exchanger III inlet, and overhead vapor and reflux line from I:

Reference temperature = 176°F

	<i>In</i>		<i>Out</i>
Feed	$(10,000)(0.96)(80 - 176) =$	-921,000	Bottoms to vanillin plant $(8333)(1.0)(106.5 - 176) = -579,000$
Reflux	$(5000)(0.85)(176 - 176) =$	0	Vapor $(6667)(0.85)(176 - 176) + (6667)(675) = 4,500,000$
Steam		ΔH_{S_1}	
		$(\Delta H_{S_1} - 921,000)$	<u>3,921,000</u>
		$\Delta H_{S_1} - 921,000 = 3,921,000$	
		$\Delta H_{S_1} = 4,842,000 \text{ Btu/hr}$	

(c) Energy balance around heat exchanger I outlet and overhead vapor and reflux from II:

Reference temperature = 172°F

	<i>In</i>		<i>Out</i>
Feed to II	$(1667)(0.85)(176 - 172) =$	5,650	Vapor $(4200)(0.72)(172 - 172) + (4200)(650) = 2,725,000$
	$\Delta H_{\text{vaporization-steam@176°F}}$		
	$+(1667)(675) =$	1,125,000	
Reflux	$(3150)(0.72)(160 - 172) =$	-27,200	Bottoms $(617)(1.0)(210 - 172) = 23,400$
Steam		ΔH_{S_2}	
		$(\Delta H_{S_2} + 1,103,450)$	<u>2,748,400</u>
		$\Delta H_{S_2} + 1,103,450 = 2,748,400$	
		$\Delta H_{S_2} = 1,645,000 \text{ Btu/hr}$	

(d) Total energy input into system:

$$\Delta H_{S_1} + \Delta H_{S_2} + \text{steam heater} = 4,842,000 + 1,645,000 + 1,125,000 = 7,612,000 \text{ Btu/hr} \leftarrow \textcircled{C}$$

(e) Energy balance on condenser I:

$W = \text{lb H}_2\text{O/hr}$; Reference temperature = 176°F

	<i>In</i>		<i>Out</i>
Vapor	$(6667)(0.85)(176 - 176) + (6667)(675) =$	4,500,000	Condensate $(6667)(0.85)(176 - 176) = 0$
Cooling H ₂ O (W)	$(W)(1.0)(80 - 176)$	$96W$	Cooling H ₂ O (W)

Boilers	$(3)(0.85)(160 - 176)$	21,600	Bottoms	$(6)(1.0)(210 - 172)$	23,100
Steam		ΔH_{S_1}			
	$(\Delta H_{S_1} + 1,103,450)$				<u>2,748,400</u>

$\Delta H_{S_1} + 1,103,450 = +8,400$
 $\Delta H_{S_1} = 1,645,000 \text{ Btu/hr}$

(d) Total energy input into system:

$$\Delta H_{S_1} + \Delta H_{S_2} + \text{steam heater} = 4,842,000 + 1,645,000 + 1,125,000 = 7,612,000 \text{ Btu/hr} \leftarrow \textcircled{c}$$

(e) Energy balance on condenser I:

	<i>In</i>	<i>Out</i>
Vapor	$(6667)(0.85)(176 - 176) + (6667)(675) =$	$(6667)(0.85)(176 - 176) =$
Cooling H ₂ O	$(W)(1.0)(80 - 176)$	$(W)(1.0)(130 - 176) =$
	$= \frac{4,500,000}{-96W}$	$= \frac{0}{-46W}$
	$\frac{(-96W + 4,500,000)}{50W} = 90,000 \text{ lb H}_2\text{O/hr}$	
	$50W = 4,500,000 \quad \text{or} \quad W = \frac{4,500,000}{50}$	
	$\frac{90,000 \text{ lb H}_2\text{O/hr}}{8.345 \text{ lb/gal}} = 10,800 \text{ gal H}_2\text{O/hr} \leftarrow \textcircled{d}_1$	

(f) Energy balance on condenser II:

	<i>In</i>	<i>Out</i>
Vapor	$(4200)(0.72)(172 - 172) + (4200)(650) =$	$(4200)(0.72)(160 - 172) =$
Cooling H ₂ O	$(W)(1.0)(80 - 172)$	$(W)(1.0)(172 - 130) =$
	$= \frac{2,725,000}{-92W}$	$= \frac{-36,000}{-42W}$
	$\frac{(-92W + 2,725,000)}{50W} = 55,200 \text{ lb H}_2\text{O/hr}$	$\frac{(-42W - 36,000)}{50W} =$
	$50W = 2,761,000 \quad \text{or} \quad W = \frac{2,761,000}{50}$	
	$\frac{55,200 \text{ lb H}_2\text{O}}{8.345 \text{ lb/gal}} = 6620 \text{ gal H}_2\text{O/hr} \leftarrow \textcircled{d}_2$	

(g) Energy balance on heat exchanger II:

	<i>In</i>	<i>Out</i>
Condensate	$(1050)(0.72)(160 - 80)$	$(1050)(0.72)(100 - 80) =$
Cooling H ₂ O	$(W)(1.0)(80 - 80)$	$(W)(1.0)(130 - 80) =$
	$= 60,500$	$= 15,120$
	$= 0$	$= \frac{50W}{50W + 15,120}$
	$60,500$	
	$50W + 15,120 = 60,500$	
	$W = 907 \text{ lb H}_2\text{O/hr} \quad \text{or} \quad 109 \text{ gal H}_2\text{O/hr} \leftarrow \textcircled{d}_3$	

WHAT YOU SHOULD HAVE LEARNED FROM THIS CHAPTER

1. By the end of this chapter you should have perfected your techniques in using material and energy balances separately or in combination to such an extent that you should be able to analyze any type of process and write and solve the appropriate balances.
2. You should know how to use humidity charts and enthalpy-concentration charts as aids in the solution of problems.

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CHAPTER

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5.1. Lime
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Unsteady-State Material and Energy Balances

6

In previous chapters all the material and all the energy balances you have encountered, except for the batch energy balances, were *steady-state* balances, i.e., balances for processes in which the accumulation term was zero. Now it is time for us to focus our attention briefly on *unsteady-state* processes. These are processes in which quantities or operating conditions *change with time*. Sometimes you will hear the word *transient state* applied to such processes. The unsteady state is somewhat more complicated than the steady state and in general problems involving unsteady-state processes are more difficult to handle mathematically than those involving steady-state processes. However, a wide variety of important industrial problems falls into this category, such as the startup of equipment, batch heating or reactions, the change from one set of operating conditions to another, and the perturbations that develop as process conditions fluctuate. In this chapter we consider only one category of unsteady-state processes, but it is the one that is the most widely used.

The basic expression in words, Eqs. (2.1) or (4.22), for either the material or the energy balance should by now be well known to you and is repeated as Eq. (6.1) below. However, you should also realize that this equation can be applied at various levels, or strata, of description. In other words, the engineer can portray the operation of a real process by writing balances on a number of physical scales. A typical illustration of this concept might be in meteorology, where the following different degrees of detail can be used on a descending scale

of magnitude in the real world:

- Global weather pattern
- Local weather pattern
- Individual clouds
- Convective flow in clouds
- Molecular transport
- The molecules themselves

Similarly, in chemical engineering we write material and energy balances from the viewpoint of various scales of information:

- (a) Molecular and atomic balances,
- (b) Microscopic balances,
- (c) Multiple gradient balances,
- (d) Maximum gradient balances, and
- (e) Macroscopic balances (overall balances)

in decreasing order of degree of detail about a process.¹ In this chapter, the type of balance to be described and applied is the simplest one, namely, the macroscopic balance [(e) in the tabulation above].

The macroscopic balance ignores all the detail within a system and consequently results in a balance about the entire system. Only time remains as an independent variable in the balance. The dependent variables, such as concentration and temperature, are not functions of position but represent overall averages throughout the entire volume of the system. In effect, the system is assumed to be sufficiently well mixed so that the output concentrations and temperatures are equivalent to the concentrations and temperatures inside the system.

To assist in the translation of Eq. (6.1)

$$\left\{ \begin{array}{l} \text{Accumulation} \\ \text{or depletion} \\ \text{within the} \\ \text{system} \end{array} \right\} = \left\{ \begin{array}{l} \text{Transport into} \\ \text{system through} \\ \text{system} \\ \text{boundary} \end{array} \right\} - \left\{ \begin{array}{l} \text{Transport out} \\ \text{of system} \\ \text{through system} \\ \text{boundary} \end{array} \right\} + \left\{ \begin{array}{l} \text{Generation} \\ \text{within} \\ \text{system} \end{array} \right\} - \left\{ \begin{array}{l} \text{Consumption} \\ \text{within} \\ \text{system} \end{array} \right\} \quad (6.1)$$

into mathematical symbols, you should refer to Fig. 6.1. Equation (6.1) can be applied to the mass of a single component or to the total amount of material or energy in the system. Let us write each of the terms in Eq. (6.1) in mathematical symbols for a very small time interval Δt . Let the accumulation be positive

¹Additional information together with applications concerning these various types of balances can be found in D. M. Himmelblau and K. B. Bischoff, *Process Analysis and Simulation*, Wiley, New York, 1968.

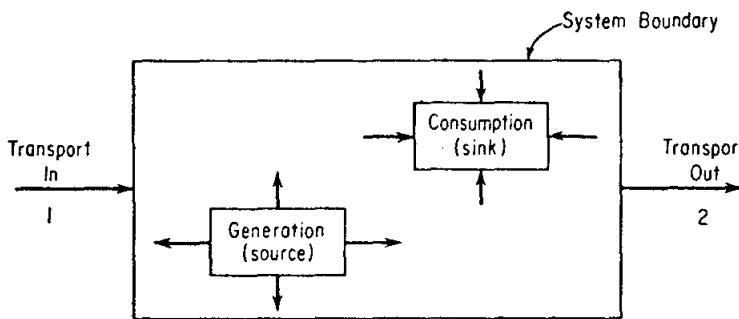


Fig. 6.1. A general unsteady-state process with transport in and out and internal generation and consumption.

in the direction in which time is positive, i.e., as time increases from t to $t + \Delta t$. Then, using the component mass balance as an example, the accumulation will be the mass of A in the system at time $t + \Delta t$ minus the mass of A in the system at time t ,

$$\text{Accumulation} = \rho_A V|_{t+\Delta t} - \rho_A V|_t$$

where²

$$\begin{aligned}\rho_A &= \text{mass of component } A \text{ per unit volume} \\ V &= \text{volume of the system}\end{aligned}$$

Note that the net dimensions of the accumulation term are the mass of A .

We shall split the mass transport across the system boundary into two parts, transport through defined surfaces S_1 and S_2 , whose areas are known, and transport across the system boundary through other (undefined) surfaces. The net transport of A into and out of the system through defined surfaces can be written as

$$\text{Net flow across boundary via } S_1 \text{ and } S_2 = \rho_A v S \Delta t|_{S_1} - \rho_A v S \Delta t|_{S_2}$$

where

$$v = \text{fluid velocity in a duct of cross section } S$$

$$S = \text{defined cross-sectional area perpendicular to material flow}$$

Again note that the net dimensions of the transport term are the mass of A . Other types of transport across the system boundary can be represented by

$$\text{Net residual flow across boundary} = \tilde{w}_A \Delta t$$

where

$$\tilde{w}_A = \text{rate of mass flow of component } A \text{ through the system boundaries other than the defined surfaces } S_1 \text{ and } S_2$$

²The symbol $|$ means that the quantities preceding the vertical line are evaluated at time t , or time $t + \Delta t$, or at surface S_1 , or at surface S_2 , as the case may be.

Finally, th
a chemical reac

where $\tilde{r}_A = \text{net reaction rate}$

Introductio
(6.3) and (6.4) c

Component mat

$$\rho_A V|_{t+\Delta t} - \rho_A V|_t$$

Total material b

Energy balance:

$$E|_{t+\Delta t} - E|_t$$

where

$$\tilde{B} = \text{rate of}$$

$$\tilde{m} = \text{rate of}$$

$$\tilde{Q} = \text{rate of}$$

$$\tilde{W} = \text{rate of}$$

$$\tilde{w} = \text{rate of}$$

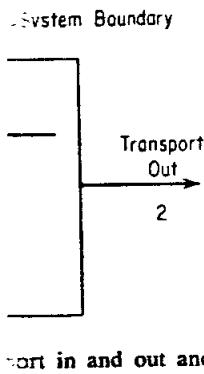
$$\text{through}$$

$$\rho = \text{total m}$$

The other nota
Chaps. 2 and 4
now all expresse

If each side

Similar relation
the limit of each



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Δt are the mass of A .
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areas are known, and trans-
ferred) surfaces. The net
surfaces can be writ-

$$\Delta t|_{S_1} - \rho_A v S \Delta t|_{S_1}$$

to material flow
term are the mass of A .
can be represented by
 $= \tilde{w}_A \Delta t$

the system boundaries

evaluated at time
may

Finally, the net generation-consumption term will be assumed to be due to a chemical reaction r_A :

$$\text{Net generation-consumption} = \tilde{r}_A \Delta t$$

where \tilde{r}_A = net rate of generation-consumption of component A by chemical reaction

Introduction of all these terms into Eq. (6.1) gives Eq. (6.2). Equations (6.3) and (6.4) can be developed from exactly the same type of analysis.

Component material balances:

$$\frac{\rho_A V|_{t+\Delta t} - \rho_A V|_t}{\text{accumulation}} = \rho_A v S \Delta t|_{S_1} - \rho_A v S \Delta t|_{S_2} + \tilde{w}_A \Delta t + \tilde{r}_A \Delta t$$

(6.2)

Total material balance:

$$\frac{\rho V|_{t+\Delta t} - \rho V|_t}{\text{accumulation}} = \rho v S \Delta t|_{S_1} + \rho v S \Delta t|_{S_2} + \tilde{w} \Delta t$$

(6.3)

Energy balance:

$$\begin{aligned} \frac{E|_{t+\Delta t} - E|_t}{\text{accumulation}} &= \left[\left(\hat{H} + \frac{v^2}{2} + gh \right) \tilde{m} \Delta t \right]_{S_1} - \left[\left(\hat{H} + \frac{v^2}{2} + gh \right) \tilde{m} \Delta t \right]_{S_2} \\ &+ \tilde{Q} \Delta t - \tilde{W} \Delta t + \tilde{B} \Delta t \end{aligned}$$

(6.4)

where

\tilde{B} = rate of energy transfer accompanying \tilde{w}

\tilde{m} = rate of mass transfer through defined surfaces

\tilde{Q} = rate of heat transfer

\tilde{W} = rate of work done by the system

\tilde{w} = rate of total mass flow through the system boundaries other than
through the defined surfaces S_1 and S_2

ρ = total mass, per unit volume

The other notation for the material and energy balances is identical to that of Chaps. 2 and 4; note that the work, heat, generation, and mass transport are now all expressed as rate terms (mass or energy per unit time).

If each side of Eq. (6.2) is divided by Δt , we obtain

$$\frac{\rho_A V|_{t+\Delta t} - \rho_A V|_t}{\Delta t} = \rho_A v S|_{S_1} - \rho_A v S|_{S_2} + \tilde{w}_A + \tilde{r}_A$$

(6.5)

Similar relations can be obtained from Eqs. (6.3) and (6.4). Next, if we take the limit of each side of Eq. (6.5) as $\Delta t \rightarrow 0$, we get

$$\frac{d(\rho_A V)}{dt} = -\Delta(\rho_A v S) + \tilde{w}_A + \tilde{r}_A$$

(6.6)

Similar treatment of the total mass balance and the energy balance yields the following two equations:

$$\frac{d(\rho V)}{dt} = -\Delta(\rho v S) + \tilde{w} \quad (6.7)$$

$$\frac{d(E)}{dt} = -\Delta \left[\left(\hat{H} + \frac{v^2}{2} + gh \right) \tilde{m} \right] + \tilde{Q} - \tilde{W} + \tilde{B} \quad (6.8)$$

The relation between the energy balance given by Eq. (6.8), which has the units of energy per unit time, and the energy balance given by Eq. (4.24), which has the units of energy, should be fairly clear. Equation (4.24) represents the integration of Eq. (6.8) with respect to time, expressed formally as follows:

$$E_t - E_{t_0} = \int_{t_0}^t \{-\Delta[(\hat{H} + \hat{K} + \hat{P})\tilde{m}] + \tilde{Q} + \tilde{B} - \tilde{W}\} dt$$

The quantities designated in Eq. (4.24) without the tilde (~) are the respective integrated values from Eq. (6.9).

To solve one or a combination of the very general equations (6.6), (6.7), or (6.8) analytically is usually quite difficult, and in the following examples we shall have to restrict our analyses to simple cases. If we make enough (reasonable) assumptions and work with simple problems, we can consolidate or eliminate enough terms of the equations to be able to integrate them and develop some analytical answers. Numerical solutions are also possible.

In the solution of unsteady-state problems you have to apply the usual procedures of problem solving initially discussed in Chap. 1. Two major tasks exist:

- (a) To set up the unsteady-state equation.
- (b) To solve it once the equation is established.

After you draw a diagram of the system and set down all the information available, you should try to recognize the important variables and represent them by letters. Next, decide which variable is the independent one, and label it. The independent variable is the one you select to have one or a series of values, and then the other variables are all dependent ones—they are determined by the first variable(s) you selected. Which is chosen as an independent and which as a dependent variable is usually fixed by the problem but may be arbitrary. Although there are no general rules applicable to all cases, the quantities which appear prominently in the statement of the problem are usually the best choices. You will need as many equations as you have dependent variables.

As mentioned before, in the macroscopic balance the independent variable is time. In mathematics, when the quantity x varies with time, we consider dx to be the change in x that occurs during time dt if the process continues through the interval beginning at time t . Let us say that t is the independent variable and x is the dependent one. In solving problems you can use one or a combination of Eqs. (6.6), (6.7), and (6.8) directly, or alternatively you can proceed, as shown in some of the examples, to set up the differential equations from scratch exactly

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EXAMPLE 6

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Solution:
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(6.8)

(6.8), which has the units given by Eq. (4.24), which has (4.24) represents the integrally as follows:

$$\tilde{Q} + \tilde{B} - \tilde{W} \} dt$$

tilde (\sim) are the respective general equations (6.6), (6.7). In the following examples we make enough (reasonable) consolidations or eliminate them and develop some sensible ways to apply the usual Chap. 1. Two major tasks

all the information available and represent them in one, and label it. These or a series of values, and they are determined by the first independent and which as a but may be arbitrary. All cases, the quantities which are usually the best choices. independent variables. Since the independent variable is with time, we consider dx/dt . The process continues through the independent variable and we use one or a combination you can proceed, as shown equations from scratch exactly.

in the same fashion as Eqs. (6.2)–(6.4) were formulated. For either approach the objective is to translate the problem statement in words into one or more simultaneous differential equations having the form

$$\frac{dx}{dt} = f(x, t) \quad (6.10)$$

Then, assuming this differential equation can be solved, x can be found as a function of t . Of course, we have to know some initial condition(s) or at one (or more) given time(s) know the value(s) of x .

If dt and dx are always considered positive when increasing, then you can use Eq. (6.1) without having any difficulties with signs. However, if you for some reason transfer an output to the left-hand side of the equation, or the equation is written in some other form, then you should take great care in the use of signs (see Example 6.2 below). We are now going to examine some very simple unsteady-state problems which are susceptible to reasonably elementary mathematical analysis. You can (and will) find more complicated examples in texts dealing with all phases of mass transfer, heat transfer, and fluid dynamics.

EXAMPLE 6.1 Unsteady-state material balance without generation

A tank holds 100 gal of a water-salt solution in which 4.0 lb of salt are dissolved. Water runs into the tank at the rate of 5 gal/min and salt solution overflows at the same rate. If the mixing in the tank is adequate to keep the concentration of salt in the tank uniform at all times, how much salt is in the tank at the end of 50 min? Assume that the density of the salt solution is essentially the same as that of water.

Solution:

We shall set up the differential equations which describe the process from scratch. Step 1: Draw a picture, and put down the known data. See Fig. E6.1.

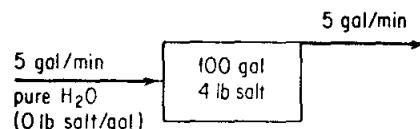


Fig. E6.1.

Step 2: Choose the independent and dependent variables. Time, of course, is the independent variable, and either the salt quantity or concentration in the tank can be the dependent variable. Suppose that we make the mass (quantity) of salt the dependent variable. Let x = lb of salt in the tank at time t .

Step 3: Write the known value of x at a given value of t . This is the initial condition:

$$\text{at } t = 0, \quad x = 4.0 \text{ lb}$$

Step 4: It is easiest to make a total material balance and a component material balance on the salt. (No energy balance is needed because the system can be assumed to be isothermal.)

Total balance:

$$\begin{aligned} \text{accumulation} &= \text{in} \\ [m_{\text{tot}} \text{ lb}]_{t+\Delta t} - [m_{\text{tot}} \text{ lb}]_t &= \frac{5 \text{ gal}}{\text{min}} \left| \frac{1 \text{ ft}^3}{7.48 \text{ gal}} \right| \left| \frac{\rho_{H_2O} \text{ lb}}{\text{ft}^3} \right| \left| \Delta t \text{ min} \right| \\ &\quad - \text{out} \\ &\quad - \frac{5 \text{ gal}}{\text{min}} \left| \frac{1 \text{ ft}^3}{7.48 \text{ gal}} \right| \left| \frac{\rho_{\text{soln}} \text{ lb}}{\text{ft}^3} \right| \left| \Delta t \text{ min} \right| = 0 \end{aligned}$$

This equation tells us that the flow of water into the tank equals the flow of solution out of the tank if $\rho_{H_2O} = \rho_{\text{soln}}$ as assumed. Otherwise there is an accumulation term.

Salt balance:

$$\begin{aligned} \text{accumulation} &= \text{in} - \text{out} \\ [x \text{ lb}]_{t+\Delta t} - [x \text{ lb}]_t &= 0 - \frac{5 \text{ gal}}{\text{min}} \left| \frac{x \text{ lb}}{100 \text{ gal}} \right| \left| \Delta t \text{ min} \right| \end{aligned}$$

Dividing by Δt and taking the limit as Δt approaches zero,

$$\lim_{\Delta t \rightarrow 0} \frac{[x]_{t+\Delta t} - [x]_t}{\Delta t} = -0.05x$$

or

$$\frac{dx}{dt} = -0.05x \quad (\text{a})$$

Notice how we have kept track of the units in the normal fashion in setting up these equations. Because of our assumption of uniform concentration of salt in the tank, the concentration of salt leaving the tank is the same as that in the tank, or $x \text{ lb}/100 \text{ gal}$ of solution.

Step 5: Solve the unsteady-state material balance on the salt. By separating the independent and dependent variables, we get

$$\frac{dx}{x} = -0.05 dt$$

This equation is easily integrated between the definite limits of

$$t = 0, \quad x = 4.0$$

$$t = 50, \quad x = \text{the unknown value } X \text{ lb}$$

$$\int_{4.0}^X \frac{dx}{x} = -0.05 \int_0^{50} dt$$

$$\ln \frac{X}{4.0} = -2.5, \quad \ln \frac{4.0}{X} = 2.5$$

$$\frac{4.0}{X} = 12.2, \quad X = \frac{4.0}{12.2} = 0.328 \text{ lb salt}$$

An equivalent differential equation to Eq. (a) can be obtained directly from the component mass balance in the form of Eq. (6.6) if we let ρ_A = concentration of salt in the tank at any time t in terms of lb/gal:

$$\frac{d(\rho_A V)}{dt} = - \left(\frac{5 \text{ gal}}{\text{min}} \left| \frac{\rho_A \text{ lb}}{\text{gal}} \right| - 0 \right)$$

If the tank holds 100 gal of solution at all times, V is a constant and equal to 100, so that

$$\frac{d\rho_A}{dt} = -\frac{5\rho_A}{100} \quad (\text{b})$$

The initial condition

The solution

EXAMPLE 1

A square tank 10 ft on a side is to be filled with a salt solution. The flow rate required

Solution:

Step 1: I

Step 2: S

independent variable is the height of the liquid in the tank.

Step 3: V

Step 4: I

time Δt , the liquid in the tank is in the

where

The dep

lb, is

An overall m

Although Δh

The accumul

The initial conditions are

$$\text{at } t = 0, \rho_A = 0.04$$

The solution of Eq. (b) would be carried out exactly as the solution of Eq. (a).

$$\frac{\Delta t}{\text{min}} = 0$$

This is the flow of solution
an accumulation term.

$$\frac{\text{min}}{\Delta t}$$

(a)

tion in setting up these
ion in the tank,
the $\text{lb}/\text{ft}^3 \times \text{lb}/100 \text{ gal}$
salt. By separating the

of

D

salt

obtained directly from
let ρ_A = concentration

constant and equal to 100.

(b)

EXAMPLE 6.2 Unsteady-state material balance without generation

A square tank 4 ft on a side and 10 ft high is filled to the brim with water. Find the time required for it to empty through a hole in the bottom 1 in.² in area.

Solution:

Step 1: Draw a diagram of the process, and put down the data. See Fig. E6.2(a).

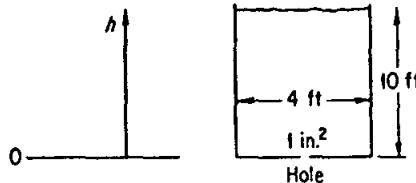


Fig. E6.2(a).

Step 2: Select the independent and dependent variables. Again, time will be the independent variable. We could select the quantity of water in the tank as the dependent variable, but since the cross section of the tank is constant, let us choose h , the height of the water in the tank, as the dependent variable.

Step 3: Write the known value of h at a given value of t :

$$\text{at } t = 0, h = 10 \text{ ft}$$

Step 4: Develop the unsteady-state balance(s) for the process. In an elemental time Δt , the height of the water in the tank drops Δh . The mass of water leaving the tank is in the form of a cylinder 1 in.² in area, and we can calculate the quantity as

$$\frac{1 \text{ in.}^2}{144 \text{ in.}^2} \left| \frac{1 \text{ ft}^2}{\text{sec}} \right| \frac{v^* \text{ ft}}{\text{ft}^3} \left| \frac{\rho \text{ lb}}{\text{ft}^3} \right| \frac{\Delta t \text{ sec}}{\text{ft}^3} = \rho v^* \frac{\Delta t}{144} \text{ lb}$$

where

ρ = the density of water

v^* = the average velocity of the water leaving the tank

The depletion of water inside the tank in terms of the variable h , expressed in lb, is

$$\frac{16 \text{ ft}^2}{\text{ft}^3} \left| \frac{\rho \text{ lb}}{\text{ft}^3} \right| \left| \frac{h \text{ ft}}{\text{ft}^3} \right|_{t+\Delta t} - \frac{16 \text{ ft}^2}{\text{ft}^3} \left| \frac{\rho \text{ lb}}{\text{ft}^3} \right| \left| \frac{h \text{ ft}}{\text{ft}^3} \right|_t = 16\rho \Delta h$$

An overall material balance indicates that

accumulation = in - out

$$16\rho \Delta h = 0 - \frac{\rho v^* \Delta t}{144} \quad (\text{a})$$

Although Δh is a negative value, our equation takes account of this automatically. The accumulation is positive if the right-hand side is positive, and the accumulation

is negative if the right-hand side is negative. Here the accumulation is really a depletion. You can see that the term ρ , the density of water, cancels out, and we could just as well have made our material balance on a volume of water.

Equation (a) becomes

$$\frac{\Delta h}{\Delta t} = - \frac{v^*}{(16)(144)}$$

Taking the limit as Δh and Δt approach zero, we get

$$\frac{dh}{dt} = -\frac{v^*}{(16)(144)} \quad (b)$$

Unfortunately, this is an equation with one independent variable, t , and two dependent variables, h and v^* . We must find another equation to eliminate either h or v^* if we want to obtain a solution. Since we want our final equation to be expressed in terms of h , the next step is to find some function that relates v^* to h and t , and then we can substitute for v^* in the unsteady-state equation.

We shall employ the steady-state mechanical energy balance for an incompressible fluid, discussed in Chap. 4, to relate v^* and h . See Fig. E6.2(b). Recall from Eq. (4.30) with $W = 0$ and $E_v = 0$ that

$$\Delta \left(\frac{v^2}{2} + gh \right) = 0 \quad (\text{c})$$

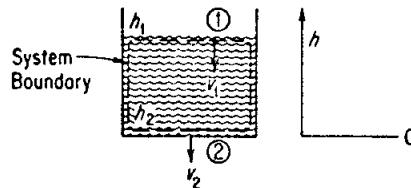


Fig. E6.2(b)

We assume that the pressures are the same at sections ① and ② of the system consisting of the water in the tank. Equation (c) reduces to

$$\frac{v_2^2 - v_1^2}{2} + g(h_2 - h_1) = 0 \quad (d)$$

where

v_2 = the exit velocity through the 1-in.² hole at boundary (2)

v_1 = the velocity of the water in the tank at boundary ①

If $v_1 \approx 0$, a reasonable assumption for the water in the large tank at any time, at least compared to v_2 , and the reference plane is located at the 1-in.² hole,

$$v_2^2 = -2g(0 - h_1) = 2gh \quad (e)$$

Because the exit-stream flow is not frictionless and because of turbulence and orifice effects in the exit hole, we must correct the value of v given by Eq. (e) for frictionless flow by an empirical adjustment factor as follows:

$$v_2 = c\sqrt{2gh} = v^* \quad (\text{f})$$

ulation is really a depletion. ers out, and we could just as water.

(b)

endent variable, t , and two equation to eliminate either h final equation to be expressed relates v^* to h and t , and then

balance for an incompressible 2(b). Recall from Eq. (4.30)

(c)

where c is an orifice correction which we could find (from a text discussing fluid dynamics) has a value of 0.62 for this case. In the American engineering system ($g = 32.2 \text{ ft/sec}^2$), $v^* = 0.62\sqrt{2(32.2)h} = 4.97\sqrt{h} \text{ ft/sec}$. Let us substitute this relation into Eq. (b) in place of v^* . Then we obtain

$$\frac{dh}{dt} = -\frac{4.97(h)^{1/2}}{(16)(144)}$$

or

$$-464 \frac{dh}{h^{1/2}} = dt \quad (g)$$

Equation (g) can be integrated between

$$h = 10 \text{ ft} \quad \text{at } t = 0$$

and

$$h = 0 \text{ ft} \quad \text{at } t = \theta, \quad \text{the unknown time}$$

$$-464 \int_{10}^0 \frac{dh}{h^{1/2}} = \int_0^\theta dt$$

to yield θ ,

$$\theta = 464 \int_0^{10} \frac{dh}{h^{1/2}} = 464 \left[2\sqrt{h} \right]_0^{10} = 2940 \text{ sec}$$

EXAMPLE 6.3 Material balance in batch distillation

A small still is separating propane and butane at 275°F and initially contains 10 lb moles of a mixture whose composition is $x = 0.30$ (x = mole fraction butane). Additional mixture ($x_F = 0.30$) is fed at the rate of 5 lb moles/hr. If the total volume of the liquid in the still is constant, and the concentration of the vapor from the still (x_D) is related to x_S as follows:

$$x_D = \frac{x_S}{1 + x_S}$$

how long will it take for the value of x_S to change from 0.30 to 0.40? What is the steady-state ("equilibrium") value of x_S in the still (i.e., when x_S becomes constant)? See Fig. E6.3.

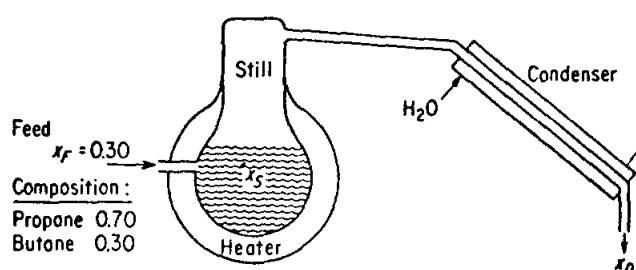


Fig. E6.3.

Solution:

Since butane and propane form ideal solutions, we do not have to worry about volume changes on mixing or separation. Only the material balance is needed to answer the questions posed. If t is the independent variable and x_s the dependent variable, we can say that

Butane balance (C_4):

The input to the still is

$$\begin{array}{c|c|c} \text{5 moles feed} & | 0.30 \text{ mole } C_4 & | \Delta t \text{ hr} \\ \hline \text{hr} & | \text{mole feed} & | \end{array}$$

The output from the still is equal to the amount condensed,

$$\begin{array}{c|c|c} \text{5 moles cond.} & | x_D \text{ moles } C_4 & | \Delta t \text{ hr} \\ \hline \text{hr} & | \text{mole cond.} & | \end{array}$$

The accumulation is

$$\frac{10 \text{ moles in still}}{\text{mole in still}_{t+\Delta t}} | x_s \text{ moles } C_4 | - \frac{10 \text{ moles in still}}{\text{mole in still}_t} | x_s \text{ moles } CH_4 | = 10\Delta x_s$$

Our unsteady-state material balance is then

$$\begin{aligned} \text{accumulation} &= \text{in} - \text{out} \\ 10\Delta x_s &= 1.5\Delta t - 5x_D\Delta t \end{aligned}$$

or, dividing by Δt and taking the limit as Δt approaches zero,

$$\frac{dx_s}{dt} = 0.15 - 0.5x_D$$

As in the previous example, it is necessary to reduce the equation to two variables by substituting for x_D :

$$x_D = \frac{x_s}{1+x_s}$$

Then

$$\begin{aligned} \frac{dx_s}{dt} &= 0.15 - \frac{x_s}{1+x_s}(0.5) \\ \frac{dx_s}{0.15 - \frac{0.5x_s}{1+x_s}} &= dt \end{aligned}$$

The integration limits are

$$\begin{aligned} \text{at } t = 0, \quad x_s &= 0.30 \\ t = \theta, \quad x_s &= 0.40 \end{aligned}$$

$$\int_{0.30}^{0.40} \frac{dx_s}{0.15 - [0.15x_s/(1+x_s)]} = \int_0^\theta dt = \theta$$

$$\int_{0.30}^{0.40} \frac{(1+x_s) dx_s}{0.15 - 0.35x_s} = \theta = \left[-\frac{x_s}{0.35} - \frac{1}{(0.35)^2} \ln(0.15 - 0.35x_s) \right]_{0.30}^{0.40}$$

$$\theta = 5.85 \text{ hr}$$

If you did not know how to integrate the equation analytically, or if you only had experimental data for x_D as a function of x_s instead of the given equation, you could always integrate the equation graphically as shown in Example 6.6 or integrate numerically on a digital computer.

have to worry about
is needed to answer
dependent variable.

The steady-state value of x_s is established at infinite time or, alternatively, when the accumulation is zero. At that time,

$$0.15 = \frac{0.5x_s}{1+x_s} \text{ or } x_s = 0.428$$

The value of x_s could never be greater than 0.428 for the given conditions.

EXAMPLE 6.4 Unsteady-state chemical reaction

A compound dissolves in water at a rate proportional to the product of the amount undissolved and the difference between the concentration in a saturated solution and the concentration in the actual solution at any time. A saturated solution of compound contains 40 g/100 g H₂O. In a test run starting with 20 lb of undissolved compound in 100 lb of pure water it is found that 5 lb are dissolved in 3 hr. If the test continues, how many pounds of compound will remain undissolved after 7 hr? Assume that the system is isothermal.

Solution:

Step 1: See Fig. E6.4.

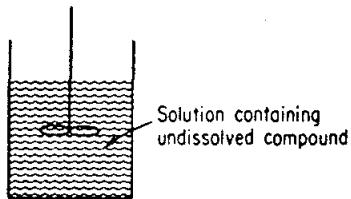


Fig. E6.4.

Step 2: Let the dependent variable x = the pounds of *undissolved* compound at time t (the independent variable).

Step 3: At any time t the concentration of dissolved compound is

$$\frac{(20-x)}{100} \frac{\text{lb compound}}{\text{lb H}_2\text{O}}$$

The rate of dissolution of compound according to the problem statement is

$$\text{rate } \frac{\text{lb}}{\text{hr}} = k(x \text{ lb}) \left(\frac{40 \text{ lb compound}}{100 \text{ lb H}_2\text{O}} - \frac{(20-x) \text{ lb compound}}{100 \text{ lb H}_2\text{O}} \right)$$

where k is the proportionality constant. We could have utilized a concentration measured on a volume basis rather than one measured on a weight basis, but this would just change the value and units of the constant k .

Next we make an unsteady-state balance for the compound in the solution (the system):

$$\begin{aligned} \text{accumulation} &= \text{in} - \text{out} + \text{generation} \\ \frac{dx}{dt} &= 0 - 0 + kx \left(\frac{40}{100} - \frac{20-x}{100} \right) \end{aligned}$$

or

$$\frac{dx}{dt} = kx \left(\frac{40}{100} - \frac{20-x}{100} \right)$$

Step 4: Solution of the unsteady-state equation:

$$\frac{dx}{x(20+x)} = \frac{k}{100} dt$$

This equation can be split into two parts and integrated,

$$\frac{dx}{x} - \frac{dx}{x+20} = \frac{k}{5} dt$$

or integrated directly for the conditions

$$t_0 = 0, \quad x_0 = 20$$

$$t_1 = 3, \quad x_1 = 15$$

$$t_2 = 7, \quad x_2 = ?$$

Since k is an unknown, one extra pair of conditions is needed in order to evaluate k .

To find k , we integrate between the limits stated in the test run:

$$\int_{20}^{15} \frac{dx}{x} - \int_{20}^{15} \frac{dx}{x+20} = \frac{k}{5} \int_0^3 dt$$

$$\left[\ln \frac{x}{x+20} \right]_{20}^{15} = \frac{k}{5} (3 - 0)$$

$$k = -0.257$$

(Note that the negative value of k corresponds to the actual physical situation in which undissolved material is consumed.) To find the unknown amount of undissolved compound at the end of 7 hr, we have to integrate again:

$$\int_{20}^{x_2} \frac{dx}{x} - \int_{20}^{x_2} \frac{dx}{x+20} = \frac{-0.257}{5} \int_0^7 dt$$

$$\left[\ln \frac{x}{x+20} \right]_{20}^{x_2} = \frac{-0.257}{5} (7 - 0)$$

$$x_2 = 10.7 \text{ lb}$$

Step 3

Step 4

(a) Total b

or

(b) Na_2SO_4

[x lb]

or

EXAMPLE 6.5 Overall unsteady-state process

A 15 percent Na_2SO_4 solution is fed at the rate of 12 lb/min into a mixer which initially holds 100 lb of a 50-50 mixture of Na_2SO_4 and water. The exit solution leaves at the rate of 10 lb/min. Assuming uniform mixing, what is the concentration of Na_2SO_4 in the mixer at the end of 10 min? Ignore any volume changes on mixing.

Solution:

In contrast to Example 6.1, both the water and the salt concentrations, and the total material in the vessel, change with time in this problem.

Step 1: See Fig. E6.5.

Step 2:

Let x = fraction Na_2SO_4 in the tank at time t in $\left(\frac{\text{lb Na}_2\text{SO}_4}{\text{lb total}} \right)$

y = total lb of material in the tank at time t

Step 5:
equations w
in Eq. (b) a

To get y , we

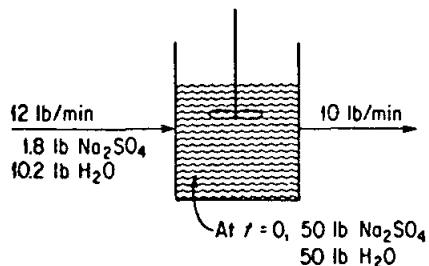


Fig. E6.5.

Step 3: At time $t = 0$, $x = 0.50$, $y = 100$.

Step 4: Material balances between time t and $t + \Delta t$:

(a) *Total balance:*

$$\frac{\text{accumulation}}{[y]_{t+\Delta t} - [y]_t = \Delta y} = \frac{\text{in}}{\frac{12 \text{ lb}}{\text{min}}} - \frac{\text{out}}{\frac{10 \text{ lb}}{\text{min}}} \quad | \Delta t \text{ min}$$

or

$$\frac{dy}{dt} = 2 \quad (\text{a})$$

(b) *Na_2SO_4 balance:*

$$\begin{aligned} & \frac{\text{accumulation}}{\left[\frac{x \text{ lb } \text{Na}_2\text{SO}_4}{\text{lb total}} \middle| \frac{y \text{ lb total}}{\text{lb total}} \right]_{t+\Delta t} - \left[\frac{x \text{ lb } \text{Na}_2\text{SO}_4}{\text{lb total}} \middle| \frac{y \text{ lb total}}{\text{lb total}} \right]_t} \\ &= \frac{\text{in}}{\frac{1.8 \text{ lb } \text{Na}_2\text{SO}_4}{\text{min}}} - \frac{\text{out}}{\frac{10 \text{ lb total}}{\text{min}}} \quad | \frac{x \text{ lb } \text{Na}_2\text{SO}_4}{\text{lb total}} | \Delta t \text{ min} \end{aligned}$$

or

$$\frac{d(xy)}{dt} = 1.8 - 10x \quad (\text{b})$$

Step 5: There are a number of ways to handle the solution of these two differential equations with two unknowns. Perhaps the easiest is to differentiate the xy product in Eq. (b) and substitute Eq. (a) into the appropriate term containing dy/dt :

$$\frac{d(xy)}{dt} = x \frac{dy}{dt} + y \frac{dx}{dt}$$

To get y , we have to integrate Eq. (a):

$$\begin{aligned} \int_{100}^y dy &= \int_0^t 2 dt \\ y - 100 &= 2t \\ y &= 100 + 2t \end{aligned}$$

Then

$$\frac{d(xy)}{dt} = x(2) + (100 + 2t)\frac{dx}{dt} = 1.8 - 10x$$

$$\frac{dx}{dt}(100 + 2t) = 1.8 - 12x$$

$$\int_{0.50}^x \frac{dx}{1.8 - 12x} = \int_0^{10} \frac{dt}{100 + 2t}$$

$$-\frac{1}{12} \ln \frac{1.8 - 12x}{1.8 - 6.0} = \frac{1}{2} \ln \frac{100 + 20}{100}$$

$$x = 0.267 \frac{\text{lb Na}_2\text{SO}_4}{\text{lb total solution}}$$

An alternative method of setting up the dependent variable would have been to let $x = \text{lb Na}_2\text{SO}_4$ in the tank at the time t . Then the Na_2SO_4 balance would be

$$\frac{dx \text{ lb Na}_2\text{SO}_4}{dt \text{ min}} = \frac{1.8 \text{ lb Na}_2\text{SO}_4}{\text{min}} - \frac{10 \text{ lb total}}{\text{min}} \mid \begin{array}{l} x \text{ lb Na}_2\text{SO}_4 \\ y \text{ lb total} \end{array}$$

$$\frac{dx}{dt} = 1.8 - \frac{10x}{100 + 2t}$$

or

$$\frac{dx}{dt} + \frac{10}{100 + 2t}x = 1.8$$

The solution to this linear differential equation gives the pounds of Na_2SO_4 after 10 min; the concentration then can be calculated as x/y . To integrate the linear differential equation, we introduce the integrating factor $e^{\int (dt/10 + 0.2t)}$:

$$xe^{\int (dt/10 + 0.2t)} = \int (e^{\int (dt/10 + 0.2t)}) (1.8) dt + C$$

$$x(10 + 0.2t)^5 = 1.8 \int (10 + 0.2t)^5 dt + C$$

at $x = 50$, $t = 0$, and $C = 35 + 10^5$;

$$x = 1.5(10 + 0.2t) + \frac{35 \times 10^5}{(10 + 0.2t)^5}$$

at $t = 10 \text{ min}$;

$$x = 1.5(12) + \frac{35 \times 10^5}{(12)^5} = 32.1$$

The concentration is

$$\frac{x}{y} = \frac{32.1}{100 + 20} = 0.267 \frac{\text{lb Na}_2\text{SO}_4}{\text{lb total solution}}$$

EXAMPLE 6.6 Unsteady-state energy balance with graphical integration

Five thousand pounds of oil initially at 60°F are being heated in a stirred (perfectly mixed) tank by saturated steam which is condensing in the steam coils at 40 psia. If the rate of heat transfer is given by Newton's heating law, i.e.,

$$\tilde{Q} = \frac{dQ}{dt} = h(T_{\text{steam}} - T_{\text{oil}})$$

where Q is the heat transferred in Btu and h is the heat transfer coefficient in the

proper unit
to 90°F ? W
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tank

10x

proper units, how long does it take for the discharge from the tank to rise from 60 to 90°F? What is the maximum temperature that can be achieved in the tank?

Additional data:

entering oil flow rate = 1018 lb/hr at a temperature of 60°F

discharge oil flow rate = 1018 lb/hr at a temperature of T

$$h = 291 \text{ Btu}/(\text{hr})(^{\circ}\text{F})$$

$$C_{\text{oil}} = 0.5 \text{ Btu}/(\text{lb})(^{\circ}\text{F})$$

Solution:

The process is shown in Fig. E6.6(a). The independent variable will be t , the time; the dependent variable will be the temperature of the oil in the tank, which is

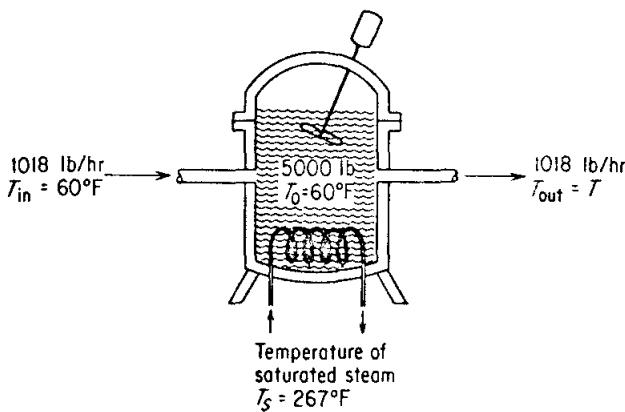


Fig. E6.6(a).

the same as the temperature of the oil discharged. The material balance is not needed because the process, insofar as the quantity of oil is concerned, is assumed to be in the steady state.

Our next step is to set up the unsteady-state energy balance for the interval Δt . Let T_s = the steam temperature and T = the oil temperature:

$$\text{accumulation} = \text{input} - \text{output}$$

A good choice for a reference temperature for the enthalpies is 60°F because this makes the input enthalpy zero.

enthalpy of the input stream	$1018 \text{ lb} \left \frac{0.5 \text{ Btu}}{\text{hr}} \right \left(\frac{(T_{\text{in}} - T_{\text{ref}})}{(^{\circ}\text{F})} \right) \left \frac{\Delta t \text{ hr}}{} \right = 0 \right\}$	input (Btu)
transfer heat	$h(T_s - T) = \frac{291 \text{ Btu}}{(\text{hr})(^{\circ}\text{F})} \left(\frac{(267 - T)^{\circ}\text{F}}{} \right) \left \frac{\Delta t \text{ hr}}{} \right \right\}$	
enthalpy of the output stream	$1018 \text{ lb} \left \frac{0.5 \text{ Btu}}{\text{hr}} \right \left(\frac{(T - 60)^{\circ}\text{F}}{(^{\circ}\text{F})} \right) \left \frac{\Delta t \text{ hr}}{} \right \right\}$	output (Btu)
enthalpy change inside tank	$\left\{ \begin{aligned} & \left[\frac{5000 \text{ lb}}{} \left \frac{0.5 \text{ Btu}}{(\text{lb})(^{\circ}\text{F})} \right \left(\frac{(T - 60)^{\circ}\text{F}}{(^{\circ}\text{F})} \right) \right]_{t+\Delta t} \\ & - \left[\frac{5000 \text{ lb}}{} \left \frac{0.5 \text{ Btu}}{(\text{lb})(^{\circ}\text{F})} \right \left(\frac{(T - 60)^{\circ}\text{F}}{(^{\circ}\text{F})} \right) \right]_t \end{aligned} \right\}$	accumulation (Btu)

The rate of change of energy inside the tank is nothing more than the rate of change of internal energy, which, in turn, is essentially the same as the rate of change of enthalpy, i.e., $dE/dt = dU/dt = dH/dt$, because $d(pV)/dt \cong 0$.

We use Eq. (6.8) with $\tilde{B} = 0$. We assume that all the energy introduced into the motor enters the tank as \tilde{W} :

$$\tilde{W} = \frac{3 \text{ hp}}{4} \left| \frac{0.7608 \text{ Btu}}{(\text{sec})(\text{hp})} \right| \frac{3600 \text{ sec}}{1 \text{ hr}} = \frac{1910 \text{ Btu}}{\text{hr}}$$

$$2500 \frac{dT}{dt} = 291(267 - T) - 509(T - 60) + 1910$$

$$\frac{dT}{dt} = 44.1 - 0.32T$$

$$\int_{60}^{90} \frac{dT}{44.1 - 0.32T} = \int_0^\theta dt = \theta$$

An analytical solution to this equation gives $\theta = 1.52 \text{ hr}$. For illustrative purposes, so you can see how equations too complex to integrate directly can be handled, let us graphically integrate the left-hand side of the equation. We set up a table and choose values of T . We want to calculate $1/(44.1 - 0.32T)$ and plot this quantity vs. T . The area under the curve from $T = 60^\circ$ to $T = 90^\circ \text{F}$ should be 1.52 hr .

T	$0.32T$	$44.1 - 0.32T$	$\frac{1}{44.1 - 0.32T} = \phi$
60	19.2	24.9	0.0402
70	22.4	21.7	0.0462
80	25.6	18.5	0.0540
90	28.8	15.3	0.0655

These data are plotted in Fig. E6.6(b).

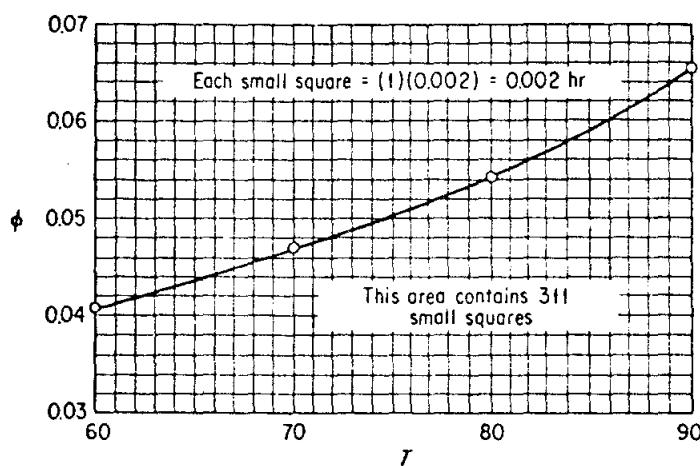


Fig. E6.6(b).

than the rate of change

the rate of change of

any introduced into the

area

1910

The area below $\phi = 0.030$ is

$$(90 - 60)(0.030 - 0) = 0.90 \text{ hr}$$

The area above $\phi = 0.030$ but under the curve is

$$(311)(0.002) = 0.622 \text{ hr}$$

The total area = $0.90 + 0.622 = 1.52 \text{ hr}$.

WHAT YOU SHOULD HAVE LEARNED FROM THIS CHAPTER

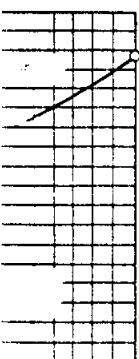
This chapter was intended to acquaint you with the basic concepts underlying unsteady-state material and energy balances and to enable you to set up the necessary differential equations for very simple physical systems.

SUPPLEMENTARY REFERENCES

1. Himmelblau, D. M., and K. B. Bischoff, *Process Analysis and Simulation*, Wiley, New York, 1968.
2. Jenson, V. G., and G. V. Jeffreys, *Mathematical Methods in Chemical Engineering*, Academic Press, New York, 1963.
3. Marshall, W. R., and R. L. Pigford, *The Application of Differential Equations to Chemical Engineering Problems*, University of Delaware, Newark, 1942.
4. Sherwood, T. K., and C. E. Reid, *Applied Mathematics in Chemical Engineering*, 2nd ed., McGraw-Hill, New York, 1957.

PROBLEMS

- 6.1. A defective tank of 1500 ft^3 volume containing 100 percent propane gas (at 1 atm) is to be flushed with air (at 1 atm) until the propane concentration is reduced to less than 1 percent. At that concentration of propane the defect can be repaired by welding. If the flow rate of air into the tank is $30 \text{ ft}^3/\text{min}$, for how many minutes must the tank be flushed out? Assume that the flushing operation is conducted so that the gas in the tank is well mixed.
- 6.2. The catalyst in a fluidized bed reactor of 200-ft^3 volume is to be regenerated by contact with a hydrogen stream. Before the hydrogen can be introduced into the reactor, the O_2 content of the air in the reactor must be reduced to 0.1 percent. If pure N_2 can be fed into the reactor at the rate of $20 \text{ ft}^3/\text{min}$, for how long should the reactor be purged with N_2 ? Assume that the catalyst solids occupy 6 percent of the reactor volume and that the gases are well mixed.
- 6.3. A plant at Canso, Nova Scotia, makes fish-protein concentrate (FPC). It takes 6.6 lb of whole fish to make 1 lb of FPC, and therein is the problem—to make money, the plant must operate most of the year. One of the operating problems



470 Appendix A

TABLE A.5 HEAT, ENERGY, OR WORK EQUIVALENTS

lb	$\text{kW}\cdot\text{hr}$	$\text{hp}\cdot\text{hr}$	Joule	calorie^*	Joule
0.7376	2.773×10^{-7}	3.725×10^{-7}	9.478×10^{-4}	0.2390	1
7.733	2.724×10^{-6}	3.653×10^{-6}	9.296×10^{-3}	2.3438	9.80665
1	3.766×10^{-7}	5.0505×10^{-7}	1.285×10^{-3}	0.3241	1.356
2.655×10^3	1	1.341	3.4128×10^3	8.6057×10^3	3.6×10^6
1.98×10^4	0.7455	1	2.545×10^3	6.4162×10^3	2.6845×10^6
74.73	2.815×10^{-5}	3.774×10^{-5}	9.604×10^{-2}	-24.218	1.0133×10^2
3.086×10^2	1.162×10^{-3}	1.558×10^{-3}	3.9657	1×10^3	4.184×10^3
7.7816×10^2	2.930×10^{-4}	3.930×10^{-4}	1	-2.52×10^2	1.055×10^3
3.086	1.162×10^{-6}	1.558×10^{-6}	3.97×10^{-3}	1	4.184

*The thermochemical calorie = 4.184 J; the IT calorie = 4.1867 J (see Sec. 4.1).

TABLE A.6 PRESSURE EQUIVALENTS

mm Hg	in. Hg	bar	atm	N/m^2
1	3.937×10^{-2}	1.333×10^{-3}	1.316×10^{-3}	1.333×10^2
25.40	1	3.387×10^1	3.342×10^{-2}	3.387×10^3
750.06	29.53	1	0.9869	1.000×10^5
760.0	29.92	1.013	1	1.013×10^5
7.502×10^{-2}	2.954×10^{-4}	1.000×10^{-5}	9.872×10^{-6}	1

The values for
of their isotopes

Name

Actinium
Aluminium
Americium
Antimony
Argon
Arsenic
Astatine
Barium
Berkelium
Beryllium
Bismuth
Boron
Bromine
Cadmium
Caesium
Calcium
Californium
Carbon
Cerium
Chlorine
Chromium
Cobalt
Copper
Curium
Dysprosium
Einsteinium
Erbium
Europium
Fermium
Fluorine
Francium
Gadolinium
Gallium
Gérmánium
Gold
Hafnium
Helium
Holmium
Hydrogen
Iodine
Iridium
Iron
Krypton
Lanthanum
Lawrencium
Lead
Lithium
Lutetium
Magnesium
Manganese
Mendelevium

SOURCE: C

Appendix C

Steam Tables

SOURCE: Combustion Engineering, Inc.
Absolute pressure = atmospheric pressure - vacuum.
 Barometer and vacuum columns may be corrected to mercury at 32°F by subtracting $0.00009 \times (t - 32) \times$ column height, where t is the column temperature in °F.
 One inch of mercury at 32°F = 0.4912 lb/in.²

Example:

Barometer reads 30.17 in. at 70°F. Vacuum column reads 28.26 in. at 80°F. Pounds pressure = $(30.17 - 0.00009 \times 38 \times 30.17) - 28.26 - 0.00009 \times 48 \times 28.26 = 1.93$ in. of mercury at 32°F.

Saturation temperature (from table) = 100°F.

TABLE C.1 SATURATED STEAM: TEMPERATURE TABLE

Temp. Fahr. <i>t</i>	Absolute pressure		Specific volume			Enthalpy		
	Lb/in. ² <i>P</i>	In. Hg 32°F	Sat. Liquid <i>v_f</i>	Evap. <i>v_{fg}</i>	Sat. Vapor <i>v_g</i>	Sat. Liquid <i>h_f</i>	Evap. <i>h_{fg}</i>	Sat. Vapor <i>h_g</i>
32	0.0886	0.1806	0.01602	3305.7	3305.7	0	1075.1	1075.1
34	0.0961	0.1957	0.01602	3060.4	3060.4	2.01	1074.9	1076.0
36	0.1041	0.2120	0.01602	2836.6	2836.6	4.03	1072.9	1076.9
38	0.1126	0.2292	0.01602	2632.2	2632.2	6.04	1071.7	1077.7
40	0.1217	0.2478	0.01602	2445.1	2445.1	8.05	1070.5	1078.6
42	0.1315	0.2677	0.01602	2271.8	2271.8	10.06	1069.3	1079.4
44	0.1420	0.2891	0.01602	2112.2	2112.2	12.06	1068.2	1080.3
46	0.1532	0.3119	0.01602	1965.5	1965.5	14.07	1067.1	1081.2
48	0.1652	0.3364	0.01602	1829.9	1829.9	16.07	1065.9	1082.0
50	0.1780	0.3624	0.01602	1704.9	1704.9	18.07	1064.8	1082.9
52	0.1918	0.3905	0.01603	1588.4	1588.4	20.07	1063.6	1083.7
54	0.2063	0.4200	0.01603	1482.4	1482.4	22.07	1062.5	1084.6
56	0.2219	0.4518	0.01603	1383.5	1383.5	24.07	1061.4	1085.5
58	0.2384	0.4854	0.01603	1292.7	1292.7	26.07	1060.2	1086.3
60	0.2561	0.5214	0.01603	1208.1	1208.1	28.07	1059.1	1087.2
62	0.2749	0.5597	0.01604	1129.7	1129.7	30.06	1057.9	1088.0
64	0.2949	0.6004	0.01604	1057.1	1057.1	32.06	1056.8	1088.9
66	0.3162	0.6438	0.01604	989.6	989.6	34.06	1055.7	1089.8
68	0.3388	0.6898	0.01605	927.0	927.0	36.05	1054.5	1090.6
70	0.3628	0.7387	0.01605	868.9	868.9	38.05	1053.4	1091.5
72	0.3883	0.7906	0.01606	814.9	814.9	40.04	1052.3	1092.3
74	0.4153	0.8456	0.01606	764.7	764.7	42.04	1051.2	1093.2
76	0.4440	0.9040	0.01607	718.0	718.0	44.03	1050.1	1094.1
78	0.4744	0.9659	0.01607	674.4	674.4	46.03	1048.9	1094.9
80	0.5067	1.032	0.01607	633.7	633.7	48.02	1047.8	1095.8
82	0.5409	1.101	0.01608	595.8	595.8	50.02	1046.6	1096.6
84	0.5772	1.175	0.01608	560.4	560.4	52.01	1045.5	1097.5
86	0.6153	1.253	0.01609	527.6	527.6	54.01	1044.4	1098.4
88	0.6555	1.335	0.01609	497.0	497.0	56.00	1043.2	1099.2
90	0.6980	1.421	0.01610	468.4	468.4	58.00	1042.1	1100.1
92	0.7429	1.513	0.01611	441.7	441.7	59.99	1040.9	1100.9
94	0.7902	1.609	0.01611	416.7	416.7	61.98	1039.8	1101.8
96	0.8403	1.711	0.01612	393.2	393.2	63.98	1038.7	1102.7
98	0.8930	1.818	0.01613	371.3	371.3	65.98	1037.5	1103.5
100	0.9487	1.932	0.01613	350.8	350.8	67.97	1036.4	1104.4
102	1.0072	2.051	0.01614	331.5	331.5	69.96	1035.2	1105.2
104	1.0689	2.176	0.01614	313.5	313.5	71.96	1034.1	1106.1
106	1.1338	2.308	0.01615	296.5	296.5	73.95	1033.0	1107.0
108	1.2020	2.447	0.01616	280.7	280.7	75.94	1032.0	1107.9

v = specific volume, ft³/lb. *h* = enthalpy, Btu/lb.

Appendix C

Steam Tables 473

Steam Tables

at 32°F by subtracting
temperature in °F.

.26 in. at 80°F. Pounds
 $48 \times 28.26 = 1.93$ in. of

ABLE

	Enthalpy		Sat. Liquid h_f	Sat. Vapor h_g
0	1075.1	1075.1		
2.01	1074.9	1076.0		
4.03	1072.9	1076.9		
6.04	1077.7			
8.05	1078.6			
10.06	1079.4			
12.06	1068.2	1080.3		
14.07	1067.1	1081.2		
16.07	1065.9	1082.0		
18.07	1064.8	1082.9		
20.07	1063.6	1083.7		
22.07	1062.5	1084.6		
24.07	1061.4	1085.5		
26.07	1060.2	1086.3		
28.07	1059.1	1087.2		
30.06	1057.9	1088.0		
32.06	1056.8	1088.9		
34.06	1055.7	1089.8		
36.05	1054.5	1090.6		
38.05	1053.4	1091.5		
40.04	1052.3	1092.3		
42.04	1051.2	1093.2		
44.03	1050.1	1094.1		
46.03	1048.9	1094.9		
48.02	1047.8	1095.8		
50.02	1046.6	1096.6		
52.01	1045.5	1097.5		
54.01	1044.4	1098.4		
56.00	1043.2	1099.2		
58.00	1042.1	1100.1		
59.99	1040.9	1100.9		
61.98	1039.8	1101.8		
63.98	1038.7	1102.7		
65.98	1037.5	1103.5		
67.97	1036.4	1104.4		
69.96	1035.2	1105.2		
71.96	1034.1	1106.1		
73.95	1033.0	1107.0		
74.94	1032.0	1107.9		

TABLE C.1 (CONT.)

Temp. Fahr. <i>t</i>	Absolute pressure		Specific volume		Enthalpy		
	Lb/in. ² <i>p</i>	In. Hg 32°F	Sat. Liquid <i>v_f</i>	Evap. <i>v_{fg}</i>	Sat. Vapor <i>v_g</i>	Sat. Liquid <i>h_f</i>	Evap. <i>h_{fg}</i>
110	1.274	2.594	0.01617	265.7	265.7	77.94	1030.9
112	1.350	2.749	0.01617	251.6	251.6	79.93	1029.7
114	1.429	2.909	0.01618	238.5	238.5	81.93	1028.6
116	1.512	3.078	0.01619	226.2	226.2	83.92	1027.5
118	1.600	3.258	0.01620	214.5	214.5	85.92	1026.4
120	1.692	3.445	0.01620	203.45	203.47	87.91	1025.3
122	1.788	3.640	0.01621	193.16	193.18	89.91	1024.1
124	1.889	3.846	0.01622	183.44	183.46	91.90	1023.0
126	1.995	4.062	0.01623	174.26	174.28	93.90	1021.8
128	2.105	4.286	0.01624	165.70	165.72	95.90	1020.7
130	2.221	4.522	0.01625	157.55	157.57	97.89	1019.5
132	2.343	4.770	0.01626	149.83	149.85	99.89	1018.3
134	2.470	5.029	0.01626	142.59	142.61	101.89	1017.2
136	2.603	5.300	0.01627	135.73	135.75	103.88	1016.0
138	2.742	5.583	0.01628	129.26	129.28	105.88	1014.9
140	2.887	5.878	0.01629	123.16	123.18	107.88	1013.7
142	3.039	6.187	0.01630	117.37	117.39	109.88	1012.5
144	3.198	6.511	0.01631	111.88	111.90	111.88	1011.3
146	3.363	6.847	0.01632	106.72	106.74	113.88	1010.2
148	3.536	7.199	0.01633	101.82	101.84	115.87	1009.0
150	3.716	7.566	0.01634	97.18	97.20	117.87	1007.8
152	3.904	7.948	0.01635	92.79	92.81	119.87	1006.7
154	4.100	8.348	0.01636	88.62	88.64	121.87	1005.5
156	4.305	8.765	0.01637	84.66	84.68	123.87	1004.4
158	4.518	9.199	0.01638	80.90	80.92	125.87	1003.2
160	4.739	9.649	0.01639	77.37	77.39	127.87	1002.0
162	4.970	10.12	0.01640	74.00	74.02	129.88	1000.8
164	5.210	10.61	0.01642	70.79	70.81	131.88	999.7
166	5.460	11.12	0.01643	67.76	67.78	133.88	998.5
168	5.720	11.65	0.01644	64.87	64.89	135.88	997.3
170	5.990	12.20	0.01645	62.12	62.14	137.89	996.1
172	6.272	12.77	0.01646	59.50	59.52	139.89	995.0
174	6.565	13.37	0.01647	57.01	57.03	141.89	993.8
176	6.869	13.99	0.01648	56.64	54.66	143.90	992.6
178	7.184	14.63	0.01650	52.39	52.41	145.90	991.4
180	7.510	15.29	0.01651	50.26	50.28	147.91	990.2
182	7.849	15.98	0.01652	48.22	48.24	149.92	989.0
184	8.201	16.70	0.01653	46.28	46.30	151.92	987.8
186	8.566	17.44	0.01654	44.43	44.45	153.93	986.6
188	8.944	18.21	0.01656	42.67	42.69	155.94	985.3
190	9.336	19.01	0.01657	40.99	41.01	157.95	984.1
192	9.744	19.84	0.01658	39.38	39.40	159.95	982.8
194	10.168	20.70	0.01659	37.84	37.86	161.96	981.5
196	10.605	21.59	0.01661	36.38	36.40	163.97	980.3
198	11.057	22.51	0.01662	34.98	35.00	165.98	979.0
200	11.525	23.46	0.01663	33.65	33.67	167.99	977.8
202	12.010	24.45	0.01665	32.37	32.39	170.01	976.6
204	12.512	25.47	0.01666	31.15	31.17	172.02	975.3
206	13.031	26.53	0.01667	29.99	30.01	174.03	974.1
208	13.568	27.62	0.01669	28.88	28.90	176.04	972.8
210	14.123	28.75	0.01670	27.81	27.83	178.06	971.5
212	14.696	29.92	0.01672	26.81	26.83	180.07	970.3
215	15.591	0.01674	25.35	25.37	186.10	968.3	
220	17.188	0.01677	23.14	23.16	188.14	965.2	
225	18.915	0.01681	21.15	21.17	193.18	961.9	
230	20.78	0.01684	19.371	19.388	198.22	958.7	
235	22.80	0.01688	17.761	17.778	203.28	955.3	
240	24.97	0.01692	16.307	16.324	208.34	952.1	
245	27.31	0.01696	15.010	15.027	213.41	948.7	
250	29.82	0.01700	13.824	13.841	218.48	945.3	

v = specific volume, ft³/lb. *h* = enthalpy, Btu/lb.

TABLE C.1 (CONT.)

Temp. Fahr. <i>t</i>	Absolute pressure		Specific volume		Enthalpy		Temp. Fahr. <i>t</i>	Absolu
	Lb/in. ² <i>p</i>	In. Hg 32°F	Sat. Liquid <i>v_f</i>	Evap. <i>v_{fg}</i>	Sat. Vapor <i>v_g</i>	Sat. Liquid <i>h_f</i>	Evap. <i>h_{fg}</i>	
255	32.53		0.01704	12.735	12.752	223.56	942.0	1165.6
260	35.43		0.01708	11.754	11.771	228.65	938.6	1167.3
265	38.54		0.01713	10.861	10.878	233.74	935.3	1169.0
270	41.85		0.01717	10.053	10.070	238.84	931.8	1170.6
275	45.40		0.01721	9.313	9.330	243.94	928.2	1172.1
280	49.20		0.01726	8.634	8.651	249.06	924.6	1173.7
285	53.25		0.01731	8.015	8.032	254.18	921.0	1175.2
290	57.55		0.01735	7.448	7.465	259.31	917.4	1176.7
295	62.13		0.01740	6.931	6.948	264.45	913.7	1178.2
300	67.01		0.01745	6.454	6.471	269.60	910.1	1179.7
305	72.18		0.01750	6.014	6.032	274.76	906.3	1181.1
310	77.68		0.01755	5.610	5.628	279.92	902.6	1182.5
315	83.50		0.01760	5.239	5.257	285.10	898.8	1183.9
320	89.65		0.01765	4.897	4.915	290.29	895.0	1185.3
325	96.16		0.01771	4.583	4.601	295.49	891.1	1186.6
330	103.03		0.01776	4.292	4.310	300.69	887.1	1187.8
335	110.31		0.01782	4.021	4.039	305.91	883.2	1189.1
340	117.99		0.01788	3.771	3.789	311.14	879.2	1190.3
345	126.10		0.01793	3.539	3.557	316.38	875.1	1191.5
350	134.62		0.01799	3.324	3.342	321.64	871.0	1192.6
355	143.58		0.01805	3.126	3.144	326.91	866.8	1193.7
360	153.01		0.01811	2.940	2.958	332.19	862.5	1194.7
365	162.93		0.01817	2.768	2.786	337.48	858.2	1195.7
370	173.33		0.01823	2.607	2.625	342.79	853.8	1196.6
375	184.23		0.01830	2.458	2.476	348.11	849.4	1197.5
380	195.70		0.01836	2.318	2.336	353.45	844.9	1198.4
385	207.71		0.01843	2.189	2.207	358.80	840.4	1199.2
390	220.29		0.01850	2.064	2.083	364.17	835.7	1199.9
395	233.47		0.01857	1.9512	1.9698	369.56	831.0	1200.6
400	247.25		0.01864	1.8446	1.8632	374.97	826.2	1201.2
405	261.67		0.01871	1.7445	1.7632	380.40	821.4	1201.8
410	276.72		0.01878	1.6508	1.6696	385.83	816.6	1202.4
415	292.44		0.01886	1.5630	1.5819	391.30	811.7	1203.0
420	308.82		0.01894	1.4806	1.4995	396.78	806.7	1203.5
425	325.91		0.01902	1.4031	1.4221	402.28	801.6	1203.9
430	343.71		0.01910	1.3303	1.3494	407.80	796.5	1204.3
435	362.27		0.01918	1.2617	1.2809	413.35	791.2	1204.6
440	381.59		0.01926	1.1973	1.2166	418.91	785.9	1204.8
445	401.70		0.01934	1.1367	1.1560	424.49	780.4	1204.9
450	422.61		0.01943	1.0796	1.0990	430.11	774.9	1205.0
455	444.35		0.0195	1.0256	1.0451	435.74	769.3	1205.0
460	466.97		0.0196	0.9745	0.9941	441.42	763.6	1205.0
465	490.43		0.0197	0.9262	0.9459	447.10	757.8	1204.9
470	514.70		0.0198	0.8808	0.9006	452.84	751.9	1204.7
475	539.90		0.0199	0.8379	0.8578	458.59	745.9	1204.5
480	566.12		0.0200	0.7972	0.8172	464.37	739.8	1204.2
485	593.28		0.0201	0.7585	0.7786	470.18	733.6	1203.8
490	621.44		0.0202	0.7219	0.7421	476.01	727.3	1203.3
495	650.59		0.0203	0.6872	0.7075	481.90	720.8	1202.7
500	680.80		0.0204	0.6544	0.6748	487.80	714.2	1202.0
505	712.19		0.0206	0.6230	0.6436	493.8	707.5	1201.3
510	744.55		0.0207	0.5932	0.6139	499.8	700.6	1200.4
515	777.96		0.0208	0.5651	0.5859	505.8	693.6	1199.4
520	812.68		0.0209	0.5382	0.5591	511.9	686.5	1198.4
525	848.37		0.0210	0.5128	0.5338	518.0	679.2	1197.2
530	885.20		0.0212	0.4885	0.5097	524.2	671.9	1196.1
535	923.45		0.0213	0.4654	0.4867	530.4	664.4	1194.8
540	962.80		0.0214	0.4433	0.4647	536.6	656.7	1193.3

 $\nu =$ specific volume, ft³/lb. $h =$ enthalpy, Btu/lb.

*Critical temp.

TABLE C.1 (CONT.)

At. Liquid <i>t</i>	Enthalpy		Absolute pressure			Specific volume			Enthalpy		
	Evap. <i>h_{fg}</i>	Sat. <i>h_f</i>	Temp., Fahr. <i>t</i>	Lb/in. ² <i>p</i>	In. Hg 32°F	Sat. Liquid <i>v_f</i>	Evap. <i>v_{fg}</i>	Sat. Vapor <i>v_g</i>	Sat. Liquid <i>h_f</i>	Evap. <i>h_{fg}</i>	Sat. Vapor <i>h_g</i>
35.56	942.0	1165.6	545	1003.6	0.0216	0.4222	0.4438	542.9	648.9	1191.8	
-2.65	938.6	1167.3	550	1045.6	0.0218	0.4021	0.4239	549.3	640.9	1190.2	
3.74	935.3	1169.0	555	1088.8	0.0219	0.3830	0.4049	555.7	632.6	1188.3	
8.84	931.8	1170.6	560	1133.4	0.0221	0.3648	0.3869	562.2	624.1	1186.3	
3.94	928.2	1172.1	565	1179.3	0.0222	0.3472	0.3694	568.8	615.4	1184.2	
-9.06	924.6	1173.7	570	1226.7	0.0224	0.3304	0.3528	575.4	606.5	1181.9	
-4.18	921.0	1175.2	575	1275.7	0.0226	0.3143	0.3369	582.1	597.4	1179.5	
-9.31	917.4	1176.7	580	1326.1	0.0228	0.2989	0.3217	588.9	588.1	1177.0	
-4.45	913.7	1178.2	585	1378.1	0.0230	0.2840	0.3070	595.7	578.6	1174.3	
-9.60	910.1	1179.7	590	1431.5	0.0232	0.2699	0.2931	602.6	568.8	1171.4	
-4.76	906.3	1181.1	595	1486.5	0.0234	0.2563	0.2797	609.7	558.7	1168.4	
-79.92	902.6	1182.5	600	1543.2	0.0236	0.2432	0.2668	616.8	548.4	1165.2	
-5.10	898.8	1183.9	605	1601.5	0.0239	0.2306	0.2545	624.1	537.7	1161.8	
-20.29	895.0	1185.3	610	1661.6	0.0241	0.2185	0.2426	631.5	526.6	1158.1	
-5.49	891.1	1186.6	615	1723.4	0.0244	0.2068	0.2312	638.9	515.3	1154.2	
-30.69	887.1	1187.8	620	1787.0	0.0247	0.1955	0.2202	646.5	503.7	1150.2	
-5.91	883.2	1189.1	625	1852.4	0.0250	0.1845	0.2095	654.3	491.5	1145.8	
-1.14	879.2	1190.3	630	1919.8	0.0253	0.1740	0.1993	662.2	478.8	1141.0	
-16.38	875.1	1191.5	635	1989.0	0.0256	0.1638	0.1894	670.4	465.5	1135.9	
-21.64	871.0	1192.6	640	2060.3	0.0260	0.1539	0.1799	678.7	452.0	1130.7	
-26.91	866.8	1193.7	645	2133.5	0.0264	0.1441	0.1705	687.3	437.6	1124.9	
-32.19	862.5	1194.7	650	2208.8	0.0268	0.1348	0.1616	696.0	422.7	1118.7	
-7.48	858.2	1195.7	655	2286.4	0.0273	0.1256	0.1529	705.2	407.0	1112.2	
-42.79	853.8	1196.6	660	2366.2	0.0278	0.1167	0.1445	714.4	390.5	1104.9	
-43.11	849.4	1197.5	665	2448.0	0.0283	0.1079	0.1362	724.5	372.1	1096.6	
-33.45	844.9	1198.4	670	2532.4	0.0290	0.0991	0.1281	734.6	353.3	1087.9	
-58.80	84	1199.2	675	2619.2	0.0297	0.0904	0.1201	745.5	332.8	1078.3	
-44.17	7	1199.9	680	2708.4	0.0305	0.0810	0.1115	757.2	310.0	1067.2	
-59.56	-1.0	1200.6	685	2800.4	0.0316	0.0716	0.1032	770.1	284.5	1054.6	
-74.97	826.2	1201.2	690	2895.0	0.0328	0.0617	0.0945	784.2	254.9	1039.1	
-80.40	821.4	1201.8	695	2992.7	0.0345	0.0511	0.0856	801.3	219.1	1020.4	
-25.83	816.6	1202.4	700	3094.1	0.0369	0.0389	0.0758	823.9	171.7	995.6	
-1.30	811.7	1203.0	705	3199.1	0.0440	0.0157	0.0597	870.2	77.6	947.8	
-96.78	806.7	1203.5	705.34*	3206.2	0.0541	0	0.0541	910.3	0	910.3	
-32.28	801.6	1203.9									
-27.80	796.5	1204.3									
-13.35	791.2	1204.6									
-18.91	785.9	1204.8									
-24.49	780.4	1204.9									
-30.11	774.9	1205.0									
-35.74	769.3	1205.0									
-41.42	763.6	1205.0									
-47.10	757.8	1204.9									
-52.84	751.9	1204.7									
-38.59	745.9	1204.5									
-4.37	739.8	1204.2									
-20.18	733.6	1203.8									
-76.01	727.3	1203.3									
-81.90	720.8	1202.7									
-87.80	714.2	1202.0									
-63.8	707.5	1201.3									
-99.8	700.6	1200.4									
-105.8	693.6	1199.4									
-11.9	686.5	1198.4									
-18.0	679.2	1197.2									
-24.2	671.9	1196.1									
-30.4	664.4	1194.8									
-36.6	656.7	1193.3									

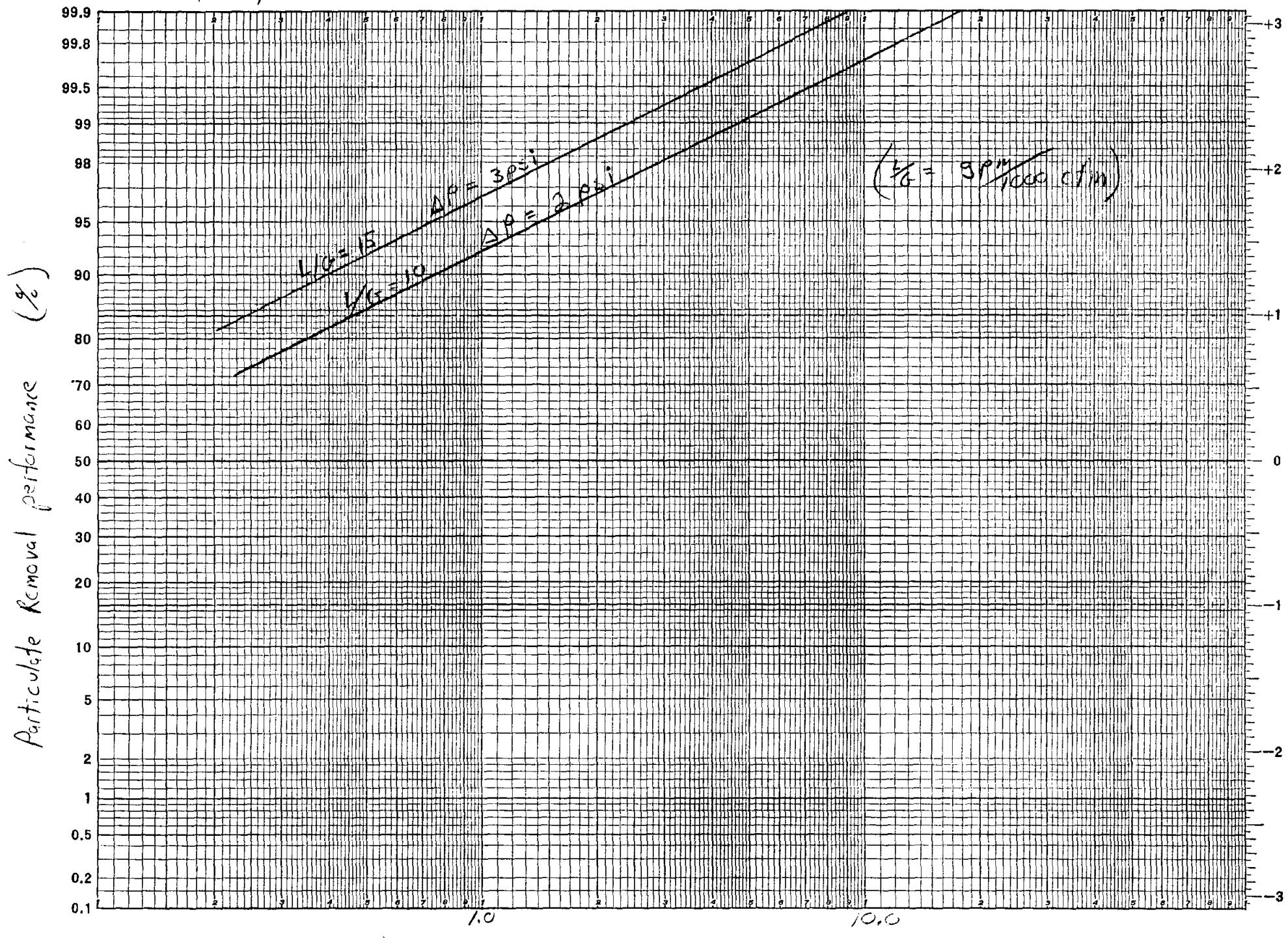
*Critical temperature.

v = specific volume, ft³/lb. *h* = enthalpy, Btu/lb.

Serial no. 60178

Croll-Reynolds model 22-6 HE

PERFORMANCE CURVE



OPERATING CONDITIONS AND PERFORMANCE DATA

Model No.: 22-6HE Croll-Reynolds Job No.: 60178

I. OPERATING CONDITIONS

- A. Gas Inlet Rate Capacity: 10 - 35 acfm
B. Gas Inlet Temperature: 10° - 140°F 170°F DESIGN
C. Gas Inlet Pressure: 3 PSIG
D. Gas Composition: 65% N₂, 25% CO₂, 3% H₂,
2% H₂O VAPOR, 5% HYDROCARBONS (MAINLY
METHANE)

- E. Liquid Inlet Rate:

1. 0.6 gpm
2. _____ gpm

- F. Δ Pressure At Liquid Inlet:

1. 15 Δ psig
x specific gravity: _____
2. _____ psig
x specific gravity: _____

- G. Liquid Composition:

1. H₂O

2. _____

- H. Maximum Liquid Temperature: 40° - 140° F

- I. ΔP Across System: 3 A. PSI inches W.S.

II. PERFORMANCE DATA

- A. 95 % Removal efficiency of 0.75 μ
B. _____ % Removal efficiency of _____
C. _____ % Removal efficiency of _____
D. _____ % Removal efficiency of _____

Based upon above operating conditions.

OPERATING CONDITIONS AND PERFORMANCE DATA

Model No.: 22-6HE Croll-Reynolds Job No.: 60178

1. OPERATING CONDITIONS

- A. Gas Inlet Rate Capacity: 10 - 35 acfm
B. Gas Inlet Temperature: 10° - 140°F 170°F DESIGN
C. Gas Inlet Pressure: 3 PSIG
D. Gas Composition: 65% N₂, 25% CO₂, 3% H₂,
2% H₂O VAPOR, 5% HYDROCARBONS (MAINLY
METHANE)

- E. Liquid Inlet Rate:

1. 0.6 gpm
2. _____ gpm

- F. Δ Pressure At Liquid Inlet:

1. 15 psig
x specific gravity: _____
2. _____ psig
x specific gravity: _____

- G. Liquid Composition:

1. H₂O

2. _____

- H. Maximum Liquid Temperature: 40° - 140° F

- I. ΔP Across System: 3 A PSI inches W.G.

II. PERFORMANCE DATA

- A. 95 % Removal efficiency of 0.75 μ
B. _____ % Removal efficiency of _____
C. _____ % Removal efficiency of _____
D. _____ % Removal efficiency of _____

Based upon above operating conditions.

CROLL - REYNOLDS COMPANY, INC.

CHEMICAL & MECHANICAL ENGINEERS

751 CENTRAL AVENUE

P. O. BOX 668

WESTFIELD, N. J. 07091

ENVIRONMENTAL CONTROL
EQUIPMENT

WET SCRUBBING EQUIPMENT:

DUST, GAS, FGD, NOX

SOLVENT REMOVAL AND SPECIAL SYSTEMS

COOLING TOWERS AND PACKING MATERIAL

TEL. 201-232-4200

TWX NO. 710-997-9642

VACUUM EQUIPMENT

EJECTOR & VACUUM PUMP SYSTEMS

THERMOCOMPRESSORS

VACUUM REFRIGERATION SYSTEMS

SURFACE & BAROMETRIC CONDENSERS

December 23, 1983

Western Research Institute
University of Wyoming Research Corp.
P. O. Box 3395
Laramie, WY 82071

Attention: Mr. T. Owen

Subject: Your Order No. 40555
Our Order No. 60178

Gentlemen:

Enclosed are two (2) certified prints and one (1) certified reproducible of our drawing FSB-20640 Rev. 1 showing the No. 22-6HE Fume Scrubber we are furnishing under the subject order. Please note that this drawing shows the location of mist eliminator pad, per your request.

Also, per your request, we have enclosed four (4) copies of Bete Fog Nozzle, Inc. drawing 2NF-4699 (2 pages).

Manufacture of this equipment is proceeding according to the enclosed. If there are any questions, please contact our Mr. Roger Kirchheim as soon as possible.

Very truly yours,

CROLL-REYNOLDS COMPANY, INC.

Mrs. M. Partelow

(Mrs.) M. Partelow

Enc.

WESTERN RESEARCH INSTITUTE

INTEROFFICE MEMORANDUM

June 20, 1984

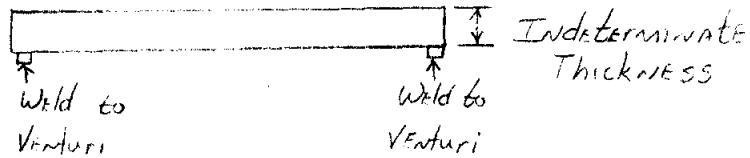
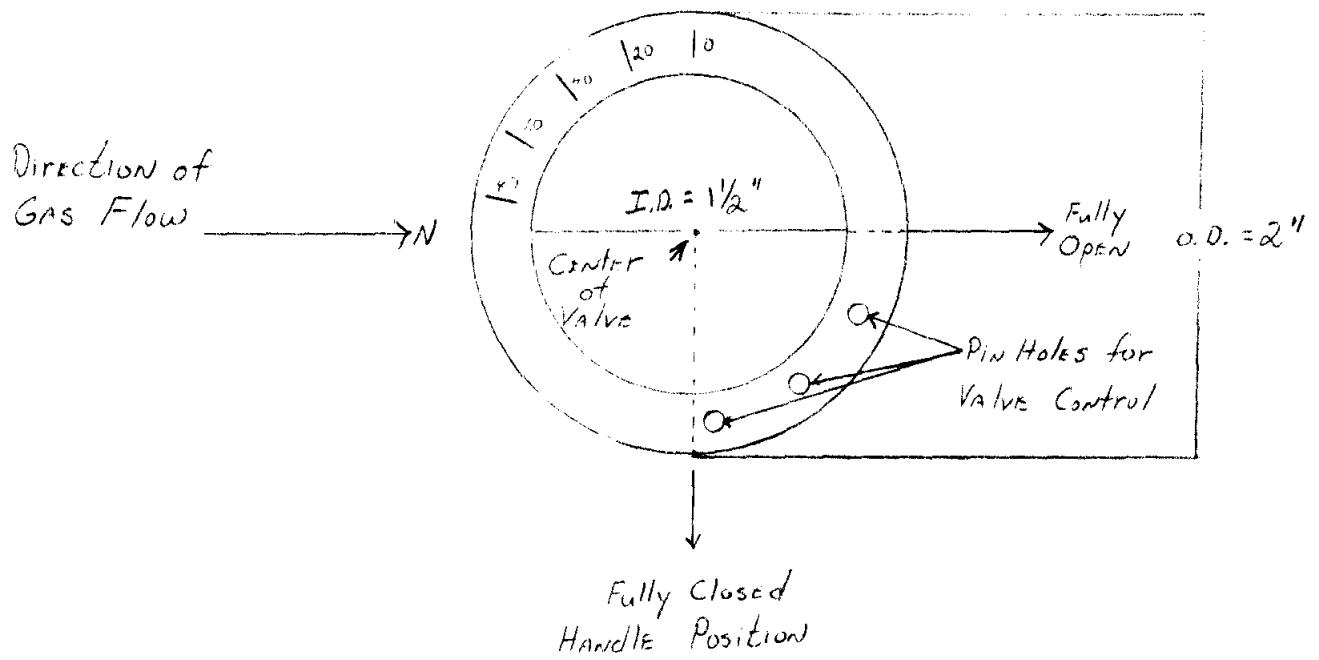
TO: Andy Long

FROM: Tom Owen, Environmental Engineering Division

SUBJECT: Drawing for Venturi Scrubber Throat Valve Control

Please find attached a copy of the proposed design for the venturi scrubber throat valve control ring. Please contact me if you have questions regarding these drawings.

cc: Place
Thomas E. Owen



All spaces in shaded area
For Use By Purchasing Or
Receiving Only

UNIVERSITY OF WYOMING RESEARCH CORPORATION

3/8/84

~~REQUISITION~~

95

H000074

41646

PURCHASE ORDER NO.

Suggested Vendor, Address, Phone No., Contact

Towne Station Express
1203 South 2nd
Laramie, Wyo 82070
(307) 745-7346

Date Ordered 3/8/84

FOB

Terms *N*

Delivery 3/18/84

Vendo

SAME

Date of Request	Date Required	Deliver To: (Name)	Ext.	Prepay & Add	Collect	Sales Order No.:	GSA Cont. No.:
3/16/84	3/16/84	1st Accts	216				

Item No.	Articles or Services	Qty.	Unit	Unit Price	Account	Amount	Obj. Cls.	Receipts
1	Freight charges to shipment of factory scrubber / cyclone separator from Cull- Reynolds.	1	mt	56.44	41142	56.44	903 635	

CROHL REYNOLDS PO# 40555

By Pam

→ Requisitioner

Signature

Date _____

Approvals

Signature

Date

Authorizer

Signature

Date

Receiver

Signature

Dato

W. McLeem

All spaces in shaded area
For Use By Purchasing Or
Receiving Only

**UNIVERSITY OF WYOMING RESEARCH CORPORATION
REQUISITION**

**VENDOR BUSINESS
CODE CODE**

PURCHASE ORDER NO.

Suggested Vendor, Address, Phone No., Contact

Date Ordered

Vendredi

F-04

T-40

1

Delivery

Date of Request	Date Required	Deliver To: (Name)	Ext.	Prepay & Add	Collect	Sales Order No.:	GSA Cont. No.:
-----------------	---------------	--------------------	------	--------------	---------	------------------	----------------

Reunions

Signature

Dat

APPENDIX

Signature

Dat

© 2007 Springer

Singapura

Ono

Buccinum

Signature

Page

CROLL - REYNOLDS COMPANY, INC.

CHEMICAL & MECHANICAL ENGINEERS

751 CENTRAL AVENUE

P. O. BOX 668

WESTFIELD, N. J. 07091

ENVIRONMENTAL CONTROL
EQUIPMENT

WET SCRUBBING EQUIPMENT:

DUST, GAS, FGD, NOX

SOLVENT REMOVAL AND SPECIAL SYSTEMS
COOLING TOWERS AND PACKING MATERIAL

TEL. 201-232-4200
TWX NO. 710-997-9642

VACUUM EQUIPMENT

EJECTOR & VACUUM PUMP SYSTEMS

THERMOCOMPRESSORS

VACUUM REFRIGERATION SYSTEMS

SURFACE & BAROMETRIC CONDENSERS

December 7, 1983

University of Wyoming Research Corp.

P. O. Box 3395

Laramie, WY 82071

Attention: Mr. T. Owen

Subject: Your Order No. 40555
Our Order No. 60178

Gentlemen:

Enclosed are four (4) certified prints of our drawing
FSB-20640 showing the No. 22-6HE Fume Scrubber we propose
to furnish under the subject order.

Print approval has been received. Manufacture of this equipment is proceeding according to the enclosed. If there are any questions, please contact our Mr. Roger Kirchheim as soon as possible.

Also enclosed are four (4) copies each of the following:

Operating Conditions and Performance Data

Performance Curve

Proposal Data Sheet

Inst. 179 Operating Instructions

Information concerning the spray nozzles will be forwarded as soon as possible after receipt from supplier.

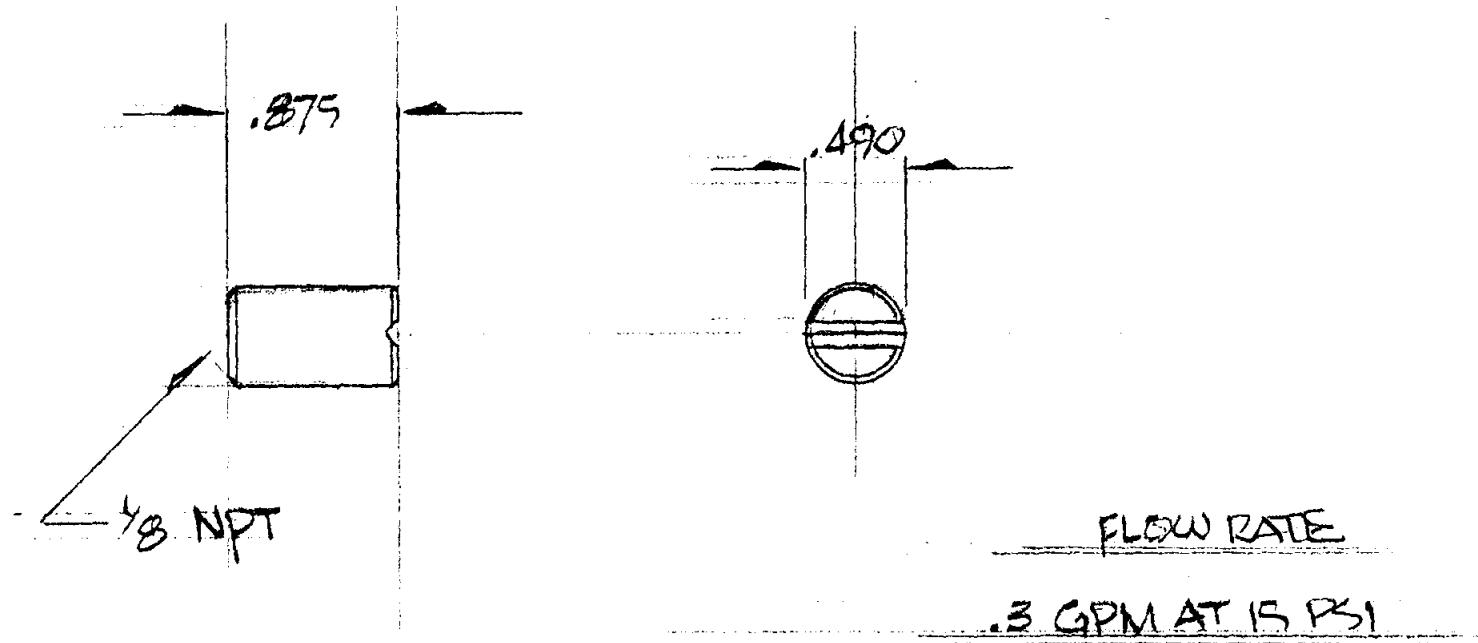
Very truly yours,

CROLL-REYNOLDS COMPANY, INC.

Mrs. M. Partelow

(Mrs.) M. Partelow

Enc.



NOTES

1. MATERIAL: 316 STL ST.

BETE FOG NOZZLE, INC.
GREENFIELD, MASS.

SHEET 1 OF 2

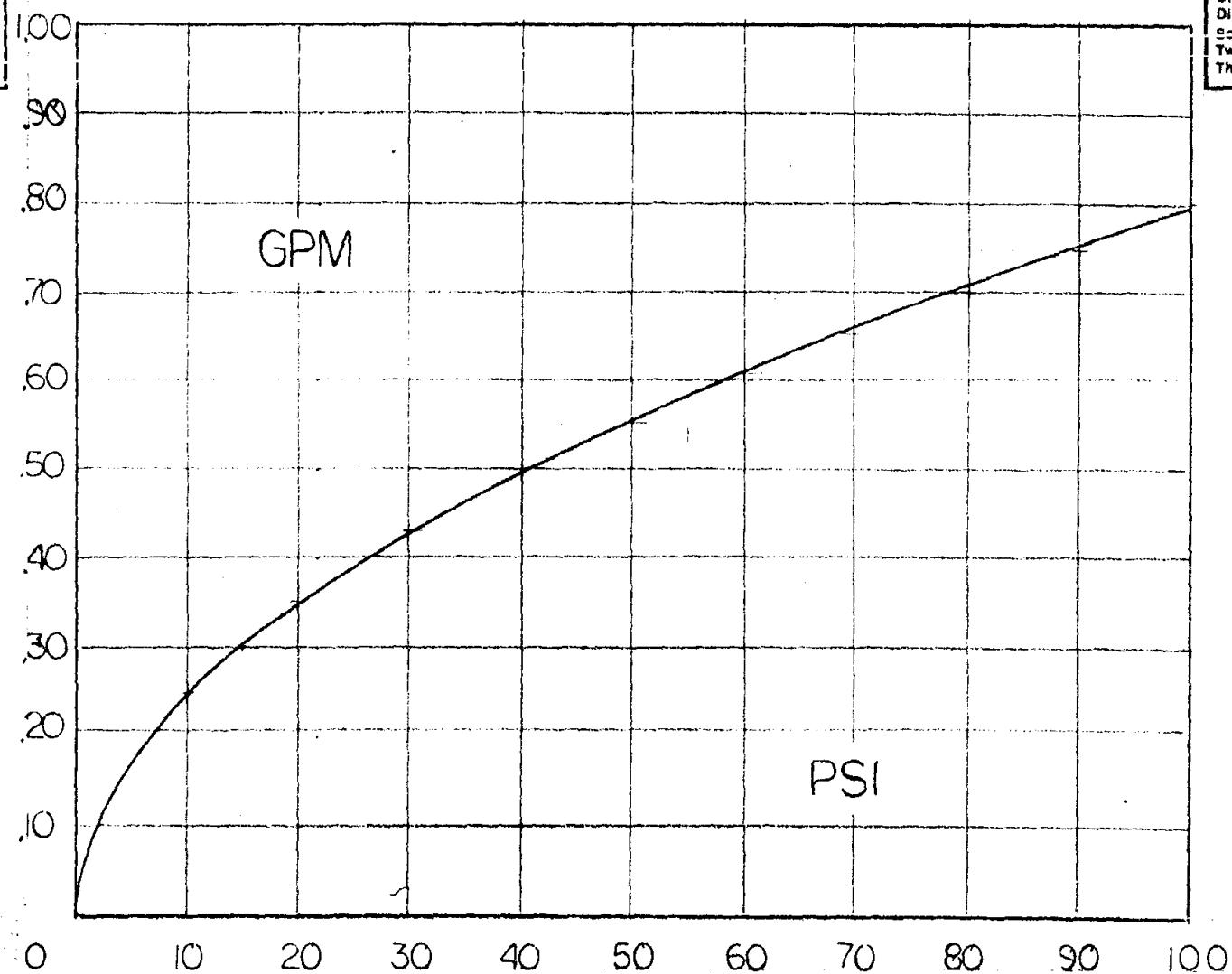
1/8 FNF 050 90

FOR CROLL-REYNOLDS

SCALE: DRAWN: CHECKED:
DATE: 12/12/04 DATE:

DRAWING No. ZNF-4C99 -

REV.	DATE	BY	CHECKED	DESCRIPTION



NOTES

1. FLOW RATE DATA

SHEET 2 of 2

BETE FOG NOZZLE, INC.
GREENFIELD, MASS.

1/8 NF 050 90

FOR CROLL-REYNOLDS

SCALE:	DRAWN:	CHECKED:	REV.
DATE: 1/12/98	DATE: 1/12/98	DATE: 1/12/98	

DRAWING No. ZNE-AC99

REV.	DATE	BY	CHECKED

DESCRIPTION

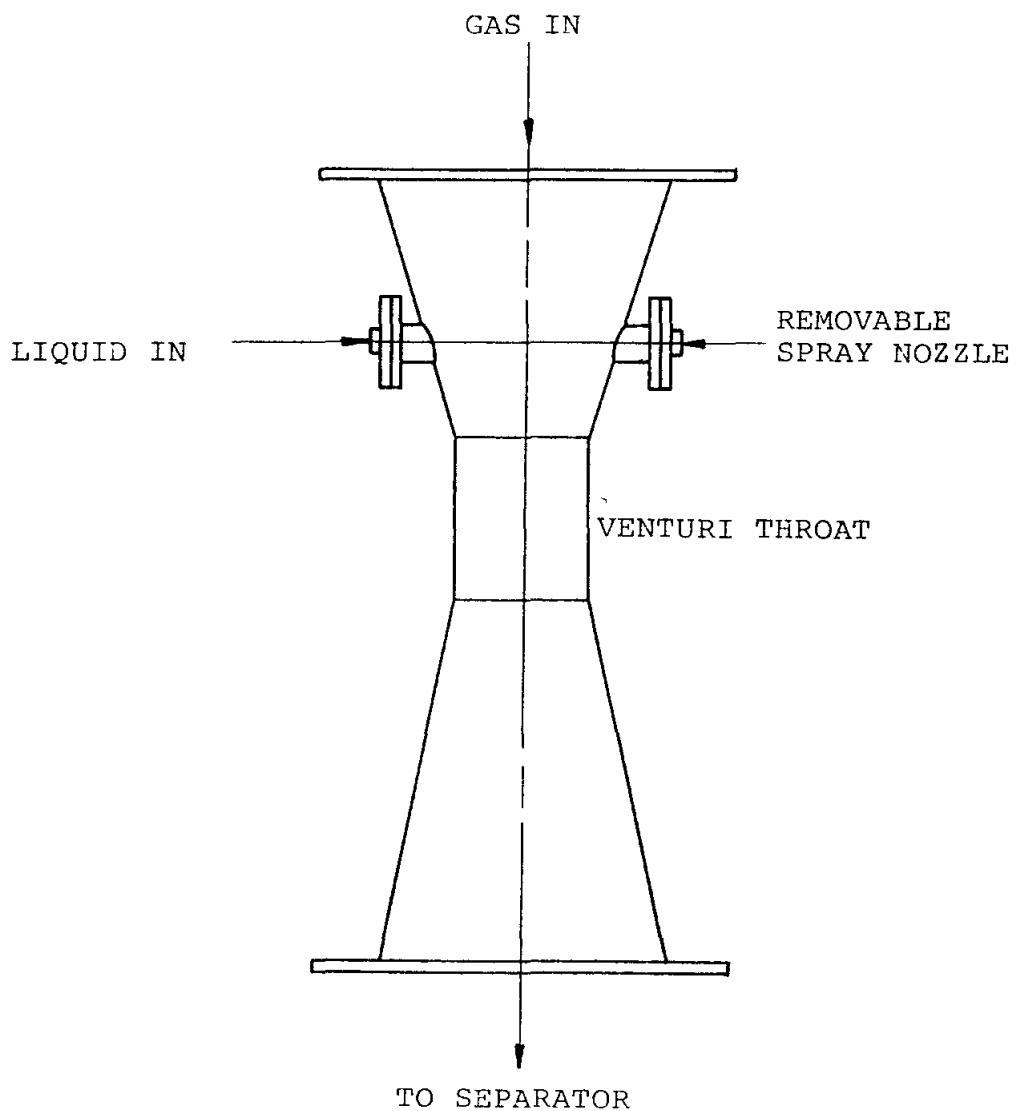
OPERATING INSTRUCTIONS
HIGH ENERGY VENTURI SCRUBBER

Operating conditions for Order No. 60178

Required gas pressure drop A P=3 PSI" W. G.

Required liquid pressure 15 A psig

Required liquid flow 0.6 gpm



OPERATING PRINCIPLES

In operation, the venturi scrubber uses the energy from a high velocity gas stream to entrain and atomize a liquid stream. The high atomization of the liquid and the extreme turbulence in the venturi throat gives this scrubber its exceptionally high ability to remove small micron or submicron dust particles. The effectiveness of this unit is dependent upon the gas velocity in the throat. This can be easily measured through the pressure drop which the unit requires. If the pressure drop is not as shown on the above information, the unit will not function properly.

This particular venturi scrubber is a fixed throat unit. The design gas velocity should be maintained at all times. The liquid recycle rate and pressure are also important. Once these values are obtained, the unit will perform satisfactorily.

Little or no maintenance is required on the venturi scrubber and separator. There are no internal moving parts which could wear or come out of alignment. The only causes of difficulty would be a build up of solid material inside of the unit. If the gas pressure drop continues to build up or the gas flow decreases, please check the throat area for the possibility of a solids build up. This can be mechanically removed if necessary. The spray nozzles are removable through the flanges provided. They should be inspected occasionally to assure that they are not eroded or that corrosion has not ruined the orifice. A slight amount of wear will not significantly affect performance of this type of scrubber. If the unit does not appear to be functioning properly; however, these nozzles should be checked and particular care taken of the possibility of plugging due to the presence of solids. The nozzles are designed to be of nonplugging design; however, excessive solid loads could still cause difficulties.

The separator for this unit is covered under a separate set of operating instructions which should be referred to.

CROLL-REYNOLDS HIGH ENERGY SCRUBBER SYSTEM

TO:

Western Research Institute
University of Wy. Res. Corp.

MODEL NO.: 22-6HE

QUANTITY: One

PRICE PER SYSTEM: \$2,640

F.O.B.: Shops - Teterboro, NJ

TERMS: Net 30

ESTIMATED DELIVERY:

10 Weeks after drawing approval

Weeks for drawings

 ITEM IN STOCK DELIVERY:

Weeks after receipt of order

Deliveries are quoted based on standard shop schedules at the time of quote. Special delivery requirements may be accommodated on an individual basis.

COMMENTS:

Since Croll-Reynolds Co. has no control over the mixture or concentration of corrosive elements which may come in contact with the equipment supplied, no guarantee is expressed or implied concerning materials of construction for corrosion resistance.

Customer should make every effort to assure suitability prior to purchase.

Proposal by: M. I. Holzman

Date: 10/3/83

SPECIFICATIONS**DIMENSIONS**

Gas Inlet/Outlet: 2" / 2"

Scrubbing Liquid Inlet: 1/2"

Separator Tank: Not Included Included

Tank Diameter: 6" Tank Height: 4' 6"

Liquid Storage: YES NO Capacity _____ Gallons

Tank Connections: Drain 1", Fill _____, Overflow _____

Manway: None

Separator Type: Mesh Mist Eliminator

Other: _____

MATERIALS OF CONSTRUCTION

ITEM	MATERIAL
------	----------

Venturi:	316L Stainless Steel
----------	----------------------

Separator:	" " "
------------	-------

Spray Nozzles:	316 Stainless Steel
----------------	---------------------

APPROXIMATE WEIGHT

Shipping: _____ Operating: _____

CONSTRUCTION DESIGN

In general accordance with:

PS 15-69 ASME Code ASME Code Stamped

or vessel designed for pressure/vacuum 15 PSIG / _____

Wall Thicknesses: 1/8" Min.

Head Thicknesses Bottom/Top 1/8" Min., 1/8" Min.

Hold down lugs Included Not included

Lifting lugs Included Not included

OPERATING CONDITIONS

Gas Inlet Rate Capacity: 10-35 scfm

Gas Inlet Temperature: 110-140°F 170°F Design

Pressure: 3-15 PSIG (Atm. Press.=580 MM Hg. Abs.)

Gas Composition: Gas Containing Hydrocarbon

Particulate & Mist

Liquid Inlet Rate: 0.6 gpm

Pressure at Liquid Inlet: 15 psig Differential

Specific Gravity: _____

Liquid Composition: Water

Maximum Liquid Temperature: 100°F

△ Pressure Drop Across System: 3 PSIG inches WG

PERFORMANCE DATA

95 % Removal efficiency of 0.75 Micron

% Removal efficiency of Particulate

% Removal efficiency of _____

% Removal efficiency of _____

% Removal efficiency of _____

Based upon above operating conditions

11/11/83

Tom -

- to Cull-Reynolds
- Draft letter as addendum to P.O. listing the attached revised specifications.
 - Note in separate paragraph that changes mainly involve the acquisition of information and are not substantive changes in the design parameters.

cc to Purchasing

T Weber
W McFernan
A Long
B Place

Do not send letter to typing until we have reviewed it and have agreed on its contents.

After the letter has been drafted and we have agreed on its contents and we have discussed what changes will take place you may

①

Design Specifications

<u>Gas Composition</u> (mole percent)	
65%	N ₂
25%	CO ₂
3%	H ₂
2%	H ₂ O
5%	Hydrocarbons

Gas Flow Rate

10 - 35 SCFM

Temperature

Operating 110°F to 140°F

Design 170°F

Pressure

Operating +3 psig

Design -3 psig to +15 psig

Scrubbing Liquid Composition

Composition - any of the following:

- Water
- Caustic Soln
- Ammonia Soln
- Amine Soln.

Scrubbing Liquid Temperature

40°F to 140°F

Barometric Pressure

880 mm Hg

Liquid to Gas Ratio

10 to 35 gallons
 1000 SCF

Approximate Gas BTU Content

30 BTU / scf

- Vendor to specify particulate removal efficiency. Vendor to supply WRI with operating data vs. efficiency, if available. Vendor to guarantee specified particulate removal efficiency for specified operating conditions.

Vendor to specify liquid inlet nozzles and provide details to WRI.

(nozzle make and orientation)

Vendor to supply ΔP vs atomization for nozzle.

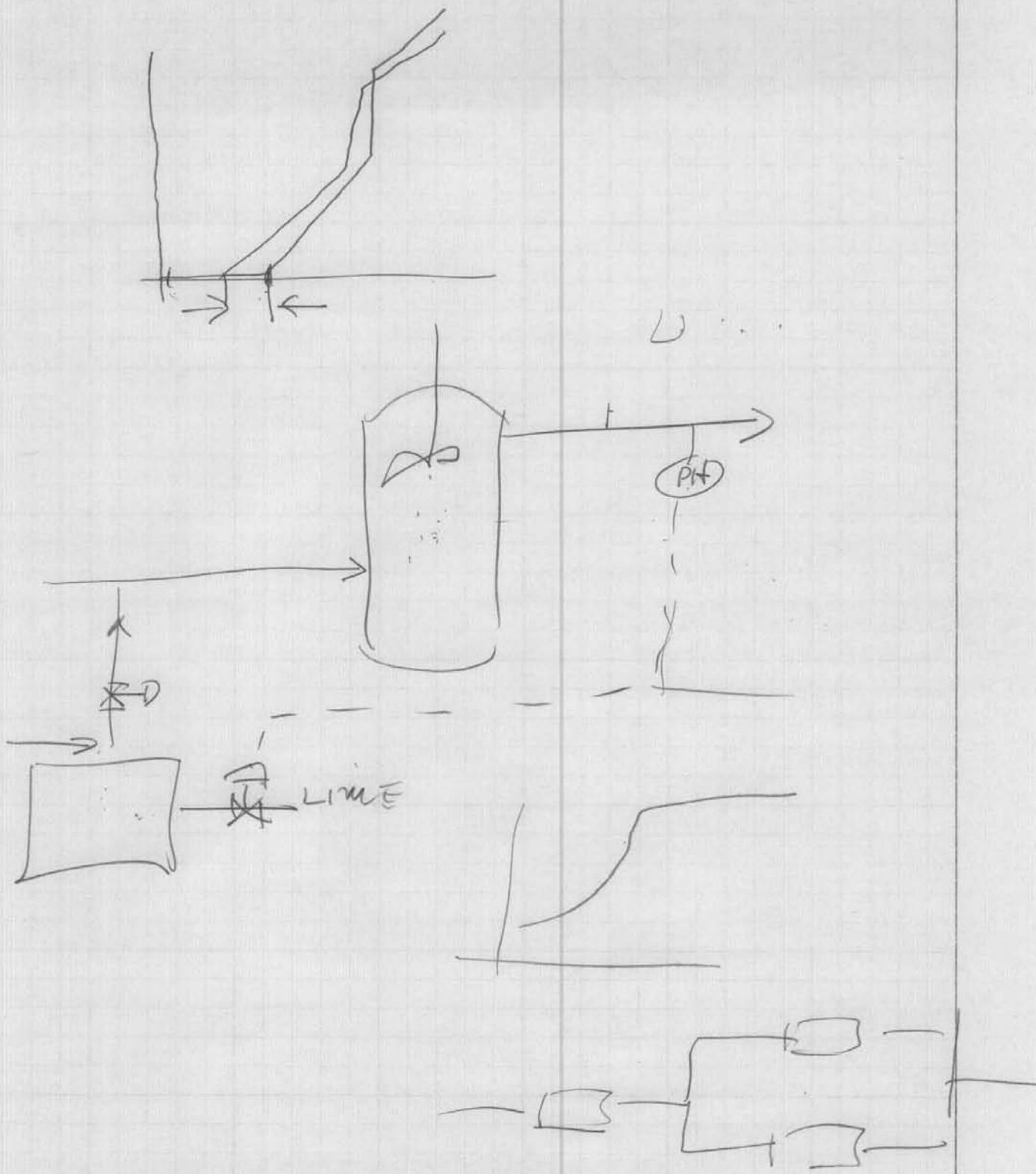
Vendor to specify variable throat specifications and supply recommended operating conditions to WRI. also vendor to supply correlations of throat valve position vs. ΔP

To WRI.

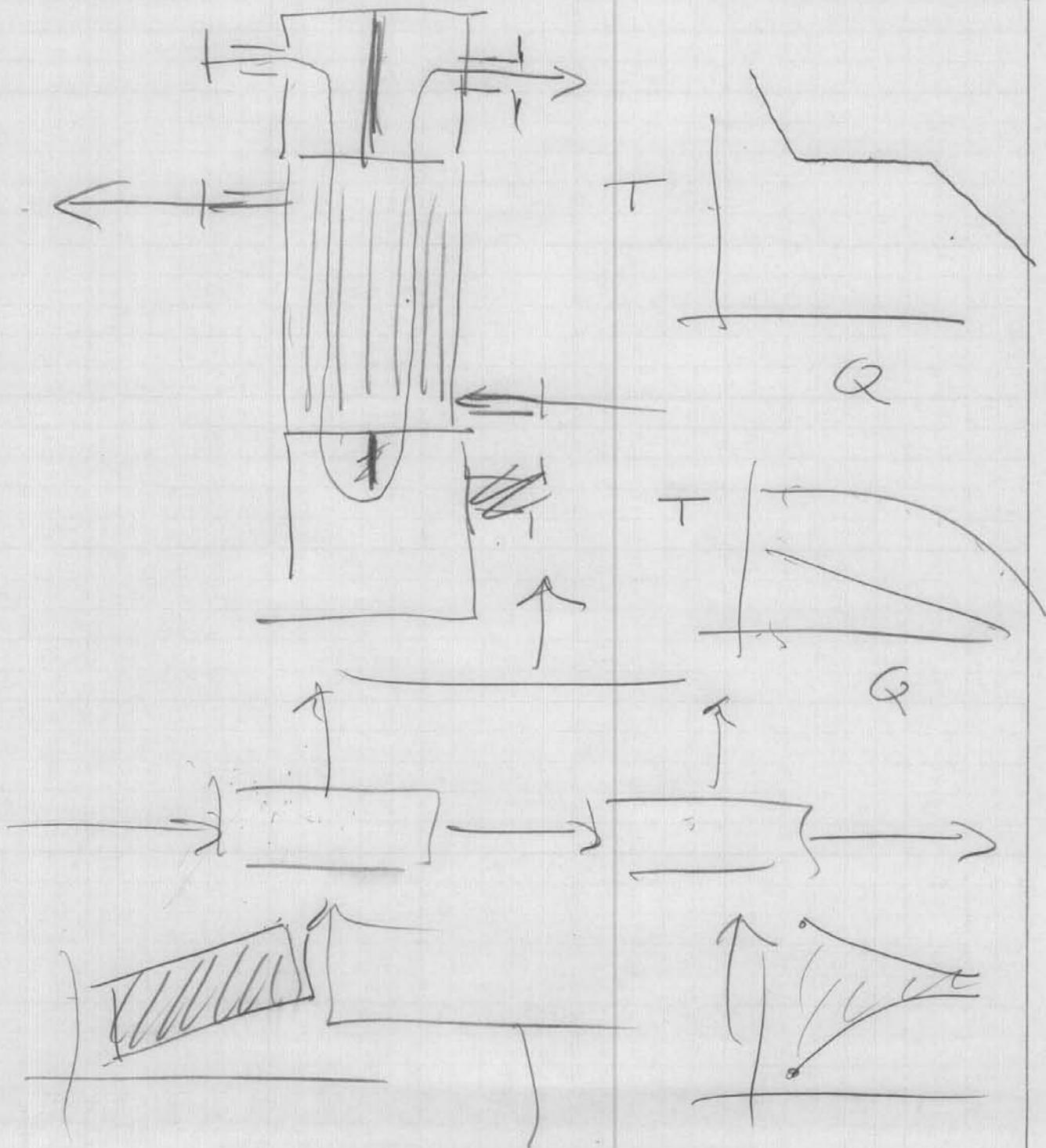
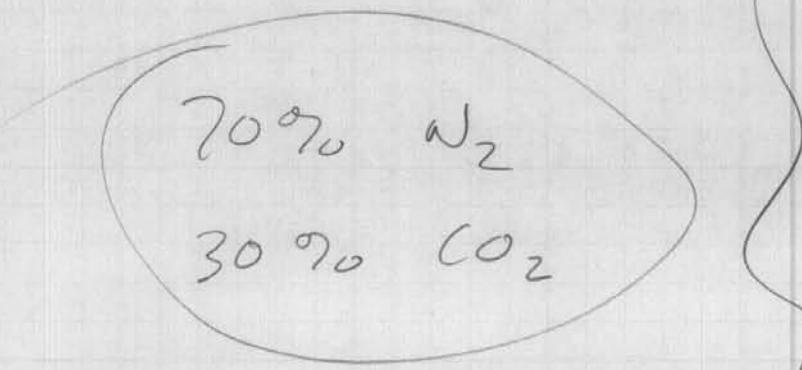
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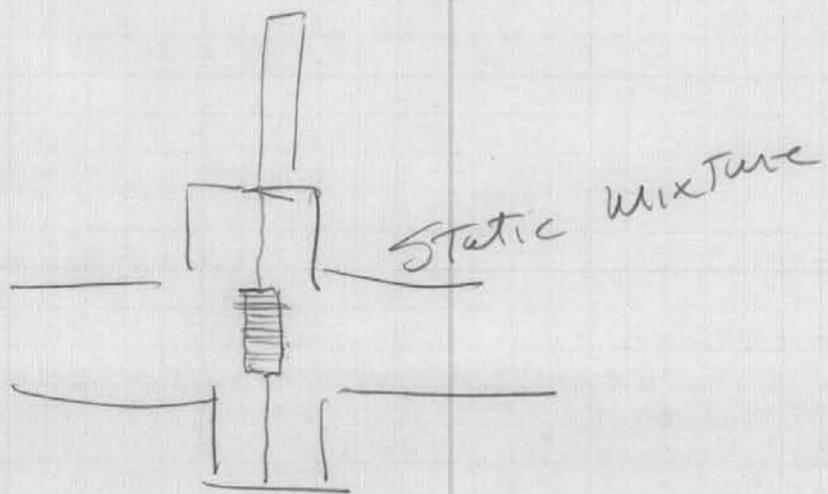
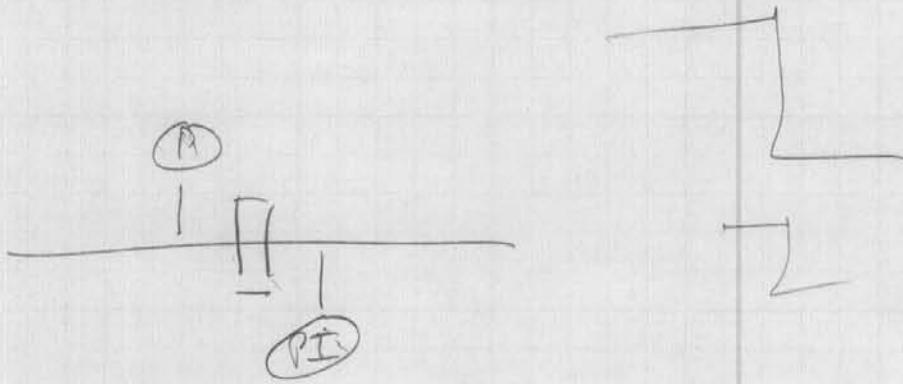
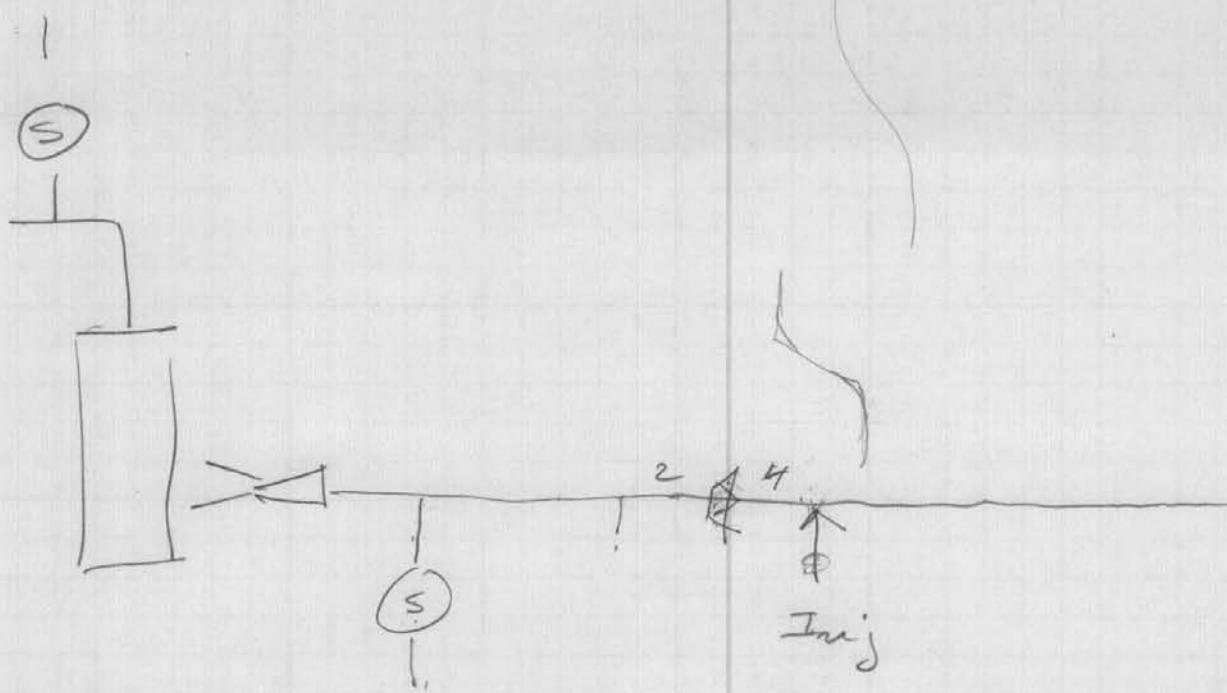
6

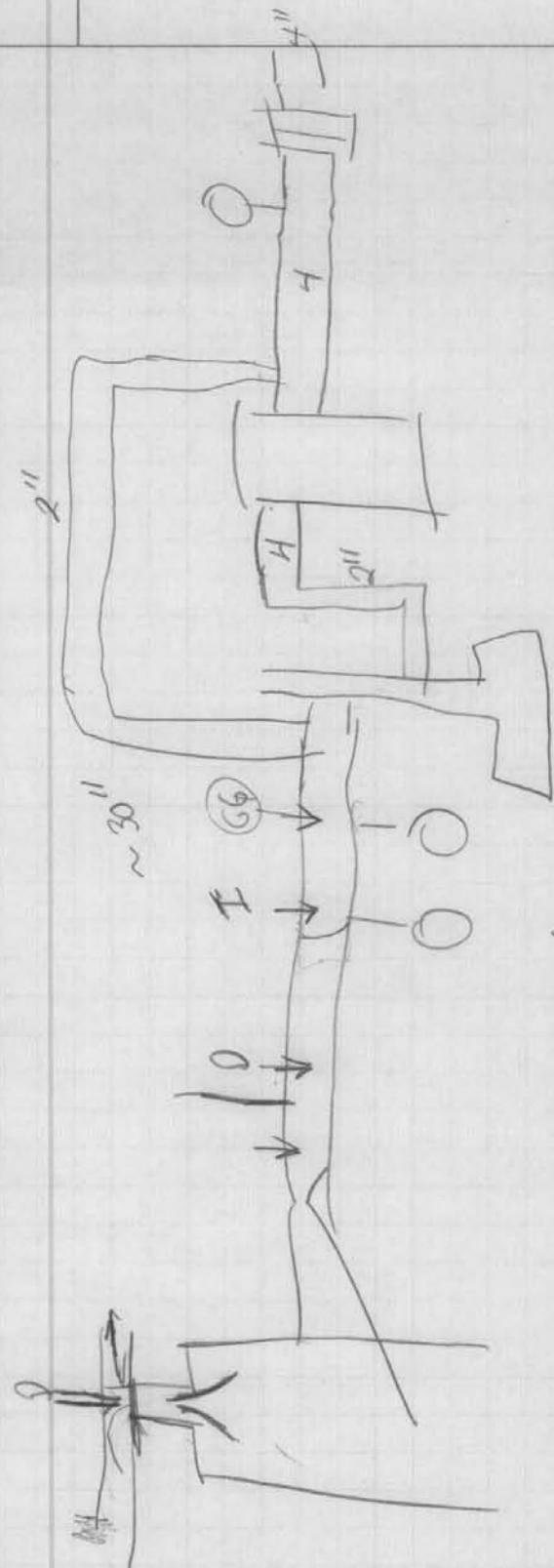
- Vendor to specify the required liquid level in Separator. WRI will provide fittings and instrumentation for level control
 - Vendor to specify materials of construction
 - Mist Eliminator in Separator is to be considered standard equipment
 - Coupling between the Scrubber and the Separator to be flanged to allow rotation in 90 degree increments



copy of Trace
Paper.







$$20 \text{ SCFM} \times \left(\frac{100 + 460}{520} \right) \left(\frac{14.7}{11.2} \right)$$

$$28.269$$

$$V = \frac{28.269}{8.4542 \times 10^{-3}} \times \frac{1}{60}$$

$$= 86.3837 \text{ ft/s}$$

$$\Delta P = \frac{(86.39)^2 (0.0612) (8.454 \times 10^{-3})^{133} (24.76)^7}{1270}$$

~~2201928 m/s~~

$$= 2.1978 \text{ " w.c.}$$

$$\frac{C_o}{C_i} = \frac{3.47}{\Delta P + 1.43} = \frac{3.47}{2.1978 + 1.43} = 1.1254$$

Assume Throat Diameter = 1.0 "

$$\overline{t}_l = 11.2 \text{ psia}$$

$$\overline{T} = 100 \text{ F}$$

~~70%~~ N₂

30% CO₂

$$w = (.7)(28) + (-3)(44) = -32.8$$

$$\rho = \left(\frac{32.8}{379.4} \right) \left(\frac{520}{100+460} \right) \left(\frac{11.2}{14.7} \right)$$
$$= .0612 \text{ lb/ft}^3$$

$$L = \frac{35 \text{ gal}}{1000 \text{ SCF}} \cancel{\text{SCF}}$$

$$L = \frac{35 \text{ gal}}{1000 \text{ SCF}} \times \frac{.0865}{.0612} \frac{\text{ACF}}{\text{SCF}}$$
$$= \frac{24.76 \text{ gal}}{1000 \text{ ACF}}$$

$$A = \frac{\pi}{4} \left(\frac{1}{12} \right)^2 = \cancel{.008} \\ 5.4542 \times 10^{-3} \text{ ft}^2$$

~~A = 20~~

$$Q = 20 \text{ SCFM} \times \frac{0.0865}{0.0612} \\ = 28.268 \text{ ACFM}$$

$$V = \frac{28.268 \text{ ft}^3/\text{min}}{5.4542 \times 10^{-3} \text{ ft}^2} \times \frac{1}{60}$$

$$= 86.388 \text{ ft/s}$$

MAX

$$35 \text{ scfm} \left(\frac{140+460}{520} \right) \left(\frac{14.7}{11.2-3} \right)$$

$$= 72.40 \text{ ACFM}$$

m³/h

$$10 \text{ scfm} \left(\frac{110+460}{520} \right) \left(\frac{14.7}{15.0+11.2} \right)$$

$$= 6.15 \text{ ACFM}$$

AUC

$$20 \text{ scfm} \left(\frac{140+460}{520} \right) \left(\frac{14.7}{11.2+3} \right)$$

$$= 23.89 \text{ ACFM}$$

MAX

$$35 \text{ scfm} \times \frac{35 \text{ gal}}{1000 \text{ scf}} = 1.23 \text{ gpm}$$
$$\times 60$$
$$\frac{}{73.5 \text{ gph}}$$

MIN

0

AVG

$$20 \text{ scfm} \times \frac{35 \text{ gal}}{1000 \text{ scf}} = 0.70 \text{ gpm}$$

$$20 \times \frac{10}{1000} = 0.2 \text{ gpm}$$

$$10 \times \frac{10}{1000} = 0.1 \text{ gpm}$$

20 scfm

$$P_m = 3 \text{ psig} = 14.2 \text{ psia}$$

$$\Delta P = 3 \text{ psig}$$

$$P_{out} = 11.2 \text{ psia}$$

$$T_m = 140^\circ F \text{ (sat)} \quad \text{UP } .9492$$

$$T_{out} = 100^\circ F \text{ (Sat)} \quad \text{UP } 2.8886$$

$$20 \text{ SCFM} \left\{ \begin{array}{c} 2.8886 \\ \hline 14.2 - 2.8886 \end{array} - \begin{array}{c} .9492 \\ \hline 11.2 - .9492 \end{array} \right\}$$

$$= 3.26 \text{ SCFM} \times \frac{1}{379.4} \times 18 \cancel{\times 1} \times \frac{1}{8.34}$$

$$= 0.0185$$

$$= 1.1 \text{ gpm}$$

$$1.1 \text{ gph}$$

$$Re = \frac{\cancel{F}}{\mu} \frac{v D P}{\mu} = \frac{4 D P \cdot 4}{\pi D^2 \mu}$$

. 3 c_{o_2}
. 7 w_2

120F

$c_{o_2} = 0.015 \text{ cp}$

$$Q = \text{SCFM} \cdot \left(\frac{T}{T_0} \right) \left(\frac{P}{P_0} \right)$$

$w_2 = 0.018$

$$P = \frac{M}{379.4} \cdot \left(\frac{T_0}{T} \right) \left(\frac{P}{P_0} \right)$$

$\mu = 0.017 \text{ cp}$

$$Q \cdot P = \text{SCFM} \cdot \frac{M}{379.4}$$

$$Re = \frac{4 \cdot \text{SCFM} \cdot M \times 60}{\pi (379.4) (D) \mu}$$

$$M = 32.8$$

$$\mu = 0.017 \times 2.42 = 0.0411 \frac{l b}{ft \cdot hr}$$

$$\text{SCFM} = 20$$

$$Re = \frac{(4)(20)(32.8)(60)}{\pi(329.4)D(0.0411)}$$
$$= \frac{3213.85}{D(\text{ft})}$$

D, in	D, ft	$Re (20 \text{ SCFM})$	$Re (15 \text{ SCFM})$
4		9641.5 - 6	7230
2		19283.12	14462

$$\frac{35 \text{ gal}}{1000 \text{ CF}} \times 35 \text{ cfm}$$

$$= 1.23 \text{ gpm}$$

$$\begin{array}{r} \div 2 \\ \hline 0.61 \\ \times 0.61 \\ \hline 0.38 (\text{gpm})^2 \end{array}$$

$$\Delta P_N = 60 \text{ psi}$$

$$H = \pi + \Delta P_N + \Delta P_v$$

$$= 15 + 60 + 60 = 135 \text{ psi}$$

$$Sc = \frac{\mu}{\rho D}$$

$$\rho = .06 \text{ lb/lft}^3$$

$$\mu = .04 \frac{lb}{lbf \cdot in}$$

$$D = 0.1 \frac{cm^2}{sec} \times \frac{3600 sec}{hr} \times \left(\frac{1 m}{2.54 cm} \times \frac{1 ft}{12 in} \right)^2$$

$$= 0.39 \text{ lft}^2/\text{hr}$$

$$Sc = \frac{0.04}{(0.06)(0.39)} = 1.72$$

$$Pe = Re \cdot Sc = 1.7 \times Re$$

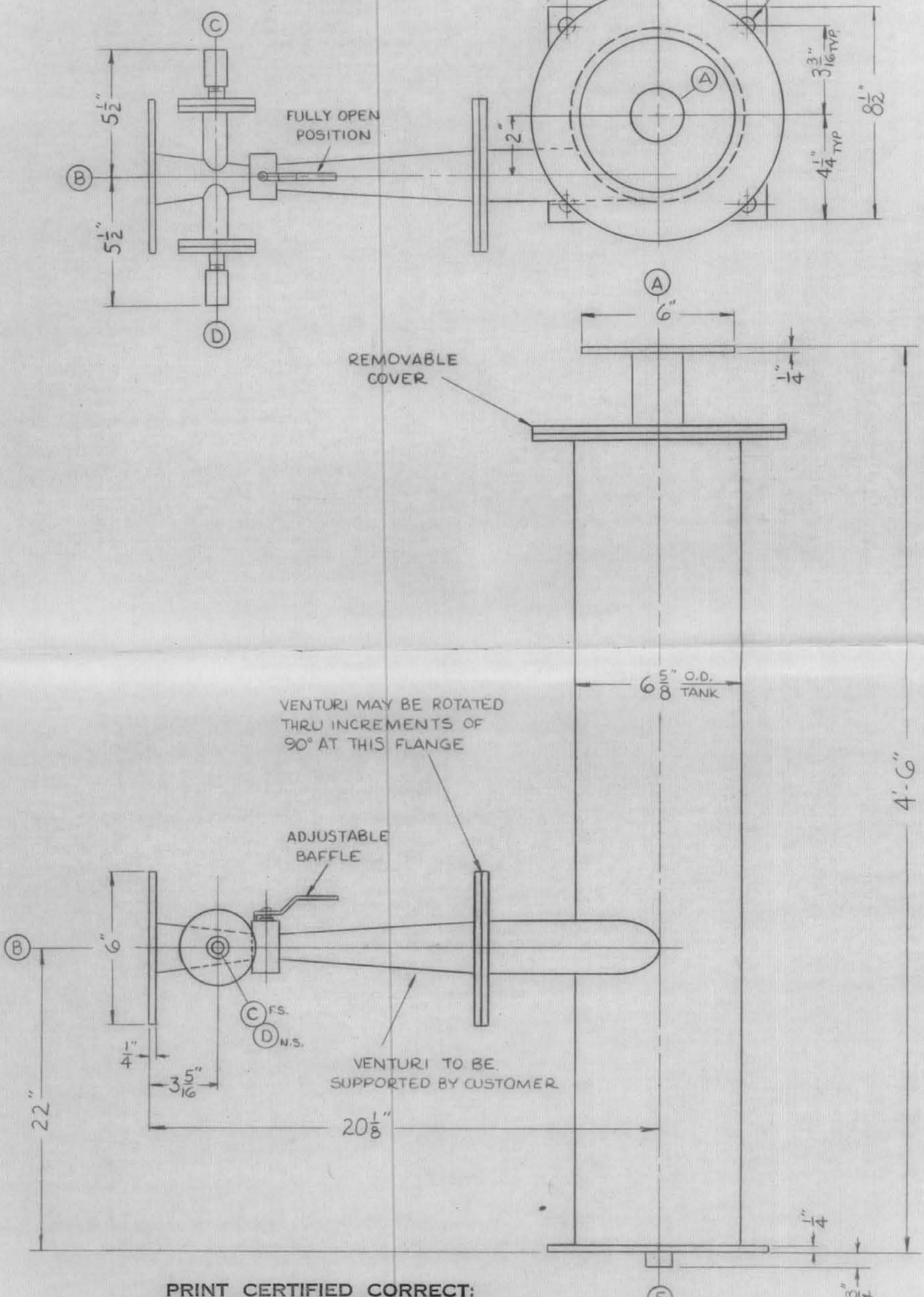
$$= 17000$$

To

$$34000$$

DESCRIPTION	DRILLING ONLY	REMARKS
(A) 2"-GAS OUTLET	150# ANSI STD.	
(B) 2"-GAS INLET	150# ANSI STD.	
(C) $\frac{1}{2}$ " LIQUID INLET		NPT (FEMALE)
(D) $\frac{1}{2}$ " LIQUID INLET		NPT (FEMALE)
(E) 1"-DRAIN		NPT (FEMALE)

4- $\frac{5}{8}$ " DIA. HOLES
SPACED AS SHOWN
IN BASEPLATE



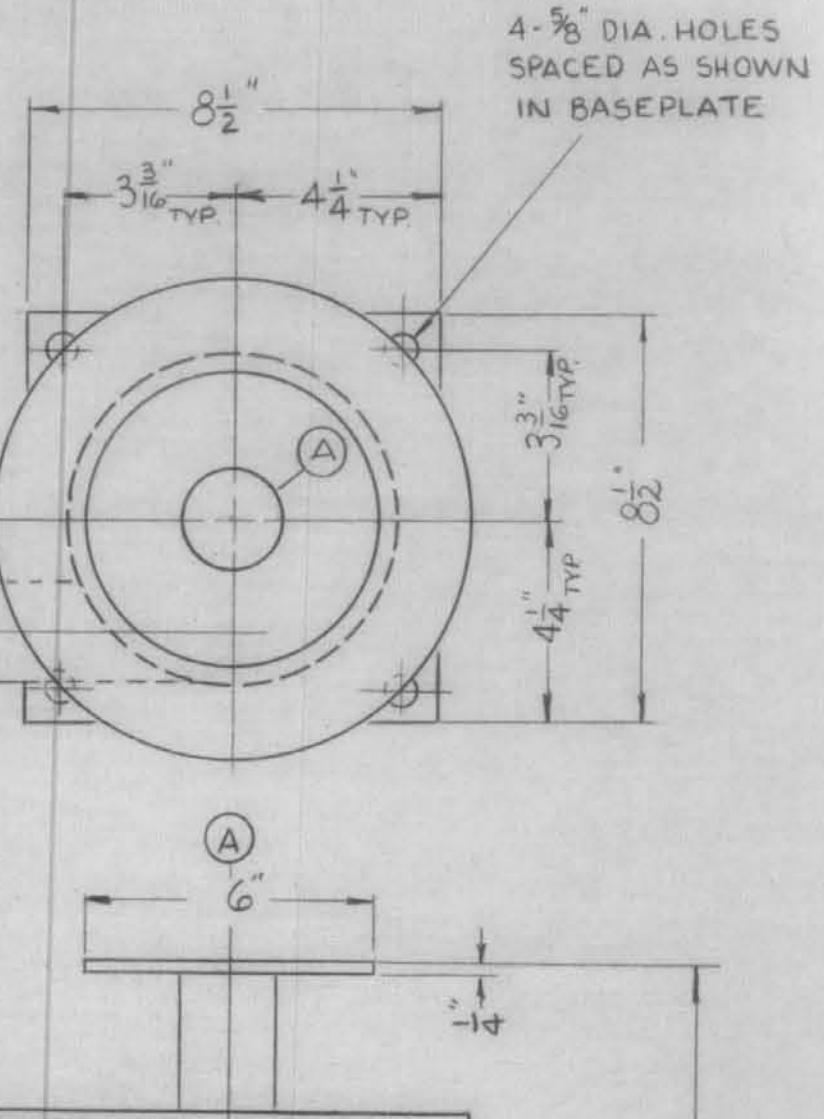
PRINT CERTIFIED CORRECT:
YOUR ORDER NO. 40555
ITEM NO.
CUR ORDER NO. 60178
ENGINEERING DEPT.
DATE: 12-7-83

NOTE:
BOLT HOLES IN ALL FLANGED CONN'S ARE
EQUALLY SPACED & STRADDLE NATURAL ES

CROLL-REYNOLDS COMPANY, INC.
WESTFIELD, N.J.

NO 22-GHE FUME SCRUBBER LAYOUT
SCALE NONE
TRM 10-24-83 FSB-20640

	DESCRIPTION	DRILLING ONLY	<u>REMARKS</u>
(A)	2"-GAS OUTLET	150# ANSI STD.	
(B)	2"-GAS INLET	150# ANSI STD.	
(C)	1/2"-LIQUID INLET		NPT(FEMALE)
(D)	1/2"-LIQUID INLET		NPT(FEMALE)
(E)	1"- DRAIN		NPT(FEMALE)



REMOVABLE
COVER

VENTURI MAY BE ROTATED
THRU INCREMENTS OF
90° AT THIS FLANGE

**ADJUSTABLE
BAFFLE**

VENTURI TO BE
SUPPORTED BY CUSTOMER

PRINT CERTIFIED CORRECT;
YOUR ORDER NO. 40555
ITEM NO.
OUR ORDER NO. 60178
ENGINEERING DEPT.
DATE: 12-7-83

NOTE:

BOLT HOLES IN ALL FLANGED CONN'S ARE
EQUALLY SPACED & STRADDLE NATURAL FS

CROLL-REYNOLDS COMPANY, INC.
WESTFIELD, N.J.

NO 22-GHE FUME SCRUBBER LAYOUT
scale: none
HRG 10-24-83 FSB-20640

Barry Place

--

November 11, 1983

Roger Kirchheim
Croll-Reynolds Company, Inc.
P. O. Box 668
Westfield, NJ 07091

Dear Mr. Kirchheim:

As per our telephone conversation on November 11, 1983, please find enclosed an approved copy of your drawing FSB-20640 showing the No. 22-6HE Fume Scrubber. This approval is based on your acknowledgment that the design parameters we discussed will not change the design of the Fume Scrubber.

The design specifications and a revised purchase order will be transmitted under separate cover from our Purchasing Office.

If you have further questions, please contact me at 307-721-2341.

Sincerely,

Thomas E. Owen

cc: ~~B. Place~~
W. McTernan
Purchasing

bcc: ~~Writer~~
~~ES File~~

TEO:ja

1/13 - North Site 10-ton Venturi/Cyclone

Address: Place, Owen

1.) Want AP across venturi nozzle vs. flow.

2.) Need to have information for design of feed pump and rotameter.

1/13 - Venturi Scrubber/Cyclone Separator

Address: Owen, Kirkham (Croll-Reynolds) 201-232-4200

1.) Received the "approved" drawings and changes in specifications from purchasing, everything is going along fine. Will send certified drawings & information as soon as possible.

2.) Pressure drop vs. gpm for nozzles

AP_v vs. Q

.6 (total)

.3 gpm @ 15 psi. EACH nozzle

.25 @ 10 psi "

.35 @ 20 psi "

.61 @ 60 psi "

.43 @ 30 "

.5 @ 40 "

.71 @ 80 "

Clark

York

10-ton

1E

46 1020

1000

15

2

5

7

9

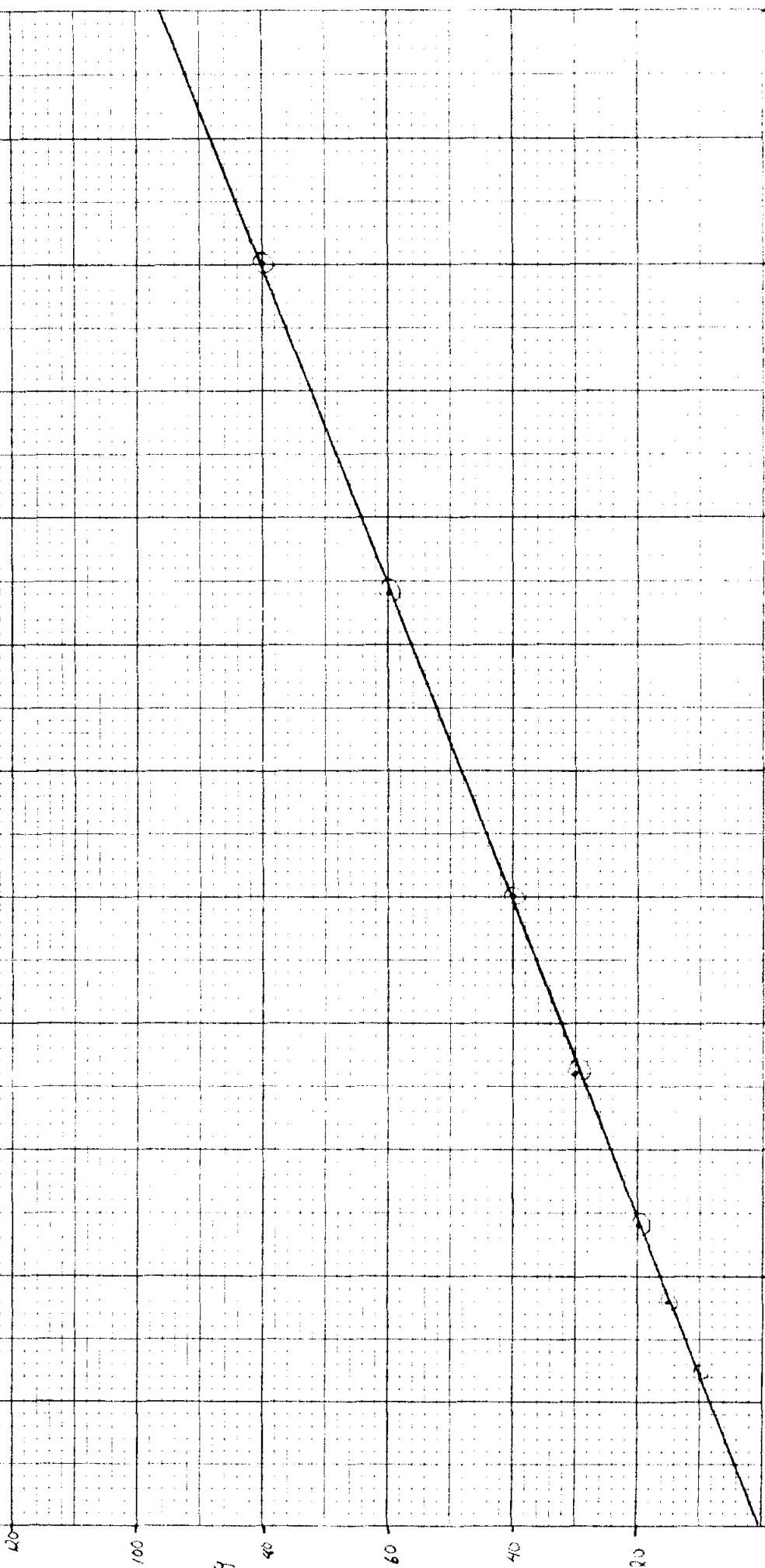
11

13

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17

19



WESTERN RESEARCH INSTITUTE

UNIVERSITY OF WYOMING RESEARCH CORPORATION
 Purchasing Office
 P.O. Box 3395, University Station
 Laramie, Wyoming 82071
 (307) 721-2272

PURCHASE ORDER

Page 1 of 2

VENDOR: Croll-Reynolds Attn: Mike Holzman P.O. Box 668 Westfield, NJ 07091		PURCHASE ORDER NUMBER 40555 The purchase order number must appear on all documents and packages.	
(201) 232-4200		SHIP TO: WESTERN RESEARCH INSTITUTE University of Wyoming Research Corp. 9th & Lewis Laramie, WY 82070	
Order Date	F.O.B.	Ship Via	Terms
10/05/83	Teterboro, NJ	*See below	Net 30
Item	Articles/Services	Qty.	Unit Price
1.	Design and fabricate a small variable throat venturi scrubber and cyclone separator for the North Site Retort Facility 10-ton Retort Building addition, Model 226HE. The Venturi is to be designed to operate over the range of the following parameters:	1	ea. \$2640.00
Gas Flow	10-35 scfm 20-23 scfm (average)		\$2640.00
Gas Temperature	110-140°F		
Gas Pressure	3 psig (average), 15 psig (maximum)		
Barometric Pressure	580 mm Hg (average)		
Upstream Pipe Interface	2 in. schedule 40		
Downstream Pipe Interface	2 in. schedule 40		
Liquid/Gas Ratio Range	10:1 to 35:1		
Liquid Injection Method	Jets		
Scrubbing Liquid	Caustic or amine solutions with some inorganic salts present and moderate to high levels of ammonia.		
Gas BTU Content	130-175 BTU/SCF		
Diameter of separator	6", 316 stainless steel		
Couplings between the scrubber and the separator	of a standard pipe size and thread such that the venturi can		

SHIP TO: Western Research Institute
 University of Wyoming Research Corporation
 Attn: Finance Office
 P.O. Box 3395, University Station
 Laramie, WY 82071

TOTAL \$2640.00

Pam C. Lebeda
 Pam C. Lebeda, Contracting Officer

be placed in different physical relationship to the separator.

*Delivery Schedule: Drawings - 3 weeks ARO
Scrubber & Separator - 9 weeks after receipt
of approved drawings.

CONFIRMING ORDER PLACED WITH MIKE HOLZMAN
BY PAM LEBEDA, 10/5/83.

B. Price

November 11, 1983

Roger Kirchheim
Croll-Reynolds Company, Inc.
751 Central Avenue
P. O. Box 668
Westfield, NJ 07091

Dear Mr. Kirchheim:

This letter is an addendum to our Purchase Order No. 40555. Please reference you Order No. 60178 for a venturi scrubber and cyclone separator. As per our telephone conversation, we are transmitting the revised design specifications below.

Design Specifications

Gas Composition (mole percent)

Nitrogen	65%
Carbon Dioxide	25%
Hydrogen	3%
Water Vapor	2%
Hydrocarbons	5%

Gas Flow Rate

10-35 scfm

Temperature

Operating	110° F to 140° F
Design	170° F

Pressure

Operating	3 psig
Design	-3 psig to 15 psig

Scrubbing Liquor Composition (Any of the following)

Water	
Caustic Solution	- 5%
Ammonia Solution	- 5%
Amine Solution	- 15%

Scrubbing Liquor Temperature

40° F to 140° F

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Barometric Pressure

580 mm HG

Liquid to Gas Ratio

10 to 35 gallons per 1000 scf

Approximate BTU Content of the Gas

30 BTU per scf

Other Specifications

Vendor to specify particulate removal efficiency.

Vendor to supply WRI with operating data verses particulate removal efficiency, if available.

Vendor to guarantee specified particulate removal efficiency for specified operating conditions.

Vendor to specify liquid inlet nozzles and provide specification details to WRI including nozzle make and orientation.

Vendor to supply required pressure verses atomization data for nozzles.

Vendor to specify variable throat specifications and supply recommended operating conditions to WRI.

Vendor to specify the required liquid level in the separator.

Vendor to supply correlations of throat valve position verses pressure drop to WRI, if possible.

The materials of construction for all components will be stainless steel. The type of stainless steel will be specified by the vendor.

A two inch mist eliminator in the separator is to be considered standard equipment.

Couplings between the scrubber and the separator to be flanged to allow rotation in 90° increments.

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These revised design specifications mainly involve the acquisition of information and are not substantive changes in the design parameters. Please contact me if you have questions regarding these specifications or if these changes will cause a change in the purchase price so that we can submit a revised purchase order.

Sincerely,

Thomas E. Owen

cc: Purchasing
J. Weber
W. McTernan
~~B. Place~~
A. Long

bcc: Writer
✓ ES File

TEO:ja

VENTURI SCRUBBER AND CYCLONE DESIGN CRITERIA

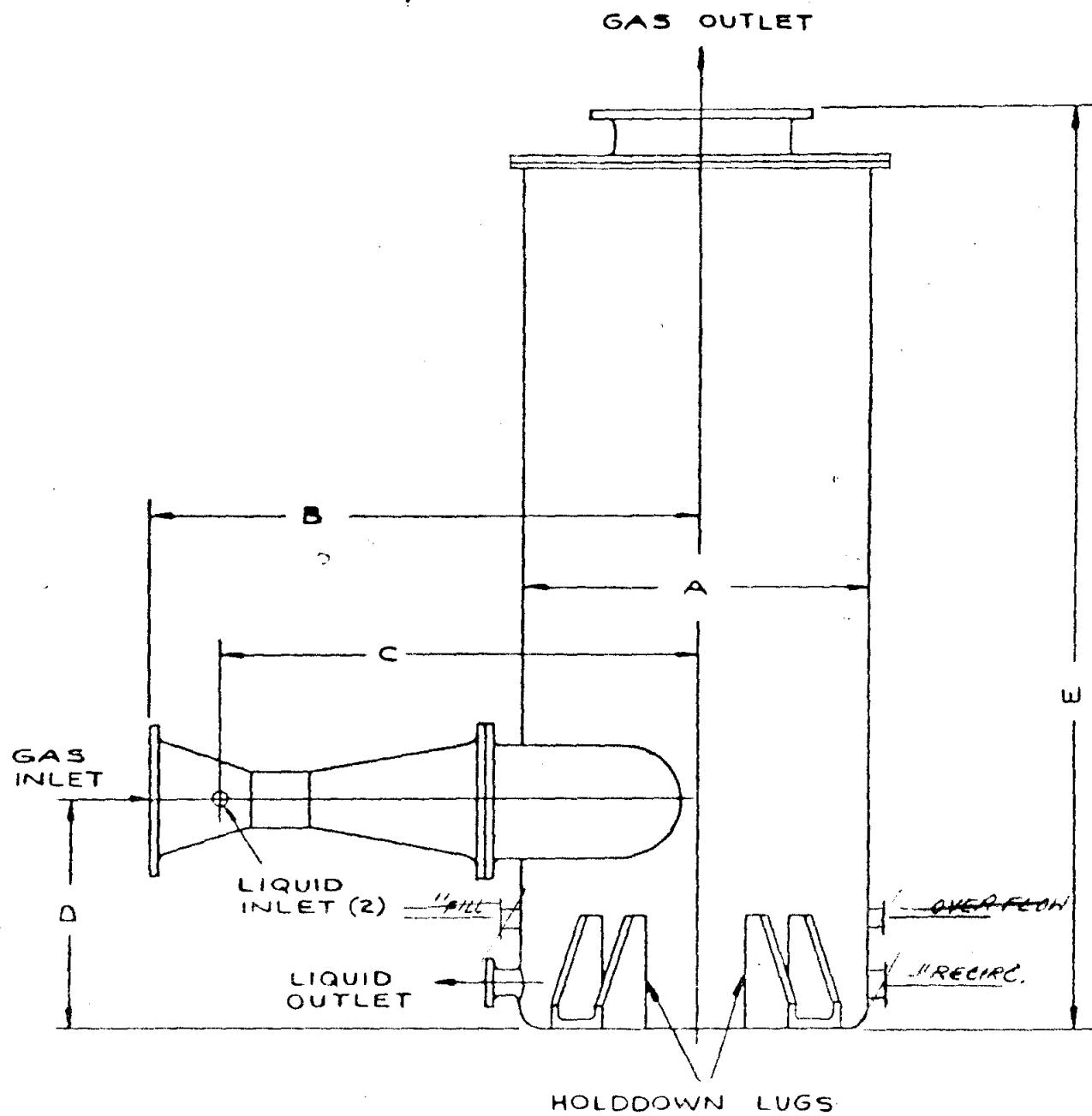
Gas Flow	10-35 scfm 20-23 scfm (average)
Gas Temperature	110-140°F
Gas Pressure	3 psig (average), 15 psig (maximum)
Barometric Pressure	580 mm Hg (average)
Upstream Pipe Interface	4 in. schedule 40
Downstream Pipe Interface	4 in. schedule 40
Liquid/Gas Ratio Range	10:1 to 35:1
Liquid Injection Method	Jets — Drop Atomization
Scrubbing Liquid	Caustic or amine solutions with some inorganic salts present and moderate to high levels of ammonia.
Gas BTU Content	130-175 BTU/SCF 30 BTU/SCF

SPECIAL FEATURES

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Couplings between the scrubber and the separator of a standard pipe size and thread such that the venturi can be placed in different physical relationship to the separator.

- Seal antisealer
- Efficiency for particle size $\sim 25\mu$, $\beta = 95\%$ what conditions are the dynamical for?
- Jets - atomization
- Mist Eliminator
- Material of construction



CONNECTIONS	SIZE	LETTER	DIMENSIONS
GAS INLET	2"	A	6"
GAS OUTLET	2"	B	1'-6"
LIQUID INLET	1"	C	1'-4"
LIQUID OUTLET	1"	D	8"
MANWAY		E	4'-6"

22-6 HE
 ALL DIMENSIONS ARE APPROXIMATE
CROLL-REYNOLDS COMPANY, INC.
 WESTFIELD, N.J.

PROPOSED LAYOUT OF VENTURI FUME SCRUBBER
 SCALE: 1" = 1'

**CROLL-REYNOLDS
HIGH ENERGY
SCRUBBER SYSTEM**

O: Western Research Institute
University of Wyo. Res. Corp.

MODEL NO.: 22-64E

QUANTITY: One

PRICE PER SYSTEM: 2640

F.O.B.: shops - Teterboro, NJ

TERMS: Net 30

ESTIMATED DELIVERY:

10 Weeks after drawing approval
Weeks for drawings

ITEM IN STOCK DELIVERY:

Weeks after receipt of order

Deliveries are quoted based on standard shop schedules at the time of quote. Special delivery requirements may be accommodated on an individual basis.

COMMENTS:

Since Croll-Reynolds Co. has no control over the mixture or concentration of corrosive elements which may come in contact with the equipment supplied, no guarantee is expressed or implied concerning materials of construction for corrosion resistance.

Customer should make every effort to assure suitability prior to purchase.

Proposal by: M. A. Holman

Date: 10/3/83

SPECIFICATIONS

DIMENSIONS

Gas Inlet/Outlet: 2", 2"
Scrubbing Liquid Inlet: ½"
Separator Tank: Not Included Included
Tank Diameter: 6" Tank Height: 4'-6"
Liquid Storage: YES NO Capacity _____ Gallons
Tank Connections: Drain 1", Fill _____, Overflow _____
Manway: None
Separator Type: mesh mist elim.
Other: _____

MATERIALS OF CONSTRUCTION

ITEM	MATERIAL
Venturi:	316 L S.S.
Separator:	same
Spray Nozzles:	316 S.S.

APPROXIMATE WEIGHT

Shipping: _____ Operating: _____

CONSTRUCTION DESIGN

In general accordance with:

PS 15-69 ASME Code ASME Code Stamped
or vessel designed for pressure/vacuum 15 psig / _____
Wall Thicknesses: ⅛" min.
Head Thicknesses Bottom/Top ⅛" min., ⅛" min.
Hold down lugs Included Not included
Lifting lugs Included Not included

OPERATING CONDITIONS

Gas Inlet Rate Capacity: 10 - 35 acfm

Gas Inlet Temperature: 110 - 140°F

Pressure: 3 - 15 psig (1 atm = 580 mm Hg)

Gas Composition: gas containing hydrocarbon
particulate & mist

Liquid Inlet Rate: 0.6 gpm

Pressure at Liquid Inlet: 15 psig

x Specific Gravity: water

Liquid Composition: water

Maximum Liquid Temperature: 100°F

Pressure Drop Across System: 3 psig (inches) W.G.

PERFORMANCE DATA

95	% Removal efficiency of 0.75 micron particulate
	% Removal efficiency of _____

Based upon above operating conditions