2.16. PREDICTION AND CORRELATION OF PHYSICAL PROPERTIES*

2.16.1. INTRODUCTION

Physical property values, sufficiently accurate for many engineering applications, can be estimated in the absence of reliable experimental data. The purpose of this section is to provide a set of recommended prediction methods for general engineering use. It is not intended to be a comprehensive review, and many additional methods are available in the literature. Methods recommended in this section were selected on the basis of accuracy, generality, and, in most cases, simplicity or ease of use. They generally correspond to the methods tested and given priority in the DIPPR 801 database project.[1]

Properties included in this subsection are divided into 10 categories: (1) physical constants including critical properties, normal melting and boiling points, acentric factor, radius of gyration, dipole moment, refractive index, and dielectric constant; (2) liquid and solid vapor pressure; (3) thermal properties including enthalpy and Gibbs energy of formation and ideal gas entropy; (4) latent enthalpies of vaporization, fusion, and sublimation; (5) heat capacities for ideal and real gases, liquids, and solids; (6) densities of gas, liquid, and solid phases; (7) gas and liquid viscosity; (8) gas and liquid thermal conductivity; (9) surface tension; and (10) flammability properties including flash point, flammability limits, and autoignition temperature. Each of the 10 subsections gives a definition of the properties and a description of one or more recommended prediction methods. Each description lists the type of method, its uncertainty, its limitations, and the expected uncertainty of the predicted value. A numerical example is also given to illustrate use of the method. For brevity, symbols used for physical properties and for variables and constants in the equations are defined under Nomenclature and are not necessarily defined after their first use except where doing so clarifies usage. A list of equation and table numbers in which variables appear is included in the Nomenclature section for quick cross-referencing. Although emphasis is on pure-component properties, some mixture estimation techniques have been included for physical constants, density, viscosity, thermal conductivity, surface tension, and flammability. Correlation and estimation of properties that are inherently multicomponent (e.g., diffusion coefficients, mixture excess properties, activity coefficients) are treated elsewhere in this handbook.

2.16.2. UNITS

The International System (SI) of metric units has been used throughout this section. Where possible, the estimation equations are set up in dimensionless groups to eliminate the need to specify units of variables and to facilitate unit conversions. For example, rather than use P_c as an equation variable, the dimensionless group (P_c/Pa) is used. When a value for P_c expressed in any units (say, P_c = 6.53 MPa) is inserted into this group, the result is dimensionless with an explicit indication of conversion factors that must be included, such as

$$\frac{P_c}{\mathrm{Pa}} = \frac{6.53\,\mathrm{MPa}}{\mathrm{Pa}} = \left(\frac{6.53\,\mathrm{MPa}}{\mathrm{Pa}}\right)\left(\frac{10^6\mathrm{Pa}}{\mathrm{MPa}}\right) = 6.53 \times 10^6$$

Appropriate unit conversion factors are found in Sec. 1 of this handbook.

Nomenclature

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Physical constants	Definition	Value
h	Planck's constant	6.626×10^{-34} J · s
k	Boltzmann's constant	1.3806×10^{-23} J/(molecule · K)
N_A	Avogadro's number	6.022×10^{26} molecule/kmol
R	Gas constant	8314.3 Pa · m^3/(kmol · K)
Properties	**Definition**	**Typical units**
A, B, C	Molecular principal moments of inertia	kg · m^2
AIT	Autoignition temperature	K
A_{vdw}	Van der Waals area	m^2/kmol
$B, B(T)$	Second virial coefficient	m^3/kmol
C_P	Isobaric molar heat capacity	J/(kmol · K)
C_p^o	Ideal gas isobaric molar heat capacity	J/(kmol · K)
C_v	Constant-volume molar heat capacity	J/(kmol · K)
H_i	Enthalpy of compound i	J/kmol
k	Thermal conductivity	W/(m · K)
LFL	Lower flammability limit	%
M	Molecular weight	kg/kmol
n	Refractive index	unitless
P	Pressure	Pa
P	Parachor	unitless
P_c	Critical pressure	Pa
P_r	Reduced pressure; $P_r = P/P_c$	unitless
P^*	Vapor pressure	Pa
P^*_{meas}	Measured vapor pressure value	Pa
P_r^*	Reduced vapor pressure; $P_r^* = P^*/P_c$	unitless
P_t^*	Vapor pressure at triple point	Pa
R_D	Molar refraction	cm^3/mol

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Physical constants	Definition	Value
R_g	Radius of gyration	m
S^o	Ideal gas entropy	J/(kmol · K)
S^s	Standard state entropy	J/(kmol · K)
S_r	Rotational contribution to entropy	J/(kmol · K)
S_{vib}	Vibrational contribution to entropy	J/(kmol · K)
T	Temperature	K
T_{ad}	Adiabatic flame temperature	K
T_b	Normal boiling point temperature	K
T_{br}	Reduced temperature at T_b; $T_{br} = T_b/T_c$	unitless
T_c	Critical temperature	K
T_{FP}	Flash point temperature	K
T_m	Melting temperature	K
T_{meas}	T at which a dependent property was measured	K
T_r	Reduced temperature; $T_r = T/T_c$	unitless
UFL	Upper flammability limit	%
V	Molar volume	m^3/kmol
V_c	Critical volume	m^3/kmol
V_r	Reduced volume; $V_r = ZT_r/P_r$	unitless
w_i	Mass fraction of component i	unitless
x_i	Mole fraction of component i	unitless
y_i	Mole fraction of component i in vapor phase	unitless
Z	Compressibility factor; $Z = PV/RT$	unitless
Z_c	Critical compressibility factor; $Z_c = P_cV_c/RT_c$	unitless
Z_i	Compressibility factor of reference fluid i	unitless
ΔG_f^o	Ideal gas standard Gibbs energy of formation	J/kmol
ΔG_f^s	Standard state Gibbs energy of formation	J/kmol

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Physical constants	Definition	Value
ΔH_f^o	Ideal gas standard enthalpy of formation	J/kmol
ΔH_f^s	Standard state enthalpy of formation	J/kmol
ΔH_{fus}	Enthalpy of fusion	J/kmol
ΔH_{rxn}	Enthalpy change per mole of reaction as written	J/kmol
ΔH_{sub}	Enthalpy of sublimation	J/kmol
ΔH_u	Enthalpy of vaporization	J/kmol
ΔS_f^s	Standard state entropy of formation	J/(kmol · K)
ΔS_f^o	Ideal gas entropy of formation	J/(kmol · K)
ΔS_{fus}	Latent entropy of fusion	J/(kmol · K)
ΔZ_v	Change in compressibility factor upon vaporization	unitless
δ	Solubility parameter	$J^{1/2} \cdot m^{-3/2}$
ε	Dielectric constant	unitless
η	Viscosity	Pa · s
η^o	Viscosity at low pressure	Pa · s
μ	Dipole moment	D
μ_r	Reduced dipole moment [defined in Eq. (2-66)]	unitless
ρ	Molar density; $\rho = V^{-1}$	$kmol/m^3$
ρ_c	Critical molar density; $\rho_c = V_c^{-1}$	$kmol/m^3$
ρ_r	Reduced molar density; $\rho_r = \rho/\rho_c$	unitless
ρ_S, ρ_L, ρ_V	Density of solid, liquid, vapor, respectively	$kmol/m^3$
σ	Surface tension	mN/m
σ_m	Surface tension of mixture	mN/m
τ	Complementary reduced temperature $(1 - T_r)$	unitless
τ_b	τ at the normal boiling point $(1 - T_{br})$	unitless
ϕ_i	Volume fraction of component i	unitless
ω	Acentric factor	unitless

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Physical constants	Definition	Value
Equation variables	**Definition**	**Appears in (Eq. 2-?) or [Table 2-?]**
a	EoS constant	(70), [172]
$a, b, c, \ldots$	GC values for C_p and η	(54), (57), (96), [174]
a, b, c	Correlation coefficients	(25), (27), (42), (43), (44), (69)
a_i	GC values	(46), (96), [164], [174]
a, b	Terms in second virial correlation	(65)
a, b	Chickos correlation parameters	(42), (43), (44)
a_i, b_i, d_i	GC values for liquid C_p	(54), [166]
$a\alpha$	EoS constant for mixture	(78)
$A, B, C, \ldots$	Correlation constants/parameters	(2), (23), (24), (26), (28), (28a), (38), (40), (53), (54), (56), (69), (71), (82), (84), (86), (87), (94), (95), (100), (101), (102)
A	Factor in liquid k correlation	(110), [176]
A_i	Constants in C_p^o correlation	(48), (49), (70)
b	EoS constant	(70), [172]
$b_i, c_i, \ldots$	Reference EoS constants	(69), [171]
b_i	GC value for AIT	(129), [180]
$\bar{b}$	EoS constant for mixture	(77)
$B^{(i)}$	Second virial expansion term	(62), (63), (64), (65)
C	Number of components in mixture	(74), (75), (76), (77), (78), (79), (80), (81), (98)
C	Parameter in modified Pachaiyappan method	(109)
C_i	GC values for some methods	(9), (10), (11), (18), (86), [175], [173]
C_{ij}	Group-group intramolecular interaction pair	(12), [156]
$(C^o{}_p)_i$	GC values for ideal gas heat capacity	(52), [165]
Cs_j	Chickos GC value for C—H group	(44), [162]
C_{st}	Fuel concentration for stoichiometric combustion	(127), (128)
Ct_j	Chickos GC value for functional group	(44), [163]

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Physical constants	Definition	Value
f_i	Halogen correction for ΔH_{sub} correlation	(46), [164]
$F^{(i)}$	Vapor pressure deviation function	(29)
F	Factor in surface tension equation	(118), (119)
GI	Group-group interaction correction term	(9), (10), (11), (12)
G_{ij}	Adjustable mixture viscosity parameter	(97)
g^E_c	UNIFAC combinatorial excess Gibbs energy	(98)
g^E_r	UNIFAC residual excess Gibbs energy	(98)
h	Parameter in Riedel vapor pressure equation	(28a)
K	Parameter in Riedel vapor pressure equation	(28a)
m	Parameter in modified Pachaiyappan method	(109)
n_{hvy}	Number of non-hydrogen atoms	(11), (12), (18)
n_A	Number of atoms in the molecule	(1), (34), (35), (51)
n_E	Number of occurrences of element E in compound	(58)
NG	Number of interacting groups	(12)
n_i	Number of occurrences of group i	(9), (10), (11), (13), (15), (16), (31), (46), (52), (54), (55), (86), (117), (124), (127), (129)
n_f	Number of different functional groups	(44)
n_s	Number of C—H groups bonded to functional groups	(44)
n_x	Number of halogen and H atoms	(46)
N	Total number of groups in molecule	(18), (31) (46), (54), (57), (58), (86), (96), (117), (124), (127), (129)
N_C	Number of C atoms	(123)
Nf_i	Number of functional groups of type i	(44)
Ng_i	Number of C—H groups of type i bonded to C	(44)
N_H	Number of H atoms	(123)
N_{CR}	Number of CH_2 groups forming cyclic paraffin	(43)
N_O	Number of O atoms	(123)

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Physical constants	Definition	Value
N_R	Number of nonaromatic rings	(43)
N_S	Number of S atoms	(123)
Ns_i	Number of C—H groups bonded to functional group	(44)
N_{Si}	Number of Si atoms	(123)
N_X	Number of halogen atoms	(123)
$\overline{P}_c$	Pseudocritical pressure for mixture	(75)
q	Rackett equation power for Z_c	(72), (80)
q_i	UNIFAC molecular surface area	following (99)
Q_k	UNIFAC group surface area	following (99)
r_i	UNIFAC molecular volume	following (99)
r^*	Dimensionless separation distance	(4)
R_k	UNIFAC group volume	following (99)
$(S^o)_i$	GC value for entropy	(31), [161]
t	Total number of functional groups	(44)
$t_{m1,i}$	First-order GC contribution for T_m	(16), [158]
$t_{m2,i}$	Second-order GC contribution for T_m	(16), [159]
$\overline{T}_c$	Pseudocritical temperature for mixture	(74), (75), (79)
$T_{c,ij}$	Cross term in mixing rule	(79)
x_P	Term in the Pailhes method [= log(1 atm/ P)]	(17)
U^*	Dimensionless intermolecular potential	(4)
UFL_i	GC contribution	(127), [178]
$Z^{(0)}$	Compressibility factor of simple fluid	(68), [169]
$Z^{(1)}$	Acentric deviation term for Z	(68), [170]
$Z_{c,ij}$	Cross term in mixing rule	(79)
Z_{RA}	Modified Rackett correlation parameter	following (72)
$\overline{Z}_{RA}$	Modified Rackett parameter for mixture	(80), (81)

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Physical constants	Definition	Value
$\alpha, \beta, \gamma, \ldots$	Correlation parameters for k	(107), (108), (110), [176]
$\alpha(T_r)$	EoS temperature-dependent function	(70), [172]
α_c	Parameter in Riedel vapor pressure equation	(28a)
α_{mn}	Viscosity group-group interactions	(99), [175]
β	Reference EoS constant	(69), [171]
β	Stoichiometric coefficient for combustion	(122), (123), (128)
β_i	Nonlinear correction term in correlation	(46), (57), [164], [167]
γ	Reference EoS constant	(69), [171]
δ	= 0 for nonlinear molecules; = 1 for linear	(1), (35), before (50), (51)
δ	EoS parameter	(70), [172]
Δ_E	Contribution of element E to heat capacity	(58), [168]
Δ_P	GC contribution to P_c	(7), [154]
Δ_T	GC contribution to T_c	(6), [154]
Δ_V	GC contribution to V_c	(8), [154]
$(\Delta H_f^o)_i$	GC value for enthalpy of formation	(31), [161]
$\Delta \mathbf{P}_i$	GC for Parachor	(117), [177]
Δpc_i	Group i contribution to critical pressure	(15)
Δs_i	GC value for group i	(44), [162, 163]
$\Delta T_{ad,i}$	Group i contribution to adiabatic flame temperature	(124)
Δtc_i	Group i contribution to critical temperature	(13)
ε	Lennard-Jones well depth parameter	following (4)
ε	EoS parameter	(70), [172]
ϕ	UNIFAC molecular volume fraction	following (99)
ν	LFL enthalpic term	(126)
ν_i	Stoichiometric coefficient (+ for product and − for reactant) for compound i in reaction	(32), (33), (34)

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Physical constants	Definition	Value
ν_j	Frequency of vibrational mode *j*	(50)
θ	UNIFAC molecular surface fraction	following (99)
Θ	UNIFAC group surface fraction	following (99)
Θ_A, Θ_B, Θ_C	Characteristic rotational *T* of molecule	before and following (35)
Θ_j	Characteristic vibrational *T* of mode *j*	(1), (35)
σ	Lennard-Jones size parameter	following (4)
σ	Rotational external symmetry number	following (35)
μ_r^*	Modified reduced dipole moment	(84), (85)
ψ	Parameter in Riedel vapor pressure equation	(28a)
ψ	Parameter in correlation of *k* for gases	(106), (107)
ψ_{mn}	UNIFAC interaction factor	(99)
ξ	Viscosity de-dimensionalizing factor	(88), (89), (90), (91), (92), (93)
$\bar{\omega}$	Pseudo-acentric factor for mixture	(76)

Acronyms and abbreviations	Definition
CC	Computational chemistry
CS	Corresponding states
DIPPR	Design Institute for Physical Properties
EoS	Equation of state
GC	Group contributions
LJ	Lennard-Jones
MC	Monte Carlo
MD	Molecular dynamics
QSPR	Quantitative structure-property relationships

2.16.3. GENERAL REFERENCES

2.16.3.1. Prediction Methods

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[PGL5] Poling, B. E., J. M. Prausnitz, and J. P. O'Connell, *The Properties of Gases and Liquids,* 5th ed., McGraw-Hill, New York, 2001.

2.16.3.2. Property Databases

[DIPPR] Rowley, R. L., et al., *DIPPR Data Compilation of Pure Chemicals Properties,* Design Institute for Physical Properties, AIChE, New York, 2007.

[TRC] *TRC Thermodynamic Tables—Non-Hydrocarbons,* Thermodynamics Research Center, The Texas A&M University System, College Station, Tex., extant 2004; *TRC Thermodynamic Tables—Hydrocarbons,* Thermodynamics Research Center, The Texas A&M University System, College Station, Tex., extant 2004.

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[SWS] Stull, D. R., F. F. Westrum, Jr., and G. C. Sinke,*The Chemical Thermodynamics of Organic Compounds*, John Wiley & Sons, New York, 1969.

[TDS] Daubert, T. E., and R. P. Danner, *Technical Data Book—Petroleum Refining,* 5th ed., American Petroleum Institute, Washington, extant 1994.

2.16.4. CLASSIFICATION OF ESTIMATION METHODS

Physical property estimation methods may be classified into six general areas: (1) theory and empirical extension of theory, (2) corresponding states, (3) group contributions, (4) computational chemistry, (5) empirical and quantitative structure-property relations (QSPR) correlations, and (6) molecular simulation. A quick overview of each class is given below to provide context for the methods and to define the general assumptions, accuracies, and limitations inherent in each.

Theory and Empirical Extension of Theory Methods based on theory generally provide better extrapolation capability than empirical fits of experimental data. Assumptions required to simplify the theory to a manageable equation suggest accuracy limitations and possible improvements, if necessary. For example, the ideal gas isobaric heat capacity, rigorously obtained from statistical mechanics under the assumption of independent harmonic vibrational modes, is (Rowley, R. L., *Statistical Mechanics for Thermophysical Property Calculations*, Prentice-Hall, Englewood Cliffs, N.J., 1994)

$$\frac{C_p^o}{R} = \frac{8-\delta}{2} + \sum_{j=1}^{3n_A-6+\delta} \left(\frac{\Theta_j}{T}\right)^2 \frac{e^{\Theta_j/T}}{\left(e^{\Theta_j/T}-1\right)^2}$$

$$\delta = \begin{cases} 0 & \text{nonlinear molecules} \\ 1 & \text{linear molecules} \end{cases}$$

(2-1)

where Θ_j is the characteristic temperature for the jth vibrational frequency in a molecule of n_A atoms. The temperature dependence of this equation is exact to the extent that the frequencies are harmonic.

Extension of theory often requires introduction of empirical models and parameters in lieu of terms that cannot be rigorously calculated. Good accuracy is expected in the region where the model parameters were fitted to experimental data, but only

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limited accuracy when an empirical model is extrapolated to other conditions. For example, a simplified theory suggests that vapor pressure should have the form

$$\ln P^* = A - \frac{B}{T}$$

(2-2)

where the empirical parameter B is given by

$$B = \frac{\Delta H_v}{R \Delta Z_v}$$

(2-3)

and ΔH_υ and ΔZ_υ are differences between the vapor and liquid enthalpies and compressibility factors, respectively. Equation (2-2) can be used to correlate vapor pressures over a moderate temperature range, but it is inadequate to represent vapor pressures over the whole liquid temperature range because ΔH_υ also varies with temperature.

Corresponding States (CS) The principle of CS applies to conformal fluids [Leland, T. L., Jr., and P. S. Chappelear,*Ind. Eng. Chem.*, **60** (1968): 15]. Two fluids are conformal if their intermolecular interactions are equivalent when scaled in dimensionless form. For example, the Lennard-Jones (LJ) intermolecular pair potential energy U can be written in dimensionless form as

$$U^* = 4\left(r^{*-12} - r^{*-6}\right)$$

(2-4)

where $r^* = r/\sigma$, $U^* = U/\varepsilon$, σ is the LJ size parameter, and ε is the LJ attractive well depth parameter. At equivalent scaled temperatures kT/ε (k is Boltzmann's constant) and pressures $P\sigma^3/\varepsilon$, all LJ fluids will have identical dimensionless properties because the molecules interact through the identical scaled intermolecular potential given by Eq. (2-4). Generalization of this scaling principle is commonly done using critical temperature T_c and critical pressure P_c as scaling factors. At the same reduced coordinates ($T_r = T/T_c$ and $P_r = P/P_c$) conformal fluids will have the same dimensionless properties. For example, $Z = Z(T_r, P_r)$ where the compressibility factor is defined as $Z = PV/RT$. A correlation of experimental data for one fluid can then be used as the reference for the properties of all conformal fluids. Nonconformality is the main accuracy limitation. For instance, interactions between nonspherical or polar molecules are not adequately represented by Eq. (2-4), and so the scaled properties of these fluids will not conform to those of a fluid with interactions well represented by Eq. (2-4). A correction for nonconformality is usually made by the addition of one or more reference fluids whose deviations from the first reference fluid are used to characterize the effect of nonconformality. For example, in the Lee-Kesler method [Lee, B. I., and M. G. Kesler, *AIChE J.*, **21** (1975): 510] *n*-octane is used as a second, nonspherical reference fluid, and deviations of *n*-octane scaled properties from those of the spherical reference fluid at equivalent reduced conditions are assumed to be a linear function of the acentric factor.

Group Contributions (GCs) Physical properties generally correlate well with molecular structure. GC methods assume a summative behavior of the structural groups of the constituent molecules. For example, ethanol ($CH_3—CH_2—OH$) properties would be obtained as the sum of contributions from the $—CH_3$, $—CH_2$, and —OH groups. The contribution of each group is obtained by regression of experimental data that include as many different compounds containing that group as possible. Structural groups must be used exactly as defined in the original correlation of the groups. A general principle when parsing a structure into constituent groups is that the more specific the group, the higher its priority. For example, the structural piece —

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$COOCH_3$ in a methyl ester could be divided in more than one way, but if the —COO— and $-CH_3$ groups are available in the method, then they should be used rather than the combination of the two less specific groups $-(C=O)-$ and —O—. These latter group values were most likely regressed only from ketone and ether data, respectively. Excellent accuracy can usually be expected from GC methods in which the group values were regressed from large quantities of experimental data. However, if the ratio of the number of groups to regressed experimental data is large, significant errors can result when the method is applied to new compounds (extrapolation). Such excessive specificity in the group definitions leads to poor extrapolation capabilities even though the fit of the regressed data may have been excellent.

First-order GC methods assume simple summations of the group values are adequate to represent the molecular value. Second-order effects, caused by steric and electron induction effects from neighboring groups, can alter group values. Second-order GC methods require considerably more experimental data to tune the method, and large tables of group values are required because differences in bonded neighbors require separate groups.

Computational Chemistry (CC) Commercial software is available that solves the Schrödinger equation by using approximate forms of the wave function. Various levels of sophistication (termed *model chemistry*) for the wave function can be chosen at the expense of computational time. Results include structural information (bond lengths, bond angles, dihedral angles, etc.), electron/charge distribution information, internal vibrational modes (for ideal gas properties), and energy of the molecule, valid for the chosen model chemistry. Because calculations are usually performed on individual molecules, the results are best suited for ideal gas properties. Relative energies for the same model chemistry are more accurately obtained than absolute energies, so enthalpies and entropies of reaction are also common industrial uses of CC predictions.

Empirical QSPR Correlations Quantitative structure-property relationship (QSPR) methods correlate physical properties with molecular descriptors that characterize the structural and electronic character of the molecule. Large amounts of experimental data are used to statistically determine the most significant descriptors to be used in the correlation and their contributions. The resultant correlations are simple to apply if the descriptors are available. Descriptors must be generated by the user with computational chemistry software or obtained from some tabulation. QSPR methods are often very accurate for specific families of compounds for which the correlation was developed, but extrapolation to other families generally results in considerable loss of accuracy.

Molecular Simulations Molecular simulations are useful for predicting properties of bulk fluids and solids. Molecular dynamics (MD) simulations solve Newton's equations of motion for a small number (on the order of 10^3) of molecules to obtain the time evolution of the system. MD methods can be used for equilibrium and transport properties. Monte Carlo (MC) simulations use a model for the potential energy between molecules to simulate configurations of the molecules in proportion to their probability of occurrence. Statistical averages of MC configurations are useful for equilibrium properties, particularly for saturated densities, vapor pressures, etc. Property estimations using molecular simulation techniques are not illustrated in the remainder of this section as commercial software implementations are not commonly available.

2.16.5. PHYSICAL CONSTANTS

Critical Properties The critical temperature T_c, pressure P_c, and volume V_c of a compound are important, widely used constants. They are important in determining the phase boundaries of a compound and (particularly T_c and P_c) are required input parameters for many property estimation methods, particularly CS methods.

The critical temperature of a compound is the temperature above which a liquid phase cannot be formed, regardless of the system pressure. The critical pressure is the vapor pressure of the compound at the critical temperature. The molar critical volume is the volume occupied by 1 mol of a chemical at its critical temperature and pressure. The critical compressibility factor Z_c is determined from the experimental or predicted values of the critical properties by its definition

$$Z_c = \frac{P_c V_c}{R T_c}$$

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(2-5)

Recommended Methods The Ambrose method is recommended for all three critical properties of hydrocarbons and *n*-alcohols. The Nannoolal method is recommended for all three critical properties of all other organic molecules. The Wilson-Jasperson method is a simple method also recommended for estimating T_c and P_c for organic and some inorganic chemicals. The first-order Wilson-Jasperson method often gives better results than the second-order method except strongly polar, hydrogen-bonding, and associating fluids.

Method: Ambrose method.

Reference: Ambrose, D., *Natl. Phys. Lab. Report Chem.* **92** (1978); *Natl. Phys. Lab Report Chem.* **98** (1979).

Classification: Group contributions.

Expected uncertainty: ~6 K for T_c (about 1 percent), ~2 bar for P_c (about 5 percent), ~8 cm^3/mol for V_c (about 3 percent).

Applicability: Organic compounds.

Input data: T_b, M, group contributions Δ_T, Δ_P, and Δ_V from Table 2-154.

Table 2-154 Ambrose Group[a] Contributions for Critical Constants

Group	Δ_T	Δ_P	Δ_V
Carbon atoms in alkyl groups	0.138	0.226	55.1
Corrections			
>CH— (each)	−0.043	−0.006	−8
>C< (each)	−0.120	−0.030	−17
Double bonds (nonaromatic)	−0.050	−0.065	−20
Triple bonds	−0.200	−0.170	−40
Delta Platt number,[b] multiply by	−0.023	−0.026	—
Aliphatic functional groups:			
—O—	0.138	0.160	20
>CO	0.220	0.282	60
—CHO	0.220	0.220	55
—COOH	0.578	0.450	80
—CO—O—OC—	1.156	0.900	160
—CO—O—	0.330	0.470	80
—NO_2—	0.370	0.420	78

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Group	Δ	Δ	Δ
—NH_2	0.208	0.095	30
—NH—	0.208	0.135	30
>N—	0.088	0.170	30
—CN	0.423	0.360	80
—S—	0.105	0.270	55
—SH	0.090	0.270	55
—SiH_3	0.200	0.460	119
—O—$Si(CH_3)_2$	0.496	—	—
—F	0.055	0.223	14
—Cl	0.055	0.318	45
—Br	0.055	0.500	67
—I	0.055	—	90
Halogen correction in aliphatic compounds:			
F is present	0.125		
F is absent, but Cl, Br, I are present	0.055		
Aliphatic alcohols[c]	[d]	[e]	15
Ring compound increments (listed only when different from aliphatic values):			
—CH_2—, >CH—, >C<	0.090	0.182	44.5
>CH— in fused ring	0.030	0.182	44.5
Double bond	−0.030	—	−15
—O—	0.090	—	10
—NH—	0.090	—	—
—S—	0.090	—	30
Aromatic compounds:			
Benzene	0.448	0.924	[f]
Pyridine	0.448	0.850	
C_4H_4 (fused as in naphthalene)	0.220	0.515	

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Group	Δ	Δ	Δ
—F	0.080	0.183	
—Cl	0.080	0.318	
—Br	0.080	0.600	
—I	0.080	0.850	
—OH	0.198	−0.025	
Corrections for nonhalogenated substitutions:			
First	0.010	0	
Each subsequent	0.030	0.020	
Ortho pairs containing —OH	−0.080	−0.050	
Ortho pairs with no —OH	−0.040	−0.050	
Highly fluorinated aliphatic compounds:			
$—CF_3$, $—CF_2—$, >CF—	0.200	0.550	
$—CF_2—$, >CF— (ring)	0.140	0.420	
>CF— (in fused ring)	0.030	—	
—H (monosubstitution)	−0.050	−0.350	
Double bond (nonring)	−0.150	−0.500	
Double bond (ring)	−0.030	—	
(other increments as in nonfluorina ted compounds)			

[a]Ambrose, D., Correlation and Estimation of Vapour-Liquid Critical Properties. I. Critical Temperatures of Organic Compounds, *Natl. Phys. Lab Report Chem.* **92** (1978); Correlation and Estimation of Vapour-Liquid Critical Properties. II. Critical Pressures and Volumes of Organic Compounds, *Natl. Phys. Lab Report Chem.* **98** (1979).

[b]The delta Platt number is defined as the Platt number of the isomer minus the Platt number of the corresponding alkane. (For *n*-alkanes the Platt number is $n - 3$.) The Platt number is the total number of groups of four carbon atoms three bonds apart [Platt, J. R., *J. Chem. Phys.*, **15**(1947): 419; **56**(1952): 328]. This correction is used only for branched alkanes.

[c]Includes naphthenic alcohols and glycols but not aromatic alcohols such as xylenol.

[d]First determine the hydrocarbon homomorph, i.e., substitute $—CH_3$ for each —OH and calculate $\Sigma\Delta_T$ for this compound. Subtract 0.138 from $\Sigma\Delta_T$ for each —OH substituted. Next, add $0.87 - 0.11n + 0.003n^2$ where $n = [T_b/\text{K (alcohol)} - 314]/19.2$. Exceptions include methanol ($\Sigma\Delta_T = 0$), ethanol ($\Sigma\Delta_T = 0.939$), and any alcohol whose value of n exceeds 10.

[e]Determine the hydrocarbon homomorph as in footnote *d*. Calculate $\Sigma\Delta_p$ and subtract 0.226 for each —OH substituted. Add $0.100 - 0.013n$, where n is computed as in footnote *d*.

[f]When estimating the critical volumes of aromatic substances, use ring compound values, if available, and correct for double bonds.

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Description: A GC method with first-order contributions and corrections (delta Platt number) for branched alkanes. Variables T_c, P_c, and V_c are given by the following relations:

$$T_c = T_b \left[1 + \left(1.242 + \sum \Delta_T \right)^{-1} \right]$$

(2-6)

$$\frac{P_c}{\text{bar}} = \frac{M}{\text{kg/kmol}} \left(0.339 + \sum \Delta_P \right)^{-2}$$

(2-7)

$$\frac{V_c}{\text{cm}^3/\text{mol}} = 40 + \sum \Delta_V$$

(2-8)

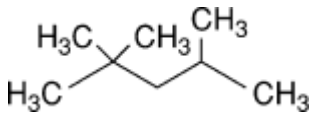
Example

Example

Use the Ambrose method to estimate the critical constants of 2,2,4-trimethylpentane.

Required data: From the DIPPR 801 database, T_b = 372.39 K and M = 114.229 kg/kmol.

Structure:



Group contributions from Table 2-154:

Group	n_i	Δ_T	Δ_P	Δ_V
Alkyl carbons	8	0.138	0.226	55.1
>CH— (correction)	1	−0.043	−0.006	−8
>C< (correction)	1	−0.120	−0.030	−17
Delta Platt no.	0	−0.023	−0.026	—

Calculations using Eqs. (2-6), (2-7), and (2-8):

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$$\sum \Delta_T = (8)\,(0.138) + (1)(-0.043) + (1)(-0.120) = 0.941$$
$$T_c = T_b(1.4581) = (372.39\ \mathrm{K})(1.4581) = 543.0\ \mathrm{K}$$
$$\sum \Delta_P = (8)(0.226) + (1)(-0.006) + (1)(-0.030) = 1.772$$

$$\frac{P_c}{\mathrm{bar}} = \frac{M}{\mathrm{kg/kmol}}\left(0.339 + \sum \Delta_P\right)^{-2} = \frac{114.229}{(0.339 + 1.772)^2} = 25.63 \qquad P_c = 25.63\,\mathrm{bar}$$

$$\sum \Delta_V = (8)(55.1) + (1)(-8) + (1)(-17) = 415.8$$
$$V_c = (40 + 415.8)\ \mathrm{cm^3/mol} = 455.8\ \mathrm{cm^3/mol}$$

Results:

Property	DIPPR recommended value	Ambrose estimation	% Difference
T_c/K	543.8	543.0	−0.15
P_c/bar	25.70	25.63	0.27
V_c/(cm^3/mol)	468.0	455.8	−2.6

Method: Nannoolal method.

Reference: Nannoolal, Y., J. Rarey, and D. Ramjugernath, *Fluid Phase Equilib.* **252** (2007): 1.

Classification: Group contributions.

Expected uncertainty: ~6 K or 1 percent for T_c; ~2 bar or 5 percent for P_c; ~8 cm^3/mol or 3 percent for V_c.

Applicability: Organic compounds.

Input data: T_b, group contributions C_i from Table 2-155, intramolecular group-group interactions C_{ij}, from Table 2-156, and the number of nonhydrogen atoms in the molecule n_{hvy}.

Table 2-155 Group Contributions for the Nannoolal et al. Method for Critical Constants[a] and Normal Boiling Point[b]

ID†	Group	Description	TC × 10^3	PC × 10^4	VC	NBP
1	CH_3—(ne)	CH_3— not connected to N, O, F, or Cl	41.8682	8.1620	28.7855	177.3066
2	CH_3—(e)	CH_3— connected to N, O, F, or Cl	33.1371	5.5262	28.8811	251.8338
3	CH_3—(a)	CH_3— connected to an aromatic atom (not necessarily C)	−1.0710	4.1660	26.7237	157.9527
4	—C(c)H_2—	—CH_2— in a chain	40.0977	5.2623	32.0493	239.4531

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ID†	Group	Description	TC × 10	PC × 10	VC	NBP
5	>C(c)H—	>CH— in a chain	30.2069	2.3009	32.1108	240.6785
6	>C(c)<	>C< in a chain	−3.8778	−2.9925	28.0534	249.5809
7	>C(c)<(e)	>C< in a chain connected to at least one F, Cl, N, or O	52.8003	3.4310	33.7577	266.8769
8	>C(c)<(Ca)	>C< in a chain connected to at least one aromatic carbon	9.4422	2.3665	28.8792	201.0115
9	—C(r)H_2—	—CH_2— in a ring	21.2898	3.4027	24.8517	239.4957
10	>C(r)H—	>CH— in a ring	26.3513	3.6162	30.9323	222.1163
11	>C(r)<	>C< in a ring	−17.0459	−5.1299	5.9550	209.9749
12	>C(r)<(e, c)	>C< in a ring; connected to at least one N, O, Cl, or F not in the ring	51.7974	4.1421	29.5901	250.9584
13	>C(r)<(e, r)	>C< in a ring connected to at least one N or O which is part of the ring	18.9549	0.8765	20.2325	492.0707
14	>C(r)<(Ca)	>C< in a ring connected to at least one aromatic carbon	−29.1568	−0.1320	10.5669	244.3581
15	═C(a)H—	aromatic ═CH—	16.1154	2.1064	19.4020	235.3462
16	═C(a)<(ne)	aromatic ═C< not connected to O, N, Cl, or F	68.2045	4.1826	25.0434	315.4128
17	═C(a)<(e)	aromatic ═C< connected to O, N, Cl, or F	68.1923	3.5500	5.6704	348.2779
18	(a) ═ C(a)<2(a)	aromatic ═C< with three aromatic neighbors	29.8039	1.0997	16.4118	367.9649
19	F—(C, Si)	F— connected to C or Si	15.6068	0.7328	−5.0331	106.5492
20	—CF═ C<	F— on a C═C (vinyl fluoride)	11.0757	4.3757	1.5646	49.2701
21	F—(C,Si)(F)(2b)	F— connected to C or Si substituted with at least one F and two other atoms	18.1302	3.4933	3.3646	53.1871
22	F—(C,Si)([F, Cl])(b)	F— connected to a C or Si substituted with one F or Cl and one other atom	19.1772	2.6558	1.0897	78.7578
23	F—(C,Si)([F, Cl]2)	F— connected to C or Si already substituted with two F or Cl atoms	20.8519	1.6547	1.1084	103.5672
24	F—(Ca)	F— connected to an aromatic carbon	−24.0220	0.5236	19.3190	−19.5575
25	Cl—(C,Si)	Cl— connected to C or Si not already substituted with F or Cl	−1.3329	−2.2611	22.0457	330.9117
26	Cl—(C,Si)([F, Cl])	Cl— connected to C or Si already substituted with one F or Cl	2.6113	−1.4992	23.9279	287.1863
27	Cl—(C, Si)([F, Cl]2)	Cl— connected to C or Si already substituted with at least two F or Cl	15.5010	0.4883	26.2582	267.4170
28	Cl—(Ca)	Cl— connected to aromatic C	−16.1905	−0.9280	36.7624	205.7363

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ID†	Group	Description	TC × 10	PC × 10	VC	NBP
29	—CCl═C<	Cl— on a C═C (vinyl chloride)	60.1907	11.8687	34.4110	292.5816
30	Br—(C,Si)	Br— connected to a nonaromatic C or Si	5.2621	−4.3170	36.0223	419.4959
31	Br—(Ca)	Br— connected to an aromatic C	−21.5199	−2.2409	30.7004	377.6775
32	I—(C, Si)	I— connected to C or Si	−8.6881	−4.7841	48.2989	556.3944
33	—OH *tert*	—OH connected to tertiary carbon	84.8567	−7.4244	10.6790	349.9409
34	HO—(C,Si) *sec*	—OH connected to secondary C or Si	79.3047	−4.4735	5.6645	390.2446
35	HO—(C,Si) long	—OH connected to primary C or Si; chain >4 C or Si	49.5968	−1.8153	2.0869	443.8712
36	HO—(C,Si) short	—OH connected to primary C or Si; chain <5 C or Si	130.1320	−6.8991	3.7778	488.0819
37	—OH (Ca)	—OH connected to an aromatic C (phenols)	14.0159	−12.1664	25.6584	361.4775
38	(C,Si)—O—(C,Si)	ether —O— connected to two C or Si	12.5082	2.0592	11.6284	146.4836
39	>(OC_2)<	>(OC_2)< (epoxide)	41.3490	0.1759	46.7680	820.7118
40	NH_2—(C, Si)	NH_2— connected to either C or Si	18.3404	−4.4164	13.2571	321.1759
41	NH_2—(Ca)	NH_2— connected to an aromatic C	−50.6419	−9.0065	73.7444	441.4388
42	(C,Si)—NH—(C,Si)	—NH— connected to two C or Si (secondary amine)	17.1780	−0.4086	20.5722	223.0992
43	(C,Si)2>N—(C,Si)	>N— connected to three C or Si (tertiary amine)	−0.5820	2.3625	6.0178	126.2952
44	COOH—(C)	—COOH connected to C	199.9042	3.9873	40.3909	1080.3139
45	(C)—COO—(C)	—COO— connected to two C (ester)	75.7089	4.3592	42.6733	636.2020
46	HCOO—(C)	HCOO— connected to C (formic acid ester)	58.0782	1.0266	36.1286	642.0427
47	—C(r)OO—	—COO— in ring, C is connected to C (lactone)	109.1930	0.4329		1142.6119
48	—CON<	—CON< disubstituted amide	102.1024	0.5172	64.3506	1052.6072
49	—CONH—	—CONH— (monosubstituted amide)				1364.5333
50	—$CONH_2$	—$CONH_2$ (amide)				1487.4109
51	O═C<(Can)2	—CO— connected to two nonaromatic C (ketones)	56.1572	0.1190	30.9229	618.9782
52	CHO—(Can)	CHO— connected to nonaromatic C (aldehydes)	44.2000	−2.3615	25.5034	553.8090
53	SH—(C)	—SH connected to C (thiols)	−7.1070	−9.4154	34.7699	434.0811
54	(C)—S—(C)	—S— connected to two C	0.5887	−8.2595	38.0185	461.5784

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ID†	Group	Description	TC × 10	PC × 10	VC	NBP
55	(C)—S—S—(C)	—S—S— (disulfide) connected to two C				864.5074
56	—S(a)—	—S— in an aromatic ring	−7.7181	−4.9259	20.3127	304.3321
57	(C)—C≡N	—C≡N (cyanide) connected to C	117.1330	5.1666	43.7983	719.2462
58	>C(c)═C(c)<	>C═C< (both C have at least one non-H neighbor)	45.1531	7.1581		475.7958
59	>C(c)═C(c)<(Ca)	noncyclic >C═C< connected to at least one aromatic C				586.1413
60	—(e)C(c)═C(c)<	noncyclic >C═C< with at least one F, Cl, N, or O	67.9821	−6.2791	51.0710	500.2434
61	H_2C(c)═C<	H_2C═C< (1-ene)	45.4406	9.6413	48.1957	412.6276
62	>C(r)═C(r)<	cyclic >C═C<	56.4059	3.4731	34.1240	475.9623
63	—C≡C—	—C≡C—	−19.9737	−2.2718	40.9263	512.2893
64	HC≡C—	HC≡C— (1-yne)	36.0883	2.4489	29.8612	422.2307
65	(Ca)—O(a)—(Ca)	—O—in an aromatic ring with aromatic C neighbors	10.4146	−0.5403	4.7476	37.1936
66	═N(a)—(r5)	aromatic —N— in a five-member ring, free electron pair	18.9903	8.3052	−25.3680	453.3397
67	═N(a)—(r6)	aromatic ═N— in a six-member ring	10.9495	−4.7101	23.6094	306.7139
68	NO_2—(C)	NO_2— connected to aliphatic C	82.6239	−5.0929	34.8472	866.5843
69	NO_2—(Ca)	NO_2— connected to aromatic C				821.4141
70	>Si<	>Si<	25.4209	5.7270	75.7193	282.0181
71	>Si<(O)	>Si< connected to at least one O	72.5587	2.7602	69.5645	207.9312
72	NO_3—	nitrate (esters of nitric acid)				920.3617
74	O═N—O—(C)	nitrites (esters of nitrous acid)				494.2668
76	—C═O—O—C═O—	anhydride connected to two C	164.3355	4.0458		1251.2675
77	COCl—	COCl— connected to C (acid chloride)				778.9151
78	>Si<(F,Cl)	>Si< connected to at least one F or Cl	157.3401	12.6786		540.0895
79	O═C(—O—)2	noncyclic carbonate	97.2830	0.2822	52.8789	879.7062
80	OCN—	OCN— connected to C or Si (cyanate)	153.7225		27.1026	660.4645
81	SCN—(C)	SCN— (thiocyanate) connected to C				1018.4865

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ID†	Group	Description	TC × 10	PC × 10	VC	NBP
82	(C)—SO_2—(C)	noncyclic sulfone connected to two C (sulfones)	90.9726	−23.9221	68.0701	1559.9840
83	(C)2>Sn<(C)2	>Sn< connected to four carbons	62.3642	0.7043		510.4223
87	>C═C═C<	cumulated double bond	53.6350	12.6128		664.0903
88	>C═C—C═C<(r)	conjugated double bond in a ring	24.7302	−10.2451	64.4616	957.6388
89	>C═C—C═C<(c)	conjugated double bond in a chain				928.9954
90	CHO—(Ca)	CHO— connected to aromatic C (aldehydes)	38.4681	−4.0133	20.0440	560.1024
91	(C,Si) ═N—	double-bonded amine connected to at least one C or Si				229.2288
92	(O═ C< (C)2)a	—CO— connected to two C with at least one aromatic C (ketones)	63.6504	−5.0403	28.7127	606.1797
93	>Si<(C,H)2	>Si< attached to two carbon or hydrogen	34.2058	3.2023	55.3822	
94	—O—O—	peroxide				273.1755
97	(C,Si)a—NH—(Ca,Si)a	—NH— connected to two C or Si, at least one aromatic (secondary amines)	27.3441	−4.3834	29.3068	201.3224
99	—OCON<	—CO connected to O and N (carbamate)				886.7613
100	>N—(C═O)—N<	—CO connected to two N (urea)				1045.0343
101	(C,Si)2>N<(C,Si)2	Quaternary amine connected to four C or Si				–109.6269
102	F—(C,Si)(Cl)(b)2	F— connected to C or Si with at least one Cl and two other atoms	1.3231	3.3971	1.3597	111.0590
103	—OCOO—	—CO connected to two O (carbonates)	764.9595	58.9190		1573.3769
104	>SO_4	S(═ O)$_2$ connected to two O (sulfates)				1483.1289
107	>S═O	sulfoxide				1379.4485
109	>N(C═O)	—CO connected to N				492.0707
111	(N)—C≡N	—C≡N (cyanide) connected to N				971.0365
113	>P<	phosphorus connected to at least 1 C or S (phosphine)				428.8911
115	—ON═(C,Si)	—ON═ connected to C or Si (isoazole)	36.0361	−5.1116	16.2688	612.9506
Corrections						
119	(C═O)—C([F,Cl]2,3)	carbonyl connected to C with two or more halogens	32.1829	7.3149	−3.8033	−82.2328

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ID†	Group	Description	TC × 10	PC × 10	VC	NBP
120	(C═O)—C([F,Cl]2,3)2	carbonyl connected to two C, each with at least two halogens	11.4437	4.1439	27.5326	–247.8893
121	C—[F,Cl]3	carbon with three halogens	−1.3023	0.4387	1.5807	−20.3996
122	(C)2—C—[F,Cl]2	secondary carbon with two halogens	−34.3037	−4.2678	−2.6235	15.4720
123	No hydrogen	component has no hydrogen	−1.3798	4.8944	−5.3091	–172.4201
124	One hydrogen	component has one hydrogen	−2.7180	2.8103	−6.1909	−99.8035
125	(3,4) ring	a three- or four-member nonaromatic ring	11.3251	−0.3035	3.2219	−62.3740
126	5-ring	a five-member nonaromatic ring	−4.7516	0.0930	−6.3900	−40.0058
127	*Ortho* pair(s)	*ortho*- position counted only once and only if no *meta* or *para* pairs	1.2823	0.7061	−3.5964	−27.2705
128	*Meta* pair(s)	*meta*- position counted only once and only if no *para* or *ortho* pairs	6.7099	−0.7246	1.5196	−3.5075
129	*Para* pair(s)	*para*- position counted only once and only if no *meta* or *ortho* pairs				16.1061
130	((C═)(C)C—CC3)	carbon with four carbon neighbors and one double-bonded carbon neighbor	−33.8201	−8.8457	−4.6483	25.8348
131	C2C—CC2	carbon with four carbon neighbors, two on each side	−18.4815	−2.2542	−5.0563	35.8330
132	C3C—CC2	carbon with five carbon neighbors	−23.6024	−3.2460	−6.3267	51.9098
133	C3C—CC3	carbon with six carbon neighbors	−24.5802	−5.3113	4.9392	111.8372
134	C═C—C═O	—C═O connected to sp^3 carbon	−35.6113	1.0934	2.8889	40.205

[a]Nannoolal, Y., et al., *Fluid Phase Equilib.* **252** (2007): 1.

[b]Nannoolal, Y., et al., *Fluid Phase Equilib.* **226** (2004): 45.

†Table-specific nomenclature: (e) = connected to N, O, F, Cl; (ne) = not connected to N, O, F, Cl; (r) = in a ring; (c) = in a chain; (a) = aromatic, not necessarily carbon; (Ca) = aromatic carbon; b = any nonhydrogen atom

Table 2-156 Intermolecular Interaction Corrections for the Nannoolal et al. Method for Critical Constants[a] and Normal Boiling Point[b]

	TC × 10^3	PC × 10^4	VC	NBP
—OH :: —OH	−434.8568	−5.6023		291.7985
—OH :: —COOH				146.7286
—OH :: —O—	−146.7881	7.3373	19.7707	135.3991

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	TC × 10	PC × 10	VC	NBP
—OH :: >(OC$_2$)<				226.4980
—OH :: —COOC—				211.6814
—OH :: —CO—				46.3754
—OH :: —O(a)—				435.0923
—OH :: —S(na)—				−74.0193
—OH :: —SH				38.6974
—OH :: —NH$_2$	120.9166	69.8200		314.6126
—OH :: >NH	−30.4354	6.1331	−8.0423	286.9698
—OH :: —CN				306.3979
—OH :: ═N(a)−(r6)				1334.6747
—OH(a) :: —OH(a)	144.4697	57.8350	97.5425	288.6155
—OH(a) :: —COOH				−1477.9671
—OH(a) :: —O—				130.3742
—OH(a) :: —COOC—				−1184.9784
—OH(a) :: —CHO				43.9722
—OH(a) :: —NH$_2$				797.4327
—OH(a) :: Nitrate				−1048.124
—OH(a) :: ═N(a)−(r6)				−614.3624
—COOH :: —COOH				117.2044
—COOH :: —O—				612.8821
—COOH :: —COOC—				−183.2986
—COOH :: —CO—				−55.9871
—O— :: —O—	162.6878	2.6751	−23.6366	91.4997
—O— :: >(OC$_2$)<	707.4116	88.8752	−329.5074	178.7845
—O— :: —COOC—	128.2740	−1.0295	−55.5112	322.5671
—O— :: —CO—				15.6980
—O— :: —CHO				17.0400

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	TC × 10	PC × 10	VC	NBP
—O— :: —O(a)—				329.0050
—O— :: —S(na)—	−654.1363	25.8246	−37.2468	394.5505
—O— :: —NH_2	−738.0515	−125.5983		124.3549
—O— :: >NH				101.8475
—O— :: —CN	741.8565			293.5974
—O— :: Nitrate				963.6518
>(OC_2)< :: >(OC_2)<				1006.388
>(OC_2)< :: —CO—				22.5208
>(OC_2)< :: —CHO				163.5475
—COOC— :: —COOC—	366.2663	0.5195	−74.8680	431.0990
—COOC— :: —CO—				22.5208
—COOC— :: —O(a)—				707.9404
—COOC— :: —NH_2				182.6291
—COOC— :: >NH				317.0200
—COOC— :: —CN				517.0677
—COOC— :: Nitrate				−205.6165
—CO— :: —CO—	1605.564	−78.2743	−413.3976	−303.9653
—CO— :: —CHO				−391.3690
—CO— :: —O(a)—				176.5481
—CO— :: —S(a)—				381.0107
—CO— :: >NH				−215.3532
—CO— :: —CN				−574.2230
—CO— :: Nitrate				−3628.903
—CO— :: ═N(a)−(r6)				124.1943
—CHO— :: —CHO—				562.1763
—CHO— :: —O(a)—				674.6858
—CHO— :: —S(a)—				397.575

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	TC × 10	PC × 10	VC	NBP
—CHO— :: Nitrate				140.9644
—O(a)— :: —NH_2				395.4093
—O(a)— :: ═N(a)—(r5)	24.0243	−35.1998	217.9243	−888.612
—S(na)— :: —S(na)—	−861.1528	43.9001	−403.1196	−11.9406
—S(na)— :: —NH_2				−562.306
—S(a)— :: —CN				−101.232
—S(a)— :: ═N(a)—(r5)	131.7924	−19.7033	164.2930	−348.740
—SH :: —SH				217.6360
—NH_2 :: —NH_2	−60.9217	−0.6754		174.0258
—NH_2 :: >NH				510.3473
—NH_2 :: Nitrate				663.8009
—NH_2 :: ═N(a)—(r6)				27.2735
>NH :: >NH	−49.7641	22.1871	−57.1233	239.8076
>NH :: ═N(a)—(r6)				758.9855
—OCN :: —OCN	−1866.097		44.1062	−356.5017
—OCN :: Nitrate				−263.0807
—CN :: ═N(a)—(r6)				−370.9729
Nitrate :: Nitrate				65.1432
═N(a)—(r6) :: ═N(a)—(r6)	−32.3208	12.5371	−26.4556	−271.9449
[a]Nannoolal, Y., et al., *Fluid Phase Equilib.* **252** (2007): 1.				
[b]Nannoolal, Y., et al., *Fluid Phase Equilib.* **226** (2004): 45.				

Description: A GC method with first-order contributions. Variables T_c, P_c, and V_c are given by the following relations:

$$T_c = T_b \left[0.6990 + \frac{1}{0.9889 + \left(\sum_i n_i C_i + \mathrm{GI} \right)^{0.8607}} \right]$$

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(2-9)

$$\frac{P_c}{\mathrm{kPa}} = \frac{\left(\frac{M}{\mathrm{kg/kmol}}\right)^{-0.14041}}{\left(0.00939 + \sum_i n_i C_i + \mathrm{GI}\right)^2}$$

(2-10)

$$\frac{V_c}{10^{-6}\mathrm{m}^3/\mathrm{mol}} = \frac{\sum_i n_i C_i + \mathrm{GI}}{n_{\mathrm{hvy}}^{-0.2266}} + 86.1539$$

(2-11)

where n_i is the number of groups of type i; C_i are group contributions from Table 2-155; M is molecular weight; and GI is the total correction for group-group interactions calculated using

$$\mathrm{GI} = \frac{1}{n_{\mathrm{hvy}}} \sum_{i=1}^{\mathrm{NG}} \sum_{j=1}^{\mathrm{NG}} \frac{C_{ij}}{\mathrm{NG} - 1}$$

(2-12)

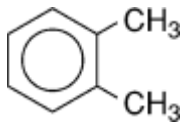
where $C_{ji} = C_{ij}$. The values for the interactions are shown in this format in Table 2-156. The sum of all group pairs within the molecule is divided by the number of nonhydrogen atoms, n_{hvy}, and by 1 less than the number of interacting groups NG. In the example below, there are no group-group interactions. The calculation of GI using Eq. (2-12) is illustrated later in an example calculation for the normal boiling point.

Example

Example

Estimate the critical constants of *o*-xylene using the Nannoolal method.

Structure:



Required input data: From the DIPPR 801 database, T_b = 417.58 K. From Table 2-155:

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Group	n_i	C_i (T_C)	C_i (P_C)	C_i (V_C)
═C(a)–	4	0.0161154	0.00021064	19.402
CH_3–(a)	2	−0.001071	0.0004166	26.7237
═C(a)<(ne)	2	0.0682045	0.00041826	25.0434
ortho	1	0.0012823	0.00007061	−3.5964
GI	–	0	0	0

From Eqs. (2-9), (2-10), and (2-11):

$$\begin{aligned}\sum C_i(T_c) &= (4)(0.0161154)+(2)(-0.001071)+(2)(0.0682045)\\ &\quad +(1)(0.0012823)=0.20001\end{aligned}$$

$$T_c = T_b\left[0.6990+\frac{1}{0.9889+(0.20001)^{0.8607}}\right]=1.5060T_b$$
$$T_c=(1.5060)(417.58\text{ K})=628.87\text{ K}$$

$$\begin{aligned}\sum C_i(P_c) &= (4)(0.00021064)+(2)(0.0004166)+(2)(0.00041826)\\ &\quad +(1)(0.00007061)=0.0025829\end{aligned}$$

$$\frac{P_c}{\text{kPa}}=\frac{(106.165)^{-0.14041}}{(0.00939+0.00258289)^2}=3623.55$$

$$\begin{aligned}\sum C_i(V_c) &= (4)(19.402)+(2)(26.7237)+(2)(25.0434)\\ &\quad +(1)(-3.5964)=177.5458\end{aligned}$$

$$n_{\text{hvy}}=8 \qquad \frac{V_c}{10^{-6}\text{m}^3/\text{mol}}=\frac{177.5458}{n_{\text{hvy}}^{-0.2266}}+86.1539=\frac{177.5458}{(8)^{-0.2266}}+86.1539=370.57$$

Results:

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Property	DIPPR 801 recommendation	Nannoolal estimation	% Difference
T_c/K	630.3	628.9	−0.2
P_c/bar	37.32	36.24	−2.9
V_c/(cm^3/mol)	370	370.6	0.2

Method: Wilson-Jasperson method.

Reference: Wilson, G. M., and L. V. Jasperson, "Critical Constants T_c, P_c, Estimation Based on Zero, First and Second Order Methods," AIChE Spring Meeting, New Orleans, La., 1996.

Classification: Group contributions.

Expected uncertainty: ~6 K or 1 percent for T_c; ~2 bar or 5 percent for P_c.

Applicability: Organic and some inorganic compounds.

Input data: M, T_b, group contributions C_i from Table 2-157, and molecular structure.

Table 2-157 Wilson-Jasperson First- and Second-Order Contributions for Critical Temperature and Pressure[a]

First-order atom	Δtc_k	Δpc_k
H, D, T	0.002793	0.12660
He	0.320000	0.43400
B	0.019000	0.91000
C	0.008532	0.72983
N	0.019181	0.44805
O	0.020341	0.43360
F	0.008810	0.32868
Ne	0.036400	0.12600
Al	0.088000	6.05000
Si	0.020000	1.34000
P	0.012000	1.22000
S	0.007271	1.04713
Cl	0.011151	0.97711
Ar	0.016800	0.79600

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First-order atom	Δtc	Δpc
Ti	0.014000	1.19000
V	0.018600	—
Ga	0.059000	—
Ge	0.031000	1.42000
As	0.007000	2.68000
Se	0.010300	1.20000
Br	0.012447	0.97151
Kr	0.013300	1.11000
Rb	−0.027000	—
Zr	0.175000	1.11000
Nb	0.017600	2.71000
Mo	0.007000	1.69000
Sn	0.020000	1.95000
Sb	0.010000	—
Te	0.000000	0.43000
I	0.005900	1.31593
Xe	0.017000	1.66000
Cs	−0.027500	6.33000
Hf	0.219000	1.07000
Ta	0.013000	—
W	0.011000	1.08000
Re	0.014000	—
Os	−0.050000	—
Hg	0.000000	−0.08000
Bi	0.000000	0.69000
Rn	0.007000	2.05000
U	0.015000	2.04000

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First-order atom	Δtc	Δpc
Second-order group	Δtc_j	Δpc_j
—OH, C_4 or less	0.0350	0.00
—OH, C_5 or more	0.0100	0.00
—O—	−0.0075	0.00
—NH_2, >NH, >N—	−0.0040	0.00
—CHO	0.0000	0.50
>CO	−0.0550	0.00
—COOH	0.0170	0.50
—COO—	−0.0150	0.00
—CN	0.0170	1.50
—NO_2	−0.0200	1.00
Organic halides (once per molecule)	0.0020	0.00
—SH, —S—, —SS—	0.0000	0.00
Siloxane bond	−0.0250	−0.50
[a]As cited in PGL5.		

Description: A GC method with first- and some second-order contributions. Variables T_c, P_c, and V_c are given by the following relations:

$$T_c = \frac{T_b}{\left(0.048271 - 0.019846 n_r + \sum_k n_k \Delta tc_k + \sum_j n_j \Delta tc_j\right)^{0.2}}$$

(2-13)

$$\frac{P_c}{\text{bar}} = \frac{0.0186233(T_c/\text{K})}{\exp(Y) - 0.96601}$$

(2-14)

$$Y = -0.00922295 - 0.0290403 n_r + 0.041\left(\sum_k n_k \Delta pc_k + \sum_j n_j \Delta pc_j\right)$$

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(2-15)

where n_r is the number of rings in the molecule; Δtc_k and Δpc_k are the first-order group contributions tabulated in Table 2-157 with n_k the number of such occurrences in the molecule; and Δtc_j and Δpc_j are the second-order group contributions, also tabulated in Table 2-157, with n_j occurrences of these second-order groups in the molecule.

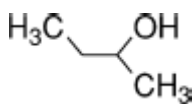
Example

Example

Estimate T_c and P_c of *sec*-butanol by using the Wilson-Jasperson method.

Required input data: From DIPPR 801 database, T_b = 372.9 K.

Structure:



Group contributions from Table 2-157:

Group	n_k	Δtc_k	Δpc_k	n_j	Δtc_j	Δpc_j
H	10	0.002793	0.12660	–	–	–
O	1	0.020341	0.43360	–	–	–
C	4	0.008532	0.72983	–	–	–
–OH, C4 or less	–	–	–	1	0.0350	0

From Eqs. (2-13), (2-14), and (2-15):

$$\begin{aligned}
\sum n_k \Delta tc_k &= (10)(0.002793) + (1)(0.020341) + (4)(0.008532) = 0.082399 \\
T_c &= \frac{T_b}{(0.048271+0.082399+0.0350)^{0.2}} = \frac{372.9\ K}{0.6980} = 534.25\ K \\
\sum n_k \Delta pc_k &= (10)(0.12660) + (1)(0.43360) + (4)(0.72983) = 4.61892 \\
Y &= -0.00922295 + 0.041(4.61892) = 0.18015 \\
\frac{P_c}{bar} &= \frac{0.0186233(T_c/K)}{\exp(Y)-0.96601} = \frac{(0.0186233)(534.25)}{\exp(0.18015)-0.96601} = 43.00
\end{aligned}$$

Results:

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Property	DIPPR 801 recommendation	Wilson-Jasperson estimation	% Difference
T_c/K	536.2	534.25	−0.4
P_c/bar	42.02	43.00	2.3

Normal Melting Point The *normal melting point* is defined as the temperature at which melting occurs at atmospheric pressure. Methods to estimate the melting point are not particularly effective because the melting point depends strongly on solid crystal structure and that structure is not effectively correlated with standard GC or CS methods.

Recommended Method The method of Constantinou and Gani is recommended with caution.

Reference: Constantinou, L., and R. Gani, *AIChE J.*, **40** (1994): 1697.

Classification: Group contributions.

Expected uncertainty: 25 percent.

Applicability: Organic compounds.

Input data: First- and second-order group contributions from molecular structure.

Description: A group contribution method given by

$$T_m = (102.425\text{K}) \cdot \ln\left(\sum_i n_i t_{m1,i} + \sum_j n_j t_{m2,j}\right)$$

(2-16)

where

n_i, n_j = number of first- and second-order groups, respectively

$t_{m1,i}$ = first-order group contributions from Table 2-158

$t_{m2,i}$ = second-order group contributions from Table 2-159

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Table 2-158 First-Order Groups and Their Contributions for Melting Point*

Group	$t_{m1,i}$	Group	$t_{m1,i}$	Group	$t_{m1,i}$
$-CH_3$	0.4640	$-COOCH_2-$	3.5572	$-CCl_3$	10.2337
$>CH_2$	0.9246	$-OOCH$	4.2250	$>ACCl$	2.7336
$>CH-$	0.3557	$-OCH_3$	2.9248	$-CH_2NO_2$	5.5424
$>C<$	1.6479	$-OCH_2-$	2.0695	$>CHNO_2$	4.9738
$-CH=CH_2$	1.6472	$-OCH<$	4.0352	$>ACNO_2$	8.4724
$-CH=CH-$	1.6322	$-OCH_2F$	4.5047	$-CH_2SH$	3.0044
$>C=CH_2$	1.7899	$-CH_2NH_2$	6.7684	$-I$	4.6089
$>C=CH-$	2.0018	$>CHNH_2$	4.1187	$-Br$	3.7442
$>C=C<$	5.1175	$-NHCH_3$	4.5341	$-C\equiv CH$	3.9106
$-CH=C=CH_2$	3.3439	$-CH_2NH-$	6.0609	$-C\equiv C-$	9.5793
$>ACH$	1.4669	$>CHNH-$	3.4100	$>C=CCl-$	1.5598
$>AC-$	0.2098	$>NCH_3$	4.0580	$>ACF$	2.5015
$>ACCH_3$	1.8635	$-NCH_2-$	0.9544	$-CF_3$	3.2411
$>ACCH_2-$	0.4177	$>ACNH_2$	10.1031	$-COO-$	3.4448
$>ACCH<$	−1.7567	$-C_5H_3(N)-$	12.6275	$-CCl_2F$	7.4756
$-OH$	3.5979	$-CH_2CN$	4.1859	$-CClF_2$	2.7523
$>ACOH$	13.7349	$-COOH$	11.5630	$-F$ (other)	1.9623
$-COCH_3$	4.8776	$-CH_2Cl$	3.3376	$-CONH_2$	31.2786
$-COCH_2-$	5.6622	$>CHCl$	2.9933	$-CON(CH_3)_2$	11.3770
$-CHO$	4.2927	$>CCl-$	9.8409	$-CH_3S$	5.0506
$-COOCH_3$	4.0823	$-CHCl_2$	5.1638	$>CH_2S$	3.1468

*Constantinou, L., and R. Gani, *AIChE J.*, **40** (1994): 1697.

Table 2-159 Second-Order Groups and Their Contributions for Melting Point*

Group	$t_{m21,i}$	Group	$t_{m21,i}$
$-CH(CH_3)_2$	0.0381	CHCOOH; CCOOH	−3.1034

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Group	t	Group	t
$-C(CH_3)_3$	−0.2355	ACCOOH	28.4324
$-CH(CH_3)CH(CH_3)-$	0.4401	CH_3COOCH; CH_3COOC	0.4838
$-CH(CH_3)C(CH_3)_2-$	−0.4923	$COCH_2COO$ or COCHCOO or COCCOO	0.0127
$-C(CH_3)_2C(CH_3)_2-$	6.0650	CO—O—CO	−2.3598
Three-member ring	1.3772	ACCOO	−2.0198
Five-member ring	0.6824	CHOH	−0.5480
Six-member ring	1.5656	COH	0.3189
Seven-member ring	6.9709	$CH_m(OH)CH_n(OH)$ [m, n = 0, 1, 2]	0.9124
$CH_n{=}CH_m{-}CH_p{=}CH_k$	1.9913	$CH_{m\ cyclic}{-}OH$ [m = 0, 1]	9.5209
[k, n, m, p = 0, 1, 2]			
$CH_3CH_m{=}CH_n$ [m, n = 0, 1, 2]	0.2476	$CH_m(OH)CH_n(NH_p)$	2.7826
		[m, n, p = 0, 1, 2, 3]	
$CH_2CH_m{=}CH_n$ [m, n = 0, 1, 2]	−0.5870	$CH_m(NH_2)CH_n(NH_2)$	2.5114
		[m, n = 0, 1, 2]	
$CHCH_m{=}CH_n$ or $CCH_m{=}CH_n$	−0.2361	$CH_{m\ cyclic}{-}NH_p{-}CH_{n\ cyclic}$	1.0729
[m, n = 0, 1, 2]		[m, n, p = 0, 1, 2]	
Alicyclic side chain: $C_{cyclic}C_m$	−2.8298	$CH_m{-}O{-}CH_n{=}CH_p$	0.2476
[m > 1]		[m, n, p = 0, 1, 2]	
CH_3CH_3	1.4880	$AC{-}O{-}CH_m$	0.1175
		[m = 0, 1, 2, 3]	
CHCHO; CCHO	2.0547	$CH_{m\ cyclic}{-}S{-}CH_{n\ cyclic}$	−0.2914
		[m, n = 0, 1, 2]	
CH_3COCH_2	−0.2951	$CH_m{=}CH_n{-}F$	−0.0514
		[m, n = 0, 1, 2]	
CH_3COCH; CH_3COC	−0.2986	$CH_m{=}CH_n{-}Br$	−1.6425
		[m, n = 0, 1, 2]	
$C_{cyclic}({=}O)$	0.7143	ACBr	2.5832

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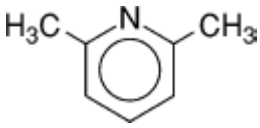
Group	t	Group	t
ACCHO	−0.6697	ACl	−1.5511
*Constantinou, L., and R. Gani, *AIChE J.*, **40** (1994): 1697.			

Example

Example

Estimate the melting point of 2,6-dimethylpyridine.

Structure and group contributions:



Group	n_i	$t_{m1,i}$	$t_{m2,i}$
$-CH_3$	2	0.4640	
$-C_5H_3(N)-$	1	12.6275	
Six-member ring	1		1.5656

Calculation using Eq. (2-16):

$$T_m = (102.425\ \mathrm{K})\ \ln\ [(2)(0.4640) + 12.6275 + 1.5656] = 278\ \mathrm{K}$$

The predicted value is 4 percent higher than the recommended experimental value of 267 K in the DIPPR 801 database.

Normal Boiling Point The normal boiling temperature T_b is the temperature at which the vapor pressure of the liquid equals 101.325 kPa (1.0 atm). If there are sufficient vapor pressure data available, then T_b may be found from a regression of the data using an appropriate vapor pressure equation [e.g., Eqs. (2-24) to (2-28)]. If two or more vapor pressure values are available in the approximate temperature range of T_b, they can be used to obtain T_b by using Eq. (2-2) to linearly interpolate ln P^* versus $1/T$ values. When one or more low-temperature vapor pressure points are available, a common occurrence, then the method of Pailhes can be used to estimate T_b. The most accurate method for prediction of normal boiling temperatures without experimental data is the Nannoolal method.

Recommended Method Pailhes method.

Reference: Pailhes, F., *Fluid Phase Equilib.*, **41** (1988): 97.

Classification: Group contributions.

Expected uncertainty: ~3 K (1 to 2 percent).

Applicability: Organic compounds.

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Input data: Molecular structure and one measured vapor pressure value P^*_{meas} (often at a low pressure). The method requires estimation of the reduced normal boiling point, T_{br}, and P_c, which in the example below are obtained using the Wilson-Jasperson first-order method and the Ambrose method, respectively.

Description: A simple group contribution method is given by

$$T_b = T_{\text{meas}} \left[\frac{\log(P_c/\text{bar}) + (1 - T_{br})x_P}{\log(P_c/\text{bar})} \right] - 3x_p - 1.49x_p^2$$

(2-17)

where

T_b = estimated normal boiling point

P_c = critical pressure estimated from group contributions

$x_P = \log(1\ \text{atm}/P^*_{\text{meas}})$

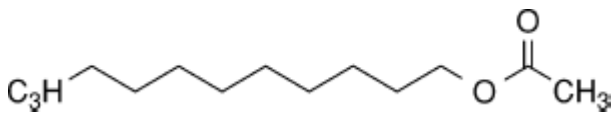
T_{meas} = temperature at which experimental vapor pressure P^*_{meas} is known

Example

Example

The vapor pressure of *n*-decylacetate (M = 200.32 kg/kmol) at 348.65 K is 106.66 Pa. Estimate the normal boiling point of this compound, using the Paihles method.

Structure and group contributions from Tables 2-154 and 2-157:



Wilson-Jasperson Groups	n_i	Δtc_i		Ambrose Groups	n_i	$\Delta_{P,i}$
H	24	0.002793		-COO-	1	0.470
O	2	0.020341		C (alkyl)	11	0.226
C	12	0.008532				

Group contribution calculations using Eq. (2-13) for T_{br} and Eq. (2-7) for P_c :

$$\begin{aligned}
\sum n_i \Delta tc_i &= (24)(0.002793) + (2)(0.020341) + (12)(0.008532) = 0.210098 \\
T_{br} &= (0.048271 + 0.210098)^{0.2} = 0.7629 \\
\sum n_i \Delta_{P,i} &= (1)(0.470) + (11)(0.226) = 2.956 \\
P_c &= \frac{200.32}{(0.339+2.956)^2}\text{bar} = 18.450\ \text{bar}
\end{aligned}$$

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Calculation of auxiliary quantities:

$$x_P = \log\left(\frac{1\ \text{atm}}{P^*_{\text{meas}}}\right) = \log\left(\frac{101{,}325\ \text{Pa}}{106.66\ \text{Pa}}\right) = 2.9777$$

Calculation of normal boiling point using Eq. (2-17):

$$\frac{T_b}{\text{K}} = (348.65)\left[\frac{\log(18.450) + (1 - 0.7629)(2.9777)}{\log(18.450)}\right] - 3(2.9777) - 1.49(2.9777)^2$$
$$T_b = 520.94\ \text{K}$$

The estimated value is 0.7 percent higher than the DIPPR 801 recommended value of 517.15 K.

Recommended Method: Nannoolal method.

Reference: Nannoolal, Y., J. Rarey, D. Ramjugernath, and W. Cordes,*Fluid Phase Equilib.*, **226** (2004): 45.

Classification: Group contributions.

Expected uncertainty: ~7 K (about 2 percent).

Applicability: Organic compounds.

Input data: C_i values in Table 2-155; intramolecular group-group interactions C_{ij} in Table 2-156; and the number of nonhydrogen atoms in the molecule.

Description: A GC method that includes second-order corrections for steric effects and intramolecular interactions. T_b is calculated from

$$\frac{T_b}{K} = \frac{\sum_{i=1}^{N} n_i \cdot C_i + \text{GI}}{n_{\text{hvy}}^{0.6583} + 1.6868} + 84.3395$$

(2-18)

where

n_{hvy} = number of nonhydrogen (heavy) atoms

n_i = number of occurrences of group *i*

C_i = group contribution from Table 2-155

GI = total group-group interaction as calculated using Eq. (2-12) and Table 2-156

Example

Example

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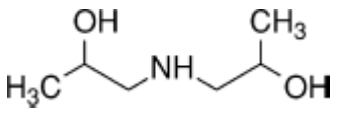
Estimate the normal boiling point of di-isopropanolamine by using the Nannoolal method.

Structure:



Group contributions and values:

Group	n_i	C_i	Group total
$-CH_3$	2	177.3066	354.6132
>C(c)<(e)	4	266.8769	1067.508
—OH sec	2	390.2446	780.4892
—NH—	1	223.0992	223.0992
GI			
—OH:: —OH	2/(9 × 2)	291.7985	32.42206
—OH:: —NH—	4/(9 × 2)	286.9698	63.77107
		Total	2521.902

Note that the frequencies of the interaction correction terms are calculated in the following manner: There are three interacting groups (—OH, —OH, —NH—) in the molecule, so NG − 1 = 2. The four —OH:: —NH— interactions and two —OH:: —OH interactions are each divided by 2 and by the number of nonhydrogen atoms n_{hvy} = 9, according to Eq. (2-12).

Calculation using Eq. (2-18):

$$\frac{T_b}{\mathrm{K}} = \frac{2521.902}{9^{0.6583} + 1.6868} + 84.3395 = 509.3 \qquad T_b = 509.3\,\mathrm{K}$$

This value differs by −2.4 percent from the DIPPR 801 recommended value of 521.9 K.

2.16.6. CHARACTERIZING AND CORRELATING CONSTANTS

Acentric Factor The acentric factor of a compound ω is defined in terms of the reduced vapor pressure evaluated at a reduced temperature of 0.7 as

$$\omega = -log\, P_r^*|_{T_r=0.7} - 1.0000$$

(2-19)

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It is primarily used as a third parameter (in addition to T_c and P_c) in CS predictions as a measure of deviations from nonspherical molecular shape, hence the name, suggesting molecular interactions that are not between centers of molecules. However, as defined in Eq. (2-19), ω also contains polarity information, and it increases with increasing polarity for molecules of similar size and shape. The value of ω is close to zero for small, spherically shaped, nonpolar molecules (argon, methane, etc.). It increases in value with larger deviations of molecular shape from spherical (longer chain lengths, less chain branching, etc.) and with increasing molecular polarity. When possible, ω should be obtained from experimental vapor pressure correlations by using Eq. (2-19), but an accurate estimation of ω can be made by using the critical constants and a single vapor pressure point by application of CS vapor pressure equations.

Recommended Method 1 Definition.

Classification: Theory and empirical extension of theory.

Expected uncertainty: Within 3 percent if an experimental vapor pressure correlation is available; within 10 percent from a predicted vapor pressure correlation.

Applicability: Most organic compounds.

Input data: Vapor pressure correlation or T_c, P_c, and T_b if an experimental vapor pressure correlation is unavailable.

Description: Equation (2-19) is applied directly to the appropriate vapor pressure equation. A predictive vapor pressure equation can also be used as in the second example.

Example

Example

Calculate the acentric factor of chlorobenzene with a known value for T_b.

Input information: From the DIPPR 801 database, T_b = 404.87 K, T_c = 632.35 K, and P_c = 45.1911 bar.

Calculation of auxiliary quantities (see Eq. (2-28a) for these equations):

$$T_{br} = \frac{T_b}{T_c} = \frac{404.87}{632.35} = 0.64 \qquad K = 0.0838$$

$$\psi = -35 + \frac{36}{T_{br}} + 42 \cdot \ln(T_{br}) - T_{br}^6 = -35 + \frac{36}{0.64} + 42 \cdot \ln(0.64) - (0.64)^6 = 2.4312$$

$$\begin{aligned} \alpha_c &= \frac{(3.758)K\psi + \ln(P_C/1.01325\text{bar})}{K\psi - \ln(T_{br})} \\ &= \frac{(3.758)(0.0838)(2.4312) + \ln\left(\frac{45.1911}{1.01325}\right)}{(0.0838)(2.4312) - \ln(0.64)} = 7.025 \end{aligned}$$

$$D = K(\alpha_c - 3.758) = (0.0838)(7.025 - 3.758) = 0.2738$$

$$A = 35D = 9.581 \quad B = -36D = -9.855 \quad C = \alpha_c - 42D = -4.473$$

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Calculation using Eq. (2-28) at T_r = 0.7:

$$\ln(P_r) = 9.581 - \frac{9.855}{0.7} - 4.473 \cdot \ln(0.7) + 0.2738 \cdot (0.7)^6 = -2.870$$

Calculation using Eq. (2-19):

$$\omega = -\frac{\ln(P_r)}{2.303} - 1.0000 = \frac{2.870}{2.303} - 1.0000 = 0.246$$

This value differs by −1.5 percent from DIPPR 801 recommended value of 0.2499.

Recommended Method 2 Corresponding states.

Reference: [PGL5].

Classification: Corresponding states.

Expected uncertainty: Generally within 5 percent, worse for strongly polar fluids.

Applicability: Most organic compounds.

Input data: T_c, P_c, and a single vapor pressure point (e.g., the normal boiling point T_b).

Description: See Eq. (2-29) for the equations used in this method. The vapor pressure equation is inverted to obtain the acentric factor from a single vapor pressure point.

Example

Example

Repeat the above calculation of the acentric factor of chlorobenzene, using the Walton-Ambrose modification of the Lee-Kesler vapor pressure equation, Eq. (2-29).

Input information: From the DIPPR 801 database, T_b = 404.87 K, T_c = 632.35 K, and P_c = 45.1911 bar.

Calculation of auxiliary quantities:

$$T_{br} = \frac{T_b}{T_c} = \frac{404.87}{632.35} = 0.64 \qquad \tau = 1 - 0.64 = 0.36$$

$$f^{(0)} = \frac{(-5.97616)(0.36) + (1.29874)(0.36)^{1.5} - (0.60394)(0.36)^{2.5} - (1.06841)(0.36)^5}{0.64} = -3.0034$$

$$f^{(1)} = \frac{(-5.03365)(0.36) + (1.11505)(0.36)^{1.5} - (5.41217)(0.36)^{2.5} - (7.46628)(0.36)^5}{0.64} = -3.1788$$

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$$f^{(2)} = \frac{(-0.64771)(0.36) + (2.41539)(0.36)^{1.5} - (4.26979)(0.36)^{2.5} - (3.25259)(0.36)^{5}}{0.64}$$
$$= -0.037$$

Calculation using Eq. (2-29) at the normal boiling point:

$$\ln \frac{1.01325}{45.1911} = -3.798 = f^{(0)} + \omega f^{(1)} + \omega^2 f^{(2)} = -3.0034 - 3.1788\omega - 0.037\omega^2$$

Back solution of the quadratic equation for ω: ω = 0.249

Radius of Gyration The radius of gyration R_g is a measure of the mass distribution about the center of mass of a molecule. Radius R_g increases with molecular size. It is useful in CS applications to separate molecular size and shape effects from polar effects. It is defined in terms of the principal moments of inertia of a molecule (*A*, *B*, and *C*) as

$$R_g = \sqrt{\frac{(AB)^{1/2} N_A}{M}}$$

(2-20)

for planar molecules and as

$$R_g = \sqrt{\frac{2\pi (ABC)^{1/3} N_A}{M}}$$

(2-21)

for nonplanar molecules. Radii of gyration can be calculated from these defining equations using principal moments of inertia obtained from spectral data or from computational chemistry software.

Recommended Method Principal moments of inertia.

Classification: Computational chemistry.

Expected uncertainty: Less than 5 percent.

Applicability: All molecules.

Input data: M and molecular structure.

Description: Computational chemistry software is used to optimize the geometry of the molecule and obtain the principal moments of inertia to be used in Eqs. (2-20) and (2-21).

Example

Example

Calculate the radius of gyration for hydrazine.

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Input information: From the DIPPR 801 database, M = 32.0452 kg/kmol. The structure of hydrazine is

$$H_2N—NH_2$$

Calculation of the principal moments of inertia: Optimizing hydrazine with HF/6-31G model chemistry gives the following principal moments of inertia:

A = 12.24050 amu · Bohr^2

B = 72.41081 amu · Bohr^2

C = 79.16893 amu · Bohr^2

Conversion from atomic units to SI gives

$$\begin{aligned} A &= (12.24050\,\text{amu}\cdot\text{Bohr}^2)\left(\frac{5.29177\times10^{-11}\text{m}}{\text{Bohr}}\right)^{-2}\left(\frac{1.66054\times10^{-27}\text{kg}}{\text{amu}}\right) \\ &= 5.692\times10^{-47}\text{kg}\cdot\text{m}^2 \\ B &= (72.41081\,\text{amu}\cdot\text{Bohr}^2)\left(\frac{4.65010^{-48}\text{kg}\cdot\text{m}^2}{\text{amu}\cdot\text{Bohr}^2}\right) = 3.367\times10^{-46}\text{kg}\cdot\text{m}^2 \\ C &= (79.16893\,\text{amu}\cdot\text{Bohr}^2)\left(\frac{4.65010^{-48}\text{kg}\cdot\text{m}^2}{\text{amu}\cdot\text{Bohr}^2}\right) = 3.681\times10^{-46}\text{kg}\cdot\text{m}^2 \end{aligned}$$

Calculation using Eq. (2-21):

$$\begin{aligned} (ABC)^{1/3} &= [(5.692\times10^{-47})(3.367\times10^{-46})(3.681\times10^{-46})]^{1/3}\,\text{kg}\cdot\text{m}^2 \\ &= 1.918\times10^{-46}\,\text{kg}\cdot\text{m}^2 \\ R_g &= \sqrt{\frac{2\pi(1.918\times10^{-46}\text{kg}\cdot\text{m}^2)(6.022\cdot10^{26}\text{kmol}^{-1})}{32.0452\,\text{kg/kmol}}} = 1.505\times10^{-10}\text{m} \end{aligned}$$

This is 3.8 percent below the DIPPR 801 database value of 1.564×10^{-10} m which was obtained from spectral principal moments of inertia.

Dipole Moment The dipole moment of a molecule is the first moment of the electric charge density expansion. All normal paraffins have a value of zero. Charge separation within the molecule due to electronegativity differences between bonded atoms increases the dipole moment. Computational chemistry software uses the electron density distribution of the optimized molecule to calculate dipole moments.

Recommended Method Electron density distribution.

Classification: Computational chemistry.

Expected uncertainty: Uncertainty varies depending upon the model chemistry chosen, but it can be as large as 60 percent.

Applicability: All molecules.

Input data: Molecular structure.

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Example

Example
Calculate the dipole moment for methanol. *Draw structure and optimize molecule by using computational chemistry software:* The dipole moment obtained from a geometry optimized with the HF/6-31G model chemistry for methanol is 2.288 D. This value is 35 percent larger than the experimental gas-phase value of 1.700 D in the DIPPR 801 database.

Refractive Index Refractive index is the ratio of the speed of light in a vacuum to the speed of light in the medium. The incident light is the sodium D line (5.896×10^{-7} m). Refractive index is dimensionless and generally ranges between 1.3 and 1.5 for organic liquids.

Recommended Method Wildman-Crippen method.

Reference: Wildman, S. A., and G. M. Crippen, *J. Chem. Inf. Comput. Sci.* **39** (1999): 868.

Classification: Theory and group contribution.

Expected uncertainty: Generally less than 3 percent for liquids.

Applicability: Most organic molecules (currently not applicable to organic acids).

Input data: Molecular structure, molecular weight, and density at the desired temperature.

Description: This method is based on the Lorentz-Lorenz relation between the molar refraction R_D and the refractive index, which can be written in the form

$$n = \sqrt{\frac{M + 2\left(\frac{\rho}{\mathrm{gm \cdot cm^{-3}}}\right) R_D}{M - \left(\frac{\rho}{\mathrm{gm \cdot cm^{-3}}}\right) R_D}}$$

(2-22)

where n is refractive index at the same temperature as the density ρ. Wildman and Crippen developed a GC method for R_D with the atomic contributions shown in Table 2-160 for each type of atom with its bonded neighbors.

Table 2-160 Wildman-Crippen Contributions for Refractive Index[a]

Type†	Description	MR		Type	Description	MR
C1 1°, 2° aliphatic	C(4H), C(3H)(C), C(2H)(2C)	2.503		N1 1° amine	N(2H)(A)	2.262
C2 3°, 4° aliphatic	C(H)(3C), C(4C)	2.433		N2 2° amine	N(H)(2A)	2.173
C3 1°, 2° aliphatic e	C(3H)(e), C(2H)(2e)	2.753		N3 1° aromatic amine	N(2H)(a)	2.827
C4 3°, 4° aliphatic e	C(H)(3e), C(4e)	2.731		N4 2° aromatic amine	N(H)(a)(A, a)	3.000

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Type†	Description	MR		Type	Description	MR
C5 olefin e	C(═e)	5.007		N5 imine	N(H)(═A, ═a)	1.757
C6 olefin	C(2H)(═A), C(H)(═A), C(═A)	3.513		N6 substituted imine	N[2(═A, ═a)]	2.428
C7 acetylene	C(#A)	3.888		N7 3° amine	N(3A)	1.839
C8 1° aromatic c	C(3H)(c)	2.464		N8 3° aromatic amine	N(a)[2(a, A)]	2.819
C9 1° aromatic e	C(3H)(ae)	2.412		N9 nitrile	N(#A)	1.725
C10 2° aromatic	C(2H)(a)	2.488		N11 aromatic N	n	2.202
C11 3° aromatic	C(H)(a)	2.582		N13 4° amine	N(4A,), N(═A)[2(A, a)]	0.2604
C12 4° aromatic	C(a)	2.576		NS supplemental N	any other N	2.134
C13 aromatic e	c(!e)	4.041		O1 aromatic	o	1.080
C14 aromatic F	c(F)	3.257		O2 alcohol	O(H), O(2H)	0.8238
C15 aromatic Cl	c(Cl)	3.564		O3 aliphatic ether	O[2(C, A)]	1.085
C16 aromatic Br	c(Br)	3.180		O4 aromatic ether	O(a)(A, a)	1.182
C17 aromatic I	c(I)	3.104		O5 oxide	O(═O, ═N), O(A)(N)	3.367
C18 aromatic	c(H)	3.350		O6 oxide	O(A)(S)	0.7774
C19 bridgehead	c(3:a)	4.346		O7 oxide	O(A)(!N, !S)	0.000
C20 4° aromatic	c(2:a)(a)	3.904		O8 aromatic carbonyl	O(═c)	3.135
C21 4° aromatic	c(2:a)(C)	3.509		O9 aliphatic carbonyl	O(═C)[2(C, H, N, A]	0.000
C22 4° aromatic	c(2:a)(N)	4.067		O10 aromatic carbonyl	O(═C)(c)(C, H, A, a)	0.2215
C23 4° aromatic	c(2:a)(O)	3.853		O11 carbonyl (e)	O(═C)(A, a)	0.3890
C24 4° aromatic	c(2:a)(S)	2.673		O12 acid	O(C═O)	—
C25 4° aromatic	c(2:a)(═C), c(2:a)(═N, ═O)	3.135		OS supplemental O	any other O	0.6865
C26 C═C aromatic	C(═C)(a)	4.305		F fluorine	F(A)	1.108
C27 aliphatic e	C(4!e)	2.693		Cl chlorine	Cl(A)	5.853
CS supplemental C	any other C	3.243		Br bromine	Br(A)	8.927
H1 hydrocarbon	H(H), H(C)	1.057		I iodine	I(A)	14.02

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Type†	Description	MR		Type	Description	MR
H2 alcohol	H(O)	1.395		P phosphorous	P(A)	6.920
H3 amine/amide	H(N), H(O)(N)	0.9627		S1 aliphatic S	S(A)	7.591
H4 acid	H(COO), H(COS), H(OO)	1.805		S3 aromatic S	s(A)	6.691
HS supplemental H	any other H	1.112		pblk all remaining p-block elements		5.754

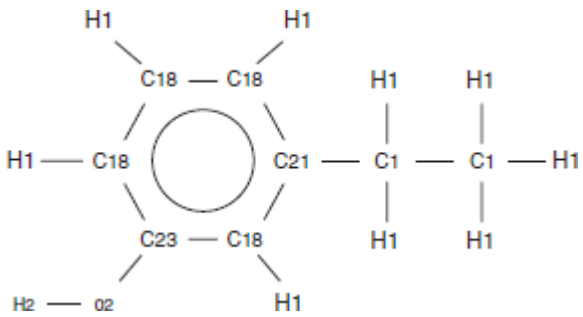
[a]Wildman, S. A., and G. M. Crippen, *J. Chem. Inf. Comput. Sci.* **39** (1999): 868.

†Table-specific nomenclature: e = N, O, P, S, F, Cl, Br, or I; ! = not (e.g., !e = not any of the e elements); c = aromatic carbon; n = aromatic nitrogen; o = aromatic oxygen; A = any nonhydrogen atom; a = aromatic, not necessarily carbon; bond types are single (—), double (═), triple (#), and aromatic (:)

Example

Example

Calculate the refractive index of *m*-ethylphenol at 298.15 K. The various types of atoms corresponding to the descriptions in Table 2-160 are identified in the 2-D structural diagram shown here.



The molecular weight of *m*-ethylphenol is 122.16 kg/kmol, and its liquid density at 298.15 K is given in the DIPPR database as 1.00651 g/cm^3. The group contributions are summed up as shown in this table:

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Type	Description	Number	Value	Contribution
C1	1° & 2° aliphatic	2	2.503	5.006
C18	aromatic	4	3.350	13.40
C21	4° aromatic –aliphatic C	1	3.509	3.509
C23	4° aromatic –O attached	1	3.853	3.853
O2	alcohol	1	0.8238	0.8238
H1	hydrocarbon	9	1.057	9.513
H2	alcohol	1	1.395	1.395
	Group Sum	19	R_D	37.4998

This value for R_D is used in Eq. (2.22) to obtain

$$n = \sqrt{\frac{122.16 + 2(1.00651)(37.4998)}{122.16 - (1.00651)(37.4998)}} = 1.530$$

The predicted value differs by 0.3 percent from the experimental value of 1.535 given in the DIPPR database.

Dielectric Constant The dielectric constant is the ratio of the electric field strength in vacuum to that in the material for the same charge distribution. Equivalently, it is the ratio of the capacitance between two parallel charged plates when filled with the material to that of a vacuum with identical charges on the plates.

Recommended Method Liu method.

Reference: Liu, J-P, W. V. Wilding, N. F. Giles, and R. L. Rowley,*J. Chem. Eng. Data* **55** (2010): 41–45.

Classification: QSPR.

Expected uncertainty: Generally less than 1 percent for nonpolar organic liquids and less than 20 percent for polar organic liquids.

Applicability: Organic liquids. Not valid if the predicted dielectric constant is greater than 50.

Input data: For hydrocarbons and nonpolar molecules, the dipole moment μ, solubility parameter δ, and refractive index n are required. For polar and nonhydrocarbon molecules, the van der Waals area A_{vdw} and number of oxygen-containing groups are additionally required.

Description: The general correlation for the dielectric constant ε is

$$\ln \varepsilon = C_0 + C_1\left(\frac{\mu}{\mathrm{D}}\right) + C_2\left(\frac{A_{\mathrm{vdw}}}{\mathrm{m}^2 \cdot \mathrm{kmol}^{-1}}\right)^{-1} + C_3\left(\frac{\delta}{\mathrm{J}^{1/2} \cdot \mathrm{m}^{-3/2}}\right) + C_4 n^2 + \sum_{i}^{\mathrm{O\ Groups}} \frac{G_i}{k_i}$$

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(2-23)

with the coefficients given by

Applicability	C_0	C_1	C_2	C_3	C_4
Hydrocarbons and nonpolar	−0.1694	0.1283	0	2.8251×10^{-5}	0.2150
	−0.3416	0.5239	4.072×10^{8}	7.408×10^{-5}	−0.3248

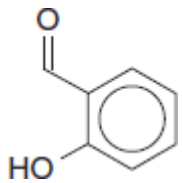
The summation term shown in Eq. (2.23) is only for oxygen-containing groups in the molecule in which G_i is the contribution shown below and k_i ($k_i > 1$) is the number of occurrences of that group in the molecule.

Group	Example	G_i	Group	Example	G_i
[S, N, P] = O	thionyl chloride	0.2879	−OH(na)	alcohol	0.2230
>C=O	ketone	0.3615	−OH(a)	phenol	0.0990
>C=O ring	2-pyrrolidone	0.0075	−OH(C < 5)*	ethanol	0.3348
−COO−	ester	−0.0650	−CHO	aldehyde	0.1617
−COOH	acid	−0.5900			
*Applied in addition to regular −OH group for molecules with fewer than 5 C atoms.					

Example

Example

Calculate the dielectric constant of salicylaldehyde at 303 K. The structure of salicylaldehyde is shown below with the two different oxygen-containing groups and their contributions that are to be used in Eq. (2.23).



Group	G_i	k_i
−CHO	0.1617	1
−OH(a)	0.0990	1

Values of the input properties for Eq. (2.23) obtained from the DIPPR database are μ = 3.08794 D, $A_{vdw} = 8.43 \times 10^{8}$ m^2/kmol, δ = 21330 $J^{1/2}m^{-3/2}$, n = 1.57017. Equation (2.23) is then used to obtain the dielectric constant:

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$$\begin{aligned}\ln\varepsilon &= -0.3416+(0.5239)(3.08794)+\tfrac{4.072}{8.43}\\ &\quad +(7.408\times10^{-5})(21330)-(0.3248)(1.57017)^2+0.1617+0.0990\\ \ln\varepsilon &= 2.799 \text{ and } \varepsilon = 16.43\end{aligned}$$

A few reported experimental values are 13.9 at 293 K, 17.1 at 303 K, and 18.35 at 293.15 K.

2.16.7. VAPOR PRESSURE

Liquids Vapor pressure is the equilibrium pressure at a given temperature of pure, coexisting liquid and vapor phases. The vapor pressure curve is a monotonic function of temperature from its minimum value (the triple point pressure) at the triple point temperature T_t, to its maximum value, P_c, at T_c.

Liquid vapor pressure data over a limited temperature range can be correlated with the Antoine equation [Antoine, C.,*C.R.*, **107** (1888): 681, 836]

$$\text{In}\,\frac{P^*}{\text{Pa}} = A - \frac{B}{T/\text{K}+C}$$

(2-24)

Data from the triple point to the critical point can be correlated with either a modified form of the Wagner equation [Wagner, W., *A New Correlation Method for Thermodynamic Data Applied to the Vapor-Pressure Curve of Argon, Nitrogen, and Water,* J. T. R. Watson (trans. and ed.), IUPAC Thermodynamic Tables Project Centre, London, 1977; Ambrose, D., *J. Chem. Thermodyn.*, **18** (1986): 45; Ambrose, D., and N. B. Ghiassee, *J. Chem. Thermodyn.*, **19** (1987): 903, 911]

$$\ln P_r^* = \frac{a\tau + b\tau^{1.5} + c\tau^{2.5} + d\tau^5}{1-\tau} \qquad \text{where}\,\tau \equiv 1 - T_r$$

(2-25)

or the Riedel equation [Riedel, L., *Chem. Ing. Tech.*, **26** (1954): 679]

$$\ln\frac{P^*}{\text{Pa}} = A + \frac{B}{T/\text{K}} + C\ln\frac{T}{\text{K}} + D\left(\frac{T}{\text{K}}\right)^E$$

(2-26)

In its original form, *E* in Eq. (2-26) was assigned a value of 6, but other integer values of*E* from 1 to 6 have been found to be more effective for different families of chemicals in representing the vapor pressure over the whole liquid range. With the best value of *E*, either the Riedel or the Wagner equation can be used to correlate most fluids over the whole liquid range, but a fifth term is used in the Wagner equation for alcohols [Poling, B. E., *Fluid Phase Equilib.*, **116** (1996): 102]:

$$\ln P_r^* = \frac{a\tau + b\tau^{1.5} + c\tau^{2.5} + d\tau^5 + e\tau^6}{1-\tau} \qquad (\text{for alcohols})$$

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(2-27)

Correlation of experimental data within a few tenths of a percent over the entire fluid range can usually be obtained with either the Wagner or Riedel equations.

Two prediction methods are recommended for liquid vapor pressure. The first method is based on the Riedel equation; the second is a CS method. Both methods require T_c and P_c as input, but these can be estimated by the methods shown earlier if experimental values are unavailable.

Recommended Method 1 Riedel method.

Reference: Riedel, L., *Chem. Ing. Tech.*, **26** (1954): 679.

Classification: Empirical extension of theory and corresponding states.

Expected uncertainty: Varies strongly depending upon relative T, but 1 percent or less above T_b is typical with uncertainties of 5 to 30 percent near the triple point.

Applicability: Most organic compounds.

Input data: T_b, T_c, P_c.

Description: Equation (2-26) in reduced form

$$\ln P_r = A + \frac{B}{T_r} + C \ln T_r + D T_r^6$$

(2-28)

is used with the constants for this equation determined from the following set of relationships:

$$\psi = -35 + \frac{36}{T_{br}} + 42 \ln T_{br} - T_{br}^6 \qquad \alpha_c = \frac{3.758 K\psi + \ln(P_c/1.01325\,\text{bar})}{K\psi - \ln T_{br}}$$
$$h = T_{br}\frac{\ln(P_c/1.01325\,\text{bar})}{1 - T_{br}} \qquad D = K(\alpha_c - 3.758)$$

(2-28a)

$$C = \alpha_c - 42D \quad B = -36D \quad A = 35D$$

Values of the constant K [Vetere, A., *Ind. Eng. Chem. Res.*, **30** (1991): 2487] are as follows:

Class	Value
Acids	$K = -0.120 + 0.025h$
Alcohols	$K = 0.373 - 0.030h$
All other organic compounds	$K = 0.0838$

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Example

Example

Estimate the vapor pressure of chlorobenzene at 50 K intervals from 300 to 600 K.

Input information: From the DIPPR 801 database, T_b = 404.87 K, T_c = 632.35 K, and P_c = 45.1911 bar.

Auxiliary Quantities:

$$K = 0.0838 \quad T_{br} = 404.87/632.35 = 0.640$$

$$\psi = -35 + \frac{36}{0.640} + 42\ln(0.640) - (0.640)^6 = 2.431$$
$$\alpha_c = \frac{(3.758)(0.0838)(2.431)+\ln(45.191/1.01325)}{(0.0838)(2.431)-\ln(0.640)} = 7.0248$$

$$D = (0.0838)(7.0248 - 3.758) = 0.2738 \quad C = 7.0248 - (42)(0.2738) = -4.4729$$
$$B = -(36)(0.2738) = -9.8552 \quad A = -(35)(0.2738) = 9.5814$$

Calculation using Eq. (2-28) at each T (detailed calculation shown for T = 500 K):

$$T_r = 500/632.35 = 0.7907$$

$$\ln P_r = 9.5814 - \frac{9.8552}{0.7907} - 4.4729\ln 0.7907 + (0.2738)(0.7907)^6 = -1.7651$$

$$P_r = \exp(-1.7651) = 0.1712 \quad P = P_r P_c = (0.1712)(45.1911\text{ bar}) = 7.74\text{ bar}$$

T/K	T_r	ln P_r	P/bar	P_{DIPPR}/bar	% Error
300	0.4744	−7.8532	0.0176	0.0175	0.3
350	0.5535	−5.5704	0.172	0.172	0.1
400	0.6326	−3.9323	0.886	0.880	0.6
450	0.7116	−2.7101	3.01	2.98	0.9
500	0.7907	−1.7651	7.74	7.67	0.9
550	0.8698	−1.0067	16.51	16.39	0.8
600	0.9488	−0.3705	31.20	31.11	0.3

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Recommended Method 2 Ambrose-Walton method.

References: Ambrose, D., and J. Walton, *Pure & Appl. Chem.*, **61** (1989): 1395; Lee, B. I., and M. G. Kesler, *AIChE J.*, **21** (1975): 510.

Classification: Corresponding states.

Expected uncertainty: Varies strongly with relative T, but less than 1 percent is typical above T_b if the acentric factor is known.

Applicability: Most organic compounds.

Input data: T_b, T_c, P_c, and ω.

Description: The acentric factor is used to interpolate within the simple-fluid and deviation terms for ln P^*. The $f^{(i)}$ terms have been obtained from correlations of the reference fluid vapor pressures with the Wagner vapor pressure equation

$$\ln P_r^* = f^{(0)} + \omega f^{(1)} + \omega^2 f^{(2)}$$
$$f^{(0)} = \frac{-5.97616\tau + 1.29874\tau^{1.5} - 0.60394\tau^{2.5} - 1.06841\tau^5}{1-\tau}$$
$$f^{(1)} = \frac{-5.03365\tau + 1.11505\tau^{1.5} - 5.41217\tau^{2.5} - 7.46628\tau^5}{1-\tau}$$
$$f^{(2)} = \frac{-0.64771\tau + 2.41539\tau^{1.5} - 4.26979\tau^{2.5} + 3.25259\tau^5}{1-\tau}$$

(2-29)

where $\tau = 1 - T_r$.

Example

Example

Repeat the calculation of the liquid vapor pressure of chlorobenzene at 50-K intervals from 300 to 600 K using the Ambrose-Walton method.

Input information: From the DIPPR 801 database, T_c = 632.35 K, P_c = 45.1911 bar, and ω = 0.249857.

Auxiliary quantities:

$$T_r = 500/632.35 = 0.7907 \quad \tau = 1 - 0.7907 = 0.2093$$

Simple-fluid and deviation vapor pressure terms at each T (shown for T = 500 K):

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$$f^{(0)} = \frac{(-5.97616)(0.2093)+(1.29874)(0.2093)^{1.5}-(0.60394)(0.2093)^{2.5}-(1.06841)(0.2093)^{5}}{0.7907}$$
$$= -1.4405$$
$$f^{(1)} = \frac{(-5.03365)(0.2093)+(1.11505)(0.2093)^{1.5}-(5.41217)(0.2093)^{2.5}-(7.46628)(0.2093)^{5}}{0.7907}$$
$$= -1.3383$$
$$f^{(2)} = \frac{(-0.64771)(0.2093)+(2.41539)(0.2093)^{1.5}-(4.26979)(0.2093)^{2.5}+(3.25259)(0.2093)^{5}}{0.7907}$$
$$= 0.0145$$

Calculation using Eq. (2-29):

$$\begin{aligned} \ln P_r^* &= -1.4405 + (0.249857)(-1.3383) + (0.249857)^2(0.0145) = -1.774 \\ P^* &= (45.1911 \text{ bar})[\exp(-1.774)] = 7.667 \text{ bar} \end{aligned}$$

T	τ	$f^{(0)}$	$f^{(1)}$	$f^{(2)}$	$\ln P^*_r$	P^*/bar	P^*_{DIPPR}/bar	% Error
300	0.5256	−5.9228	−7.5966	−0.3050	−7.840	0.0178	0.0175	1.4
350	0.4465	−4.3006	−5.0017	−0.1439	−5.559	0.174	0.172	1.5
400	0.3674	−3.1036	−3.3106	−0.0437	−3.933	0.885	0.880	0.5
450	0.2884	−2.1800	−2.1576	0.0043	−2.719	2.98	2.98	0.0
500	0.2093	−1.4405	−1.3383	0.0145	−1.774	7.67	7.67	0.0
550	0.1302	−0.8289	−0.7318	0.0036	−1.012	16.43	16.39	0.3
600	0.0512	−0.3068	−0.2612	−0.0081	−0.373	31.14	31.11	0.1

Solids Below the triple point, the pressure at which the solid and vapor phases of a pure component are in equilibrium at any given temperature is the vapor pressure of the solid. It is a monotonic function of temperature with a maximum at the triple point. Solid vapor pressures can be correlated with the same equations used for liquids. Estimation of solid vapor pressure can be made from the integrated form of the Clausius-Clapeyron equation

$$\ln \frac{P^*}{P_t^*} = \frac{\Delta H_{\text{sub}}}{RT_t}\left(1 - \frac{T_t}{T}\right)$$

(2-30)

where

T_t = triple point temperature

P_t^* = triple point pressure

ΔH_{sub} = enthalpy of sublimation

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The liquid and solid vapor pressures are identical at the triple point. A good vapor pressure correlation that is valid at the triple point may be used to obtain the triple point pressure. Estimating solid vapor pressures by using Eq. (2-30) generally requires an estimation of ΔH_{sub}, and so the illustrative example is combined with the example on enthalpy of sublimation in the section on latent enthalpy.

2.16.8. THERMAL PROPERTIES

Enthalpy of Formation The standard enthalpy (heat) of formation is the enthalpy change upon formation of 1 mole of the compound in its standard state from its constituent elements in their standard states. Two different standard enthalpies of formation are commonly defined based on the chosen standard state. The standard enthalpy of formation ΔH_f^s uses the naturally occurring phase at 298.15 K and 1 bar as the standard state while the ideal gas enthalpy (heat) of formation ΔH_f^o uses the compound in the ideal gas state at 298.15 K and 1 bar as the standard state. In both cases, the standard state for the elements is their naturally occurring state of aggregation at 298.15 K and 1 atm. Sources for data include DIPPR, TRC, SWS, JANAF, and TDB. The Domalski-Hearing method is the most accurate general method for estimating either ΔH_f^s or ΔH_f^o if the appropriate GC values are available, but a CC method is also as accurate for estimating ΔH_f^o if an isodesmic reaction can be formulated and used. The Domalski-Hearing method also applies to entropies, and the entropy predictive equations are listed in this section for convenience because they are equivalent in form to the enthalpy equations. However, discussion and illustration of the estimation methods for entropy are delayed to the next subsection.

Recommended Method Domalski-Hearing method.

Reference: Domalski, E. S., and E. D. Hearing, *J. Phys. Chem. Ref. Data*, **22** (1993): 805.

Classification: Group contributions.

Expected uncertainty: 3 percent.

Applicability: Organic compounds for which group contributions have been regressed.

Input data: Molecular structure.

Description: GC values from Table 2-161 are directly additive for both enthalpy of formation and absolute third-law entropies:

Table 2-161 Domalski-Hearing* Group Contribution Values for Standard State Thermal Properties

Group†	ΔH_f^o	S^o	ΔH_f^s liq.	S^s liq.	ΔH_f^s solid	S^s solid
CH Groups						
C—(3H)(C)	−42.26	127.32	−47.61	83.30	−46.74	56.69
C—(2H)(2C)	−20.63	39.16	−25.73	32.38	−29.41	23.01
C—(H)(3C)	−1.17	−53.60	−4.77	−23.89	−5.98	−16.89
$-CH_{3\ corr}$ (tertiary)	−2.26	0.00	−2.18	0.00	−2.34	0.00
C—(4C)	19.20	−149.49	17.99	−98.65	12.47	−33.19

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Group†	ΔH	S	ΔH liq.	S liq.	ΔH solid	S solid
$-CH_{3\ corr}$ (quaternary)	−4.56	0.00	−4.39	0.00	−4.35	0.00
$-CH_{3\ corr}$ (tert/quat)	−1.80	0.00	−1.77	0.00	−2.70	0.00
$-CH_{3\ corr}$ (quat/quat)	−0.64	0.00	−0.64	0.00	−2.24	0.00
Cd—(2H)	26.32	115.52	21.75	86.19	22.43	
Cd—(H)(C)	36.32	33.05	31.05	28.58	25.48	
Cd—(2C)	44.14	−50.84	39.16	−29.83	32.97	
Cd—(H)(Cd)	28.28	27.74	22.18	13.30	17.53	21.75
Cd—(C)(Cd)	36.78	−61.33	30.42	−41.92	27.91	
Cd—(Cd)(Cb)					56.07	
Cd—(H)(Cb)	28.28	27.74	22.18	13.30	17.53	21.75
Cd—(C)(Cb)	37.95	−51.97	38.58			
Cd—(H)(Ct)	28.28	27.74	22.18	13.30	17.53	21.75
C—(4H), Methane	−74.48	206.92				
Cd—(2Cb)	32.88		30.83		49.91	
C—(2H)(C)(Cd)	−20.88	38.20	−25.73	31.67	−24.35	
C—(H)(2C)(Cd)	−1.63	−50.38	−5.02	−28.07	−6.49	
$-CH_{3\ corr}$ (tertiary)	−2.26	0.00	−2.18	0.00	−2.34	0.00
C—(3C)(Cd)	22.13	−150.23	20.79	−108.20	12.51	
$-CH_{3\ corr}$ (quaternary)	−4.56	0.00	−4.39	0.00	−4.35	0.00
C—(H)(C)(2Cd)	−1.17	−53.60	−4.77	−23.89	−5.98	−16.89
C—(2H)(2Cd)	−18.92	42.08	−24.43	19.32	−21.60	
C—(2H)(Cd)(Cb)			−24.73			
C—(H)(C)(Cd)(Cb)			−6.90			
cis (unsat) $_{corr}$	4.85	5.06	5.27	0.00	5.73	0.00
tert—Butyl *cis* $_{corr}$	17.24	0.00	17.48	0.00	17.57	0.00
Ct—(H)	113.50	101.96	104.47	67.57	110.34	
Ct—(C)	115.10	26.32	107.15	14.25	101.66	

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Group†	ΔH	S	ΔH liq.	S liq.	ΔH solid	S solid
Ct—(Cd)	121.42	39.92	114.77			
Ct—(Cb)	120.76	17.77	119.00		103.28	
Ct—(Ct)	120.76	25.94	104.80		103.28	
C—(2H)(C)(Ct)	−19.70	42.80	−22.13	32.36	−29.41	
C—(H)(2C)(Ct)	−3.16	−45.69				
$—CH_{3\ corr}$ (tertiary)	−2.26	0.00	−2.18	0.00	−2.34	0.00
C—(3C)(Ct)			22.83		26.38	
$—CH_{3\ corr}$ (quaternary)	−4.56	0.00	−4.39	0.00	−4.35	0.00
C—(2H)(2Ct)	−41.14		−39.08			
C—(2C)(2Ct)			20.67			
Ca	142.67	26.28	134.68	14.39	131.08	
Cb—(H)(2Cb)	13.81	48.31	8.16	28.87	6.53	22.75
Cb—(C)(2Cb)	23.64	−35.61	19.16	−19.50	13.90	−5.50
Cb—(Cd)(2Cb)	24.17	−33.85	19.12	−9.04	20.27	−10.00
Cb—(Ct)(2Cb)	24.17	−33.85	19.12	−9.04	20.07	−10.00
Cb—(3Cb)	21.66	−36.57	17.21		17.03	−6.00
C—(2C)(2Cb)					52.81	
C—(2H)(C)(Cb)	−21.34	42.59	−24.81	47.40	−22.10	26.90
C—(H)(2C)(Cb)	−4.52	−48.00	−5.82	−13.90	−3.50	
C—(Cb)(3C)	18.28	−147.19	18.70	−96.10	21.57	
C—(2H)(2Cb)	−46.43		−26.50	51.97	−21.44	22.85
C—(H)(C)(2Cb)			−21.47	28.12	16.40	
C—(H)(3Cb)	−6.86				34.48	−12.62
C—(3Cb)(C)					116.25	
C—(4Cb)	27.04				64.89	
Cbf—(Cbf)(2Cb)	20.10	0.00	15.83	−5.54	14.10	−6.00
Cbf—(Cb)(2Cbf)	16.00		11.50		12.00	2.00

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Group†	ΔH	S	ΔH liq.	S liq.	ΔH solid	S solid
Cbf—(3Cbf)	3.59		−0.90		1.94	7.00
Cb—(2Cb)(Cbf)					−8.77	
Cb—(Cb)(2Cbf)	22.46				47.93	
ortho $_{corr,}$ hydrocarbons	1.26	−2.50	3.26	0.00	5.00	0.00
meta $_{corr,}$ hydrocarbons	−0.63	0.00	0.00	0.00	2.00	0.00
Cyclopropane rsc (unsub)	115.15	134.86	111.58			
Cyclobutane rsc	110.89	126.04	106.64	51.48	114.43	
Cyclopentane rsc (unsub)	26.75	116.22	22.84	42.24	34.00	
Cyclohexane rsc (unsub)	0.68	78.18	−1.77	10.07	10.94	
Cycloheptane rsc	26.34	73.97	23.50	15.89		
Cyclooctane rsc	40.65	70.78	38.10	2.96		
Cyclononane rsc	52.91		50.40			
Cyclodecane rsc	51.99		50.61			
CHO Groups						
CO—(2H), formaldehyde	−108.60	224.54				
CO—(C)(CO)	−121.29		−135.04		−140.75	
CO—(H)(CO)	−105.98					
CO—(CO)(Cb)	−112.30				−117.75	
CO—(O)(CO)	−123.75		−123.30		−120.81	
CO—(Cd)(O)	−136.73	62.59	−155.56		−134.10	32.90
CO—(C)(O)	−137.24	62.59	−149.37	32.72	−153.60	32.13
CO—(H)(O)	−124.39	147.03	−142.42	94.68		
CO—(2O)	−111.88		−122.00		−123.00	−42.92
CO—(H)(Cd)	−126.96		−153.05			
CO—(2Cb)	−110.00		−119.00		−116.00	
CO—(C)(Cb)	−148.82		−145.22		−143.70	23.72

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Group†	ΔH	S	ΔH liq.	S liq.	ΔH solid	S solid
CO—(H)(Cb)	−121.35		−138.12		−160.18	
CO—(O)(Cb)	−125.00		−140.00		−145.00	32.13
CO—(2C)	−132.67	64.31	−152.76	33.81	−157.95	
CO—(H)(C)	−124.39	147.03	−142.42	93.55		
CO—(C)(Cd)						
O—(2CO), aliphatic	−214.50	34.16	−230.50		−235.00	
O—(2CO), aromatic	−238.30		−220.90		−207.00	
O—(Cd)(CO)	−198.03		−201.42			
O—(C)(CO)	−188.87	36.03	−196.02	38.28	−210.60	12.09
O—(H)(CO)	−254.30	101.71	−285.64	38.28	−282.15	21.78
O—(Cb)(CO)	−167.00		−165.50		−170.00	45.32
O—(C)(O)	−20.75		−23.50		−30.20	
O—(H)(O)	−72.26		−101.75		−105.30	
O—(2Cd)	−139.29		−137.32			
O—(H)(Cd)						
O—(C)(Cd)	−129.33		−133.72			
O—(2Cb)	−77.66		−85.27	23.31	−96.20	3.14
O—(C)(Cb)	−92.55		−104.85		−122.87	
O—(H)(Cb)	−160.30	121.50	−191.75	43.89	−199.25	28.62
O—(2C)	−101.42	29.33	−110.83	26.78	−119.00	
O—(H)(C)	−159.33	121.50	−191.50	43.89	−199.66	28.62
Cd—(H)(CO)	32.30	35.19	26.61		7.82	27.53
Cd—(C)(CO)						
Cd—(O)(Cd)	36.78	−61.34	30.42	−41.92	27.91	
Cd—(O)(C)	44.14	−50.84	39.08	−29.83	32.97	
Cd—(O)(H)	36.32	33.05	31.05	28.58	25.48	
Ct—(CO)					144.52	

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Group†	ΔH	S	ΔH liq.	S liq.	ΔH solid	S solid
Cb—(CO)(2Cb)	15.50		10.50		8.15	0.08
Cb—(O)(2Cb)	−4.75	−43.72	−5.61	−10.59	1.00	1.59
C—(2H)(2CO)	−30.74		−23.06		−19.10	
C—(CO)(3C)	23.93		26.15	−85.98	24.02	
C—(H)(CO)(2C)	−0.25		−3.89	−24.52	−9.83	
C—(2H)(CO)(C)	−21.84	39.58	−24.14	39.87	−27.90	24.73
C—(3H)(CO)	−42.26	127.32	−47.61	83.30	−46.74	56.69
C—(2H)(CO)(Cd)	−16.95		−19.62			
C—(2H)(CO)(Ct)	−25.48		−26.61			
C—(2H)(CO)(Cb)	−16.20		−11.67			
C—(H)(CO)(C)(Cb)					14.81	
C—(H)(O)(CO)(C)	126.63		123.43	−46.71	−14.39	8.08
C—(4O)	−152.46		−133.34			
C—(H)(3O)	−113.97		−107.74			
C—(3O)(C)	−114.39		−99.54			
C—(2O)(2C)	−53.56		−41.30			
C—(H)(2O)(C)	−57.78		−51.42			
C—(2H)(2O)	−62.22		−62.89	23.85		
C—(2H)(O)(Cb)	−33.76		−29.17			
C—(2H)(O)(Cd)	−27.49	37.49	−28.62			
C—(H)(CO)(C)(Cb)					−14.39	
C—(H)(CO)(2Cb)					3.72	
C—(O)(3Cb)					60.46	
C—(O)(3C) (ethers, esters)	9.50	−141.92	0.79	−94.68	−0.50	
C—(H)(O)(2C) (ethers, esters)	−19.46	−52.80	−21.00	−25.31	−20.08	
C—(O)(3C) (alcohols, peroxides)	−13.50	−144.60	−11.13	−122.48	−12.25	−14.77

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Group†	ΔH	S	ΔH liq.	S liq.	ΔH solid	S solid
C—(H)(O)(2C) (alcohols, peroxides)	−26.10	−43.05	−27.60	−29.83	−29.08	6.95
C—(2H)(O)(C)	−32.90	43.43	−35.80	32.59	−33.00	24.73
C—(3H)(O)	−42.26	127.32	−47.61	83.30	−46.74	56.69
O—(CO)(O)	−88.00		−90.00		−80.50	
C—(2C)(O)(Cb)	15.30		25.80		29.30	
C—(H)(C)(2O)					−52.50	
CHN and CHNO Groups						
C—(3H)(N)	−42.26	127.32	−47.61	83.30	−46.74	56.69
C—(2H)(C)(N)	−28.30	42.26	−30.80	32.38	−34.00	23.01
C—(H)(2C)(N)	−16.70	−63.55	−14.65	−20.00	−13.90	
$-CH_{3\ corr}$ (tertiary)	−2.26	0.00	−2.18	0.00	−2.34	0.00
C—(3C)(N)	0.29	−152.59	5.10	−87.99	1.00	
$-CH_{3\ corr}$ (quaternary)	−4.56	0.00	−4.39	0.00	−4.35	0.00
C—(2H)(2N)	−30.00				−26.00	
C—(2H)(Cb)(N)	−24.14		−26.09		−33.31	
N—(2H)(C) (first, amino acids)	19.25	124.40	0.33	71.71	−6.30	39.00
N—(2H)(C) (second, amino acids)	19.25	126.90	0.33	71.71	−46.00	48.75
N—(H)(2C)	67.55	33.96	51.50	32.09	47.80	
N—(3C)	116.50	−61.71	112.00	−38.62	101.00	
N—(2H)(N)	47.70	122.18	25.30	60.58	18.97	
N—(H)(C)(N)	89.16		75.00	22.05		
N—(2C)(N)	120.71		119.00	−26.94		
N—(2Cb)(N)					137.35	
N—(H)(Cb)(N)	87.50		73.40		66.90	
N—(2CO)(N)					73.62	
N—(H)(2Cd)	83.55		50.50		45.40	
N—(C)(2Cd)	120.64		97.38		88.92	

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Group†	ΔH	S	ΔH liq.	S liq.	ΔH solid	S solid
N—(2H)(Cb)	19.25	126.90	−11.00	71.71	−21.60	70.00
N—(H)(C)(Cb)	59.00		26.25		36.55	
N—(2C)(Cb)	126.40		109.40		96.50	
N—(C)(2Cb)	120.44		97.38		89.30	
N—(H)(2Cb)	83.55		50.50		45.40	
N—(3Cb)	123.15		121.80		107.50	
N_I—(C)	81.46		73.68			
N_I—(Cb)	69.00	47.01	54.50	36.40	57.00	
N_A—(C)	109.50		104.85		103.00	
N_A—(Cb)	109.50		104.85		103.00	
N_A—(oxide)(C)	40.80		22.65			
C—(2H)(C)(N_A)	−20.70		−25.70		−29.41	
C—(H)(2C)(N_A)	−2.66		−5.42			
C—(3C)(N_A)	11.50		15.50		10.50	
Cd—(H)(N)	−16.00		−15.50		−13.00	
Cd—(C)(N)	−5.74		−5.62		−3.95	
Cb—(N)(2Cb)	−1.30	−43.53	1.50	−24.43	9.75	−37.57
Cb—(NO)(2Cb)	21.50				23.00	
Cb—(NO_2)(2Cb)	−1.45		−28.30	79.95	−32.50	110.46
Cb—(CNO)(2Cb)	−177.63				155.69	
Cb—(CN)(2Cb)	151.00	85.25	122.38	64.75	121.20	50.45
Cb—(N_A)(2Cb)	22.55		20.08		18.65	
Cb—(H)(2N_I)	6.30				0.25	
CO—(H)(N)	−124.39	147.03	−188.00	93.55		
CO—(C)(N)	−133.26	56.70	−185.00		−194.60	40.00
CO—(Cb)(N) (amides)					−177.75	
CO—(Cb)(N) (amino acids)					−177.75	

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Group†	ΔH	S	ΔH liq.	S liq.	ΔH solid	S solid
CO—(Cd)(N)	−171.80					
CO—(2N)	−111.00	96.00	−190.50		−203.10	69.00
N—(2H)(CO) (amides, ureas)	−63.00	88.25	−63.90		−65.25	18.00
N—(2H)(CO) (amino acids)	−63.00		−63.90		−59.75	33.03
N—(H)(C)(CO) (amides, ureas)	−16.28		−17.10		−9.80	
N—(H)(C)(CO) (amino acids)	−16.28		−17.10		5.50	
N—(2C)(CO)	45.00		62.00		55.00	
N—(H)(Cb)(CO)	−20.84				−3.50	
N—(H)(2CO)	−91.00				−30.80	
N—(C)(2CO)	−11.64		56.20		64.00	
N—(Cb)(2CO)	9.12					
N-(2Cb)(CO)					60.85	
N—(C)(Cb)(CO)					72.00	
C—(3H)(CN), acetonitrile	74.04	252.60	40.56	149.62		
C—(2H)(C)(CN)	94.52	167.25	66.07	106.02	69.85	96.15
C—(H)(2C)(CN)	113.50	67.86	81.50		69.00	
C—(3C)(CN)	137.96		116.20	−17.91	102.07	
C—(2C)(2CN)						74.57
C—(2H)(Cd)(CN)	95.31		66.40			
Cd—(H)(CN)	146.65	158.41	117.28	92.72		
Ct—(CN)	264.60		250.20			
C—(3H)(NO_2), nitromethane	−74.86	284.14	−112.60	171.75		
C—(2H)(2NO_2), dinitromethane	−58.90		−104.90			
C—(H)(3NO_2), trinitromethane	−0.30		−32.80		−48.00	
C—(4NO_2), tetranitromethane	82.30		38.30			
C—(2H)(C)(NO_2)	−60.50	203.60	−93.50		−99.00	
CHN and CHNO Groups						

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Group†	ΔH	S	ΔH liq.	S liq.	ΔH solid	S solid
C—(H)(2C)(NO_2)	−53.00	115.32	−82.50		−89.00	
C—(3C)(NO_2)	−36.65		−61.20		−76.55	
C—(2H)(Cb)(NO_2)	−62.00		−82.76		−81.00	
C—(H)(C)(2NO_2)	−36.80		−88.80		−91.50	
C—(2C)(2NO_2)	−28.50		−77.20		−90.30	
C—(H)(C)(CO)(N)	−18.70				−11.65	−4.00
C—(2H)(CO)(N)	−3.10				−30.95	24.00
C—(H)(Cb)(CO)(N)						
O—(C)(NO)	−24.23	166.11	−46.50			
O—(C)(NO_2)	−79.71	191.92	−108.96	127.50	−124.00	
N—(H)(C)(NO_2)					16.50	
N—(H)(Cb)(NO_2)						
N—(H)(CO)(NO_2)					−14.00	
N—(C)(2NO_2)	100.30		53.50			
N—(C)(Cb)(NO_2)	183.00		167.00		150.50	
N—(2C)(NO)	90.00		59.00		55.00	
N—(2C)(NO_2)	88.00		50.00		40.00	
C—(2H)(C)(N_3)			321.70			
C—(H)(2C)(N_3)	274.00		255.00			
C—(2H)(Cb)(N_3)	347.00		327.40			
C—(3Cb)(N_3)	328.60				346.50	
Cb—(N_3)(2Cb)	320.00		303.50			
CHS and CHSO Groups						
C—(3H)(S)	−42.26	127.32	−47.61	83.30	−46.74	56.69
C—(2H)(C)(S)	−23.17	41.87	−26.77	41.09		
C—(H)(2C)(S)	−5.88	−47.36	−6.07	−16.61		
—CH_3 $_{corr}$ (tertiary)	−2.26	0.00	−2.18	0.00	−2.34	0.00

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Group†	ΔH	S	ΔH liq.	S liq.	ΔH solid	S solid
C—(3C)(S)	13.52	−145.38	16.69	−86.86		
—CH_3 corr (quaternary)	−4.56	0.00	−4.39	0.00	−4.35	0.00
—CH_3 corr (tert/quat)	−1.80	0.00	−1.77	0.00	−2.70	0.00
—CH_3 corr (quat/quat)	−0.64	0.00	−0.64	0.00	−2.24	0.00
C—(2H)(Cb)(S)	−18.53		−23.82			
C—(2H)(Cd)(S)	−25.93		−32.44			
C—(2H)(2S)	−25.10					
Cb—(S)(2Cb)	−4.75	43.72	−5.61	−10.59	1.00	1.59
Cd—(H)(S)	36.32	33.05	31.05	28.58	25.48	
Cd—(C)(S)	45.73	−51.92				
S—(C)(H)	18.64	137.67	0.06	85.95		
S—(Cb)(H)	48.10	57.34	28.51	89.04		
S—(2C)	46.99	55.19	29.82	29.80		
S—(H)(Cd)	25.52					
S—(C)(Cd)	54.39					
S—(2Cd)	102.60	68.59				
S—(Cb)(C)	76.21		58.20	35.44	42.00	
S—(C)(S)	27.62	50.50	14.36	30.84		
S—(Cb)(S)	57.45				40.60	
S—(2S)	12.59	56.07				
S—(2Cb)	102.60	68.59	93.02			
S—(H)(S)	7.95					
S—(H)(CO)	−5.90	130.54				
CO—(C)(S)	−132.67	64.31	−152.76	33.81		
C—(3H)(SO)	−42.26	127.32	−47.61	83.30	−46.74	56.69
C—(2H)(C)(SO)	−29.16		−36.88			

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Group†	ΔH	S	ΔH liq.	S liq.	ΔH solid	S solid
C—(H)(2C)(SO)						
—CH_3 corr (tertiary)	−2.26	0.00	−2.18	0.00	−2.34	0.00
C—(3C)(SO)	4.56		0.97			
—CH_3 corr (quaternary)	−4.56	0.00	−4.39	0.00	−4.35	0.00
C—(2H)(Cd)(SO)	−27.56		−32.63			
cis correction	4.11	5.06	5.27	0.00	5.73	0.00
Cb—(SO)(2Cb)	15.48		25.44		7.55	0.08
O—(SO)(H)	−158.60					
O—(C)(SO)	−92.60					
SO—(2C)	−66.78	75.73	−108.98	22.18		
SO—(2Cb)	−62.26					
SO—(2O)	−213.00					
SO—(C)(Cb)	−72.00					
C—(3H)(SO_2)	−42.26	127.32	−47.61	83.30	−46.74	56.69
C—(2H)(C)(SO_2)	−27.03		−33.76		−35.96	
C—(H)(2C)(SO_2)	−14.00					
—CH_3 corr (tertiary)	−2.26	0.00	−2.18	0.00	−2.34	0.00
C—(3C)(SO_2)	1.52		2.00		3.78	
—CH_3 corr (quaternary)	−4.56	0.00	−4.39	0.00	−4.35	0.00
CHN and CHNO Groups						
—CH_3 corr (quat/quat)	−0.64		−0.64		−2.24	
C—(2H)(Cd)(SO_2)	−29.49		−49.05			
C—(H)(C)(Cd)(SO_2)	−71.99					
C—(2H)(Cb)(SO_2)	−29.80					
C—(2H)(Ct)(SO_2)	16.36					
Cb—(SO_2)(2Cb)	15.48		25.44		7.55	0.08

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Group†	ΔH	S	ΔH liq.	S liq.	ΔH solid	S solid
Cd—(H)(SO_2)	51.58					
Cd—(C)(SO_2)	64.01					
Ct—(SO_2)	177.10					
SO_2—(Cd)(Cb)	−291.55					
SO_2—(2Cd)	−306.70					
SO_2—(2C)	−288.58	87.37	−341.14		−356.62	32.10
SO_2—(C)(Cb)	−289.10					
SO_2—(2Cb)	−287.76				−305.40	
SO_2—(SO_2)(Cb)	−325.18				−361.75	
SO_2—(2O)	−417.30					
SO_2—(C)(Cd)	−316.80					
SO_2—(Ct)(Cb)	−296.30					
O—(SO_2)(H)	−158.60					
O—(C)(SO_2)	−91.40					
CHX and CHXO Groups						
C—(3H)(F), methyl fluoride	−247.00	231.93				
C—(3H)(Cl), methyl chloride	−81.90	243.60				
C—(3H)(Br), methyl bromide	−37.66	254.94	−61.10			
C—(3H)(I), methyl iodide	14.30	263.14	−11.70			
C—(C)(3F)	−673.81	178.22	−709.07	135.56		
C—(2H)(C)(F)	−221.12	146.80				
C—(H)(2C)(F)	−204.46	55.76				
C—(3C)(F)	−202.92					
C—(H)(C)(2F)	−454.74	164.32	−487.23			
C—(2C)(2F)	−411.39	74.48	−400.37		−428.77	
C—(C)(Cl)(2F)	−462.70	169.45	−466.00	138.31		
C—(H)(C)(Cl)(F)	−271.14					

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Group†	ΔH	S	ΔH liq.	S liq.	ΔH solid	S solid
C—(C)(3Cl)	−81.98	202.14	−112.93	145.91		
C—(H)(C)(2Cl)	−79.10	183.28	−102.60	128.45		
C—(2H)(C)(Cl)	−69.45	159.24	−86.90	104.27	−85.65	
C—(2C)(2Cl)	−79.56	95.41	−101.80			
C—(H)(2C)(Cl)	−55.61	71.34	−71.17			
C—(3C)(Cl)	−43.70	−24.26	−56.78			
C—(C)(3Br)		233.05				
C—(H)(C)(2Br)						
C—(2H)(C)(Br)	−21.78	173.31	−42.65	113.00		
C—(2C)(2Br)						
C—(H)(2C)(Br)	−10.75	84.69	−27.31			
C—(3C)(Br)	7.26	−13.46	−7.40			
C—(C)(3I)						
C—(H)(C)(2I)	108.78	228.45				
C—(2H)(C)(I)	33.54	177.78	4.14		3.65	
C—(2C)(2I)						
C—(H)(2C)(I)	48.74	88.10	24.78			
C—(3C)(I)	68.46	−3.21	48.60			
C—(H)(C)(Br)(Cl)	−18.45	191.21				
N—(C)(2F)	−32.64					
C—(H)(C)(Cl)(O)	−90.37	66.53				
C—(2H)(I)(O)	15.90	170.29				
C—(C)(2Cl)(F)	−322.54		−343.87	141.71		
C—(C)(Br)(2F)	−394.55			149.70		
C—(C)(2Br)(F)						
C—(Br)(Cl)(F)						

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Group†	ΔH	S	ΔH liq.	S liq.	ΔH solid	S solid
Cd—(H)(F)	−165.12	137.24				
Cd—(H)(Cl)	4.37	147.85	−12.67			
Cd—(H)(Br)	50.94	159.91				
Cd—(H)(I)	102.36	169.45				
Cd—(C)(Cl)	−5.06	62.76	−2.23			
Cd—(2F)	−329.90	155.63				
Cd—(2Cl)	−11.51	175.41	−32.08	115.35		
Cd—(2Br)		199.16				
Cd—(2I)						
Cd—(Cl)(F)	−235.10	175.61				
Cd—(Br)(F)		177.82				
Cd—(Cl)(Br)		188.70				
Ct—(F)						
CHX and CHXO Groups						
Ct—(Cl)		140.00				
Ct—(Br)		151.30				
Ct—(I)	35.53					
Cb—(F)(2Cb)	−181.26	67.52	−191.20	54.19	−194.00	39.79
Cb—(Cl)(2Cb)	−17.03	77.08	−32.20	55.47	−32.00	43.37
Cb—(Br)(2Cb)	36.35	88.60	19.90	74.85	13.50	54.45
Cb—(I)(2Cb)	94.50	98.26	73.70	61.08	70.40	
cis $_{corr}$—(I)(I)	3.00	0.00	0.00	0.00	0.00	0.00
C—(2H)(CO)(Cl)	−44.26		−58.41		−74.75	
C—(H)(CO)(2Cl)	−40.40		−55.11			
CO—(C)(F)	−379.84		−419.59			
C—(Cb)(3F)	−691.79	179.08	−696.66			

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Group†	ΔH	S	ΔH liq.	S liq.	ΔH solid	S solid
C—(2H)(Cb)(Br)	−29.49		−44.06			
C—(2H)(Cb)(I)	7.31		−7.24			
C—(2H)(Cb)(Cl)	−73.79		−92.56			
CO—(C)(Cl)	−200.54	176.66	−225.29			
CO—(Cb)(Cl)			−216.67		−212.99	
CO—(C)(Br)	−148.54		−175.49			
CO—(C)(I)	−83.94		−117.09			
C—(H)(C)(CO)(Cl)	−39.88		−35.46			
C—(C)(CO)(2Cl)						
ortho $_{corr}$—(I)(I)	7.56	0.00	6.96	0.00	5.50	0.00
ortho $_{corr}$—(F)(F)	20.90	0.00	25.00	0.00	25.50	0.00
ortho $_{corr}$—(Cl)(Cl)	9.50	0.00	14.00	0.00	8.50	0.00
ortho $_{corr}$—(alkyl)(X)	2.51	0.00	6.30	0.00	0.00	0.00
cis $_{corr}$—(Cl)(Cl)	−4.00	0.00	0.00	0.00	0.00	0.00
cis $_{corr}$—(CH_3)(Br)	−4.00	0.00	0.00	0.00	0.00	0.00
ortho $_{corr}$—(F)(Cl)	13.50	0.00	18.50	0.00	19.50	0.00
ortho $_{corr}$—(F)(Br)	37.25	0.00	40.60	0.00	42.50	0.00
ortho $_{corr}$—(F)(I)	85.40	0.00	83.55	0.00	85.20	0.00
meta $_{corr}$—(I)(I)	0.00	0.00	0.00	0.00	20.08	0.00
meta $_{corr}$—(COCl)(COCl)	0.00	0.00	0.00	0.00	16.06	0.00
ortho $_{corr}$—(COCl)(COCl)	0.00	0.00	0.00	0.00		0.00
ortho $_{corr}$—(F)(CF_3)	111.00	0.00	112.00	0.00	0.00	0.00
meta $_{corr}$—(F)(CF_3)	2.00	0.00	6.00	0.00	0.00	0.00
ortho $_{corr}$—(F)(CH_3)	−3.30	0.00	−6.00	0.00	0.00	0.00
ortho $_{corr}$—(F)(F')	8.00	0.00	8.00	0.00	8.00	0.00
ortho $_{corr}$—(Cl)(Cl')	8.00	0.00	8.00	0.00	8.00	0.00
meta $_{corr}$—(F)(F)	0.00	0.00	6.00	0.00	8.50	0.00

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Group†	ΔH	S	ΔH liq.	S liq.	ΔH solid	S solid
meta $_{corr}$—(Cl)(Cl)	−5.00	0.00	10.00	0.00	4.00	0.00
ortho $_{corr}$—(Cl)(CHO)	−6.75	0.00	8.50	0.00	0.00	0.00
ortho $_{corr}$—(F)(COOH)	20.00	0.00	0.00	0.00	20.00	0.00
ortho $_{corr}$—(Cl)(COCl)	0.00	0.00	34.43	0.00	0.00	0.00
ortho $_{corr}$—(F)(OH)	25.50	0.00	23.00	0.00	20.00	0.00
ortho $_{corr}$—(Cl)(COOH)	0.00	0.00	0.00	0.00	20.00	0.00
ortho $_{corr}$—(Br)(COOH)	0.00	0.00	0.00	0.00	20.00	0.00
ortho $_{corr}$—(I)(COOH)	0.00	0.00	0.00	0.00	20.00	0.00
ortho $_{corr}$—(NH_2)(NH_2)	−10.00	0.00	0.00	0.00	0.00	0.00
meta $_{corr}$—(NH_2)(NH_2)	0.00	0.00	0.00	0.00	14.00	0.00
ortho $_{corr}$—(OH)(Cl)	7.50	0.00	0.00	0.00	11.00	0.00
cis $_{corr}$—(CH_3)(I)	−4.00	0.00	0.00	0.00	0.00	0.00

*Domalski, E. S., and E. D. Hearing, *J. Phys. Chem. Ref. Data*, **22** (1993): 805.

†This table is a partial listing of GC values available from the original Domalski-Hearing tables. Table-specific nomenclature: Cd = carbon with double bond; Ct = carbon with triple bond; Cb = carbon in benzene ring; Ca = allenic carbon; corr = correction term; Cbf = fused benzene ring; N_A = azo nitrogen; N_I = imino nitrogen.

$$\frac{\Delta H_f^o}{\mathrm{kJ/mol}} = \sum_{i=1}^{N} n_i (\Delta H_f^o)_i \qquad \frac{S^o}{\mathrm{J \cdot mol^{-1} K^{-1}}} = \sum_{i=1}^{N} n_i (S^o)_i$$

(2-31)

where
$(\Delta H_f^o)_i =$ enthalpy of formation GC value and $(S^o)_i$ = entropy GC value, both obtained from Table 2-161.

Group values in Table 2-161 are defined by the central, nonhydrogen group and the atoms bonded to that group. Thus, C—(2H)(2C) represents a C atom to which 2 H and 2 C atoms are bonded. For example, propane (CH_3—CH_2—CH_3) is composed of three groups: two C—(3H)(C) and one C—(2H)(2C).

Example

Example

Estimate the standard and ideal gas enthalpies of formation of *o*-toluidine.

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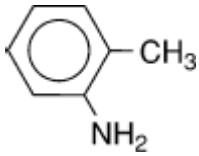
Input information: Because the melting point (256.8 K) and boiling point (473.49 K) for *o*-toluidine bracket 298.15 K, the standard state phase at 298.15 K and 1 bar is liquid.

Structure:



Group contributions:

Group	n_i	ΔH^o_f gas	ΔH^o_f liq.	S^o gas	S^s liq.
Cb—(H)(2Cb)	4	13.81	8.16	48.31	28.87
Cb—(C)(2Cb)	1	23.64	19.16	−35.61	−19.50
Cb—(N)(2Cb)	1	−1.30	1.50	−43.53	−24.43
C—(3H)(C)	1	−42.26	−47.61	127.32	83.30
N—(2H)(Cb)	1	19.25	−11.00	126.90	71.71
	Total	54.57	−5.31	368.32	226.56

Calculation from Eq. (2-31):

$$\frac{\Delta H_f^{\mathrm{o}}}{\mathrm{kJ/mol}} = 54.57 \qquad \frac{\Delta H_f^{\mathrm{S}}}{\mathrm{kJ/mol}} = -5.31$$

$$\frac{S^{\mathrm{o}}}{\mathrm{J/(mol \cdot K)}} = 368.32 \qquad \frac{S^{\mathrm{s}}}{\mathrm{J/(mol \cdot K)}} = 226.56$$

The recommended DIPPR 801 standard enthalpies of formation are
ΔH_f^{o} = 53.20 kJ/mol and
ΔH_f^{s} = −4.72 kJ/mol. The estimated values are higher than the recommended values by 2.6 and 12.5 percent, respectively. The recommended DIPPR 801 standard entropies are S^o = 355.8 J/(mol · K) and S^s = 231.2 J/(mol · K). The estimated values differ from these by 3.5 and −2.0 percent, respectively.

Recommended Method Isodesmic reaction.

Reference: Foresman, J. B., and A. Frisch, *Exploring Chemistry with Electronic Structure Methods*, 2d ed., Gaussian Inc., Pittsburgh, Pa., 1996.

Classification: Computational chemistry.

Expected uncertainty: 5 to 10 percent depending upon the level of theory and basis set size used.

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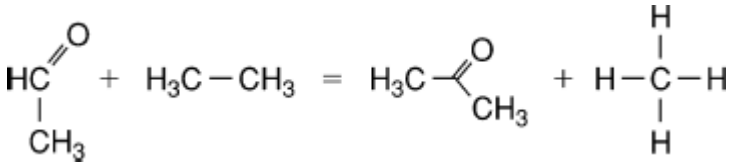
Applicability: Compounds for which an isodesmic reaction can be formulated.

Input data: Experimental
ΔH_f^o values for all *other* participants in the isodesmic reaction.

Description: While *ab initio* calculations of *absolute* enthalpies are not currently as accurate as GC methods,*relative* enthalpies of molecules calculated with the same level of theory and basis set can be very accurate, as in the case of isodesmic reactions. An isodesmic reaction is one in which the number and type of bonds are preserved during the reaction. For example, the reaction of acetaldehyde with ethane to form acetone and methane is



isodesmic with 12 single bonds and 1 double bond in both reactants and products. To use this method, one devises an isodesmic reaction involving the compound for which
ΔH_f^o is to be determined with other compounds for which experimental
ΔH_f^o values are available. *Ab initio* calculations are performed on all the participating compounds, all at the same level of theory and basis set size, to obtain the enthalpy for each at 298.15 K. The enthalpy of reaction is then calculated from

$$\Delta H_{\text{rxn}} = \sum \nu_i H_i$$

(2-32)

where ν_i = stoichiometric coefficient of *i* (+ for products, − for reactants). The enthalpy of reaction is also related to ΔH_f^o by

$$\Delta H_{\text{rxn}} = \sum \nu_i (\Delta H_f^o)_i$$

(2-33)

With experimental values available for all
ΔH_f^o except the desired compound, its value can be back-calculated fromEq. (2-33).

Example

Example

Estimate the standard ideal gas enthalpy of formation of acetaldehyde.

Input information: The isodesmic reaction shown above will be used. The recommended ΔH_f^o values from DIPPR 801 for the other three compounds are as follows:

Acetone	Methane	Ethane
−215.70 kJ/mol	−74.52 kJ/mol	−83.82 kJ/mol

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Ab initio calculations of enthalpy: With structures optimized using HF/6-31G(d) model chemistry and energies calculated with B3LYP/6-311+G(3df,2p), the following enthalpies are obtained (including the zero-point energy):

Acetone	Methane	Ethane	Acetaldehyde
−5.071 × 10^5 kJ/mol	−1.063 × 10^5 kJ/mol	−2.095 × 10^5 kJ/mol	−4.039 × 10^5 kJ/mol

Calculation using Eq. (2-32):

$$\Delta H_{\text{rxn}} = (-1.063 - 5.071 + 2.095 + 4.039) \times 10^5 \text{ kJ/mol} = -41.67 \text{ kJ/mol}$$

Calculation using Eq. (2-33):

$$\Delta H^0_{f,\text{acetaldehyde}} = \Delta H^0_{f,\text{acetone}} + \Delta H^0_{f,\text{methane}} - \Delta H^0_{f,\text{ethane}} - \Delta H_{\text{rxn}}$$
$$\Delta H^0_{f,\text{acetaldehyde}} = (-215.70 - 74.52 + 83.82 + 41.67)\,\frac{\text{kJ}}{\text{mol}} = -164.73\frac{\text{kJ}}{\text{mol}}$$

The estimated value is 1.0 percent above the DIPPR 801 recommended value of −166.40 kJ/mol.

Entropy Absolute or third-law entropies (relative to a perfectly ordered crystal at 0 K) of a compound in its standard state S^s or of an ideal gas S^o at 298.15 K and 1 bar can be found in various literature sources (DIPPR, JANAF, TRC, SWS, and TDB). Very good estimates for S^s or S^o can be obtained by using the Domalski-Hearing method. Excellent S^o values can also be obtained from statistical mechanics by using experimental vibrational frequencies or values of the frequencies generated from computational chemistry.

The standard ΔS^{s}_f and ideal gas ΔS^{o}_f entropies of formation at 298.15 K and 1 bar are related to the standard entropies by

$$\Delta S^{\text{s}}_f = S^{\text{s}}_{\text{compound}} - \sum_{i=1}^{nA} \nu_i S^{\text{s}}_{\text{element},\,i} \qquad \Delta S^{\text{o}}_f = S^{\text{o}}_{\text{compound}} - \sum_{i=1}^{nA} \nu_i S^{\text{s}}_{\text{element},\,i}$$

(2-34)

where $S^s_{\text{element},i}$ is the absolute entropy of element i in its standard state at 298.15 K and 1 bar.

Recommended Method Domalski-Hearing method.

Reference: Domalski, E. S., and E. D. Hearing, *J. Phys. Chem. Ref. Data*, **22** (1993): 805.

Classification: Group contributions.

Expected uncertainty: 3 percent.

Applicability: Organic compounds for which group contributions have been regressed.

Input data: Molecular structure.

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Description: See description given under Enthalpy of Formation above.

Example

Example

Estimate the standard and ideal gas entropies of formation of *o*-toluidine.

Standard state entropies: Estimation of S^s and S^o using the Domalski-Hearing method was illustrated above in the Enthalpy of Formation section. The standard entropies of formation can be obtained from the values determined in that example.

Formula: C_7H_9N. The standard entropies of the elements from the DIPPR 801 database are as follows:

Compound	N_2	H_2	C, graphite
ν_i	1/2	9/2	7
S_i^s/[J(kmol · K)]	1.9151×10^5	1.3057×10^5	5740

Entropies of formation can be calculated from these values by using Eq. (2-34):

$$\Delta S_f^s = \left[2.2656 - \left(\tfrac{1}{2}\right)(1.9151) - \left(\tfrac{9}{2}\right)(1.3057) - (7)(0.0574)\right] \frac{10^5 \mathrm{J}}{\mathrm{kmol{\cdot}K}}$$
$$= -4.969 \cdot 10^5 \frac{\mathrm{J}}{\mathrm{kmol{\cdot}K}}$$
$$\Delta S_f^o = \left[3.6832 - \left(\tfrac{1}{2}\right)(1.9151) - \left(\tfrac{9}{2}\right)(1.3057) - (7)(0.0574)\right] \frac{10^5 \mathrm{J}}{\mathrm{kmol{\cdot}K}}$$
$$= -3.552 \cdot 10^5 \frac{\mathrm{J}}{\mathrm{kmol{\cdot}K}}$$

Recommended Method Statistical mechanics.

Classification: Theory and computational chemistry.

Expected uncertainty: 0.2 percent if vibrational frequencies (or their characteristic temperatures) are experimentally available; uncertainty depends upon model chemistry if frequencies are determined from computational chemistry, but generally within about 5 percent.

Applicability: Ideal gases.

Input data: M; σ (external symmetry number); characteristic rotational temperature(s) (Θ_A for linear molecules; Θ_A, Θ_B, and Θ_C for nonlinear molecules); and $3n_A - 6 + \delta$ characteristic vibrational temperatures Θ_j.

Description: For harmonic frequencies, the rigorous temperature dependence of S^o is given by

$$\frac{S^o}{R} = \frac{3}{2}\ln\left(6175\frac{M}{\mathrm{kg/kmol}}\right) + \frac{S_r}{R} + \sum_{j=1}^{3n_A-6+\delta}\left[\left(\frac{\Theta_j}{T}\right)\left(e^{\Theta_j/T}-1\right)^{-1} - \ln\left(1-e^{-\Theta_j/T}\right)\right]$$

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(2-35)

$$\text{where}\,\delta = \begin{cases} 0 & \text{nonlinear} \\ 1 & \text{linear} \end{cases}$$

$$\text{and}\,\frac{S_r}{R} = \begin{cases} \ln\left[\frac{1}{\sigma}\left(\frac{\pi T^3 e^3}{\Theta_A \Theta_B \Theta_C}\right)^{1/2}\right] & \text{nonlinear} \\ \ln\left[\left(\frac{Te}{\sigma \Theta_A}\right)\right] & \text{linear} \end{cases}$$

Example

Example

Calculate S^o for ammonia.

Structure: NH_3.

Input data: M = 17 kg/kmol. McQuarrie [McQuarrie, D. A., *Statistical Mechanics*, Harper & Row, New York, 1976] gives the following $3n_A - 6 + \delta = 12 - 6 + 0 = 6$ characteristic vibrational temperatures (in K): 1360, 2330, 2330, 4800, 4880, 4880. The characteristic rotational temperatures given by McQuarrie are Θ_A = 13.6 K, Θ_B = 13.6 K, and Θ_C = 8.92 K. For NH_3, σ = 3.

Vibrational contribution: The table below shows a spreadsheet calculation of the vibrational terms inside the summation sign in Eq. (2-35).

Θ_j/K	Θ_j/(298.15 K)	S_{vib}
1207.91	4.051	0.08929
1850.16	6.205	0.01457
1850.16	6.205	0.01457
3688.19	12.370	0.00006
3821.36	12.817	0.00004
3821.36	12.817	0.00004
		Sum 0.1186

Rotational contribution:

$$\frac{S_r}{R} = \ln\left\{\frac{1}{3}\cdot\left[\frac{(298.15\,\text{K})^3 \pi e^3}{(13.6\,\text{K})(13.6\,\text{K})(8.92\,\text{K})}\right]^{1/2}\right\} = 5.81593$$

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Calculation using Eq. (2-35):

$$\frac{S^{o}_{298}}{R} = \frac{3}{2}\ln(6175.17) + 5.81593 + 0.1186 = 23.277$$
$$S^{o}_{298} = 1.935 \times 10^{5}\frac{\mathrm{J}}{\mathrm{kmol}\cdot\mathrm{K}}$$

The calculated value differs from the DIPPR 801 recommended value of 1.927×10^5 J/(kmol · K) by 0.5 percent.

Gibbs Energy of Formation The standard Gibbs energy of formation is the Gibbs energy change upon formation of 1 mole of the compound in its standard state from its constituent elements in their standard states. The standard Gibbs energy of formation ΔG_f^s uses the naturally occurring phase at 298.15 K and 1 bar as the standard state, while the ideal gas Gibbs energy of formation ΔG_f^o uses the compound in the ideal gas state at 298.15 K and 1 bar as the standard state. In both cases, the standard state for the elements is their naturally occurring state of aggregation at 298.15 K and 1 bar. Sources for data include DIPPR, TRC, JANAF, and TDB. The Gibbs energies of formation are related to the corresponding enthalpies and entropies of formation by

$$\Delta G^{o}_{f} = \Delta H^{o}_{f} - T\Delta S^{o}_{f} \qquad \text{and} \qquad \Delta G^{s}_{f} = \Delta H^{s}_{f} - T\Delta S^{s}_{f}$$

(2-36)

and predicted values of
ΔG^{s}_{f} and
ΔG^{o}_{f} are obtained from Eq. (2-36) by estimating the enthalpies and entropies of formation as shown above.

2.16.9. LATENT ENTHALPY

Enthalpy of Vaporization The enthalpy (heat) of vaporization ΔH_υ is the difference between the molar enthalpies of the saturated vapor and saturated liquid at a temperature between the triple point and critical point (at the corresponding vapor pressure). Variable ΔH_υ is related to the vapor pressure P^* by the thermodynamically exact Clapeyron equation

$$\Delta H_\upsilon = -R\Delta Z_\upsilon \frac{d\ln P^*}{d(1/T)} = RT^2\Delta Z_\upsilon \frac{d\ln P^*}{dT}$$

(2-37)

where $\Delta Z_\upsilon = Z_G - Z_L$, $Z_G = Z$ of saturated vapor, and $Z_L = Z$ of saturated liquid. Experimental heats of vaporization can be effectively correlated with

$$\Delta H_\upsilon = A(1 - T_r)^{B + CT_r + DT_r^2 + ET_r^3}$$

(2-38)

A simple method for obtaining ΔH_υ at one temperature from a known value at a reference temperature, say at the normal boiling point, is to truncate Eq. (2-38) after the B term, set B = 0.38, and take a ratio of the ΔH_υ values at the two conditions to

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give the Watson [Thek, R. E., and L. I. Stiel, *AIChE J.*, **12** (1966): 599; **13** (1967): 626] correlation

$$\Delta H_v = \Delta H_{v,\mathrm{ref}} \left(\frac{1 - T_r}{1 - T_{r,\,\mathrm{ref}}} \right)^{0.38}$$

(2-39)

If an accurate correlation for P^* and accurate values for Z_G and Z_L are available, Eq. (2-37) is the preferred method for obtaining enthalpies of vaporization. Otherwise, the CS methods shown below should be used.

Recommended Method 1 Vapor pressure correlation.

Classification: Extension of theory.

Expected uncertainty: The uncertainty varies significantly with temperature and with the quality and temperature range of the vapor pressure data used in the correlation.

Applicability: Organic compounds for which group contributions have been regressed.

Input data: Correlations for P^*, Z_G, and Z_L.

Description: An expression for ΔH_υ can be obtained from Eq. (2-37) by using an appropriate vapor pressure correlation. If one differentiates the Riedel vapor pressure correlation, Eq. (2-26), in accordance with Eq. (2-37), one obtains the heat of vaporization as

$$\Delta H_v = R \Delta Z_v \left(-B + CT + DET^{\mathrm{E}+1} \right)$$

(2-40)

The Z_G and Z_L values can be evaluated using the methods given in the section on densities below.

Example

Example

Calculate ΔH_υ for anisole at 452 K.

Input data: The vapor pressure coefficients in the DIPPR 801 database for Eq. (2-26) are

$$A = 128.06 \quad B = -9307.7 \quad C = -16.693 \quad D = 0.014919 \quad E = 1$$

The vapor pressure at 452 K is therefore

$$\ln\left(\frac{P^*}{\mathrm{Pa}}\right) = 128.06 - \frac{9307.7}{452} - 16.693 \ln(452) + 0.014919\,(452)^1 = 12.155$$
$$P^* = \exp\,(12.155) \cdot \mathrm{Pa} = 1.901 \times 10^5\,\mathrm{Pa}$$

Determine ΔZ: Required data from the DIPPR 801 database for this calculation are T_c = 645.6 K, P_c = 4.25 MPa, and ω = 0.35017. These values are used to determine the reduced conditions,

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$$T_r = \frac{452}{645.6} = 0.7 \qquad P_r = \frac{0.1901}{4.25} = 0.045$$

and the values of Z_G and Z_L from the Lee-Kesler corresponding states method as discussed in the section on density. Interpolation of the P_r values in Tables 2-169 and 2-170 at a T_r of 0.7 gives

$$Z_G^{(0)} = 0.9904 + \frac{0.045 - 0.010}{0.050 - 0.010}(0.9504 - 0.9904) = 0.9554$$
$$Z_G^{(1)} = -0.0064 + \frac{0.045 - 0.010}{0.050 - 0.010}(-0.0507 + 0.0064) = -0.0452$$
$$Z_G = Z_G^{(0)} + \omega Z_G^{(1)} = 0.9554 + (0.35017)(-0.0452) = 0.94$$

At this low pressure, Z_L is very small compared to Z_G and may be neglected; so

$$\Delta Z_V = Z_G - Z_L = 0.94$$

Calculation using Eq. (2-40):

$$\Delta H_v = \left(8.314\frac{\mathrm{J}}{\mathrm{mol}\cdot\mathrm{K}}\right)(0.94)\left[9307.7 - (16.693)(452) + (0.014919)(1)(452)^2\right]$$
$$= 37.59\frac{\mathrm{kJ}}{\mathrm{mol}\cdot\mathrm{K}}$$

This value is 0.2 percent higher than the value of 37.51 kJ/(mol · K) obtained from the DIPPR 801 database.

Recommended Method 2 Corresponding states correlation.

Reference: [PGL5], p. 7.18.

Classification: Corresponding states.

Expected uncertainty: Less than about 6 percent.

Applicability: Organic compounds.

Input data: T_c, P_c, and ω.

Description: The following correlation is used:

$$\frac{\Delta H_v}{RT_c} = 7.08\tau^{0.354} + 10.95\omega\tau^{0.456} \qquad \text{where } \tau = 1 - T_r$$

(2-41)

Example

Example

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Repeat the above calculation for anisole's ΔH_v at 452 K.

Input data: T_c = 645.6 K, P_c = 4.25 MPa, and ω = 0.35017.

Auxiliary quantities: From the previous example, the reduced temperature variables are

$$T_r = 0.7 \quad \tau = 1 - 0.7 = 0.3$$

Calculation using Eq. (2-41):

$$\frac{\Delta H_v}{RT_c} = 7.08(0.3)^{0.354} + 10.95\,(0.35017)(0.3)^{0.456} = 6.838$$
$$\Delta H_v = (6.838)\left(8.314\frac{\mathrm{J}}{\mathrm{mol}\cdot\mathrm{K}}\right)(645.6\ \mathrm{K}) = 36.70\frac{\mathrm{kJ}}{\mathrm{mol}\cdot\mathrm{K}}$$

This value is 2.2 percent below the DIPPR 801 recommended value of 37.51 kJ/(mol · K).

Enthalpy of Fusion The enthalpy (heat) of fusion ΔH_{fus} is the difference between the molar enthalpies of the equilibrium liquid and solid at the melting temperature and 1.0 atm pressure. There is no generally applicable, high-accuracy estimation method for ΔH_{fus}, but the GC method of Chickos can be used to obtain approximate results if the melting temperature is known.

Recommended Method Chickos method.

Reference: Chickos, J. S., C. M. Braton, D. G. Hesse, and J. R. Liebman, *J. Org. Chem.*, **56** (1991): 927.

Classification: QSPR and group contributions.

Expected uncertainty: Considerable variation but generally less than 50 percent.

Applicability: Only valid at the melting temperature. The method is based on the ΔS_{fus} between a solid at 0 K and the liquid at the T_m so no solid-solid transitions are taken into account. Values of ΔH_{fus} will be overestimated if there are solid-solid transitions for the actual material.

Input data: T_m and molecular structure.

Description:

$$\frac{\Delta H_{\text{fus}}}{\mathrm{J/mol}} = \frac{\Delta S_{\text{fus}}}{\mathrm{J/(mol\cdot K)}}\left(\frac{T_m}{\mathrm{K}}\right) = (T_m/\mathrm{K})\,(a+b)$$

(2-42)

$$a = \begin{cases} 0 & \text{no nonaromatic rings} \\ 35.19N_R + 4.289(N_{CR} - 3N_R) & \text{nonaromatic rings} \end{cases}$$

(2-43)

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$$b = \sum_{i=1}^{ng} Ng_i \Delta s_i + \sum_{j=1}^{ns} Ns_j Cs_j \Delta s_j + \sum_{k=1}^{nf} Nf_k Ct_k \Delta s_k$$

(2-44)

where

Ng_i = number of C—H groups of type *i* bonded to other carbon atoms

n_g = number of different nonring or aromatic C—H groups bonded to other carbon atoms

Ns_j = number of C—H groups of type *j* bonded to at least one functional group or atom

n_s = number of different nonring or aromatic C—H groups bonded to at least one functional group or atom

Nf_k = number of functional groups of type *k*

n_f = number of different functional groups or atoms

t = total number of functional groups or atoms with the exception that F atoms count as one regardless of number of occurrences

Cs_j = value from Table 2-162 for C—H group *j* bonded to at least one functional group or atom

Ct_k = value from Table 2-163 for functional group *k*

N_R = number of nonaromatic rings

N_{CR} = number of $—CH_2—$ groups in nonaromatic ring(s) required to form cyclic paraffin of same ring size(s)

Δs_i = contribution from Table 2-162 for group *i*

Δs_k = contribution from Table 2-163 for group *k*

Table 2-162 Cs (C—H) Group Values for Chickos Estimation* of ΔH_{fus}

Group	Description	*Cs*	Δ*s*	Group	Description	*Cs*	Δ*s*
$—CH_3$	methyl	1.0	18.33	$—CH_{Ar}$	aromatic C	1.0	6.44
$>CH_2$	methylene	1.0	9.41	$—C_{Ar}—$	ar. C bonded to paraffinic C	1.0	−10.33
>CH—	secondary C	0.69	−16.91	$—C_{Ar}—$	ar. C bonded to olefinic C or non-C group	1.0	−4.27
>C<	tertiary C	0.67	−38.70	$—C_{Ar}—$	ar. C bonded to acetylinic C	1.0	−2.51
$CH_2{=}$	terminal alkene	1.0	14.56	$>C_rH—$	ring structure	0.76	−15.98
—CH=	alkene	3.23	4.85	$>C_r<$	ring structure	1.0	−32.97
>C=	subst. alkene	1.0	−11.38	$—C_rH{=}$	ring structure	0.62	−4.35
≡CH	term. alkyne	1.0	10.88	$>C_r{=}$	ring structure	0.86	−11.72
≡C—	alkyne	1.0	2.18	$≡C_r—$ or $=C_r=$	ring structure	1.0	−5.36

*Chickos, J. S., et al., *J. Org. Chem.*, **56** (1991): 927.

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Table 2-163 Ct (Functional) Group Values for Chickos Estimation* of ΔH_{fus}

Group	Description	C_1	C_2	C_3	C_4	Δs
—OH	alcohol	1.0	12.6	18.9	26.4	1.13
—OH	phenol	1.0	1.0	1.0	1.0	16.57
—O—	nonring ether	1.0	1.0	1.0	1.0	1.09
—O—	ring ether	1.0	1.0	1.0	1.0	1.34
>C═O	nonring ketone	1.0	1.0			3.14
>C═O	ring ketone	1.0	1.0			−1.88
—CHO	aldehyde	1.0	1.0			19.66
—COOH	acid	1.0	1.83	1.88	1.72	14.90
—COO—	ester	1.0	1.0	1.0	1.0	3.68
$—NH_2$	aliphatic	1.0	1.0			16.23
$—NH_2$	aromatic	1.0	1.0			15.48
>NH	nonring	1.0	1.0			−2.18
>NH	ring	1.0	1.0			1.84
>N—	nonring	1.0	1.0			−15.90
>N—	ring	1.0	1.0			−17.07
═N—	ring	1.0	1.0			1.67
═N—	aromatic	1.0	1.0	1.0		7.32
—CN	nitrile	1.0	1.4			9.62
$—NO_2$	nitro	1.0	1.0	1.0		17.36
$—CONH_2$	primary amide	1.0	1.0			26.19
—CONH—	secondary amide	1.0	1.0			−0.42
—SH		1.0	1.0			17.99
—S—	nonring	1.0	1.0		0.36	7.20
—S—	ring	1.0	1.0			2.18
$—SO_2$	nonring	1.0	1.0			3.26
—F	on aliph. C	1.0	1.0	1.0	1.0	14.73

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Group	Description	C	C	C	C	Δs
—F	on olefinic C	1.0	1.0	1.0	1.0	13.01
—F	on ring C	1.0	1.0	1.0	1.0	15.90
—Cl		1.0	2.0	2.0	1.93	8.37
—Br		1.0	1.0	1.0	0.82	17.95
—I		1.0	1.0			16.95
*Chickos, J. S., et al., *J. Org. Chem.*, **56** (1991): 927.						

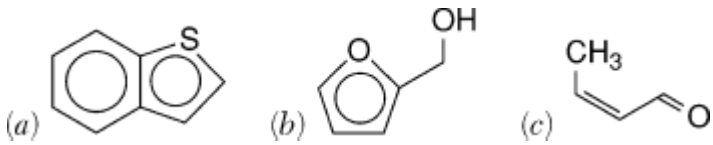
Note that nonaromatic ring —CH_2 groups are accounted for in the *a* term and are *not* included in the *b* term.

Example

Example

Calculate ΔH_{fus} at the melting point for (*a*) benzothiophene, (*b*) furfuryl alcohol, and (*c*) *cis*-crotonaldehyde.

Structures:



(*a*) *t* = 1 (1 total "functional group"), so the C_1 column in Table 2-163 is used.

$$N_R = 1 \quad N_{CR} = 5 \quad a = 35.19 + (5-3)(4.289) = 43.77$$

Group	Description	*N*	*C*	Δ*s*	Total
═CH—	aromatic (*Ng* type)	4	1	6.44	25.76
═C—	ring (*Ng* type)	1	1	−11.72	−11.72
═C—	ring (*Ns* type)	1	0.86	−11.72	−10.08
═CH—	ring (*Ng* type)	1	1	−4.35	−4.35
═CH—	ring (*Ns* type)	1	0.62	−4.35	−2.70
—S—	ring	1	1	2.18	2.18
					Total −0.91

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$$\begin{aligned} T_m &= 304.5\ \mathrm{K} \qquad \text{from DIPPR 801 database} \\ \Delta H_{\mathrm{fus}} &= (T_m/\mathrm{K})(a+b)\ \mathrm{J/mol} = (304.5)(43.77-0.91)\ \mathrm{J/mol} = 13.05\ \mathrm{kJ/mol} \end{aligned}$$

This value is 10 percent higher than the DIPPR 801 recommended value of 11.83 kJ/mol.

(*b*) *t* = 2 (2 total "functional groups"), so the C_2 column in Table 2-163 is used.

$$N_R = 1 \quad N_{CR} = 5 \quad a = 35.19 + (5-3)(4.289) = 43.77$$

Group	Description	*N*	*C*	Δ*s*	Total
═CH–	ring (*Ng* type)	2	1	−4.35	−8.70
═CH–	ring (*Ns* type)	1	0.62	−4.35	−2.70
═C<	ring (*Ns* type)	1	0.86	−11.72	−10.08
═O–	ring ether	1	1	1.34	1.34
$-CH_2-$	*Ns* type	1	1	9.41	9.41
–OH	alcohol	1	12.6	1.13	14.24
					Total 3.51

$$\begin{aligned} T_m &= 258.52\ \mathrm{K} \qquad \text{from DIPPR 801 database} \\ \Delta H_{\mathrm{fus}} &= (T_m/\mathrm{K})(a+b)\ \mathrm{J/mol} = (258.52)(43.77+3.51)\ \mathrm{J/mol} = 12.22\ \mathrm{kJ/mol} \end{aligned}$$

This value is 7 percent lower than the DIPPR 801 recommended value of 13.13 kJ/mol.

(*c*) *t* = 1 $N_R = 0$ *a* = 0

Group	Description	*N*	*C*	Δ*s*	Total
$-CH_3$	nonring (*Ng* type)	1	1	18.33	18.33
═CH–	nonring (*Ng* type)	1	1	4.85	4.85
═CH–	nonring (*Ns* type)	1	3.23	4.85	15.67
–CHO	aldehyde	1	1	19.66	19.66
					Total 58.51

$$\begin{aligned} T_m &= 158.38\ \mathrm{K} \qquad \text{from DIPPR 801 database} \\ \Delta H_{\mathrm{fus}} &= (T_m/\mathrm{K})(a+b)\ \mathrm{J/mol} = (158.38)(0+58.51)\ \mathrm{J/mol} = 9.27\ \mathrm{kJ/mol} \end{aligned}$$

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This value is 5 percent higher than the DIPPR 801 recommended value of 8.86 kJ/mol.

Enthalpy of Sublimation The enthalpy (heat) of sublimation ΔH_{sub} is the difference between the molar enthalpies of the equilibrium vapor and solid along the sublimation curve below the triple point. The effects of pressure on ΔH_{sub} and melting temperature are very small so that T_t and the normal melting point are nearly equal and

$$\Delta H_{\text{sub}}(T_t) = \Delta H_v(T_t) + \Delta H_{\text{fus}}(T_t)$$

(2-45)

Equation (2-45) can be used to estimate ΔH_{sub} at the triple point if ΔH_v is accurately known at T_t. Because ΔH_v is usually obtained from Eq. (2-37), $\Delta H_v(T)$ correlations may be less accurate near T_t where $P^*(T_t)$ is very small and difficult to measure. In this case, it is better to estimate ΔH_{sub} directly by using the following recommended method. ΔH_{sub} is only a weak function of temperature and can generally be treated as a constant from the triple point temperature down to the first solid-solid phase transition.

Recommended Method Goodman method.

Reference: Goodman, B. T., W. V. Wilding, J. L. Oscarson, and R. L. Rowley, *Int. J. Thermophys.* **25** (2004): 337.

Classification: QSPR and group contributions.

Expected uncertainty: 6 percent.

Applicability: Organic compounds for which group contributions have been regressed.

Input data: Molecular structure and radius of gyration R_G.

Description:

$$\frac{\Delta H_{\text{sub}}(T_t)}{R\text{K}} = 698.04 + 3.83798 \times 10^{12}\left(\frac{R_G}{\text{m}}\right) + \sum_{i=1}^{N} n_i a_i + \sum_{i=1}^{N} n_i^2 \beta_i + \sum_{i=1}^{N} \frac{n_i}{n_x} f_i$$

(2-46)

where

a_i = GC values from Table 2-164

β_i = nonlinear corrections for >CH_2 and Ar—CH = groups

f_i = halogen corrections

n_x = total number of all halogen and hydrogen atoms attached to C and Si atoms

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Table 2-164 Group Contributions and Corrections* for ΔH_{sub}

Group	Description	a_i	Group	Description	a_i
$-CH_3$	methyl	736.5889	>C═O	ketone	1816.093
$>CH_2$	methylene	561.3543	—COO—	ester	2674.525
>CH—	secondary C	111.0344	—COOH	acid	5006.188
>C<	tertiary C	−800.517	$-NH_2$	primary amine	2219.148
CH_2═	terminal alkene	572.6245	—NH—	sec. amine	1561.222
—CH═	alkene	541.2918	>N—	tertiary amine	325.9442
>C═	substituted alkene	117.9504	$-NO_2$	nitro	3661.233
Ar —CH═	aromatic C	626.7621	—SH	thiol/mercaptan	1921.097
Ar >C═	subst. aromatic C	348.8092	—S—	sulfide	1930.84
Ar —O—	furan O	763.284	—SS—	disulfide	2782.054
Ar —N═	pyridine N	1317.056	—F	fluoride	626.4494
Ar —S—	thiophene S	911.2903	—Cl	chloride	1243.445
—O—	ether	970.4474	—Br	bromide	669.9302
—OH	alcohol	3278.446	>Si<	silane	−83.7034
—COH	aldehyde	2402.093	>Si(O—)—	siloxane	−16.0597
Nonlinear terms		β_i	Halogen correction terms		f_i
$>CH_2$	methylene	9.5553	—F	F fraction	−1397.4
Ar—CH═	aromatic C	−2.21614	—Cl	Cl fraction	−1543.66
			—Br	Br fraction	5812.49

*Goodman, B., et al., *Int. J. Thermophys.*, **25** (2004): 337.

Example

Example

Calculate ΔH_{sub} and the solid vapor pressure for 1,2,3-trichlorobenzene at 301.15 K.

Structure:

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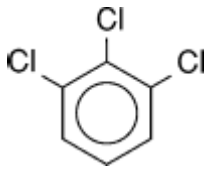

Group contributions:

Linear groups			Nonlinear and correction terms			
Group	n_i	a_i	Group	n_i	β_i	f_i
Ar—CH═	3	626.7621	Ar—CH═	3	−2.21614	
Ar>C═	3	348.8092	—Cl	3		−1543.66
—Cl	3	1243.445	n_x	6		
	$\sum_i n_i a_i = 6657.049$					

Input data: The value of R_G from the DIPPR 801 database is 4.455×10^{-10} m.

Calculation using Eq. (2-46):

$$\frac{\Delta H_{\text{sub}}(T_t)}{RK} = 698.04 + (3.838 \times 10^{12})(4.455 \times 10^{-10}) + 6657.05 + (3^2)(-2.21614) + \left(\frac{3}{6}\right)(-1543.66)$$

$$\Delta H_{\text{sub}}(T_t) = (8273\ \text{K})\left(0.008314\frac{\text{kJ}}{\text{mol}\cdot\text{K}}\right) = 68.78\frac{\text{kJ}}{\text{mol}}$$

The estimated value is 5.6 percent above the DIPPR 801 recommended value of 65.11 kJ/mol.

Estimate the solid vapor pressure at 301.15 K: The solid vapor pressure can be calculated from Eq. (2-30) by using the estimated ΔH_{sub} and one additional solid vapor pressure point. In this example the triple point temperature and vapor pressure (T_t = 325.65 K; P_t^* = 182.957 Pa) from the DIPPR 801 database are used in Eq. (2-30):

$$\ln\frac{P^*}{182.957\,\text{Pa}} = \frac{68.78\,\text{kJ/mol}}{[0.008314\,\text{kJ/(mol}\cdot\text{K)}](325.65\,\text{K})}\left(1-\frac{325.65}{301.15}\right) = -2.067$$

$$P^* = (182.957\ \text{Pa})\,[\exp(-2.067)] = 23.16\ \text{Pa}$$

The estimated value is 0.3 percent above the DIPPR 801 recommended value of 23.09 Pa.

2.16.10. HEAT CAPACITY

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The isobaric heat capacity C_P is defined as the energy required to change the temperature of a unit mass (specific heat) or mole (molar heat capacity) of the material by one degree at constant pressure. Typical units are J/(kg · K).

Gases The isobaric heat capacity of a gas is related rigorously to the ideal gas value C_P^o by

$$C_P = C_P^o - T\int_0^P \left(\frac{\partial^2 V}{\partial T^2}\right)_P dP$$

(2-47)

The second term, giving the deviation of the real fluid heat capacity from the ideal gas value, can be neglected at low to moderate pressures, or it can be calculated directly from an appropriate EoS.

Ideal gas heat capacities are available from several sources (DIPPR, JANAF, TRC, and SWS). Two common correlating equations for C_P^o are the Aly-Lee equation [Aly, F. A., and L. L. Lee, *Fluid Phase Equilib.*, **6** (1981): 169]

$$C_P^o = A_0 + A_1\left[\frac{A_2/T}{\sinh(A_2/T)}\right]^2 + A_3\left[\frac{A_4/T}{\cosh(A_4/T)}\right]^2$$

(2-48)

and a polynomial form (generally fourth-order)

$$C_P^o = \sum_{i=0}^{4} A_i T^i$$

(2-49)

Ideal gas heat capacities may also be estimated from several techniques, of which two of the most accurate and commonly used are recommended here.

Recommended Method 1 Statistical mechanics.

Reference: Rowley, R. L., *Statistical Mechanics for Thermophysical Property Calculations,* Prentice-Hall, Englewood Cliffs, N.J., 1994.

Classification: Theory and computational chemistry.

Expected uncertainty: 0.2 percent if vibrational frequencies (or their characteristic temperatures) are experimentally available; accuracy depends upon model chemistry if frequencies are determined from computational chemistry, but generally within 3 percent.

Applicability: Ideal gases.

Input data: $3n_A - 6 + \delta$ vibrational frequencies ν_j, or the corresponding characteristic vibrational temperatures Θ_j. The two are related by

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$$\Theta_j = h\nu_j/k$$

(2-50)

Description: For harmonic frequencies, the rigorous temperature dependence of C_P^o is given by

$$\frac{C_P^o}{R} = \frac{8-\delta}{2} + \sum_{j=1}^{3n_A-6+\delta} \left(\frac{\Theta_j}{T}\right)^2 \left[\frac{e^{\Theta_j/T}}{\left(e^{\Theta_j/T}-1\right)^2}\right] \qquad \delta = \begin{cases} 0 & \text{nonlinear} \\ 1 & \text{linear} \end{cases}$$

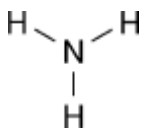
(2-51)

Example

Example

Calculate the ideal gas heat capacity of ammonia at 300 K.

Structure:



Input data: McQuarrie (McQuarrie, D. A., *Statistical Mechanics*, Harper & Row, New York, 1976) gives the following $3n_A - 6 + \delta = 12 - 6 + 0 = 6$ characteristic vibrational temperatures (in K): 1360, 2330, 2330, 4800, 4880, and 4880. Alternatively, a computational chemistry package gives the following *scaled* frequencies for HF/6-31G+ model chemistry (10^{13} Hz): 3.24, 4.97, 4.97, 9.90, 10.26, and 10.26.

Calculation: The table on the left uses the experimental Θ values to determine the individual terms in the summation of Eq. (2-51). The table on the right uses the scaled frequencies from computational chemistry software and Eq. (2-50) to obtain Θ values and the individual terms in Eq. (2-51).

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Experimental frequencies			HF/6-31G+ scaled frequencies*			
Θ/K	Θ/(300 K)	Term	$\nu_{scaled}/10^{13}$ Hz	Θ/K	Θ/(300 K)	Term
1360	4.533	0.2256	3.24	1555.0	5.183	0.1524
2330	7.767	0.0256	4.97	2385.3	7.951	0.0223
2330	7.767	0.0256	4.97	2385.3	7.951	0.0223
4800	16.000	0.0000	9.90	4751.4	15.838	0.0000
4880	16.267	0.0000	10.26	4924.2	16.414	0.0000
4880	16.267	0.0000	10.26	4924.2	16.414	0.0000
	Sum:	0.2768			Sum:	0.1970

*Empirical scaling factors have been developed for each model chemistry to help correct theoretical frequencies for anharmonic effects [Scott, A. P., and L. Radom, *J. Phys. Chem.*, **100** (1996): 16502].

From experimental frequencies:

$$C_P^o = \left(\frac{8}{2} + 0.2768\right) R = (4.2768)\left(8.3143\frac{\mathrm{J}}{\mathrm{mol}\cdot\mathrm{K}}\right) = 35.56\frac{\mathrm{J}}{\mathrm{mol}\cdot\mathrm{K}}$$

From computational chemistry frequencies:

$$C_P^o = \left(\frac{8}{2} + 0.197\right) R = (4.197)\left(8.3143\frac{\mathrm{J}}{\mathrm{mol}\cdot\mathrm{K}}\right) = 34.90\frac{\mathrm{J}}{\mathrm{mol}\cdot\mathrm{K}}$$

The value calculated from experimental frequencies is 0.1 percent lower than the DIPPR 801 recommended value of 35.61 J/(mol · K); the value calculated from frequencies generated from computational chemistry software is 2.0 percent lower than the DIPPR 801 value.

Recommended Method 2 Benson method as implemented in CHETAH program.

References: Benson, S. W., et al., *Chem. Rev.*, **69** (1969): 279; CHETAH Version 8.0: The ASTM Computer Program for Chemical Thermodynamic and Energy Release Evaluation (NIST Special Database 16).

Classification: Group contributions.

Expected uncertainty: 4 percent.

Applicability: Ideal gases of organic compounds.

Input data: Table 2-165 group values at the seven specified temperatures.

Table 2-165 Benson* and CHETAH† Group Contributions for Ideal Gas Heat Capacity

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Group†	298 K	400 K	500 K	600 K	800 K	1000 K	1500 K
CH_3 Groups							
CH_3—(Cb)	25.91	32.82	39.35	45.17	54.5	61.83	73.59
CH_3—(CO)	25.91	32.82	39.35	45.17	54.5	61.83	73.59
CH_3—(Ct)	25.91	32.82	39.35	45.17	54.5	61.83	73.59
CH_3—(C)	25.91	32.82	39.35	45.17	54.5	61.83	73.59
CH_3—(N)	25.95	32.65	39.35	45.21	54.42	61.95	73.67
CH_3—(O)	25.91	32.82	39.35	45.17	54.54	61.83	73.59
CH_3—(PO)	25.91	32.82	39.35	45.17	54.54	61.83	73.59
CH_3—(P)	25.91	32.82	39.35	45.17	54.54	61.83	73.59
CH_3—(P═N)	25.91	32.82	39.35	45.17	54.54	61.83	73.59
CH_3—(Si)	25.91	32.82	39.35	45.17	54.5	61.83	73.59
CH_3—(SO_2)	25.91	32.82	39.35	45.17	54.5	61.83	
CH_3—(SO)	25.91	32.82	39.35	45.17	54.5	61.83	
CH_3—(S)	25.91	32.82	39.35	45.17	54.5	61.83	
CH_3—(═C)	25.91	32.82	39.35	45.17	54.5	61.83	73.59
Ct Groups							
Ct—(Cb)	10.76	14.82	14.65	20.59	22.35	23.02	24.28
Ct—(Ct)	14.82	16.99	18.42	19.42	20.93	21.89	23.32
Ct—(C)	13.1	14.57	15.95	17.12	19.25	20.59	26.58
Ct—(═C)	10.76	14.82	14.65	20.59	22.35	23.02	24.28
CtBr	34.74	36.42	37.67	38.51	39.77	40.6	
CtCl	33.07	35.16	36.42	37.67	39.35	40.18	
CtF	28.55	31.65	33.99	35.79	38.3	39.85	41.77
CtH	22.06	25.07	27.17	28.76	31.27	33.32	37.04
CtI	35.16	36.84	38.09	38.93	40.18	41.02	
Ct(CN)	43.11	47.3	50.65	53.16	56.93	59.86	64.04

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Group†	298 K	400 K	500 K	600 K	800 K	1000 K	1500 K
CH_2 Groups							
CH_2—(2CO)	16.03	26.66	32.15	37.8	45.46	51.74	
CH_2—(2C)	23.02	29.09	34.53	39.14	46.34	51.65	59.65
CH_2—(2O)	11.85	21.18	31.48	38.17	43.2	47.26	
CH_2—(2═C)	19.67	28.46	35.16	40.18	47.3	52.74	60.28
CH_2—(Cb,O)	15.53	26.26	34.66	40.98	49.35	55.25	
CH_2—(Cb,SO_2)	15.53	27.5	34.66	40.98	49.77	55.25	
CH_2—(Cb,S)	38.09	49.02	57.43	63.71	72.58	78.82	
CH_2—(Cb,═C)	19.67	28.46	35.16	40.18	47.3	52.74	60.28
CH_2—(C,Cb)	24.45	31.85	37.59	41.9	48.1	52.49	57.6
CH_2—(C,CO)	25.95	32.23	36.42	39.77	46.46	51.07	
CH_2—(C,Ct)	20.72	27.46	33.19	38.01	45.46	51.03	59.44
CH_2—(C,N)	21.77	28.88	34.74	39.35	46.46	51.49	
CH_2—(C,O)	20.89	28.67	34.74	39.47	46.5	51.61	61.11
CH_2—(C,SO_2)	17.12	24.99	31.56	36.84	44.58	49.94	
CH_2—(C,SO)	19.05	26.87	33.28	38.34	45.84	51.15	
CH_2—(C,S)	22.52	29.64	36	41.73	51.32	59.23	
CH_2—(C,═C)	21.43	28.71	34.83	39.72	46.97	52.24	60.11
CH_2—(═C,O)	19.51	29.18	36.21	41.36	48.3	53.29	
CH_2—(═C,SO_2)	20.34	28.51	34.95	40.1	47.17	52.49	
CH_2—(═C,SO)	18.42	26.62	29.05	38.72	45.92	51.28	
CH_2—(═C,S)	22.23	28.59	34.45	40.85	50.98	59.48	
CH Groups							
CH—(2C,Cb)	20.43	27.88	33.07	36.63	40.73	42.9	44.7
CH—(2C,CO)	18.96	25.87	30.89	35.12	41.11	43.99	
CH—(2C,Ct)	16.7	23.48	28.67	32.57	38.09	41.44	46.55
CH—(2C,N)	19.67	26.37	31.81	35.16	40.18	42.7	

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Group†	298 K	400 K	500 K	600 K	800 K	1000 K	1500 K
CH—(2C,O)	20.09	27.79	33.91	36.54	41.06	43.53	
CH—(2C,SO_2)	18.5	26.16	31.65	35.5	40.35	43.11	
CH—(2C,S)	20.3	27.25	32.57	36.38	41.44	44.24	
CH—(2C,═C)	17.41	24.74	30.72	34.28	39.6	42.65	47.22
CH—(3C)	19	25.12	30.01	33.7	38.97	42.07	46.76
CH—(C,2O)	22.02	23.06	27.67	31.77	35.41	38.97	
C Groups							
C—(2C,2O)	19.25	19.25	23.02	25.53	27.63	28.46	
C—(3C,Cb)	19.72	28.42	33.86	36.75	38.47	37.51	31.94
C—(3C,CO)	9.71	18.33	23.86	27.17	30.43	31.69	
C—(3C,Ct)	0.33	7.33	14.36	19.97	25.2	26.71	
C—(3C,N)	18.42	25.95	30.56	33.07	35.58	35.58	
C—(3C,O)	18.12	25.91	30.35	32.23	34.32	34.49	
C—(3C,SO_2)	9.71	18.33	23.86	27.17	30.43	31.23	
C—(3C,SO)	12.81	19.17	20.26	27.63	31.56	33.32	
C—(3C,S)	19.13	26.25	31.18	34.11	36.5	33.91	
C—(3C,═C)	16.7	25.28	31.1	34.58	37.34	37.51	34.45
C—(4C)	18.29	25.66	30.81	33.99	36.71	36.67	33.99
Aromatic (Cb and Cp Groups)							
Cb—(Cb)	13.94	17.66	20.47	22.06	24.11	24.91	25.32
Cb—(CO)	11.18	13.14	15.4	17.37	20.76	22.77	
Cb—(Ct)	15.03	16.62	18.33	19.76	22.1	23.48	24.07
Cb—(C)	11.18	13.14	15.4	17.37	20.76	22.77	25.03
Cb—(N)	16.53	21.81	24.86	26.45	27.33	27.46	
Cb—(O)	16.32	22.19	25.95	27.63	28.88	28.88	
Cb—(Si)	11.18	13.14	15.4	17.37	20.76	22.77	25.03
Cb—(SO_2)	11.18	13.14	15.4	17.37	20.76	22.77	

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Group†	298 K	400 K	500 K	600 K	800 K	1000 K	1500 K
Cb—(SO)	11.18	13.14	15.4	17.37	20.76	22.77	
Cb—(S)	16.32	22.19	25.95	27.63	28.88	28.88	
Cb—(═C)	15.03	16.62	18.33	19.76	22.1	23.48	24.07
Cb—(=Nim)	16.53	21.81	24.86	26.45	27.33	27.46	
CbBr	32.65	36.42	39.35	41.44	43.11	43.95	
CbCl	30.98	35.16	38.51	40.6	42.7	43.53	
CbF	26.37	31.81	35.58	38.09	41.02	42.7	
CbH	13.56	18.59	22.85	26.37	31.56	35.2	40.73
CbI	33.49	37.25	40.18	41.44	43.11	43.95	
Cb(CHN_2)	47.3						
Cb(CN)	41.86	48.14	52.74	55.67	59.86	62.79	
Cb(N_3)	34.74						
Cb(NCO)	55.25	64.04	70.32	74.51	79.95	82.88	85.81
Cb(NCS)	32.23						
Cb(NO_2)	38.93	50.23	59.44	66.56	76.18	80.37	
Cb(SO_2OH)	65.42	79.49	84.51	97.61	109.25	113.31	
Cp—(2Cb,Cp)	12.56	15.49	17.58	19.25	21.77	23.02	
Cp—(3Cp)	8.37	12.14	14.65	16.74	19.67	21.35	
Cp—(Cb,2Cp)	12.56	15.49	17.58	19.25	21.77	23.02	
═C═,═C—,═CH—Groups							
═C—(2C)	17.16	19.3	20.89	22.02	24.28	25.45	26.62
═C—(CO,O)	23.4	29.3	31.31	32.44	33.57	34.03	
═C—(C,Cb)	18.42	22.48	24.82	25.87	27.21	27.71	28.13
═C—(C,CO)	22.94	29.22	31.02	31.98	33.53	34.32	
═C—(C,O)	17.16	19.3	20.89	22.02	24.28	25.45	
═C—(C,SO_2)	15.49	26.04	33.32	38.51	44.62	47.47	

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Group†	298 K	400 K	500 K	600 K	800 K	1000 K	1500 K
═C—(C,S)	14.65	14.94	16.03	17.12	18.46	20.93	
═C—(C,═C)	18.42	22.48	24.82	25.87	27.21	27.71	28.13
═CC—(=C,O)	18.42	22.9	24.82	26.29	27.21	27.71	
═CH—(Cb)	18.67	24.24	28.25	31.06	34.95	37.63	41.77
═CH—(CO)	31.73	37.04	38.8	40.31	43.45	46.21	
═CH—(Ct)	18.67	24.24	28.25	31.06	34.95	37.63	41.77
═CH—(C)	17.41	21.05	24.32	27.21	32.02	35.37	40.27
═CH—(O)	17.41	21.05	24.32	27.21	32.02	35.37	40.27
═CH—(SO_2)	12.72	19.55	24.82	28.63	32.94	36.29	
═CH—(S)	17.41	21.05	24.32	27.21	32.02	35.37	
═CH—(═C)	18.67	24.24	28.25	31.06	34.95	37.63	41.77
═CH_2	21.35	26.62	31.44	35.58	42.15	47.17	55.21
═C═	16.32	18.42	19.67	20.93	22.19	23.02	23.86
Oxygen Groups							
O—(2C)	14.23	15.49	15.49	15.91	18.42	19.25	
O—(2O)	15.49	15.49	15.49	15.49	17.58	17.58	20.09
O—(2 ═C)	14.02	16.32	17.58	18.84	21.35	22.6	
O—(Cb,CO)	8.62	11.3	13.02	14.32	16.24	17.5	
O—(CO,O)	1.51	6.28	9.63	11.89	15.28	17.33	
O—(C,Cb)	2.6	3.01	4.94	7.45	11.89	14.99	
O—(C,CO)	11.64	15.86	18.33	19.8	20.55	21.05	
O—(C,O)	15.49	15.49	15.49	15.49	17.58	17.58	20.09
O—(C,═C)	12.72	13.9	14.65	15.49	17.54	18.96	
O—(═C,CO)	6.03	12.47	16.66	18.79	20.8	21.77	
OH—(Cb)	18	18.84	20.09	21.77	25.12	27.63	
OH—(CO)	15.95	20.85	24.28	26.54	30.01	32.44	37.34
OH—(C)	18.12	18.63	20.18	21.89	25.2	27.67	33.65

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Group†	298 K	400 K	500 K	600 K	800 K	1000 K	1500 K
OH—(O)	21.64	24.24	26.29	27.88	29.93	31.44	34.2
O(CN)—(Cb)	34.74						
O(CN)—(C)	41.86						
O(CN)—(═C)	54.42						
$O(NO_2)$—(C)	39.93	48.3	55.5	65.3	68.61	72.75	
O(NO)—(C)	38.09	43.11	46.88	50.23	55.67	58.18	60.69
(CO)Cl—(C)	42.28	46.04	49.39	51.9	55.67	57.76	
(CO)H—(Cb)	33.53	44.2	48.77	59.48	68.56	74.01	
(CO)H—(CO)	28.13	32.78	37.25	41.4	47.84	50.73	
Oxygen Groups							
(CO)H—(C)	29.43	32.94	36.92	40.52	46.71	51.07	
(CO)H—(N)	29.43	32.94	36.92	40.52	46.71	51.07	
(CO)H—(O)	29.43	32.94	36.92	40.52	46.71	51.07	
(CO)H—(═C)	24.32	30.22	39.77	48.77	63.12	74.68	
CO—(Cb)(O)	9.12	11.51	16.65	21.05	26.32	29.54	
Halide Groups							
CBr—(3C)	39.35	47.72	52.74	55.25	56.93	56.09	
CBr_3—(C)	72.12	78.65	82.92	85.64	88.66	89.66	
CCl—(3C)	36.96	43.87	47.72	49.52	52.07	53.12	
CCl_2—(2C)	51.07	62.29	66.76	68.98	70.99	71.24	
CCl_3—(C)	68.23	75.35	79.95	82.88	86.23	87.9	
$CClF_2$—(C)	57.35	67.39	73.25	77.86	82.88	85.39	
CF—(3C)	28.46	37.09	42.7	46.71	52.03	53.24	
CF_2—(2C)	39.01	46.97	53.24	57.85	63.46	65.84	
CF_3—(Cb)	52.32	64.04	72	77.44	84.14	87.9	
CF_3—(C)	53.16	62.79	68.65	74.93	80.79	83.72	
CF_3—(S)	41.36	54.46	62.08	68.52	76.06	79.99	

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Group†	298 K	400 K	500 K	600 K	800 K	1000 K	1500 K
CH_2Br—(Cb)	30.51	46.46	52.2	57.3	65.26	69.95	
CH_2Br—(C)	38.09	46.04	52.74	57.35	64.88	70.32	
CH_2Br—(═C)	40.6	47.72	54.42	59.86	67.81	73.67	
CH_2Cl—(C)	37.25	44.79	51.49	56.09	64.04	69.9	
CH_2F—(C)	33.91	41.86	50.23	54.42	63.62	69.49	
CH_2I—(Cb)	33.91	45.17	53.7	59.9	68.15	73.8	
CH_2I—(C)	38.51	46.04	54	58.18	66.14	72	
CH_2I—(O)	34.41	43.91	51.19	56.72	64.25	69.36	
CHBr—(2C)	37.38	44.62	50.06	53.75	58.81	61.62	
CHBrCl—(C)	51.9	58.6	63.3	68.23	74.93	79.53	
CHCl—(2C)	35.45	42.7	48.89	53.41	59.82	64.38	
CHCl—(C,O)	37.67	41.44	43.95	46.88			
$CHCl_2$—(C)	50.65	58.6	64.46	69.07	74.93	78.28	
CHF—(2C)	30.56	37.84	43.83	48.39	54.83	58.64	
CHF_2—(C)	41.44	50.23	57.35	63.21	69.9	74.51	
CHI—(2C)	38.64	45.67	50.9	54.42	59.31	61.95	
CHI_2—(C)	56.93	63.42	69.61	74.17	79.7	81.58	
Cl—(3C)	41.15	49.18	54.08	56.3	57.72	56.93	
═CBr_2	51.49	55.25	58.18	59.86	62.37	63.62	
═CBrCl	50.65	53.16	56.51	59.02	61.53	62.79	
═CBrF	45.21	50.23	53.58	56.51	59.86	61.53	
═CCl_2	47.72	52.32	55.67	58.18	61.11	62.79	
═CClF	43.11	48.97	52.74	55.67	59.44	61.53	
═CF_2	40.6	46.04	50.23	53.16	57.76	60.69	
═CHBr	33.91	39.77	44.37	47.72	51.9	55.25	
═CHCl	33.07	38.51	43.11	46.88	51.49	54.83	

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Group†	298 K	400 K	500 K	600 K	800 K	1000 K	1500 K
═CHF	28.46	35.16	39.77	43.95	49.39	53.16	
═CHI	36.84	41.86	45.63	48.56	52.74	55.67	
Nitrogen Groups							
$CH_2(N_3)$—(C)	64.46						
═$CH(N_3)$	54.42						
N—(2C,Cb)	2.6	8.46	13.69	17.29	21.89	23.4	
N—(2C,CO)	13.02	19.17	23.52	26.16	28.42	28.76	
N—(2C,SO_2)	25.2	26.58	31.56	34.45	37.8	38.47	
N—(2C,SO)	17.58	24.61	25.62	27.33	28.59	34.91	
N—(2C,S)	15.99	21.64	25.99	29.05	30.93	38.68	
N—(3C)	14.57	19.09	22.73	24.99	27.46	27.92	27.21
N—(Cb,2CO)	4.1	12.81	17.71	20.3	22.1	22.14	
N—(C,2CO)	4.48	12.99	18.04	20.93	22.94	27.08	
Nb pyrid—N	10.88	13.48	15.95	17.66	20.05	21.43	
NF_2—(C)	26.5	34.58	40.9	45.63	50.9	53.54	
NH—(2Cb)	9.04	13.06	17.29	21.35	28.3	32.98	
NH—(2CO)	15.03	23.19	28.05	30.93	33.28	34.28	
NH—(2C)	17.58	21.81	25.66	28.59	33.07	36.21	39.97
NH—(Cb,CO)	2.39	6.32	9.96	13.94	16.91	18.21	
NH—(C,Cb)	15.99	20.47	23.9	26.29	30.1	32.36	
NH—(C,CO)	2.76	6.49	10.3	14.57	17.75	18.96	
NH—(C,N)	20.09	24.28	27.21	29.3	32.65	34.74	37.67
NH_2—(Cb)	23.94	27.25	30.64	33.78	39.39	43.83	51.4
NH_2—(CO)	17.04	24.03	29.85	34.7	41.69	46.97	
NH_2—(C)	23.94	27.25	30.64	33.78	39.39	43.83	51.4
NH_2—N	25.53	30.98	35.16	38.93	43.95	48.14	55.25
═Naz—(C)	11.3	17.16	20.59	22.35	23.82	23.9	

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Group†	298 K	400 K	500 K	600 K	800 K	1000 K	1500 K
═Naz—(N)	8.87	17.5	23.06	28.34	28.71	29.51	
Nitrogen Groups							
═NazH	18.33	20.47	22.77	24.86	28.34	31.06	35.33
═Nim—(Cb)	12.56						
═Nim—(C)	10.38	13.98	16.53	17.96	19.21	19.25	
═NimH	12.35	19.17	27	32.27	38.22	41.52	
Sulfur Groups							
S—(2Cb)	8.37	8.41	9.38	11.47	15.91	19.72	
S—(2C)	20.89	20.76	21.01	21.22	22.65	23.98	
S—(2S)	19.67	20.93	21.35	21.77	22.19	22.6	
S—(2 ═C)	20.05	23.36	23.15	26.33	33.24	40.73	
S—(Cb,S)	12.1	14.19	15.57	17.37	20.01	21.35	
S—(C,Cb)	12.64	14.19	15.53	16.91	19.34	20.93	
S—(C,S)	21.89	22.69	23.06	23.06	22.52	21.43	
S—(C, ═C)	17.66	21.26	23.27	24.15	24.57	24.57	
SH—(Cb)	21.43	22.02	23.32	25.24	29.26	32.82	
SH—(CO)	31.94	33.86	33.99	34.2	35.58	34.49	
SH—(C)	24.53	25.95	27.25	28.38	30.56	32.27	
SO—(2Cb)	23.94	38.05	40.6	47.93	47.97	47.09	
SO—(2C)	37.17	41.98	43.95	45.17	45.96	46.76	
SO_2—(2Cb)	34.99	46.17	56.72	62.54	66.39	66.81	
SO_2—(2C)	48.22	50.1	55.88	59.77	64.38	66.47	
SO_2—(2 ═C)	48.22	50.1	55.88	59.77	64.38	66.47	
SO_2—(Cb,SO_2)	41.06	48.14	56.59	61.66	65.76	67.1	
SO_2—(Cb, ═C)	41.4	48.14	55.88	61.16	65.8	66.64	
SO_2—(C,Cb)	41.61	48.14	56.3	60.74	65.38	66.64	

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Group†	298 K	400 K	500 K	600 K	800 K	1000 K	1500 K
S(CN)—(Cb)	39.77						
S(CN)—(C)	46.88						
S(CN)—(═C)	59.44						
Boron and Silicon Groups							
Si—(4C)	113.23	134.95	154.5	171.2	198.62	219.72	252.91
SiH_3—(C)	−39.64						
Monovalent Ligands							
CH_2(CN)—(C)	47.72	56.93	64.04	70.74	80.79	85.81	
CH_2(NCS)—(C)	61.95						
$CH_2(NO_2)$—(C)	52.7	66.22	77.52	86.48	99.58	108.41	
CH(CN)—(2C)	45.21	54	60.69	66.14	72	79.11	
$CH(NO_2)$—(2C)	50.19	63.67	74.17	82.08	92.84	99.2	
$CH(NO_2)_2$—(C)	80.79	101.3	117.2	129.76	146.09	156.13	
C(CN)—(3C)	36.21	46.71	53.96	58.81	64.92	67.77	
$C(CN)_2$—(2C)	61.62	74.47	83.72	90.46	99.54	104.48	
$C(NO_2)$—(3C)	41.4	55.84	66.39	73.75	82.92	87.32	
═CH(CHN_2)	72.42						
═CH(CN)	43.11	50.23	56.09	61.11	68.65	73.67	
═CH(NCS)	51.90						
═CH(NO_2)	51.49	63.21	72.83	80.37	90.41	97.11	105.9
═$C(CN)_2$	56.93	69.28	78.19	84.76	93.51	98.74	
3,4 Member Ring Corrections							
cyclobutane ring	−19.3	−16.28	−13.14	−11.05	−7.87	−5.78	−2.8
cyclobutene ring	−10.59	−9.17	−7.91	−7.03	−6.2	−5.57	−5.11
cyclopropane ring	−12.77	−10.59	−8.79	−7.95	−7.41	−6.78	−6.36
ethylene oxide ring	−8.37	−11.72	−12.56	−10.88	−9.63	−8.63	
ethylene sulfide ring	−11.93	−10.84	−11.13	−12.64	18.09	24.35	

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Group†	298 K	400 K	500 K	600 K	800 K	1000 K	1500 K
thietane ring	−19.21	−17.5	−16.37	−16.37	−19.25	−23.86	
trimethylene oxide ring	−19.25	−20.93	−17.58	−14.56	−10.88	0.84	
5,6 Member Ring Corrections							
1,4 dioxane ring	−19.21	−20.8	−15.91	−10.97	−6.4	−1.8	
cyclohexane ring	−24.28	−17.16	−12.14	−5.44	4.6	9.21	13.81
cyclohexene ring	−17.92	−12.72	−8.29	−5.99	−1.21	0.33	3.39
cyclopentadiene ring	−14.44	−11.85	−8.96	−6.91	−5.36	−4.35	
cyclopentane ring	−27.21	−23.02	−18.84	−15.91	−11.72	−8.08	−1.55
cylopentene ring	−25.03	−22.39	−20.47	−17.33	−12.26	−9.46	−4.52
furan ring	−20.51	−18	−15.07	−12.56	−10.88	−10.05	
piperidine ring	−24.7	−19.67	−12.14	−3.77	9.21	17.58	
pyrrolidine ring	−25.83	−23.36	−20.09	−16.74	−12.01	−9.08	
tetrahydrofuran ring	−25.12	−24.28	−20.09	−15.91	−11.3	−7.53	
thiacyclohexane ring	−26.04	−17.83	−9.38	−2.89	3.6	5.4	
thiolane ring	−20.51	−19.55	−15.4	−15.32	−18.46	−23.32	
thiophene ring	−20.51	−19.55	−15.4	−15.32	−18.46	−23.32	
7 and 8 Member Ring Corrections							
cycloheptane ring	−38.01						
cyclooctane ring	−44.16						
Gauche and 1,5 Repulsion Corrections							
but-2-ene structure C—C ═C—C	−5.61	−4.56	−3.39	−2.55	−1.63	−1.09	
but-3-ene structure C—C—C ═C	−5.61	−4.56	−3.39	−2.55	−1.63	−1.09	
cis- between 2 t-butyl groups	−5.61	−4.56	−3.39	−2.55	−1.63	−1.09	
cis- involving 1 t-butyl group	−5.61	−4.56	−3.39	−2.55	−1.63	−1.09	
cis-(not with t-butyl group)	−5.61	−4.56	−3.39	−2.55	−1.63	−1.09	
ortho- between Cl atoms	−2.09	5.02	2.09	−2.51	−1.26		
ortho- between F atoms		−0.84	−0.42	1.26	2.93		

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Group†	298 K	400 K	500 K	600 K	800 K	1000 K	1500 K
other *ortho*- (nonpolar-nonpolar)	4.69	5.65	5.44	4.9	3.68	2.76	−0.21
*Benson, S. W., et al., *Chem. Rev.*, **69** (1969): 279.							
†CHETAH Version 8.0: *The ASTM Computer Program for Chemical Thermodynamic and Energy Release Evaluation (NIST Special Database 16).*							
†Table-specific nomenclature: Cb = carbon in benzene ring; Ct = carbon with a triple bond, (═C) = carbon with a double bond; Cp = carbon in fused ring; Naz = azide; Nim = imino.							

Description: Groups are summed at each individual temperature:

$$C_P^o = \sum_{i=1}^{N} n_i \cdot (C_p^o)_i$$

(2-52)

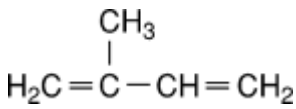
where n_i = number of occurrences of group *i* and (C_P^o)$_i$ = individual group contribution. Either Eq. (2-48) or Eq. (2-49) can be used to interpolate between the discrete temperatures.

Example

Example

Calculate the ideal gas heat capacity of isoprene (2-methyl-1,3-butadiene) at 400 K.

Structure:



Group identification and values:

Group	No.	Value, J/(mol · K)	Contribution, J/(mol · K)
═CH_2	2	26.62	53.24
═C−(2C)	1	19.3	19.3
−CH_3−(═C)	1	32.82	32.82
═CH−(C)	1	21.05	21.05
			Total 126.41

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The value of 126.4 J/(mol · K) is 3.1 percent below the DIPPR 801 recommended value of 130.4 J/(mol · K).

Liquids Liquid isobaric heat capacity increases with increasing temperature, although a minimum occurs near the triple point for many compounds. Usually liquid heat capacity is correlated as a function of temperature with a polynomial equation; a third-order polynomial is usually adequate.

Estimation of liquid heat capacity can be done by using a number of methods [Ruzicka, V., and E. S. Domalski, *J. Phys. Chem. Ref. Data*, **22** (1993): 597, 619; Chueh, C. F., and A. C. Swanson, *Chem. Eng. Prog.*, **69**, 7 (1973): 83; Lee, B. I., and M. G. Kesler, *AIChE J.*, **21** (1975): 510; Tarakad, R. R., and R. P. Danner, *AIChE J.*, **23** (1977): 944] and thermodynamic differentiation. The Ruzicka-Domalski method is generally accurate at low temperature, but the cubic behavior can overestimate the temperature rise at higher temperatures. The Lee-Kesler method is accurate for nonpolar and slightly polar fluids, but has less accuracy for strongly polar or associating fluids.

Recommended Method 1 Ruzicka-Domalski.

References: Ruzicka, V., and E. S. Domalski, *J. Phys. Chem. Ref. Data*, **22** (1993): 597, 619.

Classification: Group contributions.

Expected uncertainty: 4 percent.

Applicability: Organic compounds for which group values are available.

Input data: Molecular structure and Table 2-166 values.

Table 2-166 Liquid Heat Capacity Group Parameters for Ruzicka-Domalski Method*

†Group Definition	*a*	*b*	*d*	*T* range (K)
Hydrocarbon Groups				
C—(3H,C)	3.8452	−0.33997	0.19489	80–490
C—(2H,2C)	2.7972	−0.054967	0.10679	80–490
C—(H,3C)	−0.42867	0.93805	0.0029498	85–385
C—(4C)	−2.9353	1.4255	−0.085271	145–395
═C—(2H)	4.1763	−0.47392	0.099928	90–355
═C—(H,C)	4.0749	−1.0735	0.21413	90–355
═C—(2C)	1.9570	−0.31938	0.11911	140–315
═C—(H,═C)	3.6968	−1.6037	0.55022	130–305
═C—(C,═C)	1.0679	−0.50952	0.33607	130–305
C—(3H,═C)	3.8452	−0.33997	0.19489	80–490
C—(2H,C,═C)	2.0268	−0.20137	0.11624	90–355
C—(H,2C,═C)	−0.87558	0.82109	0.18415	110–300

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†Group Definition	*a*	*b*	*d*	*T* range (K)
C—(3C, ═C)	−4.8006	2.6004	−0.040688	165–295
C—(2H,2 ═C)	1.4973	−0.46017	0.52861	130–300
Ct—(H)	9.1633	−4.6695	1.1400	150–275
Ct—(C)	1.4822	1.0770	−0.19489	150–285
═C═	3.0880	−0.62917	0.25779	140–315
Ct—(Cb)	12.377	−7.5742	1.3760	230–550
Cb—(H)	2.2609	−0.2500	0.12592	180–670
Cb—(C)	1.5070	−0.13366	0.011799	180–670
Cb—(═C)	−5.7020	5.8271	−1.2013	230–550
Cb—(Cb)	5.8685	−0.86054	−0.063611	295–670
C—(2H,C,Ct)	2.0268	−0.20137	0.11624	90–355
C—(3H,Ct)	3.8452	−0.33997	0.19489	80–490
C—(3H,Cb)	3.8452	−0.33997	0.19489	80–490
C—(2H,C,Cb)	1.4142	0.56919	0.0053465	180–470
C—(H,2C,Cb)	−0.10495	1.0141	−0.071918	180–670
C—(3C,Cb)	1.2367	−1.3997	0.41385	220–295
C—(2H,2Cb)	−18.583	11.344	−1.4108	300–420
C—(H,3Cb)	−46.611	24.987	−3.0249	375–595
═C—(H,Cb)	3.6968	−1.6037	0.55022	130–305
═C—(C,Cb)	1.0679	−0.50952	0.33607	130–305
Cp—(Cp,2Cb)	−3.5572	2.8308	−0.39125	250–510
Cp—(2Cp,Cb)	−11.635	6.4068	−0.78182	370–510
Cp—(3Cp)	26.164	−11.353	1.2756	385–480
Halogen Groups				
C—(C,3F)	15.423	−9.2464	2.8647	125–345
C—(2C,2F)	−8.9527	10.550	−1.9986	125–345
C—(C,3Cl)	8.5430	2.6966	−0.42564	245–310

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†Group Definition	*a*	*b*	*d*	*T* range (K)
C—(H,C,2Cl)	10.880	−0.35391	0.08488	180–355
C—(2H,C,Cl)	9.6663	−1.8601	0.41360	140–360
C—(2H,═C,Cl)	9.6663	−1.8601	0.41360	140–360
C—(H,2C,Cl)	−2.0600	5.3281	−0.82721	275–360
C—(2H,C,Br)	6.3944	−0.10298	0.19403	168–360
C—(H,2C,Br)	10.784	−2.4754	0.33288	190–420
C—(2H,C,I)	0.037620	5.6204	−0.92054	245–340
C—(C,2Cl,F)	13.532	−3.2794	0.80145	240–420
C—(C,Cl,2F)	7.2295	0.41759	0.15892	180–420
C—(C,Br,2F)	8.7956	−0.19165	0.24596	165–415
═C—(H,Cl)	7.1564	−0.84442	0.27199	120–300
═C—(2F)	7.6646	−2.0750	0.82003	120–240
═C—(2Cl)	9.3249	−1.2478	0.44241	155–300
Halogen Groups				
═C—(Cl,F)	7.8204	−0.69005	0.19165	120–240
Cb—(F)	3.0794	0.46959	−0.0055745	210–365
Cb—(Cl)	4.5479	0.22250	−0.0097873	230–460
Cb—(Br)	2.2857	2.2573	−0.40942	245–370
Cb—(I)	2.9033	2.9763	−0.62960	250–320
C—(Cb,3F)	7.4477	−0.92230	0.39346	210–365
C—(2H,Cb,Cl)	16.752	−6.7938	1.2520	245–345
Nitrogen Groups				
C—(3H,N)	3.8452	−0.33997	0.19489	80–490
C-(2H,C,N)	2.4555	1.0431	−0.24054	190–375
C—(2H,Cb,N)	2.4555	1.0431	−0.24054	190–375
C—(H,2C,N)	2.6322	−2.0135	0.45109	240–370
C—(3C,N)	1.9630	−1.7235	0.31086	255–375

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†Group Definition	*a*	*b*	*d*	*T* range (K)
N—(2H,C)	8.2758	−0.18365	0.035272	185–455
N—(2H,Cb)	8.2758	−0.18365	0.035272	185–455
N—(H,2C)	−0.10987	0.73024	0.89325	170–400
N—(3C)	4.5942	−2.2134	0.55316	160–360
N—(H,C,Cb)	0.49631	3.4617	−0.57161	240–380
N—(2C,Cb)	−0.23640	16.260	−2.5258	285–390
N—(C,2Cb)	4.5942	−2.2134	0.55316	160–360
Cb—(N)	−0.78169	1.5059	−0.25287	240–455
N—(2H,N)	6.8050	−0.72563	0.15634	215–465
N—(H,C,N)	1.1411	3.5981	−0.69350	205–300
N—(2C,N)	−1.0570	4.0038	−0.71494	205–300
N—(H,Cb,N)	−0.74531	3.6258	−0.53306	295–385
C—(2H,C,CN)	11.976	−2.4886	0.52358	185–345
C—(3C,CN)	2.5774	3.5218	−0.58466	295–345
═C—(H,CN)	9.0789	−0.86929	0.32986	195–345
Cb—(CN)	1.9389	3.0269	−0.47276	265–480
C—(2H,C,NO_2)	18.520	−5.4568	1.05080	190–300
O—(C,NO_2)	−2.0181	10.505	−1.83980	180–350
Cb—(NO_2)	15.277	−4.4049	0.71161	280–415
N—(H,2Cb) (pyrrole)	−7.3662	6.3622	−0.68137	255–450
Nb—(2Cb)	0.84237	1.25560	−0.20336	210–395
Oxygen Groups				
O—(H,C)	12.952	−10.145	2.6261	155–505
O—(H,C) (diol)	5.2302	−1.5124	0.54075	195–475
O—(H,Cb) (diol)	5.2302	−1.5124	0.54075	195–475
O—(H,Cb)	−7.9768	8.10450	−0.87263	285–400

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†Group Definition	*a*	*b*	*d*	*T* range (K)
C–(3H,O)	3.8452	−0.33997	0.19489	80–490
C–(2H,C,O)	1.4596	1.4657	−0.27140	135–505
C–(2H,Cb,O)	−35.127	28.409	−4.9593	260–460
C–(2H,═C,O)	−35.127	28.409	−4.9593	260–460
C—(H,2C,O) (alcohol)	2.2209	−1.4350	0.69508	185–460
C—(H,2C,O) (ether, ester)	0.98790	0.39403	−0.016124	130–170
C—(3C,O) (alcohol)	−44.690	31.769	−4.8791	200–355
C—(3C,O) (ether, ester)	−3.3182	2.6317	−0.44354	170–310
O—(2C)	5.0312	−1.5718	0.37860	130–350
O—(C,Cb)	−22.5240	13.1150	−1.44210	320–350
O—(2Cb)	−4.5788	0.94150	0.31655	300–535
C—(2H,2O)	1.0852	1.5402	−0.31693	170–310
Oxygen Groups				
C—(2C,2O)	−12.955	9.10270	−1.53670	275–335
Cb—(O)	−1.0686	3.52210	−0.79259	285–530
C—(3H,CO)	3.8452	−0.33997	0.19489	80–490
C—(2H,C,CO)	6.6782	−2.44730	0.47121	180–465
C—(H,2C,CO)	3.92380	−2.12100	0.49646	185–375
C—(3C,CO)	−2.2681	1.75580	−0.25674	225–360
CO—(H,C)	−3.82680	7.67190	−1.27110	180–430
CO—(H,═C)	−8.00240	3.63790	−0.15377	220–430
CO—(H,Cb)	−8.00240	3.63790	−0.15377	220–430
CO—(2C)	5.4375	0.72091	−0.18312	185–380
CO—(C,═C)	41.507	−32.632	6.0326	275–355
CO—(C,Cb)	−47.21100	24.36800	−2.82740	300–465
CO—(H,O)	13.11800	16.12000	−5.12730	280–340

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†Group Definition	*a*	*b*	*d*	*T* range (K)
CO—(C,O)	29.24600	3.42610	−2.89620	180–445
CO—(═C,O)	41.61500	−12.78900	0.53631	195–350
CO—(O,CO)	23.99000	6.25730	−3.24270	320–345
O—(C,CO)	−21.43400	−4.01640	3.05310	175–440
O—(H,CO)	−27.58700	−0.16485	2.74830	230–500
═C—(H,CO)	−9.01080	15.14800	−3.04360	195–355
═C—(C,CO)	−12.81800	15.99700	−3.05670	195–430
Cb—(CO)	12.15100	−1.67050	−0.12758	175–500
CO—(Cb,O)	16.58600	5.44910	−2.68490	175–500
Sulfur Groups				
C—(3H,S)	3.84520	−0.33997	0.19489	80–490
C—(2H,C,S)	1.54560	0.88228	−0.08349	130–390
C—(H,2C,S)	−1.64300	2.30700	−0.31234	150–390
C—(3C,S)	−5.38250	4.50230	−0.72356	190–365
Cb—(S)	−4.45070	4.43240	−0.75674	260–375
S—(H,C)	10.99400	−3.21130	0.47368	130–380
S—(H,Cb)	10.99400	−3.21130	0.47368	130–380
S—(2C)	9.23060	−3.00870	0.45625	165–390
S—(2Cb)	9.23060	−3.00870	0.45625	165–390
S—(C,S)	6.65900	−1.35570	0.17938	170–350
S—(Cb,S)	9.23060	−3.00870	0.45625	165–390
S—(2Cb) (thiophene)	3.84610	0.36718	−0.06131	205–345
Ring Strain Contributions				
Hydrocarbons (ring strain)				
cyclopropane	4.4297	−4.3392	1.0222	155–240
cyclobutane	1.2313	−2.8988	0.75099	140–300
cyclopentane (unsub)	−0.33642	−2.8663	0.70123	180–300

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†Group Definition	*a*	*b*	*d*	*T* range (K)
cyclopentane (sub)	0.21983	−1.5118	0.28172	135–365
cyclohexane	−2.0097	−0.72656	0.14758	145–485
cycloheptane	−11.460	4.9507	−0.74754	270–300
cyclooctane	−4.1696	0.52991	−0.018423	295–320
spiropentane	5.9700	−3.7965	0.74612	175–310
cyclopentene	0.21433	−2.5214	0.63136	140–300
cyclohexene	−1.2086	−1.5041	0.42863	160–320
cycloheptene	−5.6817	1.5073	−0.19810	220–300
cyclooctene	−14.885	7.4878	−1.0879	260–330
cyclohexadiene	−8.9683	6.4959	−1.5272	170–300
cyclooctadiene	−7.2890	3.1119	−0.43040	205–320
cycloheptatriene	−8.7885	8.2530	−2.4573	200–310
cyclooctatetraene	−12.914	13.583	−4.0230	275–330
indan	−6.1414	3.5709	−0.48620	170–395
1H-indene	−3.6501	2.4707	−0.60531	280–375
tetrahydronaphthalene	−6.3861	2.6257	−0.19578	250–320
decahydronaphthalene	−6.8984	0.66846	−0.070012	235–485
hexahydroindan	−3.9271	−0.29239	0.048561	210–425
dodecahydrofluorene	−19.687	8.8265	−1.4031	315–485
tetradecahydrophenanthrene	−0.67632	−1.4753	−0.13087	315–485
hexadecahydropyrene	61.213	−30.927	3.2269	310–485
Nitrogen compounds				
ethyleneimine	15.281	−2.3360	−0.13720	195–330
pyrrolidine	12.703	1.3109	−1.18130	170–400
piperidine	25.681	−7.0966	0.14304	265–370
Oxygen compounds				
ethylene oxide	6.8459	−5.8759	1.2408	135–325

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†Group Definition	*a*	*b*	*d*	*T* range (K)
trimethylene oxide	−7.0148	7.3764	−2.1901	185–300
1,3-dioxolane	−2.3985	−0.48585	0.10253	175–300
furan	9.6704	−2.8138	0.11376	190–305
tetrahydrofuran	3.2842	−5.8260	1.2681	160–320
tetrahydropyran	−13.017	3.7416	−0.15622	295–325
Sulfur compounds				
thiacyclobutane	−0.73127	−1.3426	0.40114	200–320
thiacyclopentane	−3.2899	0.38399	0.089358	170–390
thiacyclohexane	−12.766	5.2886	−0.59558	295–340
*Ruzicka, V., and E. S. Domalski, *J. Phys. Chem. Ref. Data*, **22** (1993): 597, 619.				
†Table-specific nomenclature: Ct refers to a carbon atom with a triple bond; Cb refers to a carbon atom in benzene ring; ═C refers to a carbon atom with a double bond; Cp refers to a carbon atom in a fused benzene ring; ═C═ refers to an allenic carbon atom.				

Description: Groups are summed to find the temperature coefficients for a cubic polynomial correlation:

$$\frac{C_p}{R} = A + B\left(\frac{T}{100\ \mathrm{K}}\right) + D\left(\frac{T}{100\ \mathrm{K}}\right)^2$$

(2-53)

$$A = \sum_{i=1}^{N} n_i a_i \quad B = \sum_{i=1}^{N} n_i b_i \quad D = \sum_{i=1}^{N} n_i d_i$$

(2-54)

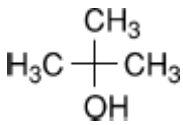
where n_i = number of occurrences of group *i* and a_i, b_i, d_i = individual group contributions.

Example

Example

Estimate the liquid heat capacity for 2-methyl-2-propanol at 340 K.

Structure:



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Group contributions:

Group	n_i	a_i	b_i	d_i
C — (3C, O) (alcohol)	1	−44.690	31.769	−4.8791
O — (H)(C)	1	12.952	−10.145	2.6261
C — (3H)(C)	3	3.8452	−0.33997	0.19489
	Sum	−20.202	20.604	−1.668

$$C_p = \left(8.3143 \frac{\mathrm{J}}{\mathrm{mol \cdot K}}\right) \left[-20.202 + 20.604 \left(\frac{304}{100}\right) - 1.668 \left(\frac{340}{100}\right)^2\right]$$
$$= 254.16 \frac{\mathrm{J}}{\mathrm{mol \cdot K}}$$

This value is 0.7 percent higher than the DIPPR 801 recommended value of 252.40 J/(mol · K).

Recommended Method 2 Lee-Kesler.

References: [PGL5]

Classification: Corresponding states.

Expected uncertainty: 4 percent.

Applicability: Organic compounds other than those that are strongly polar or associate.

Input data: T_c, ω, and the ideal gas heat capacity at the same temperature.

Description: The isobaric liquid heat capacity is calculated at the reduced temperature T_r using

$$\frac{C_p}{R} = \frac{C_p^o}{R} + 1.586 + \frac{0.49}{1 - T_r} + \omega \left[4.2775 + \frac{6.3(1 - T_r)^{1/3}}{T_r} + \frac{0.4355}{1 - T_r}\right]$$

(2-55)

Example

Example

Calculate the isobaric liquid heat capacity for 1,4-dioxane at 320 K.

Auxiliary data: From the DIPPR 801 database: T_c = 597.0 K, ω = 0.2793, and C_p^o/R = 11.94. The reduced temperature is therefore T_r = (320 K)/(597.0 K) = 0.536.

From Eq. (2.55),

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$$\frac{C_p}{R} = 11.94 + 1.586 + \frac{0.49}{1-0.536} + (0.2793)\left[4.2775 + \frac{6.3(1-0.536)^{1/3}}{0.536} + \frac{0.4355}{1-0.536}\right] = 18.58$$

and C_p = 154.5 J/(mol · K). This is 4.6 percent below the DIPPR recommended value of 162.0 J/(mol · K).

Solids Solid heat capacity increases with increasing temperature and is proportional to T^3 near absolute zero. The heat capacity at a solid-solid phase transition becomes large, and there can be a substantial difference in the heat capacity of the two equilibrium solid phases that exist on either side of the transition temperature. The heat capacity generally rises steeply with increasing temperature near the triple point.

For a quick estimation of solid heat capacity specifically at 298.15 K, the very simple modification of Kopp's rule [Kopp, H., *Ann. Chem. Pharm.* (*Liebig*), **126** (1863): 362] by Hurst and Harrison [Hurst, J. E., and B. K. Harrison, *Chem. Eng. Comm.*, **112** (1992): 21] can be used. At other temperatures and to obtain the temperature dependence of the solid heat capacity, the method given below by Goodman et al. should be used.

Recommended Method 1 Goodman method.

Reference: Goodman, B. T., W. V. Wilding, J. L. Oscarson, and R. L. Rowley, *J. Chem. Eng. Data*, **49** (2004): 24.

Classification: Group contributions.

Expected uncertainty: 10 percent.

Applicability: Organic compounds for which group values are available.

Input data: Molecular structure and Table 2-167 group values.

Table 2-167 Group Values and Nonlinear Correction Terms for Estimation of Solid Heat Capacity with the Goodman et al.* Method

Group	Description	a_i	Group	Description	a_i
$-CH_3$	methyl	0.20184	$-CO_3-$	carbonate	0.2517
$>CH_2$	methylene	0.11644	$-NH_2$	primary amine	0.056138
>CH–	secondary C	0.030492	>NH	secondary amine	−0.00717
>C<	tertiary C	−0.04064	>N–	tertiary amine	−0.01661
$CH_2{=}$	terminal alkene	0.18511	=NH	double-bond NH	0.17689
–CH=	alkene	0.11224	#N	nitrile	0.015355
>C=	subst. alkene	0.028794	–N=N–	diazide	0.3687
=C=	allene	0.053464	$-NO_2$	nitro	0.23327
#CH	terminal alkyne	−0.02914	–N=C=O	isocyanate	0.2698
#C–	alkyne	0.13298	–SH	thiol/mercaptan	0.21123

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Group	Description	*a*	Group	Description	*a*
Ar —CH═	arom. C	0.082478	—S—	sulfide	0.14232
Ar >C═	subst. arom. C	0.012958	—SS—	disulfide	0.31457
Ar —O—	furan O	0.066027	═S	sulfur double bond	0.13753
Ar —N═	pyridine N	0.056641	>S═O	sulfoxide	0.040002
Ar >N—	subst. pyrrole N	0.008938	—F	fluoride	0.15511
Ar —NH—	pyrrole N	−0.05246	—Cl	chloride	0.16995
Ar —S—	thiophene S	0.090926	—Br	bromide	0.19112
—O—	ether	0.064068	—I	iodide	0.11318
—OH	alcohol	0.10341	>Si<	silane	0.12213
—COH	aldehyde	0.15699	>Si(O—)—	linear siloxane	0.10125
>C═O	ketone	0.12939	cyc >Si(O—)—	cyclic siloxane	0.063438
—COO—	ester	0.13686	P(═O)(O—)$_3$	phosphate	0.15016
—COOH	acid	0.21019	>P—	phosphine	0.069602
—COOCO—	anhydride	0.33091	>P(═O)—	phosphine oxide	0.21875

Nonlinear Terms		
Groups	β_i	Usage
>CH_2	−0.00188	Methylene
Ar═CH—	−0.00033	Aromatic carbon

*Goodman, B. T., W. V. Wilding, J. L. Oscarson, and R. L. Rowley, *J. Chem. Eng. Data*, **49** (2004): 24.

Description:

$$\frac{C_P}{\mathrm{J/(mol \cdot K)}} = \frac{A}{1000}\left(\frac{T}{\mathrm{K}}\right)^{0.79267}$$

(2-56)

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$$A = \exp\left(6.7796 + \sum_{i=1}^{N} n_i a_i + \sum_{i=1}^{N} n_i^2 \beta_i\right)$$

(2-57)

where

n_i = number of occurrences of group *i*

a_i = individual group *i* contribution

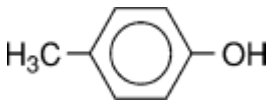
β_i = nonlinear correction terms for chain and aromatic carbons

Example

Example

Estimate the solid heat capacity for *p*-cresol at 307.93 K.

Structure:



Group contributions:

Group	n_i	a_i	β_i
$-CH_3$	1	0.20184	0
Ar—CH═	4	0.082478	−0.00033
Ar >C═	2	0.012958	0
—OH	1	0.10341	0

From Eq. (2-57):

$$\begin{aligned} A &= \exp\,[6.7796 + 0.20184 + (4)\,(0.082478) + (2)(0.012958) \\ &\quad +0.10341 + (4)^2(-0.00033)] = 1694.9 \end{aligned}$$

From Eq. (2-56):

$$C_P = \frac{1694.9}{1000}(307.93)^{0.79267}\frac{\mathrm{J}}{\mathrm{mol}\cdot\mathrm{K}} = 159.1\frac{\mathrm{J}}{\mathrm{mol}\cdot\mathrm{K}}$$

This value is 2.5 percent higher than the DIPPR 801 recommended value of 155.2 J/(mol · K).

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Recommended Method 2 Modified Kopp's rule.

Reference: Kopp, H., *Ann. Chem. Pharm.* (*Liebig*), **126** (1863): 362; Hurst, J. E., and B. K. Harrison, *Chem. Eng. Comm.*, **112** (1992): 21.

Classification: Group contributions.

Expected uncertainty: 10 percent.

Applicability: At 298.15 K; organic compounds that are solids at 298.15 K.

Input data: Compound chemical formula and element contributions of Table 2-168.

Table 2-168 Element Contributions to Solid Heat Capacity for the Modified Kopp's Rule*†

Element	Δ_E	Element	Δ_E	Element	Δ_E
C	10.89	Ba	32.37	Mo	29.44
H	7.56	Be	12.47	Na	26.19
O	13.42	Ca	28.25	Ni	25.46
N	18.74	Co	25.71	Pb	31.60
S	12.36	Cu	26.92	Si	17.00
F	26.16	Fe	29.08	Sr	28.41
Cl	24.69	Hg	27.87	Ti	27.24
Br	25.36	K	28.78	V	29.36
I	25.29	Li	23.25	W	30.87
Al	18.07	Mg	22.69	Zr	26.82
B	10.10	Mn	28.06	All others	26.63

*Kopp, H., *Ann. Chem. Pharm.* (*Liebig*), **126** (1863): 362.

†Hurst, J. E., and B. K. Harrison, *Chem. Eng. Comm.*, **112** (1992): 21.

Description:

$$\frac{C_P}{\mathrm{J/(mol \cdot K)}} = \sum_{E=1}^{N} n_E \Delta_E$$

(2-58)

where

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N = number of different elements in compound

n_E = number of occurrences of element E in compound

Δ_E = contribution of element E from Table 2-168

Example

Example

Estimate the solid heat capacity at 298.15 K for dibenzothiophene.

Structure: $C_{12}H_8S$.

Group values from Table 2-168:

$$\Delta_C = 10.89 \quad \Delta_H = 7.56 \quad \Delta_S = 12.36$$

Calculation using Eq. (2-54):

$$C_P = (12)(10.89) + (8)(7.56) + (1)(12.36) = 203.52\ \mathrm{J/(mol \cdot K)}$$

This value is 2.5 percent higher than the DIPPR 801 recommended value of 198.45 J/(mol · K).

Mixtures The molar heat capacity of liquid and vapor mixtures can be estimated as a mole fraction average of the pure-component values

$$C_{P,m} = \sum_{i=1}^{C} x_i C_{P,i}$$

(2-59)

This neglects the excess heat capacity, which, if available, can be added to the mole fraction average to improve the estimated value.

2.16.11. DENSITY

Density is defined as the mass of a substance per unit volume. Density is given in kg/m^3 in SI units, but lb$_m$/ft^3 and g/cm^3 are common AES and cgs units, respectively. Other commonly used forms of density include *molar density* (density divided by molecular weight) in kmol/m^3, *relative density* (density relative to water at 15°C), and the older term *specific gravity* (density relative to water at 60°F). Often the inverse of density, *specific volume*, and the inverse of molar density, *molar volume*, are correlated and used to convey equivalent information.

Gases Gases/vapors are compressible and their densities are strong functions of both temperature and pressure. Equations of state (EoS) are commonly used to correlate molar densities or molar volumes. The most accurate EoS are those developed for specific fluids with parameters regressed from all available data for that fluid. Super EoS are available for some of the most industrially important gases and may contain 50 or more constants specific to that chemical. Different predictive methods may be used for gas densities depending upon the conditions:

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1. At *very low densities* (high temperatures, generally above the critical, and very low pressures, generally below a few bar), the ideal gas EoS

$$Z \equiv \frac{PV}{RT} = 1$$

(2-60)

may be applied.

2. At *moderate densities* (below 40 percent of the critical density), the virial equation truncated after the second virial coefficient

$$Z = 1 + \frac{B(T)}{V}$$

(2-61)

may be used. Second virial coefficients $B(T)$ are available in the DIPPR 801 database for many chemicals and can be estimated using the Tsonopoulos method.

Recommended Method Tsonopoulos method.

Reference: Tsonopoulos, C., *AIChE J.*, **20** (1974): 263; **21** (1975): 827; **24** (1978): 1112.

Classification: Corresponding states.

Expected uncertainty: 8 percent for $B(T)$.

Applicability: Nonpolar organic compounds and some classes of polar compounds.

Input data: Class of fluid, ω, P_c, T_c, and μ.

Description:

$$\frac{BP_c}{RT_c} = B^{(0)} + \omega B^{(1)} + B^{(2)}$$

(2-62)

where

$$B^{(0)} = 0.1445 - \frac{0.330}{T_r} - \frac{0.1385}{T_r^2} - \frac{0.0121}{T_r^3} - \frac{0.000607}{T_r^8}$$

(2-63)

$$B^{(1)} = 0.0637 + \frac{0.331}{T_r^2} - \frac{0.423}{T_r^3} - \frac{0.008}{T_r^8}$$

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(2-64)

$$B^{(2)} = \frac{a}{T_r^6} - \frac{b}{T_r^8}$$

(2-65)

$$\mu_r = \left(\frac{\mu}{\mathrm{D}}\right)^2 \left(\frac{P_c}{\mathrm{bar}}\right) \left(\frac{T_c}{\mathrm{K}}\right)^{-2}$$

(2-66)

and μ = dipole moment. The values of *a* and *b* used in Eq. (2-65) depend upon the class of fluid, as given in the table below:

Class	*a*	*b*
Nonpolar fluids	0	0
Ketones, aldehydes, nitriles, ethers, esters, NH_3, H_2S, HCN	$-21.4\mu_r - 4.308 \times 10^{19}\mu_r^8$	0
Monoalkylhalides, mercaptans, sulfides	$-2.188 \times 10^{16}\mu_r^4 - 7.831 \times 10^{19}\mu_r^8$	0
1-Alcohols except methanol	0.0878	$0.00908 + 69.57\mu_r$
Methanol	0.0878	0.0525

Example

Example

Estimate the molar volume of ammonia at 430 K and 2.82 MPa.

Input properties: Recommended values from the DIPPR 801 database are T_c = 405.65 K, P_c = 11.28 MPa, μ = 1.469 D, and ω = 0.252608.

Reduced conditions:

$$T_r = (430\ \mathrm{K})/(405.65\ \mathrm{K}) = 1.06$$
$$P_r = (2.82\ \mathrm{MPa})/(11.28\ \mathrm{MPa}) = 0.25$$
$$\mu_r = (1.469)^2(112.8)/(405.65)^2 = 0.0014793$$

Second virial coefficient from Eqs. (2-63) to (2-66):

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$$
\begin{aligned}
B^{(0)} &= 0.1445 - 0.330/1.06 - 0.1385/(1.06)^2 - 0.0121/(1.06)^3 - 0.000607/(1.06)^8 = -0.301 \\
B^{(1)} &= 0.0637 + 0.331/(1.06)^2 - 0.423/(1.06)^3 - 0.008/(1.06)^8 = -0.00189 \\
a &= (-21.4)(0.0014793) - \left(4.308 \times 10^{19}\right)(0.0014793)^8 = -0.033 \\
b &= 0 \\
B^{(2)} &= (-0.033)/(1.06)^6 = -0.023
\end{aligned}
$$

From Eq. (2-62):

$$
\begin{aligned}
&BP_c/(RT_c) = -0.301 - (0.252608)(0.00189) - 0.023 = -0.324 \\
&B = (-0.324)[0.008314\ \mathrm{m^3 \cdot MPa/(kmol \cdot K)}](405.65\ \mathrm{K})/(11.28\ \mathrm{MPa}) = -0.097\ \mathrm{m^3/kmol}
\end{aligned}
$$

Molar volume from Eq. (2-61) :

$$
V = \frac{RT}{P}\left(1 + \frac{B}{V}\right) = \frac{\left(0.0083143\,\frac{\mathrm{m^3 \cdot MPa}}{\mathrm{kmol \cdot K}}\right)\ (430\ \mathrm{K})}{2.82\ \mathrm{MPa}}\left(1 + \frac{-0.097\frac{\mathrm{m^3}}{\mathrm{kmol}}}{V}\right) = 1.162\ \frac{\mathrm{m^3}}{\mathrm{kmol}}
$$

Note that the ideal gas value, 1.268 m^3/kmol, deviates by 9.1 percent from this more accurate value. The truncated virial EoS should be valid for this density since $\rho = V^{-1}$ = 0.86 kmol/m^3 is much less than 40 percent of the critical density (the DIPPR 801 recommended value for the critical density is 13.8 kmol/m^3).

3. For *higher gas densities*, the Lee-Kesler method described below provides excellent predictions for nonpolar and slightly polar fluids. Extended four-parameter corresponding-states methods are available for polar and slightly associating compounds.

Recommended Method Lee-Kesler method.

Reference: Lee, B. I., and M. G. Kesler, *AIChE J.*, **21** (1975): 510.

Classification: Corresponding states.

Expected uncertainty: 1 percent except near the critical point where errors can be up to 30 percent.

Applicability: Nonpolar and moderately polar compounds. An extended Lee-Kesler method, not described here, may be used for polar and slightly associating compounds [Wilding, W. V., and R. L. Rowley, *Int. J. Thermophys.*, **8** (1986): 525].

Input data: T_c, P_c, ω, $Z^{(0)}$, $Z^{(1)}$.

Description:

$$
Z = Z^{(0)} + \omega Z^{(1)}
$$

(2-67)

where

Z = compressibility factor

$Z^{(0)}$ = compressibility factor of simple fluid obtained from Table 2-169

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$Z^{(1)}$ = deviation from simple fluid obtained from Table 2-170

Table 2-169 Simple Fluid Compressibility Factors $Z^{(0)}$

Tr\Pr†	0.010	0.050	0.100	0.200	0.400	0.600	0.800	1.000	1.200	1.500	2.000	3.000	5.000	7.000	10.000
0.30	0.0029	0.0145	0.0290	0.0579	0.1158	0.1737	0.2315	0.2892	0.3470	0.4335	0.5775	0.8648	1.4366	2.0048	2.8507
0.35	0.0026	0.0130	0.0261	0.0522	0.1043	0.1564	0.2084	0.2604	0.3123	0.3901	0.5195	0.7775	1.2902	1.7987	2.5539
0.40	0.0024	0.0119	0.0239	0.0477	0.0953	0.1429	0.1904	0.2379	0.2853	0.3563	0.4744	0.7095	1.1758	1.6373	2.3211
0.45	0.0022	0.0110	0.0221	0.0442	0.0882	0.1322	0.1762	0.2200	0.2638	0.3294	0.4384	0.6551	1.0841	1.5077	2.1338
	(0.9648)														
0.50	0.0021	0.0103	0.0207	0.0413	0.0825	0.1236	0.1647	0.2056	0.2465	0.3077	0.4092	0.6110	1.0094	1.4017	1.9801
	(0.9741)	(0.8699)													
0.55	0.9804	0.0098	0.0195	0.0390	0.0778	0.1166	0.1553	0.1939	0.2323	0.2899	0.3853	0.5747	0.9475	1.3137	1.8520
	(0.0020)	(0.9000)	(0.7995)												
0.60	0.9849	0.0093	0.0186	0.0371	0.0741	0.1109	0.1476	0.1842	0.2207	0.2753	0.3657	0.5446	0.8959	1.2398	1.7440
	(0.0019)	(0.9211)	(0.8405)												
0.65	0.9881	0.9377	0.0178	0.0356	0.0710	0.1063	0.1415	0.1765	0.2113	0.2634	0.3495	0.5197	0.8526	1.1773	1.6519
	(0.0018)	(0.0089)	(0.8707)	(0.7367)											
0.70	0.9904	0.9504	0.8958	0.0344	0.0687	0.1027	0.1366	0.1703	0.2038	0.2538	0.3364	0.4991	0.8161	1.1241	1.5729
		(0.0086)	(0.0172)	(0.7805)											
0.75	0.9922	0.9598	0.9165	0.0336	0.0670	0.1001	0.1330	0.1656	0.1981	0.2464	0.3260	0.4823	0.7854	1.0787	1.5047
		(0.0085)	(0.0169)	(0.8181)	(0.6122)										

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Tr\Pr†	0.010	0.050	0.100	0.200	0.400	0.600	0.800	1.000	1.200	1.500	2.000	3.000	5.000	7.000	10.000
0.80	0.9935	0.9669	0.9319	0.8539	0.0661	0.0985	0.1307	0.1626	0.1942	0.2411	0.3182	0.4690	0.7598	1.0400	1.4456
			(0.0168)	(0.0332)	(0.6659)	(0.4746)									
0.85	0.9946	0.9725	0.9436	0.8810	0.0661	0.0983	0.1301	0.1614	0.1924	0.2382	0.3132	0.4591	0.7388	1.0071	1.3943
				(0.0336)	(0.7222)	(0.5346)									
0.90	0.9954	0.9768	0.9528	0.9015	0.7800	0.1006	0.1321	0.1630	0.1935	0.2383	0.3114	0.4527	0.7220	0.9793	1.3496
				(0.0364)	(0.0685)	(0.6040)	(0.4034)								
0.93	0.9959	0.9790	0.9573	0.9115	0.8059	0.6635	0.1359	0.1664	0.1963	0.2405	0.3122	0.4507	0.7138	0.9648	1.3257
					(0.7350)	(0.1047)	(0.4499)								
0.95	0.9961	0.9803	0.9600	0.9174	0.8206	0.6967	0.1410	0.1705	0.1998	0.2432	0.3138	0.4501	0.7092	0.9561	1.3108
					(0.0822)	(0.1116)	0.4853)								
0.97	0.9963	0.9815	0.9625	0.9227	0.8338	0.7240	0.5580	0.1779	0.2055	0.2474	0.3164	0.4504	0.7052	0.9480	1.2968
						(0.1312)	(0.1532)								
0.98	0.9965	0.9821	0.9637	0.9253	0.8398	0.7360	0.5887	0.1844	0.2097	0.2503	0.3182	0.4508	0.7035	0.9442	1.2901
							(0.1703)								
0.99	0.9966	0.9826	0.9648	0.9277	0.8455	0.7471	0.6138	0.1959	0.2154	0.2538	0.3204	0.4514	0.7018	0.9406	1.2835
							(0.2324)								
1.00	0.9967	0.9832	0.9659	0.9300	0.8509	0.7574	0.6353	0.2901	0.2237	0.2583	0.3229	0.4522	0.7004	0.9372	1.2772
1.01	0.9968	0.9837	0.9669	0.9322	0.8561	0.7671	0.6542	0.4648	0.2370	0.2640	0.3260	0.4533	0.6991	0.9339	1.2710
1.02	0.9969	0.9842	0.9679	0.9343	0.8610	0.7761	0.6710	0.5146	0.2629	0.2715	0.3297	0.4547	0.6980	0.9307	1.2650

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Tr\Pr†	0.010	0.050	0.100	0.200	0.400	0.600	0.800	1.000	1.200	1.500	2.000	3.000	5.000	7.000	10.000
1.05	0.9971	0.9855	0.9707	0.9401	0.8743	0.8002	0.7130	0.6026	0.4437	0.3131	0.3452	0.4604	0.6956	0.9222	1.2481
1.10	0.9975	0.9874	0.9747	0.9485	0.8930	0.8323	0.7649	0.6880	0.5984	0.4580	0.3953	0.4770	0.6950	0.9110	1.2232
1.15	0.9978	0.9891	0.9780	0.9554	0.9081	0.8576	0.8032	0.7443	0.6803	0.5798	0.4760	0.5042	0.6987	0.9033	1.2021
1.20	0.9981	0.9904	0.9808	0.9611	0.9205	0.8779	0.8330	0.7858	0.7363	0.6605	0.5605	0.5425	0.7069	0.8990	1.1844
1.30	0.9985	0.9926	0.9852	0.9702	0.9396	0.9083	0.8764	0.8438	0.8111	0.7624	0.6908	0.6344	0.7358	0.8998	1.1580
1.40	0.9988	0.9942	0.9884	0.9768	0.9534	0.9298	0.9062	0.8827	0.8595	0.8256	0.7753	0.7202	0.7761	0.9112	1.1419
1.50	0.9991	0.9954	0.9909	0.9818	0.9636	0.9456	0.9278	0.9103	0.8933	0.8689	0.8328	0.7887	0.8200	0.9297	1.1339
1.60	0.9993	0.9964	0.9928	0.9856	0.9714	0.9575	0.9439	0.9308	0.9180	0.9000	0.8738	0.8410	0.8617	0.9518	1.1320
1.70	0.9994	0.9971	0.9943	0.9886	0.9775	0.9667	0.9563	0.9463	0.9367	0.9234	0.9043	0.8809	0.8984	0.9745	1.1343
1.80	0.9995	0.9977	0.9955	0.9910	0.9823	0.9739	0.9659	0.9583	0.9511	0.9413	0.9275	0.9118	0.9297	0.9961	1.1391
1.90	0.9996	0.9982	0.9964	0.9929	0.9861	0.9796	0.9735	0.9678	0.9624	0.9552	0.9456	0.9359	0.9557	1.0157	1.1452
2.00	0.9997	0.9986	0.9972	0.9944	0.9892	0.9842	0.9796	0.9754	0.9715	0.9664	0.9599	0.9550	0.9772	1.0328	1.1516
2.20	0.9998	0.9992	0.9983	0.9967	0.9937	0.9910	0.9886	0.9865	0.9847	0.9826	0.9806	0.9827	1.0094	1.0600	1.1635
2.40	0.9999	0.9996	0.9991	0.9983	0.9969	0.9957	0.9948	0.9941	0.9936	0.9935	0.9945	1.0011	1.0313	1.0793	1.1728
2.60	1.0000	0.9998	0.9997	0.9994	0.9991	0.9990	0.9990	0.9993	0.9998	1.0010	1.0040	1.0137	1.0463	1.0926	1.1792
2.80	1.0000	1.0000	1.0001	1.0002	1.0007	1.0013	1.0021	1.0031	1.0042	1.0063	1.0106	1.0223	1.0565	1.1016	1.1830
3.00	1.0000	1.0002	1.0004	1.0008	1.0018	1.0030	1.0043	1.0057	1.0074	1.0101	1.0153	1.0284	1.0635	1.1075	1.1848
3.50	1.0001	1.0004	1.0008	1.0017	1.0035	1.0055	1.0075	1.0097	1.0120	1.0156	1.0221	1.0368	1.0723	1.1138	1.1834
4.00	1.0001	1.0005	1.0010	1.0021	1.0043	1.0066	1.0090	1.0115	1.0140	1.0179	1.0249	1.0401	1.0741	1.1136	1.1773

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Tr\Pr†	0.010	0.050	0.100	0.200	0.400	0.600	0.800	1.000	1.200	1.500	2.000	3.000	5.000	7.000	10.000

†Values in parentheses are for the opposite phase and may be used to interpolate to or near the phase boundary [PGL4; Wilding, W. V., J. K. Johnson, and R. L. *Rowley, Int. J. Thermophys*., **8**(1987):717].

Table 2-170 Acentric Deviations $Z^{(1)}$ from the Simple Fluid Compressibility Factor

Tr\Pr†	0.010	0.050	0.100	0.200	0.400	0.600	0.800	1.000	1.200	1.500	2.000	3.000	5.000	7.000	10.000
0.30	−0.008	−0.040	−0.081	−0.161	−0.323	−0.484	−0.645	−0.806	−0.966	−0.1207	−0.1608	−0.2407	−0.3996	−0.5572	−0.7915
0.35	−0.009	−0.046	−0.093	−0.185	−0.370	−0.554	−0.738	−0.921	−0.1105	−0.1379	−0.1834	−0.2738	−0.4523	−0.6279	−0.8863
0.40	−0.010	−0.048	−0.095	−0.190	−0.380	−0.570	−0.758	−0.946	−0.1134	−0.1414	−0.1879	−0.2799	−0.4603	−0.6365	−0.8936
0.45	−0.009	−0.047	−0.094	−0.187	−0.374	−0.560	−0.745	−0.929	−0.1113	−0.1387	−0.1840	−0.2734	−0.4475	−0.6162	−0.8606
	(−0.0740)														
0.50	−0.009	−0.045	−0.090	−0.181	−0.360	−0.539	−0.716	−0.893	−0.1069	−0.1330	−0.1762	−0.2611	−0.4253	−0.5831	−0.8099
	(−0.0457)	(−0.2270)													
0.55	−0.0314	−0.043	−0.086	−0.172	−0.343	−0.513	−0.682	−0.849	−0.1015	−0.1263	−0.1669	−0.2465	−0.3991	−0.5446	−0.7521
	(−0.0009)	(−0.1438)	(−0.2864)												
0.60	−0.0205	−0.041	−0.082	−0.164	−0.326	−0.487	−0.646	−0.803	−0.960	−0.1192	−0.1572	−0.2312	−0.3718	−0.5047	−0.6928
	(0.0008)	(0.0949)	(−0.1857)												
0.65	−0.0137	−0.0772	−0.078	−0.156	−0.309	−0.461	−0.611	−0.759	−0.906	−0.1122	−0.1476	−0.2160	−0.3447	−0.4653	−0.6346
	(−0.0008)	(0.0039)	(−0.1262)	(−0.2424)											
0.70	−0.093	−0.507	−0.1161	−0.148	−0.294	−0.438	−0.579	−0.718	−0.855	−0.1057	−0.1385	−0.2013	−0.3184	−0.4270	−0.5785

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Tr\Pr†	0.010	0.050	0.100	0.200	0.400	0.600	0.800	1.000	1.200	1.500	2.000	3.000	5.000	7.000	10.000
		(−0.0038)	(−0.0075)	(−0.1685)											
0.75	−0.0064	−0.0339	−0.0744	−0.0143	−0.0282	−0.0417	−0.0550	−0.0681	−0.0808	−0.0996	−0.1298	−0.1872	−0.2929	−0.3901	−0.5250
		(−0.0037)	(−0.0072)	(−0.1298)	(−0.2203)										
0.80	−0.0044	−0.0228	−0.0487	−0.1160	−0.0272	−0.0401	−0.0526	−0.0648	−0.0767	−0.0940	−0.1217	−0.1736	−0.2682	−0.3545	−0.4740
			(−0.0073)	(−0.0139)	(−0.1682)	(−0.2185)									
0.85	−0.0029	−0.0152	−0.0319	−0.0715	−0.0268	−0.0391	−0.0509	−0.0622	−0.0731	−0.0888	−0.1138	−0.1602	−0.2439	−0.3201	−0.4254
				(−0.0144)	(−0.1503)	(−0.1692)									
0.90	−0.0019	−0.0099	−0.0205	−0.0442	−0.1118	−0.0396	−0.0503	−0.0604	−0.0701	−0.0840	−0.1059	−0.1463	−0.2195	−0.2862	−0.3788
				(−0.0179)	(−0.0286)	(−0.1580)	(−0.1464)								
0.93	−0.0015	−0.0075	−0.0154	−0.0326	−0.0763	−0.1662	−0.0514	−0.0602	−0.0687	−0.0810	−0.1007	−0.1374	−0.2045	−0.2661	−0.3516
					(−0.0340)	(−0.0424)	(−0.1418)								
0.95	−0.0012	−0.0062	−0.0126	−0.0262	−0.0589	−0.1110	−0.0540	−0.0607	−0.0678	−0.0788	−0.0967	−0.1310	−0.1943	−0.2526	−0.3339
					(−0.0444)	(−0.0490)	(−0.1532)								
0.97	−0.0010	−0.0050	−0.0101	−0.0208	−0.0450	−0.0770	−0.1647	−0.0623	−0.0669	−0.0759	−0.0921	−0.1240	−0.1837	−0.2391	−0.3163
						(−0.0714)	(−0.0643)								
0.98	−0.0009	−0.0044	−0.0090	−0.0184	−0.0390	−0.0641	−0.1100	−0.0641	−0.0661	−0.0740	−0.0893	−0.1202	−0.1783	−0.2322	−0.3075

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Tr\Pr†	0.010	0.050	0.100	0.200	0.400	0.600	0.800	1.000	1.200	1.500	2.000	3.000	5.000	7.000	10.000
							(−0.0828)								
0.99	−0.0008	−0.0039	−0.0079	−0.0161	−0.0335	−0.0531	−0.0796	−0.0680	−0.0646	−0.0715	−0.0861	−0.1162	−0.1728	−0.2254	−0.2989
							(−0.1621)								
1.00	−0.0007	−0.0034	−0.0069	−0.0140	−0.0285	−0.0435	−0.0588	−0.0879	−0.0609	−0.0678	−0.0824	−0.1118	−0.1672	−0.2185	−0.2902
1.01	−0.0006	−0.0030	−0.0060	−0.0120	−0.0240	−0.0351	−0.0429	−0.0223	−0.0473	−0.0621	−0.0778	−0.1072	−0.1615	−0.2116	−0.2816
1.02	−0.0005	−0.0026	−0.0051	−0.0102	−0.0198	−0.0277	−0.0303	−0.0062	0.0227	−0.0524	−0.0722	−0.1021	−0.1556	−0.2047	−0.2731
1.05	−0.0003	−0.0015	−0.0029	−0.0054	−0.0092	−0.0097	−0.0032	0.0220	0.1059	0.0451	−0.0432	−0.0838	−0.1370	−0.1835	−0.2476
1.10	0.0000	0.0000	0.0001	0.0007	0.0038	0.0106	0.0236	0.0476	0.0897	0.1630	0.0698	−0.0373	−0.1021	−0.1469	−0.2056
1.15	0.0002	0.0011	0.0023	0.0052	0.0127	0.0237	0.0396	0.0625	0.0943	0.1548	0.1667	0.0332	−0.0611	−0.1084	−0.1642
1.20	0.0004	0.0019	0.0039	0.0084	0.0190	0.0326	0.0499	0.0719	0.0991	0.1477	0.1990	0.1095	−0.0141	−0.0678	−0.1231
1.30	0.0006	0.0030	0.0061	0.0125	0.0267	0.0429	0.0612	0.0819	0.1048	0.1420	0.1991	0.2079	0.0875	0.0176	−0.0423
1.40	0.0007	0.0036	0.0072	0.0147	0.0306	0.0477	0.0661	0.0857	0.1063	0.1383	0.1894	0.2397	0.1737	0.1008	0.0350
1.50	0.0008	0.0039	0.0078	0.0158	0.0323	0.0497	0.0677	0.0864	0.1055	0.1345	0.1806	0.2433	0.2309	0.1717	0.1058
1.60	0.0008	0.0040	0.0080	0.0162	0.0330	0.0501	0.0677	0.0855	0.1035	0.1303	0.1729	0.2381	0.2631	0.2255	0.1673
1.70	0.0008	0.0040	0.0081	0.0163	0.0329	0.0497	0.0667	0.0838	0.1008	0.1259	0.1658	0.2305	0.2788	0.2628	0.2179
1.80	0.0008	0.0040	0.0081	0.0162	0.0325	0.0488	0.0652	0.0816	0.0978	0.1216	0.1593	0.2224	0.2846	0.2871	0.2576
1.90	0.0008	0.0040	0.0079	0.0159	0.0318	0.0477	0.0635	0.0792	0.0947	0.1173	0.1532	0.2144	0.2848	0.3017	0.2876
2.00	0.0008	0.0039	0.0078	0.0155	0.0310	0.0464	0.0617	0.0767	0.0916	0.1133	0.1476	0.2069	0.2819	0.3097	0.3096

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Tr\Pr†	0.010	0.050	0.100	0.200	0.400	0.600	0.800	1.000	1.200	1.500	2.000	3.000	5.000	7.000	10.000
2.20	0.0007	0.0037	0.0074	0.0147	0.0293	0.0437	0.0579	0.0719	0.0857	0.1057	0.1374	0.1932	0.2720	0.3135	0.3355
2.40	0.0007	0.0035	0.0070	0.0139	0.0276	0.0411	0.0544	0.0675	0.0803	0.0989	0.1285	0.1812	0.2602	0.3089	0.3459
2.60	0.0007	0.0033	0.0066	0.0131	0.0260	0.0387	0.0512	0.0634	0.0754	0.0929	0.1207	0.1706	0.2484	0.3009	0.3475
2.80	0.0006	0.0031	0.0062	0.0124	0.0245	0.0365	0.0483	0.0598	0.0711	0.0876	0.1138	0.1613	0.2372	0.2915	0.3443
3.00	0.0006	0.0029	0.0059	0.0117	0.0232	0.0345	0.0456	0.0565	0.0672	0.0828	0.1076	0.1529	0.2268	0.2817	0.3385
3.50	0.0005	0.0026	0.0052	0.0103	0.0204	0.0303	0.0401	0.0497	0.0591	0.0728	0.0949	0.1356	0.2042	0.2584	0.3194
4.00	0.0005	0.0023	0.0046	0.0091	0.0182	0.0270	0.0357	0.0443	0.0527	0.0651	0.0849	0.1219	0.1857	0.2378	0.2994

†Values in parentheses are for the opposite phase and may be used to interpolate to or near the phase boundary [PGL4; Wilding, W. V., J. K. Johnson, and R. L. Rowley, *Int. J. Thermophys*., 8(1987):717].

Analytical expressions for $Z^{(0)}$ and $Z^{(1)}$ can also be generated by using

$$Z^{(0)} = Z_0 \qquad Z^{(1)} = \frac{Z_1 - Z_0}{0.3978}$$

(2-68)

where Z_0 and Z_1 are determined from

$$Z_i = \frac{P_r V_r}{T_r} = 1 + \frac{B}{V_r} + \frac{C}{V_r^2} + \frac{D}{V_r^5} + \frac{c_4}{T_r^3 V_r^2}\left(\beta + \frac{\gamma}{V_r^2}\right)\exp\left(\frac{-\gamma}{V_r^2}\right)$$
$$B = b_1 - \frac{b_2}{T_r} - \frac{b_3}{T_r^2} - \frac{b_4}{T_r^3}$$
$$C = c_1 - \frac{c_2}{T_r} + \frac{c_3}{T_r^2}$$
$$D = d_1 + \frac{d_2}{T_r}$$

(2-69)

as applied to the simple reference fluid and to the acentric reference fluid (*n*-octane), respectively. The constants for Eq. (2-69) for the two reference fluids are given in Table 2-171.

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Table 2-171 Constants for the Two Reference Fluids Used in Lee-Kesler Method*

Constant	Simple reference fluid	Acentric reference fluid
b_1	0.1181193	0.2026579
b_2	0.265728	0.331511
b_3	0.154790	0.027655
b_4	0.030323	0.203488
c_1	0.0236744	0.0313385
c_2	0.0186984	0.0503618
c_3	0.0	0.016901
c_4	0.042724	0.041577
$d_1 \times 10^4$	0.155488	0.48736
$d_2 \times 10^4$	0.623689	0.0740336
β	0.65392	1.226
γ	0.060167	0.03754
*Lee, B. I., and M. G. Kesler, *AIChE J.*, **21** (1975): 510.		

Example

Example

Estimate the molar volume of saturated *n*-decane vapor at 540.5 K.

Input properties: Recommended values from the DIPPR 801 database are T_c = 617.7 K, P_c = 2.11 MPa, P^*(540.5 K) = 0.6799 MPa, and ω = 0.492328.

Reduced conditions:

$$T_r = (540.5\ \mathrm{K})/(617.7\ \mathrm{K}) = 0.875 \quad \text{and} \quad P_r = (0.6799\ \mathrm{MPa})/(2.11\ \mathrm{MPa}) = 0.322$$

LK compressiblity factor: Since vapor phase values are needed, the appropriate values from Tables 2-169 and 2-170 that can be used to double-interpolate are as follows:

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	$Z^{(0)}$			$Z^{(1)}$	
$T_r \backslash P_r$	0.2	0.4	$T_r \backslash P_r$	0.2	0.4
0.85	0.8810	(0.7222)	0.85	−0.0715	(−0.1503)
0.90	0.9015	0.7800	0.90	−0.0442	−0.1118

Double linear interpolation within these values gives $Z^{(0)}$ = 0.8058 and $Z^{(1)}$ = −0.1025.

From Eq. (2-67):

$$Z = 0.8058 + (0.492328)(-0.1025) = 0.7553$$

Note: If the analytical form available in Eq. (2-69) is used, the following more accurate values are obtained: $Z^{(0)}$ = 0.8131, $Z^{(1)}$ = − 0.1067, and Z = 0.7606.

Molar volume:

$$V = \frac{ZRT}{P} = \frac{(0.7553)\left(0.0083143\,\frac{\mathrm{m^3 \cdot MPa}}{\mathrm{kmol \cdot K}}\right)(540.5\,\mathrm{K})}{0.6799\,\mathrm{MPa}} = 4.992\,\frac{\mathrm{m^3}}{\mathrm{kmol}}$$

4. *Cubic EoS* can be used to obtain both vapor and liquid densities as an alternative method to those mentioned above.

Recommended Method Cubic EoS.

Classification: Empirical extension of theory.

Expected uncertainty: Varies depending upon compound and conditions, but a general expectation is 10 to 20 percent.

Applicability: Nonpolar and moderately polar compounds.

Input data: T_c, P_c, ω.

Description: The more common cubic EoS can be written in the form

$$Z = \frac{V}{V-b} - \frac{V}{V^2 + \delta V + \varepsilon}\,\frac{a\,\alpha(T_r)}{RT}$$

(2-70)

where a, b, δ, and ε are constants that depend upon the model EoS chosen, as does the temperature dependence of the function $\alpha(T_r)$. Definitions of these constants and $\alpha(T_r)$ for some of the more commonly used EoS models are shown in Table 2-172. The corresponding relations for many other EoS models in this same form are available [Soave, G., *Chem. Eng. Sci.*, **27** (1972): 1197]. The independent parameters a and b in these models can be regressed from experimental data to correlate densities or can be obtained from known critical constants to predict density data.

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Table 2-172 Relationships for Eq. (2-70) for Common Cubic EoS

EoS	δ	ε	α(T_r)	$aP_c/(RT_c)^2$	$bP_c/(RT_c)$
van der Waals*	0	0	1	0.42188	0.125
Relich-Kwong†	0	0	$T_r^{-0.5}$	0.42748	0.08664
Soave‡	b	0	$[1 + (0.48 + 1.574\omega - 0.176\omega^2)(1 - T_r^{0.5})]^2$	0.42748	0.08664
Peng-Robinson§	$2b$	$-b^2$	$[1 + (0.37464 + 1.54226\omega - 0.2699\omega^2)(1 - T_r^{0.5})]^2$	0.45724	0.0778
*van der Waal, J. H., *Z. Phys. Chem.*, **5** (1890): 133.					
†Redlich, O., and J. N. S. Kwong, *Chem. Rev.*, **44** (1949): 233.					
‡Soave, G., *Chem. Eng. Sci.*, **27** (1972): 1197.					
§Peng, D. Y., and D. B. Robinson, *Ind. Eng. Chem. Fundam.*, **15** (1976): 59.					

Of the cubic EoS given in Table 2-172, the Soave and Peng-Robinson are the most accurate, but there is no general rule for which EoS produces the best estimated volumes for specific fluids or conditions. The Peng-Robinson equation has been better tuned to liquid densities, while the Soave equation has been better tuned to vapor-liquid equilibrium and vapor densities. In solving the cubic equation for volume, a convenient initial guess to find the vapor root is the ideal gas value, while an initial value of 1.05b is convenient to locate the liquid root.

Example

Example

Estimate the molar density of liquid and vapor saturated ammonia at 353.15 K, using the Soave and Peng-Robinson EoS.

Required properties: Recommended values in the DIPPR 801 database are

$$\begin{aligned} T_c &= 405.65\ \mathrm{K} \quad P_c = 112.8\ \mathrm{bar} \quad \omega = 0.252608 \\ P^*(353.15\ \mathrm{K}) &= 41.352\ \mathrm{bar}\ (\text{vapor pressure at } 353.15\ \mathrm{K}) \end{aligned}$$

EoS parameters (shown for Soave EoS):

$$a = \frac{0.42748\,(RT_c)^2}{P_c} = \frac{0.42748\left[\left(83.145\,\frac{\mathrm{bar\cdot cm^3}}{\mathrm{mol\cdot K}}\right)(405.65\mathrm{K})\right]^2}{112.8\ \mathrm{bar}} = 4.311\times 10^6\,\frac{\mathrm{cm^6\cdot bar}}{\mathrm{mol^2}}$$

$$b = \frac{0.08664\,(RT_c)}{P_c} = \frac{0.08664\left(83.145\,\frac{\mathrm{bar\cdot cm^3}}{\mathrm{mol\cdot K}}\right)(405.65\mathrm{K})}{112.8\ \mathrm{bar}} = 25.906\,\frac{\mathrm{cm^3}}{\mathrm{mol}}$$

$$T_r = (353.15\ \mathrm{K})/(405.65\ \mathrm{K}) = 0.871$$

$$\alpha = \left\{1 + \left[0.48 + (1.574)\,(0.252608) - (0.176)\,(0.252608)^2\right]\left[1 - (0.871)^{0.5}\right]\right\}^2 = 1.119$$

Rearrange and solve Eq. (2-70) for V:

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$$P = \frac{RT}{V-b} - \frac{a\alpha}{V(V+b)} \quad \text{or} \quad PV^3 - RTV^2 + (a\alpha - bRT - Pb^2)V - ab\alpha = 0$$

$$41.352\left(\frac{V}{\mathrm{m^3/mol}}\right)^3 - \left(0.029\frac{\mathrm{m^3}}{\mathrm{mol}}\right)\left(\frac{V}{\mathrm{m^3/mol}}\right)^2 + \left(4.037\times10^{-6}\frac{\mathrm{m^6}}{\mathrm{mol^2}}\right)\left(\frac{V}{\mathrm{m^3/mol}}\right) - 1.25\times10^{-10} = 0$$

Vapor root (initial guess of V = 7.1 × 10^{-7} m^3/mol from ideal gas equation):

$$V_{\mathrm{vap}} = 5.395\times10^{-4}\mathrm{m^3/mol} \quad \text{and} \quad \rho_{\mathrm{vap}} = 1/V_{\mathrm{vap}} = 1.854\,\mathrm{kmol/m^3}$$

Liquid root (initial guess of V = 2.72 × 10^{-5} m^3/mol from 1.05b):

$$V_{\mathrm{liq}} = 4.441\times10^{-5}\mathrm{m^3/mol} \quad \text{and} \quad \rho_{\mathrm{liq}} = 1/V_{\mathrm{liq}} = 22.516\,\mathrm{kmol/m^3}$$

The corresponding values and equation for the Peng-Robinson EoS are

$$a = 4.611\times10^6\,\mathrm{cm^6\cdot bar/mol^2} \quad b = 23.262\,\mathrm{cm^3/mol} \quad \alpha = 1.103$$

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V^2+2bV-b^2}$$

or

$$PV^3 + (bP - RT)V^2 + (a\alpha - 2bRT - 3Pb^2)V + (bP^3 + RTb^2 - ab\alpha) = 0$$

$$41.352\left(\frac{V}{\mathrm{m^3/mol}}\right)^3 - \left(0.0284\frac{\mathrm{m^3}}{\mathrm{mol}}\right)\left(\frac{V}{\mathrm{m^3/mol}}\right)^2 + \left(3.651\times10^{-6}\frac{\mathrm{m^6}}{\mathrm{mol^2}}\right)\left(\frac{V}{\mathrm{m^3/mol}}\right) - 1.018\times10^{-10} = 0$$

Solve for the two physical roots of this equation:

$$V_{\mathrm{vap}} = 5.286\times10^{-4}\mathrm{m^3/mol} \text{ and } \rho_{\mathrm{vap}} = 1.892\,\mathrm{kmol/m^3}$$
$$V_{\mathrm{liq}} = 3.914\times10^{-5}\mathrm{m^3/mol} \text{ and } \rho_{\mathrm{liq}} = 25.55\,\mathrm{kmol/m^3}$$

The liquid density calculated from the Soave EoS is 24.2 percent below the DIPPR 801 recommended value of 29.69 kmol/m^3; that calculated from the Peng-Robinson EoS is 13.9 percent below the recommended value.

Liquids For most liquids, the saturated molar liquid density ρ can be effectively correlated with

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$$\rho = \frac{A}{B^{[1+(1-T/C)^D]}}$$

(2-71)

adapted from the Rackett prediction equation [Rackett, H. G., *J. Chem. Eng. Data*, **15** (1970): 514]. The regression constants *A*, *B*, and *D* are determined from the nonlinear regression of available data, while *C* is usually taken as the critical temperature. The liquid density decreases approximately linearly from the triple point to the normal boiling point and then nonlinearly to the critical density (the reciprocal of the critical volume). A few compounds such as water cannot be fit with this equation over the entire range of temperature.

The recommended method for estimation of saturated liquid density for pure organic compounds is the Rackett prediction method.

Recommended Method Rackett method.

Reference: Rackett, H. G., *J. Chem. Eng. Data*, **15** (1970): 514.

Classification: Corresponding states.

Expected uncertainty: 15 percent as purely predictive equation; 2 percent if a liquid density value is available.

Applicability: Saturated liquid densities of organic compounds.

Input data: T_c, P_c, and Z_c (or, equivalently, V_c).

Description: A predictive form of the equation is given by

$$\frac{1}{\rho} = V = \left(\frac{RT_c}{P_c}\right) Z_c^q \quad \text{where } q = 1 + (1 - T_r)^{2/7}$$

(2-72)

When one or more liquid density data points are available, Z_c in Eq. (2-72) can be replaced with an adjustable parameter fitted from the data (Z_{RA} in the notation of Spencer and Danner [Spencer, C. F., and R. P. Danner, *J. Chem. Eng. Data* **17** (1972): 236]). This produces densities in good agreement with experiment and permits accurate interpolation of the densities over most of the liquid temperature range, but it does not give the correct critical density unless $Z_{RA} = Z_c$.

Example

Example

Estimate the saturated liquid density of acetonitrile at 376.69 K.

Required properties: The recommended values from the DIPPR 801 database are

$$T_c = 545.5\ \text{K} \quad P_c = 4.83\ \text{MPa} \quad Z_c = 0.184$$

Calculate supporting quantities:

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$$T_r = (376.69\ \mathrm{K})/(545.5\ \mathrm{K}) = 0.691$$
$$q = 1 + (1 - 0.691)^{2/7} = 1.715$$

Calculate saturated liquid density from Eq. (2-72):

$$\rho = \left[\frac{4.83 \times 10^6\,\mathrm{Pa}}{\left(8.314\frac{\mathrm{Pa\cdot m^3}}{\mathrm{mol\cdot K}}\right)\ (545.5\,\mathrm{K})}\right]\ (0.184)^{-1.715} = 19.42\frac{\mathrm{kmol}}{\mathrm{m^3}}$$

The estimated density is 16 percent above the DIPPR 801 value of 16.73 kmol/m^3.

Calculate ρ_{sat} *from Eq. (2-72) with a known liquid density:* Kratzke and Muller [Kratzke, H., and S. Muller, *J. Chem. Thermo.*, **17** (1985): 151] reported an experimental density of 18.919 kmol/m^3 at 298.08 K. Use of this experimental value in Eq. (2-72) to calculate Z_{RA} gives

$$T_r = (298.08\ \mathrm{K})/(545.5\ \mathrm{K}) = 0.546 \quad q = 1 + (1 - 0.546)^{2/7} = 1.798$$

$$Z_{RA} = \left[\frac{4.83 \times 10^6\,\mathrm{Pa}}{\left(8.314\frac{\mathrm{Pa\cdot m^3}}{\mathrm{kmol\cdot K}}\right)\ (545.5\,\mathrm{K})\left(18.919\frac{\mathrm{kmol}}{\mathrm{m^3}}\right)}\right]^{1/1.798} = 0.202$$
$$\rho = \left[\frac{4.83 \times 10^6\,\mathrm{Pa}}{\left(8.314\frac{\mathrm{Pa\cdot m^3}}{\mathrm{mol\cdot K}}\right)\ (545.5\,\mathrm{K})}\right]\ (0.202)^{-1.715} = 16.577\frac{\mathrm{kmol}}{\mathrm{m^3}}$$

The value obtained by the modified Rackett method is 0.9 percent below the DIPPR 801 recommended value. Note, however, that with Z_{RA} = 0.202 instead of Z_c, Eq. (2-72) gives ρ_c = 5.28 kmol/m^3 instead of $\rho_c = P_c/(Z_cRT_c)$ = 5.79 kmol/m^3.

Solids Solid density data are sparse and usually available only within a narrow temperature range. For most solids, density decreases approximately linearly with increasing temperature. No accurate method for prediction of solid densities is available, but an approximate correlation has been found between the density of the liquid phase at the triple point and the solid that is stable at the triple point conditions.

Recommended Method Goodman method.

Reference: Goodman, B. T., W. V. Wilding, J. L. Oscarson, and R. L. Rowley, *J. Chem. Eng. Data*, **49** (2004): 1512.

Classification: Empirical correlation.

Expected uncertainty: 6 percent.

Applicability: Organic compounds; applicable to the stable solid phase at the triple point temperature T_t; applicable T range is from T_t down to either the first solid-phase transition temperature or to approximately $0.3T_t$.

Input data: Liquid density at the triple point.

Description: The density for the solid phase that is stable at the triple point has been correlated as a function of temperature and the liquid density at T_t as

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$$\rho_s = \left(1.28 - 0.16\frac{T}{T_t}\right)\rho_L(T_t)$$

(2-73)

Example

Example

Estimate the density of solid naphthalene at 281.46 K.

Required properties: The recommended values from the DIPPR 801 database for T_t and the liquid density at T_t are

$$T_t = 353.43\ \mathrm{K} \quad \rho_L(T_t) = 7.6326\ \mathrm{kmol/m^3}$$

From Eq. (2-73):

$$\rho_s = \left(1.28 - 0.16\frac{281.46\ \mathrm{K}}{353.43\ \mathrm{K}}\right)\left(7.6326\frac{\mathrm{kmol}}{\mathrm{m^3}}\right) = 8.797\frac{\mathrm{kmol}}{\mathrm{m^3}}$$

The estimated value is 4.3 percent lower than the DIPPR 801 recommended value of 9.1905 kmol/m^3.

Mixtures Both liquid and vapor densities can be estimated using pure-component CS and EoS methods by treating the fluid as a pseudo-pure component with effective parameters calculated from the pure-component parameters using ad hoc mixing rules.

To apply the Lee-Kesler CS method to mixtures, pseudo-pure fluid constants are required. One of the simplest set of mixing rules for these quantities is [Prausnitz, J. M., and R. D. Gunn, *AIChE J.*, **4** (1958): 430, 494; Joffe, J., *Ind. Eng. Chem. Fundam.*, **10** (1971): 532]:

$$\overline{T}_c = \sum_{i=1}^{C} x_i T_{c,i}$$

(2-74)

$$\overline{P}_c = \frac{\sum_{i=1}^{C} x_i Z_{c,i}}{\sum_{i=1}^{C} x_i V_{c,i}} R\overline{T}_c$$

(2-75)

$$\overline{\omega} = \sum_{i=1}^{C} x_i \omega_i$$

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(2-76)

The procedures are identical to those for pure components with the replacement of T_c, P_c, and ω with the effective mixture values obtained from the above equations.

To use a cubic EoS for a mixture, mixing rules are used to calculate effective mixture parameters in terms of the pure-component values. Although more complex mixing rules may improve prediction accuracy, the simple forms recommended here provide reasonable accuracy without adjustable parameters:

$$\bar{b} = \sum_{i=1}^{C} x_i b_i$$

(2-77)

$$\overline{a\alpha} = \left[\sum_{i=1}^{C} x_i (a_i \alpha_i)^{1/2}\right]^2$$

(2-78)

Mixture calculations are then identical to the pure-component calculations using these effective mixture parameters for the pure-component *a*α and *b* values.

The modified Rackett method has also been extended to liquid mixtures [Spencer, C. F., and R. P. Danner,*J. Chem. Eng. Data*, **17** (1972): 236] using the following combining and mixing rules as modified by Li [Li, C. C.,*Can. J. Chem. Eng.*, **19** (1971): 709]:

$$T_{c,ij} = \sqrt{T_{c,i} T_{c,j}} \qquad \phi_i = \frac{x_i V_{c,i}}{\sum_{j=1}^{C} x_j V_{c,j}} \qquad \overline{T}_c = \sum_{i=1}^{C} \sum_{j=1}^{C} \phi_i \phi_j T_{c,ij}$$

(2-79)

Recommended Method Spencer-Danner-Li mixing rules with Rackett equation.

References: Spencer, C. F., and R. P. Danner, *J. Chem. Eng. Data*, **17** (1972): 236; Li, C. C.,*Can. J. Chem. Eng.*, **19** (1971): 709.

Classification: Corresponding states.

Expected uncertainty: About 7 percent on average; higher near the T_c of any of the components.

Applicability: Saturated (at the bubble point) liquid mixtures.

Input data: T_c, V_c, and x_i.

Description: The predictive form of the equation is given by

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$$\frac{1}{\rho} = V = R\left(\sum_{i=1}^{C} \frac{x_i T_{c,i}}{P_{c,i}}\right) \overline{Z}_{RA}^{\,q} \qquad q = 1.0 + (1.0 - T_r)^{2/7}$$

(2-80)

where

$$\overline{Z}_{RA} = 0.29056 - 0.08775 \sum_{i=1}^{C} x_i \omega_i \qquad \text{and} \qquad T_r = \frac{T}{\overline{T}_c}$$

(2-81)

Example

Example

Estimate the saturated liquid density of a liquid mixture of 50 mol% ethane(1) and 50 mol% *n*-decane(2) at 377.6 K.

Required properties: The recommended values from the DIPPR 801 database for the required properties are as follows:

	T_c/K	V_c/(m^3 · kmol^{-1})	P_c/bar	ω
Ethane	305.32	0.1455	48.72	0.0995
Decane	617.7	0.617	21.1	0.4923

Auxiliary quantities from Eq. (2-79):

$$\begin{aligned}
\phi_1 &= \frac{(0.5)\,(0.1455)}{(0.5)(0.1455) + (0.5)(0.617)} = 0.191; \qquad \phi_2 = 0.809 \\
T_{c,12} &= \sqrt{(305.32\,\mathrm{K})\,(617.7\,\mathrm{K})} = 434.3\,\mathrm{K} \\
\frac{\overline{T}_c}{\mathrm{K}} &= \phi_1^2 T_{c,1} + 2\phi_1\phi_2 T_{c,12} + \phi_2^2 T_{c,2} \\
&= (0.191)^2(305.32) + (2)(0.191)(0.809)(434.3) + (0.809)^2(617.7) \\
\overline{T}_c &= 549.68\,\mathrm{K}
\end{aligned}$$

Calculations from Eqs. (2-80) and (2-81):

$$T_r = (377.6\ \mathrm{K})\,/\,(549.63\ \mathrm{K}) = 0.687 \quad q = 1 + (1 - 0.687)^{2/7} = 1.718$$
$$\overline{Z}_{\mathrm{RA}} = 0.29056 - 0.08775\,[(0.5)\,(0.0995) + (0.5)\,(0.4923)] = 0.2646$$

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$$V = \left(0.08314 \frac{\mathrm{m}^3 \cdot \mathrm{bar}}{\mathrm{K} \cdot \mathrm{kmol}}\right) \left[\frac{(0.5)(305.32\,\mathrm{K})}{48.72\ \mathrm{bar}} + \frac{(0.5)\,(617.7\,\mathrm{K})}{21.1\ \mathrm{bar}}\right] (0.2646)^{1.718} = 0.151 \frac{\mathrm{m}^3}{\mathrm{kmol}}$$

The experimental value [Reamer, H. H., and B. H. Sage, *J. Chem. Eng. Data*, **7** (1962): 161] is 0.149 m^3/kmol, and the error in the estimated value is 1.3 percent.

2.16.12. VISCOSITY

Viscosity is defined as the shear stress per unit area at any point in a confined fluid, divided by the velocity gradient in the direction perpendicular to the direction of flow. The *absolute viscosity* η is the shear stress at a point, divided by the velocity gradient at that point. The SI unit of viscosity is Pa · s [1 kg/(m · s)], but the cgs units of poise (P) [1 g/(cm · s)] and centipoise (cP = 0.01 P) are also frequently used (1 cP = 1 mPa · s). The *kinematic viscosity* v is defined as the ratio of the absolute viscosity to density at the same temperature and pressure. The SI unit for v is m^2/s, but again cgs units are very common and v is often given in stokes (1 St = 1 cm^2/s) or centistokes (1 cSt = 0.01 cm^2/s).

Gases Experimental data for gases and vapors at low density are often correlated with

$$\eta^o = \frac{AT^B}{1 + C/T + D/T^2}$$

(2-82)

Over smaller temperature ranges, parameters *C* and *D* may not be necessary as ln(η) is often reasonably linear with ln(*T*). Care should be taken in extrapolating using Eq. (2-82) as there can be unintended mathematical poles where the denominator approaches zero.

Numerous methods have been developed for estimation of vapor viscosity. For nonpolar vapors, the Yoon-Thodos CS method works well, but for polar fluids the Reichenberg method is preferred. Both methods are illustrated below.

Recommended Method 1 Yoon-Thodos method.

Reference: Yoon, P., and G. Thodos, *AIChE J.*, **16** (1970): 300.

Classification: Corresponding states.

Expected uncertainty: 5 percent.

Applicability: Nonpolar and slightly polar organic vapors.

Input data: T_c, P_c, and *M.Description:* The correlation for viscosity as a function of reduced temperature is

$$\frac{\eta^o}{\mathrm{Pa} \cdot \mathrm{s}} = \frac{46.1 T_r^{0.618} - 20.4 \exp(-0.449 T_r) + 19.4 \exp(-4.058 T_r) + 1}{2.173424 \times 10^{11} (T_c/\mathrm{K})^{1/6} (M/\mathrm{g} \cdot \mathrm{mol}^{-1})^{-1/2} (P_c/\mathrm{Pa})^{-2/3}}$$

(2-83)

Example

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Example

Estimate the low-pressure vapor viscosity of propane at 353 K.

Required constants: The DIPPR 801 database recommends the following values:

$$T_c = 369.83\ \mathrm{K} \quad P_c = 4.248\ \mathrm{MPa} \quad M = 44.0956\ \mathrm{g/mol}$$

Reduced temperature:

$$T_r = (353\ \mathrm{K})\,/\,(369.83\ \mathrm{K}) = 0.9545$$

Calculation using Eq. (2-83):

$$\frac{\eta^o}{\mathrm{Pa \cdot s}} = \frac{(46.1)\,(0.9545)^{0.618} - 20.4\exp[-(0.449)\,(0.9545)] + 19.4\exp[-4.058(0.9545)] + 1}{(2.173424 \times 10^{11})\,(369.83)^{-1/6}(44.0956)^{-1/2}(4.248 \times 10^6)^{-2/3}} = 9.84 \times 10^{-6}$$

This value is 1.5 percent higher than the DIPPR 801 recommended value of 9.70×10^{-6} Pa · s.

Recommended Method 2 Reichenberg method.

Reference: Reichenberg, D., *AIChE J.*, **21** (1975): 181.

Classification: Group contributions and corresponding states.

Expected uncertainty: 5 percent.

Applicability: Nonpolar and polar organic and inorganic vapors.

Input data: T_c, P_c, M, μ, and molecular structure.

Description: The temperature dependence of the viscosity is given by

$$\frac{\eta^o}{\mathrm{Pa \cdot s}} = \frac{AT_r^2}{[1 + 0.36T_r(T_r - 1)]^{1/6}}\left[\frac{1 + 270(\mu_r^*)^4}{T_r + 270(\mu_r^*)^4}\right]$$

(2-84)

where the parameter A is determined from group contributions and the modified reduced dipole μ_r^* is found from

$$\mu_r^* = 52.46\mu_r$$

(2-85)

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and Eq. (2-66).

For organic compounds, A is found from the group values C_i, listed in Table 2-173, using

Table 2-173 Reichenberg* Group Contribution Values

Group	C_i	Group	C_i
$-CH_3$	9.04	—F	4.46
$>CH_2$	6.47	—Cl	10.06
>CH—	2.67	—Br	12.83
>C<	−1.53	—OH alcohol	7.96
$=CH_2$	7.68	>O	3.59
=CH—	5.53	>C=O	12.02
>C=	1.78	—CHO	14.02
≡CH	7.41	—COOH	18.65
≡C—	5.24	—COO— or HCOO—	13.41
$>CH_2$ ring	6.91	$-NH_2$	9.71
>CH— ring	1.16	>NH	3.68
>C< ring	0.23	=N— ring	4.97
=CH— ring	5.90	—CN	18.13
>C= ring	3.59	>S ring	8.86
*Reichenberg, D., *AIChE J.*, **21** (1975): 181.			

$$A = 10^{-7} \frac{\left(\frac{M}{\mathrm{kg/kmol}}\right)^{1/2} (T_c/\mathrm{K})}{\sum_{i=1}^{N} n_i C_i}$$

(2-86)

For inorganic gases, A is obtained from

$$A = 1.6104 \times 10^{-10} \left[\left(\frac{M}{\mathrm{g/mol}}\right)^{1/2} \left(\frac{P_c}{\mathrm{Pa}}\right)^{2/3} \left(\frac{T_c}{\mathrm{K}}\right)^{-1/6} \right]$$

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(2-87)

Example

Example

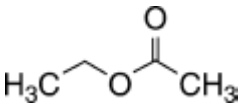
Estimate the low-pressure vapor viscosity of ethyl acetate at 401.25 K.

Required constants: The DIPPR 801 database recommends the following values:

$$M = 88.1051\ \mathrm{g/mol} \quad T_c = 523.3\ \mathrm{K} \quad P_c = 3.88\ \mathrm{MPa} \quad \mu = 1.78\ D$$

Supporting quantities:

Structural groups:



Group	n_i	C_i	Contribution
$-CH_3$	2	9.04	18.08
$>CH_2$	1	6.47	6.47
$-COO-$	1	13.41	13.41
			Total 37.96

$$T_r = (401.25\ \mathrm{K})/(523.3\ \mathrm{K}) = 0.767$$

From Eqs. (2-66) and (2-85):

$$\mu_r^* = 52.46\frac{(1.78)^2(38.8)}{(523.3)^2} = 0.024$$

From Eq. (2-86):

$$A = 10^{-7}\frac{(88.1051)^{1/2}(523.3)}{37.96} = 1.294 \times 10^{-5}$$

Calculation using Eq. (2-84):

$$\frac{\eta^o}{\mathrm{Pa \cdot s}} = \frac{(1.294 \times 10^{-5})\,(0.767)^2}{(1 + (0.36)\,(0.767)\,(0.767 - 1)]^{1/6}}\,\frac{1 + (270)\,(0.024)^4}{0.767 + (270)\,(0.024)^4} = 1.003 \times 10^{-5}$$

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The estimated value is 1.5 percent lower than the DIPPR 801 recommended value of 1.018×10^{-5} Pa · s.

The dependence of viscosity upon pressure is principally a density effect. Estimation of vapor viscosity at elevated pressures is commonly done by correlating density deviations from the low-pressure values estimated. Several methods are available, but the method developed by Jossi et al. and extended to polar fluids by Stiel and Thodos is relatively accurate and easy to apply.

Recommended Method Jossi-Stiel-Thodos method.

References: Stiel, L. I., and G. Thodos, *AIChE J.*, **10** (1964): 26; Jossi, J. A., L. I. Stiel, and G. Thodos, *AIChE J.*, **8** (1962): 59.

Classification: Empirical correlation and corresponding states.

Expected uncertainty: 9 percent—often less for nonpolar gases, larger for polar gases.

Applicability: Nonassociating gases; $\rho_r < 2.6$.

Input data: M, T_c, P_c, Z_c, μ, η^o (low-pressure viscosity at same T may be estimated by using methods given above), and ρ (may be calculated from T and P by using density methods given above).

Description: Deviation of η from the low-pressure value η^o is given by one of the following correlations depending upon its polarity and reduced density range:

For nonpolar gases, $0.1 < \rho_r < 3.0$:

$$\left[\left(\frac{\eta-\eta^o}{\mathrm{mPa\cdot s}}\right)\xi+1\right]^{1/4}=1.0230+0.23364\rho_r+0.58533\rho_r^2-0.40758\rho_r^3+0.093324\rho_r^4$$

(2-88)

For polar gases, $\rho_r \le 0.1$:

$$\left(\frac{\eta-\eta^o}{\mathrm{mPa\cdot s}}\right)\xi=1.656\rho_r^{1.111}$$

(2-89)

For polar gases, $0.1 < \rho_r \le 0.9$:

$$\left(\frac{\eta-\eta^o}{\mathrm{mPa\cdot s}}\right)\xi=0.0607\left(9.045\rho_r+0.63\right)^{1.739}$$

(2-90)

For polar gases, $0.9 < \rho_r \le 2.2$:

$$\log\left\{4-\log\left[\left(\frac{\eta-\eta^o}{\mathrm{mPa\cdot s}}\right)\xi\right]\right\}=0.6439-0.1005\rho_r$$

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(2-91)

For polar gases, 2.2 < ρ_r ≤ 2.6:

$$\log\left\{4-\log\left[\left(\frac{\eta-\eta^o}{\mathrm{mPa\cdot s}}\right)\xi\right]\right\}=0.6439-0.1005\rho_r-0.000475(\rho_r^3-10.65)^2$$

(2-92)

where $\rho_c = P_c/(Z_cRT_c)$ and

$$\xi=2173.4\left(\frac{T_c}{\mathrm{K}}\right)^{1/6}\left(\frac{M}{\mathrm{kg/kmol}}\right)^{-1/2}\left(\frac{P_c}{\mathrm{MPa}}\right)^{-2/3}$$

(2-93)

Example

Example

Estimate the vapor viscosity of CO_2 at 350 K and 20 MPa if η° = 0.0174 mPa · s and Z = 0.4983 (estimated from Lee-Kesler method, see section on density).

Required properties: From the DIPPR 801 database,

$$\begin{aligned} &M=44.01\ \mathrm{kg/kmol} \quad T_c=304.21\ \mathrm{K} \quad P_c=7.383\ \mathrm{MPa}\\ &Z_c=0.274 \qquad\qquad \mu=0\ \mathrm{D\ (nonpolar)}\end{aligned}$$

Auxiliary quantities:

$$\xi=(2173.4)\,(304.21)^{1/6}(44.01)^{-1/2}(7.383)^{-2/3}=224.1$$

$$\rho_c=\frac{7.383\,\mathrm{MPa}}{0.274\,[0.008314\,\mathrm{m^3MPa/(K\cdot kmol)}](304.21\,\mathrm{K})}=10.654\frac{\mathrm{kmol}}{\mathrm{m^3}}$$

$$\rho_r=\frac{\rho}{\rho_c}=\frac{P}{ZRT\rho_c}=\frac{20\,\mathrm{MPa}}{0.4983[0.008314\ \mathrm{m^3\cdot MPa/(K\cdot kmol)}]\,(350\,\mathrm{K})\,(10.654\,\mathrm{m^3\cdot kmol})}=1.295$$

Calculation using Eq. (2-88) for nonpolar fluids:

$$\left[224.1\left(\frac{\eta-\eta^o}{\mathrm{mPa\cdot s}}\right)+1\right]^{1/4}=1.0230+0.23364(1.295)+0.58533(1.295)^2$$
$$-0.40758(1.295)^3+0.093324(1.295)^4=1.684$$
$$\eta=\frac{1.684^4-1}{224.1}\mathrm{mPa\cdot s}+0.0174\,\mathrm{mPa\cdot s}=0.0489\ \mathrm{mPa\cdot s}$$

This differs from the experimental value of 0.0473 mPa · s by 3.4 percent.

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Liquids Liquid viscosity can be correlated as a function of temperature for low pressures. Usually the correlation is based on the Andrade equation [Andrade, E. N. da C., *Nature*, **125** (1930): 309]

$$\ln(\eta) = A + \frac{B}{T}$$

(2-94)

or an extension of it. For example, the DIPPR 801 database uses the equation

$$\ln(\eta) = A + \frac{B}{T} + C\ln T + DT^E$$

(2-95)

which is analogous to the Riedel [Riedel, L., *Chem. Ing. Tech.*, **26** (1954): 83] vapor pressure equation.

Currently the most accurate method for predicting pure liquid viscosity is the GC method by Hsu et al. It has been found that most liquids have a viscosity between 0.15 mPa · s (or cP) and 0.55 mPa · s at the normal boiling point, and this "rule" can be used as a valuable criterion to validate estimated viscosities as a function of temperature.

Recommended Method Hsu method.

Reference: Hsu, H.-C., Y.-W. Sheu, and C.-H. Tu, *Chem. Eng. J.*, **88** (2002): 27.

Classification: Group contributions.

Expected uncertainty: 20 percent.

Applicability: Organic liquids; $T_r < 0.75$.

Input data: P_c and molecular structure.

Description: The temperature dependence of the liquid viscosity is given by

$$\ln\left(\frac{\eta}{\mathrm{mPa \cdot s}}\right) = \sum_{i=1}^{N} a_i + T\sum_{i=1}^{N} b_i + \frac{\sum_{i=1}^{N} c_i}{T^2} + \left(\sum_{i=1}^{N} d_i\right) \ln\left(\frac{P_c}{\mathrm{bar}}\right)$$

(2-96)

where P_c is critical pressure and a_i, b_i, c_i, and d_i are the group contributions obtained from Table 2-174.

Table 2-174 Group Contributions for the Hsu et al. Method*

Group†	*a*	100*b*	0.0001*c*	*d*
C, H Groups				

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Group†	*a*	100*b*	0.0001*c*	*d*
CH_4	−1.7296	−1.0563	0.8928	−0.0019
$-CH_3$	0.0570	−0.2382	0.7556	−0.1765
$-CH_2-$	−0.1497	0.0060	1.4157	0.0751
>CH−	−2.2942	0.4028	4.5094	0.6679
>C<	1.0031	−0.3677	−6.0316	1.1972
$=CH_2$	0.9256	−0.2656	0.9860	−0.4417
=CH−	1.3365	0.1612	1.9408	0.2507
=C<	−3.5020	0.4305	3.1287	1.0465
≡CH	87.6040	−0.1106	4.4245	−24.1836
≡C−	−91.6154	−0.0111	0.3265	25.0542
$(-CH_2-)_R$	6.0416	−0.1778	0.8437	−1.5184
$(>CH-)_R$	−33.8745	0.7637	7.2433	8.5951
$(=CH-)_R$ cycloalkene	1.2028	−0.0120	2.0143	−0.3677
$(>C<)_R$ spirocyclane	−56.2158	1.7694	19.0452	13.3885
$(=CH-)_A$	−0.8570	−0.0098	2.4376	0.1311
$(=C<)_A$ cycloalkene	0.7896	−0.0231	−0.9222	0.1928
$(=C<)_A$ bi/terphenyl	2.0973	0.0444	8.1690	−0.4351
$(=C<)_A$ naphthalene	0.4392	0.0683	8.8426	−0.1685
$(=C<)_A$ turpentine	27.3350	1.2165	34.2857	−11.6500
$(=C<)_A$ tetralin	14.2586	−0.8665	−14.7474	−2.7574
O, S Groups				
−OH primary for C<3	5.7852	−0.5310	9.5499	−1.0300
−OH primary for C>2	1.4351	−1.0010	13.8366	0.3418
−OH secondary	−2.6895	−0.3645	29.8404	0.4246
−OH tertiary	−18.5630	2.4275	78.5417	0.9650
$(-OH)_{RC}$	16.7808	0.8509	77.1759	−6.9285
−OH polyhydric	−0.0125	−0.3634	23.2329	−0.0172

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Group†	*a*	100*b*	0.0001*c*	*d*
$(-OH)_{AC}$	−2.0856	0.6362	50.0840	−1.0539
—OH alkoxyalcohol	−2.6991	−0.4377	17.2243	0.7139
—O—	−0.7185	0.0985	2.9405	0.1149
$(-O-)_R$	−29.8045	−0.2847	−4.3145	8.3131
$(-O-)_{AC}$	−2.3454	0.0872	6.4296	0.5389
—CHO	−0.8288	−0.2612	3.7241	0.2386
>CO	−2.6622	0.1142	6.7008	0.7348
$(>CO)_R$	45.9143	−0.2405	3.8828	−12.4994
HCOOH	−2.7291	0.0413	27.4079	0.0002
—COOH for C<7	−4.0451	−0.1841	12.6878	1.1139
—COOH for C>6	−0.6721	−0.1693	20.0309	0.0279
HCOO—	−3.3731	−0.0113	9.4694	0.6071
—COO— for C<8	−0.0635	−0.2162	1.9325	0.4686
—COO— for C>7	−2.5390	0.0006	5.4231	0.8717
>CHO—	−5.4872	1.5834	34.5474	−0.4244
—(CO)—O—(CO)— anhydride	−11.8236	0.0111	7.2831	3.6587
—O—(CO)—O— carbonate	−8.0314	0.2848	9.3746	2.1486
$(>NO)_R$	−16.9531	1.0614	49.1049	2.8583
$-NO_2$	−13.0333	0.1801	12.9392	2.8987
$=CHNO_2$	−1.9653	0.1322	15.8672	−0.0701
$(-NO_2)_{AC}$	−1.2954	0.0427	12.1837	−0.0948
—S—	−3.2767	0.0779	4.4123	0.9549
—SH primary	−2.1030	−0.0965	6.0066	0.3464
—SH secondary	−0.2481	−0.3285	1.9387	0.1148
—SH tertiary	−12.3498	1.2621	23.1473	1.3950
—CSO— for C<13	−15.2678	0.5248	14.2694	3.7646

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Group†	*a*	100*b*	0.0001*c*	*d*
—CSO— for C>12	3.7475	−1.2592	−23.9353	0.8329
>SO	−32.8607	0.6232	27.5184	7.7525
N, X Groups				
$—NH_2$	−1.1345	−0.2126	7.0544	0.1336
—NH—	−6.9489	−0.1723	5.7804	1.6467
—N<	−2.1403	0.4842	6.1893	0.4718
$(—NH_2)_{AC}$	−6.3646	−0.0180	23.2752	1.0653
$(—NH—)_{AC}$	−1.7592	0.2208	14.9707	0.1171
$(—N<)_{AC}$	−1.2982	0.5975	14.0415	−0.0031
$HCONH_2$	−1.5435	−0.2774	31.8007	0.0001
HCONH—	−8.1097	0.0432	20.9135	1.8795
HCON<	−122.3280	26.4615	394.1670	0.3530
$—CONH_2$	−6.7363	0.1316	45.5193	1.2172
—CONH—	8.9977	1.5664	60.8742	−4.6399
$—COONH_2$	17.8400	−4.5188	−62.0987	1.2353
—COONH—	−10.1316	0.6712	37.9465	1.9199
$(>NH)_R$	−0.1589	0.1910	12.0578	−0.0276
N, X Groups				
$(=N—)_R$	−4.7601	0.1120	6.98437	0.9719
$—C\equiv N$	−2.7194	−0.1324	7.7955	0.6293
$(—C\equiv N)_{AC}$	0.9435	−0.0086	8.6310	−0.6443
—Cl primary	−1.7997	−0.3851	3.0118	0.5524
=CHCl	1.5851	−0.1934	3.7798	−0.4748
$(—Cl)_2$	−3.0561	−1.0770	0.1882	1.2223
$(—Cl)_3$	−1.3357	−0.3220	8.8683	0.1702
$(—Cl)_4$	4.2070	−0.4130	13.3194	−1.1972
$(—Cl)_{AC}$	−0.3083	−0.0623	4.1382	−0.2644

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Group†	*a*	100*b*	0.0001*c*	*d*
—F primary	−9.4982	0.2607	11.3406	1.8461
$(—F)_2$	−10.3980	−1.1189	1.3134	2.6681
$(—F)_3$	1.5394	0.8465	17.8121	−2.9915
$(—F)_{AC}$	0.4079	−0.2352	−0.1505	−0.2893
(—F)(—Cl)	−0.8565	−0.3682	4.6451	−0.0751
$(—F)(—Cl)_2$	−3.4552	−0.5629	3.6831	0.3613
$(—F)_2(—Cl)$	54.2824	0.0109	5.9474	−14.5771
$(—F)_2(—Cl)_2$	−2.1710	0.1403	10.3743	−1.1972
—Br primary	−0.7586	−0.6623	−2.4228	0.7385
—Br secondary	−279.0030	−0.3420	1.4253	73.6293
$(—Br)_{AC}$	−8.1919	−0.1635	3.0150	0.0621
—I primary	−1.4672	−0.2787	4.3362	0.5635
$(—I)_{AC}$	70.9918	−0.0245	7.2061	−18.9106
—(CO)—Cl	−2.3300	−0.0470	8.2815	0.4485

*Hsu, H.-C., Y.-W. Sheu, and C.-H. Tu, *Chem. Eng. J.*, **88** (2002): 27

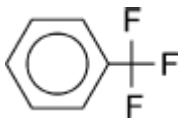
†Table-specific nomenclature: R = in nonaromatic ring, A = in aromatic ring, RC = attached to nonaromatic ring, AC = attached to aromatic ring, X = halogen, $(-X)_n$ = *n* X atoms attached to same C atom

Example

Example

Estimate the liquid viscosity of benzotrifluoride at 303.15 K.

Structural information:



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Group	Number	*a*	100*b*	0.0001*c*	*d*
>C<	1	1.0031	−0.3677	−6.0316	1.1972
(═CH−)$_A$	5	−0.8570	−0.0098	2.4376	0.1311
(═C<)$_A$	1	0.7896	−0.0231	−0.9222	0.1928
(−F)$_3$	1	1.5394	0.8465	17.8121	−2.9915
		Total −0.9529	0.4067	23.0463	−0.9460

Supporting values:

$$P_c = 32.1 \text{ MPa}$$

Calculation using Eq. (2-96):

$$\frac{\eta}{\text{mPa}\cdot\text{s}} = \exp\left[-0.9529 + (0.004067)(303.15) + \frac{230{,}463}{(303.15)^2} - 0.9460\ln(32.1)\right] = 0.610$$

The estimated value is 20 percent higher than the DIPPR 801 value of 0.509 mPa · s. Note that when the calculation is repeated at the normal boiling point (375.2 K), one obtains 0.343 mPa · s which is within the range of the aforementioned empirical rule.

Liquid Mixtures Most methods for estimating liquid mixture viscosity interpolate between the pure-component values at the same temperature. The Grunberg-Nissan equation [Grunberg, L., and A. H. Nissan, *Nature*, **164** (1949): 799]

$$\ln\eta = \sum_{i}^{C} x_i \ln\eta_i + \frac{1}{2}\sum_{i=1}^{C}\sum_{j=1}^{C} x_i x_j G_{ij}$$

(2-97)

is commonly used for nonaqueous mixtures. The parameter G_{ij} generally must be regressed from an experimental mixture viscosity. However, G_{ij} can be set to zero for hydrocarbon mixtures with expected errors in the mixture viscosity of about 15 percent.

Estimation of liquid mixture viscosity without any mixture data is difficult because the viscosity is strongly affected by large molecular size differences and strong cross-interactions between different types of molecules. The UNIFAC-VISCO method described below can be used to predict liquid viscosity of organic mixtures without any mixture data. It can estimate mixture viscosity to a limited accuracy, but it is limited in scope by the small number of group contributions currently available.

Recommended Method UNIFAC-VISCO method.

Reference: Chevalier, J. L., P. Petrino, and Y. Gaston-Bonhomme, *Chem. Eng. Sci.*, **43** (1988): 1303; Gaston-Bonhomme, Y., P. Petrino, and J. L. Chevalier, *Chem. Eng. Sci.*, **49** (1994): 1799.

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Classification: Group contributions.

Expected uncertainty: 20 percent.

Applicability: Organic liquids.

Input data: Molecular structure; pure-component molar volumes and viscosities at the mixture temperature.

Description: Liquid mixture viscosity can be estimated in a manner similar to the UNIFAC method employed for mixture excess Gibbs energy and activity coefficients. The primary equation is

$$\ln\left(\frac{\eta}{\mathrm{mPa}\cdot\mathrm{s}}\right) = \sum_{i=1}^{C} x_i \ln\left(\frac{\eta_i}{\mathrm{mPa}\cdot\mathrm{s}}\cdot\frac{V_i}{V_m}\right) + \frac{g_c^E}{RT} - \frac{g_r^E}{RT}$$

(2-98)

where V_m is the mixture molar volume and V_i is the pure-component molar volume of component *i*. The combinatorial and residual excess Gibbs energies are calculated as in the standard UNIFAC method for activity coefficients (see [PGL5]) and for brevity is not shown here. However, the group interactions ψ_{mn} are calculated using the interaction parameters α_{mn} obtained from Table 2-175 in the equation

Table 2-175 UNIFAC-VISCO* Group Interaction Parameters α_{mn}

m/n	CH_2	CH_3	CH_{2cy}	CH_{ar}	Cl	CO	COO	OH	CH_3OH
CH_2	0	66.53	224.9	406.7	60.30	859.5	1172.0	498.6	−219.7
CH_3	−709.5	0	−130.7	−119.5	82.41	11.86	−172.4	594.4	−228.7
CH_{2cy}	−538.1	187.3	0	8.958	251.4	−125.4	−165.7	694.4	−381.53
CH_{ar}	−623.7	237.2	50.89	0	177.2	128.4	−49.85	419.3	−88.81
Cl	−710.3	375.3	−163.3	−139.8	0	−404.3	−525.4	960.2	−165.4
CO	586.2	−21.56	740.6	−117.9	−4.145	0	29.20	221.5	55.52
COO	541.6	−44.25	416.2	−36.17	240.5	22.92	0	186.8	69.62
OH	−634.5	1209.0	−138	197.7	195.7	664.1	68.35	0	416.4
CH_3OH	−526.1	653.1	751.3	51.31	−140.9	−22.59	−286.2	−23.91	0

*Chevalier, J. L., P. Petrino, and Y. Gaston-Bonhomme, *Chem. Eng. Sci.*, **43** (1988): 1303; Gaston-Bonhomme, Y., P. Petrino, and J. L. Chevalier, *Chem. Eng. Sci.*, **49** (1994): 1799.

$$\psi_{mn} = \exp\left(-\frac{\alpha_{mn}}{298.15}\right)$$

(2-99)

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Example

Example

Estimate the viscosity of a mixture of 51.13 mol% ethanol(1) and 48.87 mol% benzene(2) at 298.15 K.

Required input: Values from the DIPPR 801 database for the pure components at 298.15 K are η_1 = 1.0774 mPa · s, η_2 = 0.5997 mPa · s, V_1 = 0.05862 m^3/kmol, and V_2 = 0.08948 m^3/kmol.

Groups, area fractions, and volume fractions:

Group	*R*	*Q*	N_1	N_2
CH_3	0.9011	0.8480	1	0
CH_2	0.6744	0.5400	1	0
CH_{ar}	0.5313	0.4000	0	6
OH	1.0000	1.2000	1	0
Group	r_1	q_1	r_2	q_2
CH_3	0.9011	0.848	0	0
CH_2	0.6744	0.54	0	0
CH_{ar}	0	0	3.1878	2.4
OH	1	1.2	0	0
	Total 2.5755	2.588	3.1878	2.4

where in the above table

$$q_i = \sum_{k=1}^{N} N_{i,k} Q_k \qquad \text{and} \qquad r_i = \sum_{k=1}^{N} N_{i,k} R_k$$

$$\theta_1 = \frac{x_1 q_1}{\sum_{i=1}^{4} x_i q_i} = \frac{(0.5113)(2.588)}{(0.5113)(2.588)+(0.4887)(2.4)} = 0.53 \qquad \theta_2 = 0.47$$

$$\phi_1 = \frac{x_1 r_1}{\sum_{i=1}^{4} x_i r_i} = \frac{(0.5113)(2.5755)}{(0.5113)(2.5755)+(0.4887)(3.1878)} = 0.458 \qquad \phi_2 = 0.542$$

UNIFAC combinatorial term:

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$$\frac{g_C^E}{RT} = \sum_{i=1}^{2} x_i \ln\frac{\phi_i}{x_i} + 5\sum_{i=1}^{2} x_i q_i \ln\frac{\theta_i}{\phi_i} = 0.124$$

Group interactions:

	α_{mn}			
m/n group	CH_3	CH_2	CH_{ar}	OH
CH_3	0	−709.5	−119.5	594.4
CH_2	66.53	0	406.7	498.6
CH_{ar}	237.2	−623.7	0	419.3
OH	1209	−634.5	197.7	0

	ψ_{mn}			
m/n group	CH_3	CH_2	CH_{ar}	OH
CH_3	1.000	10.801	1.493	0.136
CH_2	0.800	1.000	0.256	0.188
CH_{ar}	0.451	8.100	1.000	0.245
OH	0.017	8.399	0.515	1.000

The α_{mn} values were obtained from Table 2-175, and ψ_{mn} values were calculated from Eq. (2-99).

Group fractions in the mixture:

Group	*N*	*X*	*XQ*	Θ	ln γ
CH_3	0.5113	0.1145	0.097083	0.17370	0.293
CH_2	0.5113	0.1145	0.061822	0.11061	−0.873
CH_{ar}	2.9322	0.6565	0.262618	0.46988	0.066
OH	0.5113	0.1145	0.137382	0.24581	1.077
	Sum 4.4661		0.558905		

$$\text{Here } \Theta_m = \frac{X_m Q_m}{\sum_{i=1}^{4} X_i Q_i} \quad \text{and} \quad \ln\gamma_m = Q_m\left[1 - \ln\left(\sum_{i=1}^{4}\Theta_i\psi_{i,m}\right) - \sum_{i=1}^{4}\left(\frac{\Theta_i\psi_{m,i}}{\sum_{i=1}^{4}\Theta_j\psi_{j,i}}\right)\right]$$

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Group fractions in pure components:

Ethanol					
Group	*N*	*X*	*XQ*	Θ	lnγ
CH_3	1	0.3333	0.283	0.3277	0.5306
CH_2	1	0.3333	0.180	0.2087	−0.9405
CH_{ar}	0	0.0000	0.000	0.0000	0.2095
OH	1	0.3333	0.400	0.4637	0.6179
	Sum 3		0.863		

Benzene					
Group	*N*	*X*	*XQ*	Θ	lnγ
CH_3	0	0	0	0	0.257
CH_2	0	0	0	0	−0.728
CH_{ar}	6	1	0.4	1	0.000
OH	0	0	0	0	2.270
	Sum 6		0.4		

The pure-component Θ and ln γ equations are the same as shown above for the mixture groups.

UNIFAC residual term:

$$\frac{g_r^E}{RT} = \sum_{i=1}^{2} x_i \left[\sum_{m=1}^{4} N_{m,i} (\ln \gamma_m - \ln \gamma_{m,i}) \right] = 0.3425$$

where N_m and ln γ_m refer to the mixture and $N_{m,i}$ and ln $\gamma_{m,i}$ refer to the pure-component values.

Mixture volume:

$$V_m = \sum_{i=1}^{2} x_i V_i = 0.5113 \left(0.05862 \frac{\mathrm{m}^3}{\mathrm{kmol}} \right) + 0.4887 \left(0.08948 \frac{\mathrm{m}^3}{\mathrm{kmol}} \right)$$
$$= 0.07370 \frac{\mathrm{m}^3}{\mathrm{kmol}}$$

Using Eq. (2-98):

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$$\ln\left(\frac{\eta}{\mathrm{mPa}\cdot\mathrm{s}}\right) = 0.5113\ln\left[1.0774\left(\frac{0.05862}{0.07370}\right)\right]$$
$$+0.4887\ln\left[0.5997\left(\frac{0.08948}{0.07370}\right)\right] + 0.124 - 0.3425 = -0.4523$$

$$\eta = \exp(-0.4523)\,\mathrm{mPa}\cdot\mathrm{s} = 0.636\,\mathrm{mPa}\cdot\mathrm{s}$$

The estimated value is 6.6 percent below the reported experimental value of 0.681 mPa · s [Kouris, S., and C. Panayiotou, *J. Chem. Eng. Data*, **34** (1989): 200].

2.16.13. THERMAL CONDUCTIVITY

Thermal conductivity, *k*, is a measure of the rate at which heat conducts through the material and is defined as the proportionality constant in Fourier's law of heat conduction that relates the gradient of temperature to the heat flux or flow per unit area. In SI, it has the units of W/(m · K). The conduction mechanism in gases is primarily via molecular collisions, and *k* increases with increasing temperature (increasing molecular velocity). The temperature dependence of low-pressure, gas-phase thermal conductivity is adequately correlated with

$$k = \frac{AT^B}{1 + \frac{C}{T}}$$

(2-100)

In dense media such as liquids, energy transfers more efficiently through the intermolecular force fields than through collisions. As a result, liquid thermal conductivity generally decreases with increasing temperature (except for water, aqueous solutions, and a few multihydroxy and multiamine compounds), corresponding to the decrease in density with increased temperature. The temperature dependence of liquid thermal conductivity at low to moderate pressures has been found to be well correlated by [Jamieson, D. T., *J. Chem. Eng. Data* **24** (1979): 244]

$$k = A(1 + B\tau^{1/3} + C\tau^{2/3} + D\tau)$$

(2-101)

where $\tau = 1 - T/T_C$. For nonassociating liquids, this equation can be simplified to two parameters by setting $C = 1 - 3B$ and $D = 3B$, generally without much loss in accuracy. Below or near the normal boiling point, the temperature dependence of liquid thermal conductivity is nearly linear for modest temperature ranges and can be represented by

$$k = A - BT$$

(2-102)

where *B* is generally in the range of 1×10^{-4} to 3×10^{-4} W/(m · K^2).

Gases Methods for estimating low-pressure gas thermal conductivities are based on kinetic theory and generally correlate the dimensionless group $kM/\eta C_\upsilon$ (M = molecular weight, η = viscosity, C_υ = isochoric heat capacity), known as the Eucken

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factor. The method of Stiel and Thodos is recommended for pure nonpolar compounds, and the method of Chung is recommended for pure polar compounds.

Recommended Method Stiel-Thodos method.

Reference: Stiel, L. I., and G. Thodos, *AIChE J.*, **10** (1964): 26.

Classification: Empirical extension of theory.

Expected uncertainty: 15 percent.

Applicability: Pure nonpolar gases at low pressure.

Input data: M, T_c, η, and C_v.

Description: The following equations may be used depending upon the molecular shape:

$$\frac{kM}{\eta C_v} = 2.5 \qquad \text{monatomic}$$

(2-103)

$$\frac{kM}{\eta C_v} = 1.30 + \left(\frac{R}{C_v}\right)\left(1.7614 - \frac{0.3523}{T_r}\right) \qquad \text{linear molecules}$$

(2-104)

$$\frac{kM}{\eta C_v} = 1.15 + 2.033\left(\frac{R}{C_v}\right) \qquad \text{nonlinear molecules}$$

(2-105)

where η = viscosity at same conditions as desired for k. Because this method is only applicable at low pressures, C_v may usually be calculated as
$C_p^o - R$, where
C_p^o is the ideal gas isobaric heat capacity.

Example

Example

Estimate the low-pressure thermal conductivity of toluene vapor at 500 K.

Required properties from the DIPPR 801 database:

$$T_c = 591.75\ \mathrm{K} \quad M = 92.138\ \mathrm{g/mol} \quad \eta(500\ \mathrm{K}) = 1.1408 \times 10^{-5}\,\mathrm{Pa \cdot s}$$
$$C_v = C_p^o - R = (170.78 - 8.314)\,\mathrm{J/(mol \cdot K)} = 162.47\ \mathrm{J/(mol \cdot K)}$$

Auxiliary quantities:

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$$T_r = 500/591.75 = 0.845 \quad R/C_v = (8.314)/(162.47) = 0.0512$$

From Eq. (2-105):

$$k = [1.15 + (2.033)(0.0512)] \left[\frac{(1.1408 \times 10^{-5}\,\mathrm{Pa \cdot s})\left(162.47 \frac{\mathrm{J}}{\mathrm{mol \cdot K}}\right)}{92.138 \frac{\mathrm{g}}{\mathrm{mol}}} \right] = 25.2 \frac{\mathrm{mW}}{\mathrm{m \cdot K}}$$

The estimated value is 18 percent below the DIPPR 801 value of 30.76 mW/(m · K).

Recommended Method Chung-Lee-Starling method.

Reference: Chung, T.-H., L. L. Lee, and K. E. Starling, *Ind. Eng. Chem. Fundam.*, **23** (1984): 8.

Classification: Corresponding states.

Expected uncertainty: 15 percent.

Applicability: Pure organic gases at low pressure.

Input data: C_v, ω, T_c, M, and η.

Description: The following equations apply:

$$\frac{kM}{\eta C_v} = 3.75\,\Psi\left(\frac{R}{C_v}\right)$$

(2-106)

$$\Psi = 1 + \alpha\left(\frac{0.215 + 0.28288\alpha - 1.061\beta + 0.26665\gamma}{0.6366 + \beta\gamma + 1.061\alpha\beta}\right)$$

(2-107)

$$\alpha = \frac{C_v}{R} - 1.5 \quad \beta = 0.7862 - 0.7109\omega + 1.3168\omega^2$$
$$\gamma = 2.0 + 10.5T_r^2$$

(2-108)

Example

Example

Estimate the low-pressure thermal conductivity of naphthalene vapor at 500 K.

Required properties from the DIPPR 801 database:

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$$
\begin{aligned}
T_c &= 748.4\,\mathrm{K} \quad M = 128.17\,\mathrm{g/mol} \quad \omega = 0.30203 \\
\eta\,(500\,\mathrm{K}) &= 1.0173 \times 10^{-5}\mathrm{Pa \cdot s} \\
C_v &= C_p^o - R = (219.82 - 8.314)\,\mathrm{J/(mol \cdot K)} = 211.51\ J/(\mathrm{mol \cdot K})
\end{aligned}
$$

Auxiliary quantities [Eqs. (2-107) and (2-108)]:

$$
\begin{aligned}
T_r &= 500/748.4 = 0.6681 \quad R/C_v = (8.314)/(211.51) = 0.0393 \\
\gamma &= 2.0 + (10.5)(0.6681)^2 = 6.6866 \quad \alpha = (0.0393)^{-1} - 1.5 = 23.9388 \\
\beta &= 0.7862 - (0.7109)(0.30203) + (1.3168)(0.30203)^2 = 0.6916
\end{aligned}
$$

$$
\begin{aligned}
\Psi &= 1 + (23.9388)\left[\frac{0.215 + 0.28288\,(23.9388) - 1.061\,(0.6916) + 0.26665\,(6.6866)}{0.6366 + 0.6916\,(6.6866) + 1.061\,(23.9388)\,(0.6916)}\right] \\
&= 9.4273
\end{aligned}
$$

From Eq. (2-106):

$$
k = (3.75)(9.4273)\left[\frac{(1.1408 \times 10^{-5}\mathrm{Pa \cdot s})\left(8.314\frac{\mathrm{J}}{\mathrm{mol \cdot K}}\right)}{128.17\frac{\mathrm{g}}{\mathrm{mol}}}\right] = 23.33\frac{\mathrm{mW}}{\mathrm{m \cdot K}}
$$

The estimated value is 1.0 percent above the DIPPR 801 value of 23.09 mW/(m·K).

Liquids For hydrocarbons at low to moderate pressures, a modification of the Pachaiyappan method should be used. For nonhydrocarbons, the Baroncini method provides accurate liquid thermal conductivity estimates for compounds clearly belonging to one of the chemical families specified below. Otherwise, the Missenard method is recommended as a general method for estimating thermal conductivity of pure liquids at ambient pressure.

Recommended Method Modified Pachaiyappan.

Reference: Pachaiyappan, V., S. H. Ibrahim, and N. R. Kuloor, *Chem. Eng.* **74**(4) (1967): 140; *API Technical Databook,* 10th ed., chap. 12, 2017.

Classification: Empirical correlation.

Expected uncertainty: 10 percent.

Applicability: Hydrocarbons only; low to moderate pressures.

Input data: M, T_b, and T_c.

Description:

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$$\frac{k}{\mathrm{W \cdot m^{-1}K^{-1}}} = \frac{C\left(\dfrac{M}{\mathrm{g \cdot mol^{-1}}}\right)^m}{\left(\dfrac{V_{293}}{\mathrm{cm^3 \cdot mol^{-1}}}\right)} \left[\frac{3+20(1-T_r)^{2/3}}{3+20(1-T_{r,293})^{2/3}}\right]$$

(2-109)

where M is molecular weight, V_{293} is the molar volume at 293.15 K, T_r is the reduced temperature, $T_{r,293}$ = (293.15 K)/(T_c) and the correlation parameters C and m are obtained from the table below:

Classification	C	m
Unbranched, straight-chain hydrocarbon	0.1811	1.001
All branched, cyclic and aromatic hydrocarbons	0.4407	0.7717

Example

Example

Estimate the thermal conductivity of liquid *n*-butylbenzene at low pressure and 333.15 K.

Required properties from DIPPR 801 database:

$$M = 134.218\ \mathrm{g/mol} \quad T_c = 660.5\ \mathrm{K} \quad V_{293} = 162.01\ \mathrm{cm^3/mol}$$

Auxiliary properties:

$$T_r = (333.15\ \mathrm{K})/(660.5\ \mathrm{K}) = 0.5044 \quad T_{r,293} = (293.15\ \mathrm{K})/(660.5\ \mathrm{K}) = 0.4438$$

Since this is an aromatic hydrocarbon,

$$C = 0.4407 \text{ and } m = 0.7717 \quad \text{(from the above table)}$$

From Eq. (2-109):

$$\frac{k}{(\mathrm{W \cdot m^{-1}K^{-1}})} = \frac{(0.4407)(134.218)^{0.7717}}{162.01}\left[\frac{3+20(1-0.5044)^{2/3}}{3+20(1-0.4438)^{2/3}}\right] = 0.112$$

The estimated value is 5 percent below the experimental value of 0.118 W/(m · K) reported by Rastorguev and Pugach [Rastorguev, Yu. L., and V. V. Pugach, *Izv. Vyssh. Uchebn. Zaved., Neft Gaz*, **13** (1970): 69].

Recommended Method 1 Baroncini method.

Reference: Baroncini, C., F. DiFilippo, G. Latini, and M. Pacetti, *Int. J. Thermophys.*, **2** (1981): 21.

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Classification: Empirical correlation.

Expected uncertainty: 10 percent.

Applicability: Particularly accurate for the following families: acetates, aliphatic ethers, halogenated compounds, dicarboxylic acids, ketones, aliphatic alcohols, aliphatic acids, propionates and butyrates, and unsaturated aliphatic esters.

Input data: M, T_b, and T_c.

Description:

$$\frac{k}{\mathrm{W/(m \cdot K)}} = A\left(\frac{T_b}{\mathrm{K}}\right)^{\alpha}\left(\frac{M}{\mathrm{g/mol}}\right)^{-\beta}\left(\frac{T_c}{\mathrm{K}}\right)^{-\gamma}\frac{(1-T_r)^{0.38}}{T_r^{1/6}}$$

(2-110)

where A, α, β, and γ are obtained from Table 2-176.

Table 2-176 Correlation Parameters for Baroncini et al. Method* for Estimation of Thermal Conductivity

Family	A	α	β	γ
Saturated hydrocarbons	0.00350	1.2	0.5	0.167
Olefins	0.0361	1.2	1	0.167
Cycloparaffins	0.0310	1.2	1	0.167
Aromatics	0.0346	1.2	1	0.167
Alcohols	0.00339	1.2	0.5	0.167
Organic acids	0.00319	1.2	0.5	0.167
Ketones	0.00383	1.2	0.5	0.167
Esters	0.0415	1.2	1	0.167
Ethers	0.0385	1.2	1	0.167
Refrigerants				
R20, R21, R22, R23	0.562	0	0.5	−0.167
Others	0.494	0	0.5	−0.167

*Baroncini, C., et al., *Int. J. Thermophys.*, **2** (1981): 21.

Example

Example

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Estimate the thermal conductivity of liquid *p*-cresol at 400 K.

Required properties from DIPPR 801 database:

$$M = 108.1378\ \mathrm{g/mol} \quad T_c = 704.65\ \mathrm{K} \quad T_b = 475.133\ \mathrm{K}$$

Auxiliary properties:

$$T_r = T/T_c = (400\ \mathrm{K})/(704.65\ \mathrm{K}) = 0.5677$$

From Table 2-176 for alcohols:

$$A = 0.00339 \qquad \alpha = 1.2 \qquad \beta = \frac{1}{2} \qquad \gamma = 0.167$$

From Eq. (2-110):

$$\frac{k}{\mathrm{W/(m \cdot K)}} = (0.00339)(475.13)^{1.2}(108.1378)^{-1/2}(704.65)^{-0.167}\frac{(1-0.5677)^{0.38}}{0.5677^{1/6}} = 0.142$$

The estimated value is 7.6 percent higher than the DIPPR 801 value of 0.132 W/(m · K).

Recommended Method 2 Missenard method.

Reference: Missenard, A., *Comptes Rendus*, **260** (1965): 5521.

Classification: Corresponding states.

Expected uncertainty: 20 percent.

Applicability: Organic compounds; nonassociating.

Input data: T_c, n_A (number of atoms in molecule), ρ_{273} (liquid density at 273.15 K), T_b, M, $C_{p,273}$ (liquid heat capacity at 273.15 K).

Description:

$$\frac{k_{273}}{\mathrm{mW/(m \cdot K)}} = \left(\frac{8.4}{N_A{}^{1/4}}\right)\left(\frac{T_b}{\mathrm{K}}\right)^{1/2}\left(\frac{\rho_{273}}{\mathrm{g/m^3}}\right)^{1/2}\left(\frac{M}{\mathrm{g/mol}}\right)^{-1/2}\left[\frac{C_{p,273}}{\mathrm{J/(mol \cdot K)}}\right]$$

(2-111)

$$k = \frac{k_{273}[3 + 20(1-T_r)^{2/3}]}{3 + 20(1-T_{r,273})^{2/3}}$$

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(2-112)

where $T_{r,273}$ = (273 K)/T_c.

Example

Example

Estimate the thermal conductivity of *m*-xylene at 350 K.

Required properties from DIPPR 801 database:

$$\begin{array}{lll} T_c = 617\ \mathrm{K} & n_A = 18 & \rho_{273} = 7.6812\ \mathrm{kmol/m^3} \\ T_b = 412.27\ \mathrm{K} & M = 106.165\ \mathrm{kg/kmol} & C_{p,273} = 200.64\ \mathrm{kJ/(kmol \cdot K)} \end{array}$$

Auxiliary properties:

$$\begin{array}{ll} T_r = 350/617 = 0.5673 & T_{br} = 412.27/617 = 0.6682 \\ T_{r,273} = 273/617 = 0.4425 & \end{array}$$

From Eq. (2-111):

$$\frac{k_{273}}{\mathrm{mW/(m \cdot K)}} = (8.4)(412.27)^{1/2}(0.007681)^{1/2}(106.165)^{-1/2}(200.64)(18)^{-0.25} = 141.3$$

From Eq. (2-112):

$$k = \frac{k_{273}[3 + 20(1 - T_r)^{2/3}]}{3 + 20(1 - T_{r,273})^{2/3}} = \frac{\left(141.3 \dfrac{\mathrm{mW}}{\mathrm{m \cdot K}}\right)[3 + 20(1 - 0.5673)^{2/3}]}{3 + 20(1 - 0.4425)^{2/3}} = 123.3 \frac{\mathrm{mW}}{\mathrm{m \cdot K}}$$

The estimated value is 4.5 percent above the DIPPR 801 value of 118.0 mW/(m·K).

Liquid Mixtures The thermal conductivity of liquid mixtures generally shows a modest negative deviation from a linear mass-fraction average of the pure-component values. Although more complex methods with some improved accuracy are available, two simple methods are recommended here that require very little additional information. The first method applies only to binary mixtures while the second can be used for multiple components.

Recommended Method Filippov correlation.

References: Filippov, L. P., *Vest. Mosk. Univ., Ser. Fiz. Mat. Estestv. Nauk,* **10** (1955): 67; Filippov, L. P., and N. S. Novoselova, Sugden, *Vest. Mosk. Univ., Ser. Fiz. Mat. Estestv. Nauk,* **10** (1955): 37.

Classification: Empirical correlation.

Expected uncertainty: 4 to 8 percent.

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Applicability: Binary liquid mixtures.

Input data: Pure-component thermal conductivities k_i at mixture conditions; w_i.

Description: The mixture thermal conductivity is calculated from the pure-component values using

$$k = w_1 k_1 + w_2 k_2 - 0.72 w_1 w_2 |k_2 - k_1|$$

(2-113)

where w_i is the mass fraction of pure fluid i and k_i is the thermal conductivity of pure component i at the mixture temperature.

Recommended Method Li correlation.

References: Li, C. C., *AIChE J.*, **22** (1976): 927.

Classification: Empirical correlation.

Expected uncertainty: 4 to 8 percent.

Applicability: Liquid mixtures.

Input data: Pure-component thermal conductivities k_i at mixture conditions; $\rho_{L,i}$

Description: The mixture thermal conductivity is correlated as a function of the mixture volume fractions ϕ_i:

$$k = \sum_{i=1}^{C} \sum_{j=1}^{C} \phi_i \phi_j \frac{2 k_i k_j}{k_i + k_j}$$

$$\text{where } \phi_i = \frac{x_i \rho_{L,i}^{-1}}{\sum_{j=1}^{C} x_j \, \rho_{L,j}^{-1}}$$

(2-114)

Example

Example

Estimate the thermal conductivity of a mixture containing 30.2 mol% diethyl ether(1) and 69.8 mol% methanol(2) at 273.15 K and 0.1 MPa, using the Filippov and Li correlations.

Auxiliary data: The pure-component thermal conductivities and molar densities at 273.15 K recommended in the DIPPR 801 database are

$$\begin{aligned} k_1 &= 0.1383 \text{ W/(m} \cdot \text{K)} & \rho_1 &= 9.9335 \text{ kmol/m}^3 & M_1 &= 74.1216 \text{ kg/kmol} \\ k_2 &= 0.2069 \text{ W/(m} \cdot \text{K)} & \rho_2 &= 25.371 \text{ kmol/m}^3 & M_2 &= 32.0419 \text{ kg/kmol} \end{aligned}$$

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The mass fractions corresponding to the mole fractions given above are

$$w_1 = 0.5 \quad w_2 = 0.5$$

The volume fractions are

$$\phi_1 = \frac{(0.302)(9.9335)^{-1}}{(0.302)(9.9335)^{-1} + (0.698)(25.371)^{-1}} = 0.525 \qquad \phi_2 = 0.475$$

Calculation using Eq. (2-113):

$$\begin{aligned} k &= [(0.5)(0.1383) + (0.5)(0.2069) - (0.72)(0.5)(0.5)\,|0.2069 - 0.1383|]\frac{\mathrm{W}}{\mathrm{m \cdot K}} \\ &= 0.160\ \mathrm{W/(m \cdot K)} \end{aligned}$$

Calculation using Eq. (2-114):

$$\begin{aligned} k &= \left[(0.525)^2(0.1383) + 2 \cdot \frac{(0.525)\,(0.475)\,(2)\,(0.1383)\,(0.2069)}{0.1383 + 0.2069} + (0.475)^2(0.2069)\right]\frac{\mathrm{W}}{\mathrm{m \cdot K}} \\ &= 0.167\ \mathrm{W/(m \cdot K)} \end{aligned}$$

The Filippov value is 7.5 percent lower than the experimental value of 0.173 W/(m · K) [Jamieson, D. T., and B. K. Hastings, *Thermal Conductivity, Proceedings of the Eighth Conference,* C. Y. Ho and R. E. Taylor, eds., Plenum Press, New York, 1969]; the Li value is 3.5 percent lower than the experimental value.

2.16.14. SURFACE TENSION

The surface at a vapor-liquid interface is in tension due to the difference in attractive forces experienced by molecules at the interface between the dense liquid phase and the low-density gas phase. This causes the liquid to contract to minimize the surface area. *Surface tension* is defined as the force in the surface plane per unit length. Jasper [Jasper, J. J., *J. Phys. Chem. Ref. Data*, **1** (1972): 841] has made a critical evaluation of experimental surface tension data for approximately 2200 pure chemicals and correlated surface tension σ (mN/m = dyn/cm) with temperature as

$$\sigma = A - BT$$

(2-115)

Jasper's evaluation also includes values of *A* and *B* for most of the tabulated chemicals. Surface tension decreases with increasing temperature and increasing pressure.

Pure Liquids An approach suggested by Macleod [Macleod, D. B., *Trans. Faraday Soc.*, **19** (1923): 38] and modified by Sugden [Sugden, S. J., *Chem. Soc.*, **125** (1924): 32] relates σ to the liquid and vapor *molar* densities and a temperature-independent parameter called the Parachor **P**

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$$\frac{\sigma}{\mathrm{mN/m}} = \left[\mathrm{P} \cdot \left(\frac{\rho_L - \rho_v}{10^3 \mathrm{kmol/m^3}}\right)\right]^4$$

(2-116)

where ρ_L and ρ_V are the saturated molar liquid and vapor densities, respectively. At low temperatures, where $\rho_L >> \rho_V$, the vapor density can be neglected, but at higher temperatures the density of both phases must be calculated. The surface tension is zero at the critical point where $\rho_L = \rho_V$. Quayle [Quayle, O. R., *Chem. Rev.*, **53** (1953): 439] proposed a group contribution method for estimating **P** that has been improved in recent years by Knotts et al. [Knotts, T. A., et. al.,*J. Chem. Eng. Data*, **46** (2001): 1007]. This method using **P** is recommended when groups are available; otherwise, the Brock-Bird [Brock, J. R., and R. B. Bird, *AIChE J.*, **1** (1955): 174] corresponding-states method as modified by Miller [Miller, D. G.,*Ind. Eng. Chem. Fundam.*, **2** (1963): 78] may be used to estimate surface tension for compounds that are not strongly polar or associating.

Recommended Method 1 Parachor method.

References: Macleod, D. B., *Trans. Faraday Soc.*, **19** (1923): 38; Sugden, S. J., *Chem. Soc.*, **125** (1924): 32; Knotts, T. A., W. V. Wilding, J. L. Oscarson, and R. L. Rowley, *J. Chem. Eng. Data*, **46** (2001): 1007.

Classification: Group contributions and QSPR.

Expected uncertainty: 4 percent.

Applicability: Organic compounds for which group values are available.

Input data: ρ_L, molecular structure, and Table 2-177.

Table 2-177 Knotts* Group Contributions for the Parachor in Estimating Surface Tension

Group	ΔP_i	Group	ΔP_i
(a) Nonring C		**(e) Nitrogen groups**	
$-CH_3$	55.25	$R-NH_2$ (primary R)	44.98
$>CH_2$ (n = 1–11)	39.92	$R-NH_2$ (sec R)	44.63
$>CH_2$ (n = 12–20)	40.11	$R-NH_2$ (tert R)	46.44
$>CH_2$ (n > 20)	40.51	$A-NH_2$ (attached to arom ring)	46.53
>CH–	28.90	>NH (nonring)	29.04
>C<	15.76	>NH (ring)	31.97
$=CH_2$	49.76	>NH (in arom ring)	33.92
=CH–	34.57	>N- (nonring)	10.77
=C<	24.50	>N- (ring)	15.71
=C=	24.76	–N= (nonring)	23.24
≡CH	43.64	>N (aromatic)	26.49

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Group	ΔP	Group	ΔP
≡C—	28.64	HC≡N (hyd cyanide)	80.94
Branch corrections		—C≡N	65.23
Per branch	−6.02	—C≡N (aromatic)	67.54
sec-sec adjacency	−2.73	**(f) Nitrogen and oxygen groups**	
sec-tert adjacency	−3.61	—C═ONH_2 (amides)	93.43
tert-tert adjacency	−6.10	—C═ONH- (amides)	73.64
(b) Nonaromatic ring C		—C═ON< (amides)	57.05
—CH_2—	39.21	—NHCHO	91.69
>CH—	23.94	>NCHO	77.12
>C<	7.19	—N═O	64.32
═CH—	34.07	—NO_2	73.86
═C<	18.85	—NO_2 (aromatic)	75.05
>CH— (fused ring)	22.05	**(g) Sulfur groups**	
Ring corrections		R-SH (primary R)	66.89
Three-member ring	12.67	R-SH (sec R)	63.34
Four-member ring	15.76	R-SH (tert R)	65.33
Five-member ring	7.04	—SH (aromatic)	68.30
Six-member ring	5.19	—S— (nonring)	51.37
Seven-member ring	3.00	—S— (ring)	51.75
(c) Aromatic ring C		—S— (aromatic)	51.47
>CH	34.36	>S═O (nonring)	72.21
>C—	16.07	>SO_2 (nonring)	93.20
—C— (fused arom/arom)	19.73	>SO_2 (ring)	90.13
—C— (fused arom/aliph)	14.41	**(h) Halogen groups**	
Arom ring corr		—F	21.81
ortho	−0.60	—Cl	26.24
para	3.40	—Br	51.16

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Group	ΔP	Group	ΔP
meta	2.24	—I	54.56
subst. naphthalene corr	−7.07	—F (aromatic)	66.30
(d) Oxygen groups		—Cl (aromatic)	70.39
—OH (alc, primary)	31.42	—Br (aromatic)	90.84
—OH (alc, sec)	22.68	—I (aromatic)	92.04
—OH (alc, tertiary)	20.66	**(i) Si groups**	
—OH (phenol)	30.32	SiH_4	105.11
—O— (nonring)	20.61	>SiH—	54.50
—O— (ring)	21.67	>Si<	44.93
—O— (aromatic)	23.54	>Si< (ring)	28.64
>C═O (nonring)	47.02	**(j) Other inorganic groups**	
>C═O (ring)	50.04	$—PO_4$	115.59
O═CH— (aldehyde)	66.06	>P—	48.84
CHOOH (formic)	94.01	>B—	22.65
—COOH (acid)	74.57	>Al—	25.06
—OCHO (formate)	82.29	$—ClO_3$	106.03
—COO— (ester)	64.97		
—COOCO— (acid anhyd)	115.07		
—OC(═O)O— (ring)	84.05		
*Knotts, T. A., et al., *J. Chem. Eng. Data*, **46** (2001): 1007.			

Description: Equation (2-116) is used with **P** calculated from

$$\mathrm{P} = \sum_{i=1}^{N} n_i \Delta P_i$$

(2-117)

Group values for the Parachor are given in Table 2-177.

Example

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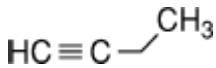
Example

Estimate the surface tension of ethylacetylene at 237.45 K.

Structure:



Group	n_i	ΔP_i	$n_i\,\Delta P_i$
≡CH	1	43.64	43.64
≡C–	1	28.64	28.64
>CH_2 (n = 1–11)	1	39.92	39.92
CH_3	1	55.25	55.25
			Total 167.45

Required properties: The DIPPR 801 database gives ρ_L = 13.2573 kmol/m^3 at 237.45 K.

Calculation using Eq. (2-116):

$$\sigma = \left[(167.45)\left(\frac{13.2573}{1000}\right)\right]^4 \frac{\mathrm{mN}}{\mathrm{m}} = 0.02429\frac{\mathrm{N}}{\mathrm{m}}$$

The estimated value is 0.9 percent above the DIPPR801 recommended value of 0.02407 N/m.

Recommended Method 2 Brock-Bird method.

Reference: Brock, J. R., and R. B. Bird, *AIChE J.*, **1** (1955): 174; Miller, D. G., *Ind. Eng. Chem. Fundam.*, **2** (1963): 78.

Classification: Corresponding states.

Expected uncertainty: 5 percent.

Applicability: Nonpolar and moderately polar organic compounds.

Input data: T_c, P_c, and T_b.

Description:

$$\frac{\sigma}{\mathrm{mN/m}} = (5.553 \times 10^{-5})\left(\frac{P_c}{\mathrm{Pa}}\right)^{2/3}\left(\frac{T_c}{\mathrm{K}}\right)^{1/3} F(1-T_r)^{11/9}$$

(2-118)

where

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$$F = \frac{T_{br}[\ln(P_c/\mathrm{Pa}) - 11.5261]}{1 - T_{br}} - 1.3281$$

(2-119)

Example

Example

Estimate the surface tension for ethyl mercaptan at 303.15 K.

Required properties from DIPPR 801:

$$T_c = 499.15\ \mathrm{K} \quad P_c = 5.49 \times 10^6\,\mathrm{Pa} \quad T_b = 308.15\ \mathrm{K}$$

Supporting quantities:

$$\begin{aligned} T_r &= (303.15\ \mathrm{K})/(499.15\ \mathrm{K}) = 0.6073 \\ T_{br} &= (308.15\ \mathrm{K})/(499.15\ \mathrm{K}) = 0.6173 \\ F &= \{0.6173[\ln\ (5.49 \times 10^6) - 11.5261]/(1 - 0.6173)\} - 1.3281 = 5.113\ [\,\mathrm{from\ Eq.}\ (2-119)] \end{aligned}$$

From Eq. (2-118):

$$\begin{aligned} \sigma &= (5.553 \times 10^{-5})(5.49 \times 10^6)^{2/3}(499.15)^{1/3}(5.113)(1 - 0.6073)^{11/9}\mathrm{mN/m} \\ &= 22.36\ \mathrm{mN/m} \end{aligned}$$

The estimated value is 1.4 percent lower than the DIPPR 801 value of 22.68 mN/m.

Liquid Mixtures Compositions at the liquid-vapor interface are not the same as in the bulk liquid, and so simple (bulk) composition-weighted averages of the pure-fluid values do not provide quantitative estimates of the surface tension at the vapor-liquid interface of a mixture. The behavior of aqueous mixtures is more difficult to correlate and estimate than that of nonpolar mixtures because small amounts of organic material can have a pronounced effect upon the surface concentrations and the resultant surface tension. These effects are usually modeled with thermodynamic methods that account for the activity coefficients. For example, a UNIFAC method [Suarez, J. T., C. Torres-Marchal, and P. Rasmussen, *Chem. Eng. Sci.*, **44** (1989): 782] is recommended and illustrated in [PGL5]. For nonaqueous systems the extension of the Parachor method, used above for pure fluids, is a simple and reasonably effective method for estimating σ for mixtures.

Recommended Method Parachor correlation.

Reference: Hugill, J. A., and A. J. van Welsenes, *Fluid Phase Equilib.*, **29** (1986): 383; Macleod, D. B., *Trans. Faraday Soc.*, **19** (1923): 38; Sugden, S. J., *Chem. Soc.*, **125** (1924).

Classification: Corresponding states.

Expected uncertainty: 3 to 10 percent.

Applicability: Nonaqueous mixtures.

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Input data: Liquid and vapor ρ at mixture *T*; Parachors of pure components; x_i.

Description:

$$\frac{\sigma_m}{\mathrm{mN/m}} = \left(\mathrm{P}_{L,m} \frac{\rho_{L,m}}{10^3 \mathrm{kmol/m^3}} - \mathrm{P}_{v,m} \frac{\rho_{V,m}}{10^3 \mathrm{kmol/m^3}} \right)^4$$

(2-120)

where σ_m = surface tension of the mixture

$\mathbf{P}_{L,m}$, $\mathbf{P}_{V,m}$ = Parachor of liquid and vapor mixtures, respectively

$\rho_{L,m}$, $\rho_{V,m}$ = mixture molar density of liquid and vapor, respectively

The following definitions are used for the liquid and vapor mixture Parachors:

$$\mathrm{P}_{L,m} = \frac{1}{2} \sum_{i=1}^{C} \sum_{\mathrm{j}=1}^{C} x_i x_j (\mathrm{P}_i + \mathrm{P}_j) \qquad \mathrm{P}_{V,m} = \frac{1}{2} \sum_{i=1}^{C} \sum_{\mathrm{j}=1}^{C} y_i y_j (\mathrm{P}_i + \mathrm{P}_j)$$

(2-121)

where x_i is the mole fraction of component *i* in the liquid and y_i is the mole fraction of component *i* in the vapor.

Note that ρ_V is generally very small compared to ρ_L at temperatures substantially lower than T_c and can often be neglected.

Example

Example

Estimate the surface tension for a 16.06 mol% *n*-pentane(1) + 83.94 mol% dichloromethane(2) mixture at 298.15 K.

Required properties from DIPPR 801:

	P	ρ_L/(kmol · m^{-3}) at 298.15 K
n-Pentane	231.1	8.6173
Dichloromethane	146.6	15.5211

Mixture Parachor from Eq. (2-121) and mixture density:

$$\mathrm{P}_{L,m} = (0.1606)^2(231.1) + (0.1606)(0.8394)(231.1 + 146.6) + (0.8394)^2(146.6) = 160.17$$

$$\rho_{L,m} = \left(\sum_{i=1}^{C} \frac{x_i}{\rho_i} \right)^{-1} = \left(\frac{0.1606}{8.6173} + \frac{0.8394}{15.5211} \right)^{-1} \frac{\mathrm{kmol}}{\mathrm{m^3}} = 13.752 \frac{\mathrm{kmol}}{\mathrm{m^3}}$$

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Calculation using Eq. (2-120): Because the temperature is low, the density of the vapor can be neglected, and

$$\frac{\sigma_m}{\mathrm{mN/m}} = [(160.17)(0.013752)]^4 = 23.54\frac{\mathrm{mN}}{\mathrm{m}}$$

The estimated value is 2.9 percent below the experimental value of 24.24 mN/m reported by De Soria [De Soria, M. L. G., et al., *J. Colloid Interface Sci.*, **103** (1985): 354].

2.16.15. FLAMMABILITY PROPERTIES

Flash Point The flash point is the lowest temperature at which a liquid gives off sufficient vapor to form an ignitable mixture with air near the surface of the liquid or within the vessel used. ASTM test methods include procedures using a closed-cup apparatus (ASTM D 56, ASTM D 93, and ASTM D 3828), which is preferred, and an open-cup apparatus (ASTM D 92 and ASTM D 1310). Closed-cup values are typically lower than open-cup values. Estimation methods cannot take into account the apparatus and procedural influences on the observed flash point.

Recommended Method Leslie-Geniesse method.

Reference: Leslie, E. H., and J. C. Geniesse, *International Critical Tables,* vol. 2, McGraw-Hill, New York, 1927, p. 161.

Classification: GC (element contributions).

Expected uncertainty: ~4 K or about 1.5 percent.

Applicability: Organic compounds.

Input data: Chemical structure and vapor pressure correlation.

Description: The flash point T_{FP} is obtained from the moles of oxygen required for stoichiometric combustion β, by back-solving from the vapor pressure correlation using

$$\frac{P^*(T_{\mathrm{FP}})}{\mathrm{atm}} = \frac{1}{8\beta}$$

(2-122)

where P^* = vapor pressure at the flash point

$$\beta = N_{\mathrm{C}} + N_{\mathrm{Si}} + N_{\mathrm{S}} + \frac{N_{\mathrm{H}} - N_{\mathrm{X}} - 2N_{\mathrm{O}}}{4}$$

(2-123)

N_C, N_{Si}, N_S, N_H, N_X, N_O = number of carbon, silicon, sulfur, hydrogen, halogen, and oxygen atoms in the molecule, respectively

Example

Example

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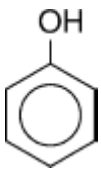
Estimate the flash point of phenol.

Structure:



Atomic contributions:

Atom type	Number
C	6
H	6
O	1

From Eq. (2-123), β = 6 + (6 − 2·1)/4 = 7

The DIPPR 801 correlation for the vapor pressure of phenol is

$$\frac{P^*}{\mathrm{Pa}} = \exp\left[95.444 - \frac{10{,}113\,\mathrm{K}}{T} - 10.09\,\mathrm{In}\left(\frac{T}{\mathrm{K}}\right) + 6.7603 \times 10^{-18}\left(\frac{T}{\mathrm{K}}\right)^6\right]$$

When this expression is used in Eq. (2-122) and solved for temperature, one obtains T_{FP} = 350.84 K, which is 0.4 percent below the DIPRR recommended value of 352.15 K.

Flammability Limits The lower flammability limit (LFL) is the equilibrium-mixture boundary-line volume percent of vapor or gas in air which if ignited will just propagate a flame away from the ignition source. Similarly, the upper flammability limit (UFL) is the upper volume percent boundary at which a flame can propagate in an ignited fuel/air equilibrium mixture. Each of these limits has a temperature at which the corresponding volumetric percent is reached. The lower flammability limit temperature corresponds approximately to the flash point, but since the flash point is determined with downward flame propagation and nonuniform mixtures and the lower flammability temperature is determined with upward flame propagation and uniform vapor mixtures, the measured lower flammability temperature is generally slightly lower than the flash point.

Recommended Method Rowley method.

Reference: Rowley, J. R., R. L. Rowley, and W. V. Wilding, *J. Hazard. Materials*, **186** (2011): 551; Rowley, J. R., "Flammability Limits, Flash Points, and Their Consanguinity: Critical Analysis, Experimental Exploration, and Prediction," Ph.D. Dissertation, Brigham Young University, 2010.

Classification: GC and extended theory.

Expected uncertainty: 10 percent for the lower limit; 25 percent for the upper limit.

Applicability: Organic compounds.

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Input data: Group contributions from Tables 2-178, ΔH_f^o, and the thermal properties (ideal gas heat of formation and average isobaric heat capacity) of the combustion products. These latter quantities are given in Table 2-179. A vapor pressure correlation is also required to obtain the corresponding flammability limit temperature.

Table 2-178 Group Contributions for Quantities Used to Estimate Flammability Limits by Rowley et al.* Method for Organic Compounds (special notation: lower case indicates aromatic atom; # = triple bond; R = ring)

Group	Example	$\Delta T_{ad,i}$	UFL_i	Group	Example	$\Delta T_{ad,i}$	UFL_i
#C—	vinyl acetate	991.44	−8.65	n	pyridine	2622.13	4.46
#CH	acetylene	1237.85	61.25	n	piperazine	2124.88	13.32
═C<	isobutene	1834.42	−7.15	>NH	*n*-pentylamine	1566.76	−0.78
═CH	*trans*-2-butene	1751.82	0.30	>N—(c)	N-ethylaniline	2695.31	−7.25
═CH_2	1-hexene	1558.49	3.06	N#C	benzonitrile	939.73	−9.72
═CH—(c)	styrene	−76.72	−11.24	N═C═O	methyl isocyanate	1147.48	4.95
═C—(c)	α-methylstyrene	2091.10	−5.13	—NO_2	nitroethane	1777.58	−11.46
>C<	neopentane	1957.78	−0.23	—S—	thiophene	1056.05	23.55
—CH	isopropanol	1558.73	0.62	—SH	ethyl mercaptan	1727.5	12.67
—CH_2	propane	1705.21	−0.30	S═	carbon disulfide	272.36	53.67
—CH_3	butane	1856.30	−1.12	Si	trimethylsilane	−55.66	78.90
CH_3—c	toluene	1862.04	−4.49	Si(O_3)	tetraethoxysilane	2095.22	120.24
c—	toluene	1719.69	5.50	(Si)—O—	octamethyltrisiloxane	2347.17	−67.75
cH	benzene	1731.92	−1.25	Si-(Cl)	monochlorosilane	1062.27	−13.93
OH—(C)	1-methylcyclohexanol	786.14	4.90	Si—(Cl_2)	dichlorosilane	554.54	62.48
OH—(CH)	isopropanol	1508.33	0.12	Si—(Cl_3)	methyl trichlorosilane	−34.35	−18.52
OH—(CH_2)	butanol	1397.73	5.32	F_2—(C)	1,1-difluoroethane	2556.15	−4.95
OH—(c)	phenol	1337.25	9.15	F_2—(C═C)	1,1-difluoroethylene	2088.23	3.43
OH—(CC#C)	propargyl alcohol	2209.35	15.57	F_3—(C)	3,3,3-trifluoropropene	2451.95	−12.81
O═C	3-pentanone	1532.45	2.50	F—(C)	methyl fluoride	1841.54	0.80
O═C_R	cyclohexanone	954.03	−11.84	F—(C═C)	vinyl fluoride	1477.04	15.38
O═C—C═C	methacrolein	1761.66	6.00	Cl_2—(C)	dichloromethane	2882.45	−22.73
O═COC	hexyl formate	1492.23	0.47	Cl_2—(C═C)	1,1-dichloroethylene	2956.55	−15.50

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Group	Example	ΔT ,	UFL	Group	Example	ΔT ,	UFL
(C)—O—(C)	diethyl ether	1325.57	13.38	Cl_3—(C)	1,1,1-trichloroethane	3046.39	−26.31
—COOH	formic acid	1252.38	−5.12	Cl—(C)	isopropyl chloride	1948.51	−5.20
$—O_R—$	furan	1402.11	26.05	Cl—(C═C)	chloropropene	2294.79	0.16
—O—O—	ethyl peroxide	−728.23	0.76	Cl—(cc—Cl)	*o*-dichlorobenzene	3257.79	−13.14
>N—	triethylamine	1442.71	8.85	Br—	methylbromide	3389.83	−24.38

*Rowley, J. R., R. L. Rowley, and W. V. Wilding, *J. Hazard. Materials*, **186** (2011): 551; Rowley, J. R., "Flammability Limits, Flash Points, and Their Consanguinity: Critical Analysis, Experimental Exploration, and Prediction," Ph.D. Dissertation, Brigham Young University, 2010.

Table 2-179 Ideal Gas Enthalpies of Formation and Average Heat Capacities of Combustion Gases for Use in Eq. (2-125)

Species	$H°$/(kJ/mol)	C_p/[J/(mol · K)]
Air	0	28.9937
O_2	0	29.3468
N_2	0	29.1260
CO_2	−393.51	37.2433
H_2O	−241.81	33.5780
SO_2	−296.84	39.8980
SiO_2	−305.43	44.0254
HF	−273.30	29.1361
HCl	−92.31	29.1436
HBr	−36.29	29.1327
HI	−26.50	29.1583

Description: A GC method is used to obtain the adiabatic flame temperature (T_{ad}) of a lower-limit fuel-air mixture using the $\Delta T_{ad,j}$ contributions shown in Table 2-178:

$$T_{\mathrm{ad}} = \frac{\sum_{\mathrm{j}} n_{\mathrm{j}} \cdot \Delta T_{\mathrm{ad,j}}}{N}$$

(2-124)

where N is the total number of groups in the molecule. The ideal gas enthalpies H_i of the combustion products and oxygen at

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T_{ad} are then calculated from the ideal gas enthalpies of formation at 298 K and the average isobaric heat capacities (given in Table 2-179) with Eq. (2-125):

$$\frac{H_i(T_{\mathrm{ad}})}{\mathrm{kJ/mol}} = \frac{\Delta H_{f,i}^o}{\mathrm{kJ/mol}} + \frac{C_{p,i}}{(\mathrm{kJ/mol \cdot K})}(T_{\mathrm{ad}} - 298)\mathrm{K}$$

(2-125)

The lower flammability limit in volume percent is then calculated from

$$\mathrm{LFL} = \frac{100\%}{1+\nu} \quad \nu = \frac{\Delta H_{f,\mathrm{fuel}}^o - \sum_{\mathrm{products}} n_i H_i(T_{\mathrm{ad}}) + \beta H_{\mathrm{O}_2}(T_{\mathrm{ad}})}{C_{p,\mathrm{air}}(T_{\mathrm{ad}} - 298)\,\mathrm{K}}$$

(2-126)

where β is defined in Eq. (2-123).

The upper flammability limit in volume percent is obtained from the UFL group values given in Table 2-178 and

$$\frac{\mathrm{UFL}}{\%} = \left[4.30 C_{\mathrm{st}}^{0.72} + \frac{\sum_j n_j \cdot \mathrm{UFL}_j}{N}\right]$$

(2-127)

where C_{st} is the fuel concentration required for stoichiometric combustion given by

$$C_{\mathrm{st}} = \frac{100}{1 + 4.773\beta}$$

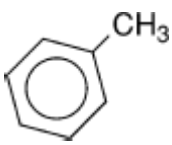
(2-128)

Example

Example

Estimate the lower and upper flammability limits of toluene.

Structure:



Group contributions:

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Group	n_j	ΔT_{ad}	UFL_j
CH_3—c	1	1862.04	−4.49
c—	1	1719.69	5.50
c—H	5	1731.92	−1.25

Auxiliary calculations:

$$\begin{aligned} T_{\mathrm{ad}} &= [1862.04 + 1719.69 + (5)(1731.92)]/7 = 1748.8 \\ \beta &= 7 + 8/4 = 9 \end{aligned}$$

Calculation of $H(T_{ad})$ from Eq. (2-125) and Table 2-179:

Species	$H°$(298 K)/(kJ/mol)	C_p/[kJ/(mol · K)]	$H(T_{ad})$/(kJ/mol)
Toluene	50.17	—	—
CO_2	−393.51	0.0372433	−339.48
H_2O	−241.81	0.0335780	−193.10
O_2	0	0.0293468	42.58
Air	0	0.0289937	—

From Eq. (2-126) and the stoichiometry of the combustion reaction, $C_7H_8 + 9O_2 = 7CO_2 + 4H_2O$:

$$\nu = \left[\frac{50.17 - [(7)(-339.48) + (4)(-193.10)] + (9)(42.58)}{(0.0289937)(1749 - 298)}\right] = 85.148$$

$$\mathrm{LFL} = \frac{100\%}{1 + 85.148} = 1.16\%$$

The UFL is found from Eqs. (2-127) and (2-128):

$$\mathrm{UFL} = (4.30)\left[\frac{100}{1 + (4.773)(9)}\right]^{0.72} + \frac{-4.49 + 5.50 + (5)(-1.25)}{7} = 7.02\%$$

These values agree well with the DIPPR 801 recommended values of 1.2 and 7.1 percent, respectively.

Flammability limit temperatures are found by determining the temperature at which the vapor pressure equals the partial pressure corresponding to the LFL or UFL. The vapor pressure correlation for toluene from DIPPR 801 is

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$$\frac{P^*}{\mathrm{Pa}} = \exp\left[76.945 - \frac{6729.8\,\mathrm{K}}{T} - 8.179\ln\left(\frac{T}{\mathrm{K}}\right) + 5.3017\times10^{-6}\left(\frac{T}{\mathrm{K}}\right)^2\right]$$

Back-solving for T using the partial pressures of 0.0116 atm for LFL and 0.0702 atm for UFL gives

$$T_{\mathrm{LFL}} = 277\ \mathrm{K}\ \text{and}\ T_{\mathrm{UFL}} = 311\ \mathrm{K}$$

Autoignition Temperature The autoignition temperature (AIT) is the minimum temperature for a substance to initiate self-combustion in air in the absence of an ignition source. Methods to estimate AIT are in general rather approximate. The method illustrated here may provide reasonable estimates, but significant errors can also result. Estimated values should not be assumed to be reliable for design and safety purposes.

Recommended Method Pintar method.

Reference: Pintar, A. J., *Estimation of Autoignition Temperature,* Technical Support Document DIPPR Project 912, Michigan Technological University, Houghton, 1996.

Classification: Group contributions.

Expected uncertainty: 25 percent.

Applicability: Organic compounds.

Input data: Group contributions from Table 2-180.

Table 2-180 Group Contributions for Pintar* Autoignition Temperature Method for Organic Compounds

Group	b_i	Group	b_i	Group	b_i
$-CH_3$	301.91	$-Cl_3$	1073.47	$-SO_3-$	–
$>CH_2$	-10.86	$-F$	360.60	$-SO_4-$	-31.71
$>CH-$	-275.17	$-F_2$	755.54	$-CO_3-$	442.26
$>C<$	-570.43	$-F_3$	1082.00	$-P=$	-334.91
$-H$	391.48	$-Br$	420.96	$-PO-$	-549.59
$-OH$	324.10	$-Br_2$	607.69	$-OPO_2-$	–
$-O-$	-18.60	$-Br_3$	1260.00	$-PO_4=$	-329.45
$-O-O-$	-397.61	$-I$	310.53	$Si-C^{\dagger}$	-147.69
$=C=O$	57.65	$-I_2$	–	$Si-O^{\dagger}$	-136.99
$-CHO$	195.20	$-I_3$	–	$Si-H^{\dagger}$	-310.52
$-COOH$	370.75	$-NH_2$	354.11	$Si-Cl^{\dagger}$	-200.88

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Group	*b*	Group	*b*	Group	*b*
—COO—	43.90	>NH	9.88	Si—N†	—
—CO—O—CO—	46.11	—N═	−249.91	Si—Si	—
$-C_6H_5$	380.27	—CN	469.67	Al	—
$m-C_6H_4$	153.15	═C═N—	−273.70	B	—
$o-C_6H_4$	77.48	═N—NH_2	378.27	Cr	—
$p-C_6H_4$	99.87	>N—NH_2	−215.02	Na	534.29
Aromatic ring	−1339.65	—NO_2	292.57	*cis*	−29.19
═	578.72	—SH	273.84	*trans*	−38.31
≡	1116.50	—S—	−60.75	Nonarom.ring	605.97
—Cl	347.39	—SO—	−91.10	Add'l.ring	565.11
$-Cl_2$	726.03	—SO_2—	—	Zn	349.02

*Pintar, A. J., *Estimation of Autoignition Temperature*, Technical Support Document DIPPR Project 912, Michigan Technological University, Houghton, 1996.

†Does not include contribution of atoms attached to silicon.

Description: A simple GC method with first-order contributions is given by

$$\mathrm{AIT} = \sum_{i=1}^{N} n_i b_i$$

(2-129)

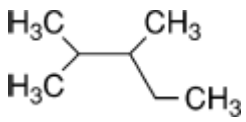
where n_i is the number of groups of type *i* in the molecule and b_i is the contribution of group *i* to the autoignition temperature. A more accurate but somewhat more complicated logarithmic GC method was also developed by Pintar in the same reference cited here.

Example

Example

Estimate the autoignition temperature of 2,3-dimethylpentane.

Structure and group information:



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Group	n_i	b_i
$-CH_3$	4	301.91
$>CH_2$	1	−10.86
$>CH-$	2	−275.17

Calculation using Eq. (2-129):

$$\mathrm{AIT} = 4(301.91) - 10.86 + 2(-275.17) = 646.4\ \mathrm{K}$$

The estimated value is 6.3 percent above the DIPPR 801 recommended value of 608.15 K.

[1] The Design Institute for Physical Properties (DIPPR) is an industrial consortium under the auspices of AIChE; Project 801, Evaluated Process Design Data, is a pure-component database of industrially important compounds. Values and procedures used with permission of the DIPPR 801 Technical Committee.

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