

Handbook of Chemical Engineering Calculations

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Preface

This handbook shows how to solve the main process-related problems that crop up often in chemical engineering practice.

The book is an outgrowth of the highly successful *Standard Handbook of Engineering Calculations*, which contained separate sections devoted to the various engineering disciplines, including a comparatively short section on chemical engineering. The desirability of publishing a similar handbook that focused exclusively on chemical engineering was obvious. Tyler Hicks, editor of the previously mentioned volume, is co-editor of the present book, which has helped to assure continuity in employing the well-accepted approach that the earlier book featured.

The essence of that approach is the use of solved, numerical illustrative examples. Except for introductory paragraphs in a few of the sections where introduction seemed especially appropriate, this entire volume consists of solved examples. In most cases, the given example closes with a "Related Calculations" discussion that explains the applicability of the particular solution technique and puts it into context. In any given section, examples have been chosen in such a way as to bring out the most important problems that crop up in that particular area of chemical engineering practice (omitted, however, are those problems that are too unwieldy and complex to be appropriate for the approach). In some of their work situations, readers will use the solution techniques directly, with a calculator; in other situations, the examples and techniques will provide the understanding that is necessary for implementing a computer-based solution.

The first section illustrates how to estimate or calculate the numerous physical and chemical properties that are relevant for chemical engineering practice. Next come sections on the basic chemical-process principles: stoichiometry, phase and chemical-reaction equilibrium, and reaction kinetics. The following two sections deal with the most pervasive unit operations: fluid flow (plus some examples in flow of solids) and heat transfer. And the final seven sections deal mainly with the most important of the other unit operations.

All of the section on flow of fluids and solids comes from the *Standard Handbook of Engineering Calculations*, and that book was the source for part of the material in the stoichiometry section as well as most of the final section, "Other Chemical Engineering Calculations." Virtually everything else in this volume was prepared specifically for it. Each section was prepared by one or more experts in the given field, and to a large extent the actual choice of examples was made by the expert(s) in question. Thus, we owe a doubly deep debt of gratitude to our contributors.

Nicholas P. Chopey

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1-1 Molar Gas Constant

Calculate the molar gas constant *R* in the following units:

- a. (atm)(cm³)/(g·mol)(K)
- b. (psia)(ft³)/(lb·mol)(°R)
- c. (atm)(ft³)/(lb·mol)(K)
- d. kWh/(lb·mol)(°R)
- e. hp·h/(lb·mol)(°R)
- f. (kPa)(m³)/(kg·mol)(K)
- g. cal/(g·mol)(K)

Calculation Procedure:**1. Assume a basis.**

Assume gas is at standard conditions, that is, 1 g·mol gas at 1 atm (101.3 kPa) pressure and 0°C (273 K, or 492°R), occupying a volume of 22.4 L.

2. Compute the gas constant.

Apply suitable conversion factors and obtain the gas constant in various units. Use $PV = RT$; that is, $R = PV/T$. Thus,

$$a. R = (1 \text{ atm})[22.4 \text{ L}/(\text{g} \cdot \text{mol})](1000 \text{ cm}^3/\text{L})/273 \text{ K} = 82.05 (\text{atm})(\text{cm}^3)/(\text{g} \cdot \text{mol})(\text{K})$$

$$b. R = (14.7 \text{ psia})[359 \text{ ft}^3/(\text{lb} \cdot \text{mol})]/492^\circ\text{R} = 10.73 (\text{psia})(\text{ft}^3)/(\text{lb} \cdot \text{mol})(^\circ\text{R})$$

$$c. R = (1 \text{ atm})[359 \text{ ft}^3/(\text{lb} \cdot \text{mol})]/273 \text{ K} = 1.315 (\text{atm})(\text{ft}^3)/(\text{lb} \cdot \text{mol})(\text{K})$$

$$d. R = [10.73 (\text{psia})(\text{ft}^3)/(\text{lb} \cdot \text{mol})(^\circ\text{R})](144 \text{ in}^2/\text{ft}^2)[3.77 \times 10^{-7} \text{ kWh}/(\text{ft} \cdot \text{lbf})] = 5.83 \times 10^{-4} \text{ kWh}/(\text{lb} \cdot \text{mol})(^\circ\text{R})$$

$$e. R = [5.83 \times 10^{-4} \text{ kWh}/(\text{lb} \cdot \text{mol})(^\circ\text{R})](1/0.746 \text{ hp} \cdot \text{h}/\text{kWh}) = 7.82 \times 10^{-4} \text{ hp} \cdot \text{h}/(\text{lb} \cdot \text{mol})(^\circ\text{R})$$

$$f. R = (101.325 \text{ kPa}/\text{atm})[22.4 \text{ L}/(\text{g} \cdot \text{mol})][1000 \text{ g} \cdot \text{mol}/(\text{kg} \cdot \text{mol})]/(273 \text{ K})(1000 \text{ L}/\text{m}^3) = 8.31 (\text{kPa})(\text{m}^3)/(\text{kg} \cdot \text{mol})(\text{K})$$

$$g. R = [7.82 \times 10^{-4} \text{ hp} \cdot \text{h}/(\text{lb} \cdot \text{mol})(^\circ\text{R})][6.4162 \times 10^5 \text{ cal}/(\text{hp} \cdot \text{h})][1/453.6 \text{ lb} \cdot \text{mol}/(\text{g} \cdot \text{mol})](1.8^\circ\text{R}/\text{K}) = 1.99 \text{ cal}/(\text{g} \cdot \text{mol})(\text{K})$$

1-2 Estimation of Critical Temperature from Empirical Correlation

Predict the critical temperature of (a) *n*-eicosane, (b) 1-butene, and (c) benzene using the empirical correlation of Nokay. The Nokay relation is

$$\log T_c = A + B \log SG + C \log T_b$$

where T_c is critical temperature in kelvins, T_b is normal boiling point in kelvins, and SG is specific gravity of liquid hydrocarbons at 60°F relative to water at the same temperature. As for A , B , and C , they are correlation constants given in Table 1-1.

TABLE 1-1 Correlation Constants for Nokay's Equation

Family of compounds	<i>A</i>	<i>B</i>	<i>C</i>
Alkanes (paraffins)	1.359397	0.436843	0.562244
Cycloalkanes (naphthenes)	0.658122	-0.071646	0.811961
Alkenes (olefins)	1.095340	0.277495	0.655628
Alkynes (acetylenes)	0.746733	0.303809	0.799872
Alkadienes (diolefins)	0.147578	-0.396178	0.994809
Aromatics	1.057019	0.227320	0.669286

Calculation Procedure:**1. Obtain normal boiling point and specific gravity.**

Obtain T_b and SG for these three compounds from, for instance, Reid, Prausnitz, and Sherwood [1]. These are (a) for *n*-eicosane ($C_{20}H_{42}$), $T_b = 617$ K and $SG = 0.775$; (b) for 1-butene (C_4H_8), $T_b = 266.9$ K and $SG = 0.595$; and (c) for benzene (C_6H_6), $T_b = 353.3$ K and $SG = 0.885$.

2. Compute critical temperature using appropriate constants from Table 1-1.

Thus (a) for *n*-eicosane:

$$\log T_c = 1.359397 + 0.436843 \log 0.775 + 0.562244 \log 617 = 2.87986$$

so $T_c = 758.3$ K (905°F). (b) For 1-butene:

$$\log T_c = 1.095340 + 0.277495 \log 0.595 + 0.655628 \log 266.9 = 2.62355$$

so $T_c = 420.3$ K (297°F). (c) For benzene:

$$\log T_c = 1.057019 + 0.22732 \log 0.885 + 0.669286 \log 353.3 = 2.75039$$

so $T_c = 562.8$ K (553°F).

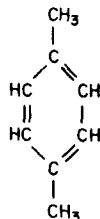
Related Calculations: This procedure may be used to estimate the critical temperature of hydrocarbons containing a single family of compounds, as shown in Table 1-1. Tests of the equation on paraffins in the range C_1 – C_{20} and various other hydrocarbon families in the range C_3 – C_{14} have shown average and maximum deviations of about 6.5 and 35°F (3.6 and 19 K), respectively.

1-3 Critical Properties from Group-Contribution Method

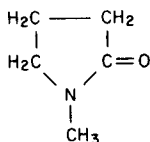
Estimate the critical properties of *p*-xylene and *n*-methyl-2-pyrrolidone using Lydersen's method of group contributions.

Calculation Procedure:**1. Obtain molecular structure, normal boiling point T_b , and molecular weight MW .**

From handbooks, for *p*-xylene (C_8H_{10}), $MW = 106.16$, $T_b = 412.3$ K, and the structure is



For *n*-methyl-2-pyrrolidone (C_5H_9NO), $MW = 99.1$, $T_b = 475.0$ K, and the structure is



2. Sum up structural contributions of the individual property increments from Table 1-2.

The calculations can be set out in the following arrays, in which N stands for the number of groups. For *p*-xylene:

Group type	N	ΔT	ΔP	ΔV	$(N)(\Delta T)$	$(N)(\Delta P)$	$(N)(\Delta V)$
—CH ₃ (nonring)	2	0.020	0.227	55	0.04	0.454	110
—C= (ring)	2	0.011	0.154	36	0.022	0.308	72
HC= (ring)	4	0.011	0.154	37	0.044	0.616	148
Total					0.106	1.378	330

For *n*-methyl-2-pyrrolidone:

Group type	N	ΔT	ΔP	ΔV	$(N)(\Delta T)$	$(N)(\Delta P)$	$(N)(\Delta V)$
—CH ₃ (nonring)	1	0.020	0.227	55	0.020	0.227	55
—CH ₂ — (ring)	3	0.013	0.184	44.5	0.039	0.552	133.5
C=O (ring)	1	0.033	0.2	50	0.033	0.20	50
—N— (ring)	1	0.007	0.13	32	0.007	0.13	32
Total					0.099	1.109	270.5

3. Compute the critical properties.

The formulas are

$$T_c = T_b \{ [(0.567) + \Sigma(N)(\Delta T) - [\Sigma(N)(\Delta T)]^2]^{-1} \}$$

$$P_c = MW[0.34 + (N)(\Delta P)]^{-2}$$

$$V_c = [40 + (N)(\Delta V)]$$

$$Z_c = P_c V_c / RT_c$$

where T_c , P_c , V_c , and Z_c are critical temperature, critical pressure, critical volume, and critical compressibility factor, respectively. Thus, for *p*-xylene,

$$T_c = 412.3[0.567 + 0.106 - (0.106)^2]^{-1}$$

$$= 623.0 \text{ K (661.8}^\circ\text{F) (literature value is 616.2 K)}$$

$$P_c = 106.16(0.34 + 1.378)^{-2} = 35.97 \text{ atm (3644 kPa) (literature value is 34.7 atm)}$$

TABLE 1-2 Critical-Property Increments—Lydersen's Structural Contributions

Symbols	ΔT	ΔP	ΔV
Nonring increments			
$-\text{CH}_3$	0.020	0.227	55
$ \text{---CH}_2$	0.020	0.227	55
$ \text{---CH}$	0.012	0.210	51
$ \text{---C---}$	0.00	0.210	41
$=\text{CH}_2$	0.018	0.198	45
$ \text{---CH}$	0.018	0.198	45
$=\text{C---}$	0.0	0.198	36
$=\text{C=}$	0.0	0.198	36
$\equiv\text{CH}$	0.005	0.153	(36)
$\equiv\text{C---}$	0.005	0.153	(36)
Ring increments			
$-\text{CH}_2-$	0.013	0.184	44.5
$ \text{---CH}$	0.012	0.192	46
$ \text{---C---}$	(-0.007)	(0.154)	(31)
$ \text{---CH}$	0.011	0.154	37
$=\text{C---}$	0.011	0.154	36
$=\text{C=}$	0.011	0.154	36
Halogen increments			
$-\text{F}$	0.018	0.221	18
$-\text{Cl}$	0.017	0.320	49
$-\text{Br}$	0.010	(0.50)	(70)
$-\text{I}$	0.012	(0.83)	(95)
Oxygen increments			
$-\text{OH}$ (alcohols)	0.082	0.06	(18)
$-\text{OH}$ (phenols)	0.031	(-0.02)	(3)
$-\text{O---}$ (nonring)	0.021	0.16	20
$-\text{O---}$ (ring)	(0.014)	(0.12)	(8)
$ \text{---C=O}$ (nonring)	0.040	0.29	60

Symbols	ΔT	ΔP	ΔV
Oxygen increments (cont)			
$\begin{array}{c} \\ -C=O \text{ (ring)} \end{array}$	(0.033)	(0.2)	(50)
$\begin{array}{c} \\ HC=O \text{ (aldehyde)} \end{array}$	0.048	0.33	73
$-COOH \text{ (acid)}$	0.085	(0.4)	80
$-COO- \text{ (ester)}$	0.047	0.47	80
$=O \text{ (except for combinations above)}$	(0.02)	(0.12)	(11)
Nitrogen increments			
$-NH_2$	0.031	0.095	28
$\begin{array}{c} \\ -NH \text{ (nonring)} \end{array}$	0.031	0.135	(37)
$\begin{array}{c} \\ -NH \text{ (ring)} \end{array}$	(0.024)	(0.09)	(27)
$\begin{array}{c} \\ -N- \text{ (nonring)} \end{array}$	0.014	0.17	(42)
$\begin{array}{c} \\ -N- \text{ (ring)} \end{array}$	(0.007)	(0.13)	(32)
$-CN$	(0.060)	(0.36)	(80)
$-NO_2$	(0.055)	(0.42)	(78)
Sulfur increments			
$-SH$	0.015	0.27	55
$-S- \text{ (nonring)}$	0.015	0.27	55
$-S- \text{ (ring)}$	(0.008)	(0.24)	(45)
$=S$	(0.003)	(0.24)	(47)
Miscellaneous			
$\begin{array}{c} \\ -Si- \end{array}$	0.03	(0.54)	
$\begin{array}{c} \\ -B- \end{array}$	(0.03)		

Note: There are no increments for hydrogen. All bonds shown as free are connected with atoms other than hydrogen. Values in parentheses are based on too few experimental data to be reliable.

Source: A. L. Lydersen, U. of Wisconsin Eng. Exp. Station, 1955.

$$V_c = 40 + 330$$

$$= 370 \text{ cm}^3/(\text{g} \cdot \text{mol}) [5.93 \text{ ft}^3/(\text{lb} \cdot \text{mol})] [\text{literature value} = 379 \text{ cm}^3/(\text{g} \cdot \text{mol})]$$

And since $R = 82.06 \text{ (cm}^3\text{)(atm)/(g} \cdot \text{mol)(K)}$,

$$Z_c = (35.97)(370)/(82.06)(623) = 0.26$$

For *n*-methyl-2-pyrrolidone,

$$T_c = 475[0.567 + 0.099 - (0.099)^2]^{-1} = 723.9 \text{ K } (843^\circ\text{F})$$

$$P_c = 99.1(0.34 + 1.109)^{-2} = 47.2 \text{ atm } (4780 \text{ kPa})$$

$$V_c = 40 + 270.5 = 310.5 \text{ cm}^3/(\text{g} \cdot \text{mol}) [4.98 \text{ ft}^3/(\text{lb} \cdot \text{mol})]$$

$$Z_c = (47.2)(310.5)/(82.06)(723.9) = 0.247$$

Related Calculations: Extensive comparisons between experimental critical properties and those estimated by several other methods have shown that the Lydersen group-contribution method is the most accurate. This method is relatively easy to use for both hydrocarbons and organic compounds in general, provided that the structure is known. Unlike Nokay's correlation (see Example 1-2), it can be readily applied to hydrocarbons containing characteristics of more than a single family, such as an aromatic with olefinic side chains. A drawback of the Lydersen method, however, is that it cannot distinguish between isomers of similar structure, such as 2,3-dimethylpentane and 2,4-dimethylpentane.

Based on tests with paraffins in the C_1 - C_{20} range and other hydrocarbons in the C_3 - C_{14} range, the average deviation from experimental data for critical pressure is 18 lb/in² (124 kPa), and the maximum error is around 70 lb/in² (483 kPa). In general, the accuracy of the correlation is lower for unsaturated compounds than for saturated ones. As for critical temperature, the typical error is less than 2 percent; it can range up to 5 percent for nonpolar materials of relatively high molecular weight (e.g., 7100). Accuracy of the method when used with multifunctional polar groups is uncertain.

1-4 Redlich-Kwong Equation of State

Estimate the molar volume of isopropyl alcohol vapor at 10 atm (1013 kPa) and 473 K (392°F) using the Redlich-Kwong equation of state. For isopropyl alcohol, use 508.2 K as the critical temperature T_c and 50 atm as the critical pressure P_c . The Redlich-Kwong equation is

$$P = RT/(V - b) - a/T^{0.5}V(V - b)$$

where P is pressure, T is absolute temperature, V is molar volume, R is the gas constant, and a and b are equation-of-state constants given by

$$a = 0.4278R^2T_c^{2.5}/P_c \quad \text{and} \quad b = 0.0867RT_c/P_c$$

when the critical temperature is in kelvins, the critical pressure is in atmospheres, and R is taken as 82.05 (atm)(cm³)/(g·mol)(K).

In an alternate form, the Redlich-Kwong equation is written as

$$Z = 1/(1 - h) - (A/B)[h/(1 + h)]$$

where $h = b/V = BP/Z$, $B = b/RT$, $A/B = a/bRT^{1.5}$, and Z , the compressibility factor, is equal to PV/RT .

Calculation Procedure:**1. Calculate the compressibility factor Z .**

Since the equation is not explicit in Z , solve for it by an iterative procedure. For Trial 1, assume that $Z = 0.9$; therefore,

$$h = 0.0867(P/P_c)/Z(T/T_c) = \frac{0.087(10/50)}{(0.9)(473/508.2)} = 0.0208$$

Substituting for the generalized expression for A/B in the Redlich-Kwong equation,

$$\begin{aligned} Z &= \frac{1}{1-h} - \left[\frac{(0.4278R^2T_c^{2.5}/P_c)}{(0.0867RT_c/P_c)(RT^{1.5})} \right] \left(\frac{h}{1+h} \right) \\ &= \frac{1}{1-h} - (4.9343)(T_c/T)^{1.5} \left(\frac{h}{1+h} \right) \\ &= \frac{1}{1-0.0208} - \left[(4.9343) \left(\frac{508.2}{473} \right)^{1.5} \right] \left[\frac{0.0208}{1+0.0208} \right] \\ &= 0.910. \end{aligned}$$

For Trial 2, then, assume that $Z = 0.91$; therefore,

$$h = \frac{0.0867(10/50)}{0.91(473/508.2)} = 0.0205$$

and

$$Z = \frac{1}{1-0.0205} - (4.9343)(508.2/473)^{1.5} \frac{0.0205}{1+0.0205} = 0.911$$

which is close enough.

2. Calculate molar volume.

By the definition of Z ,

$$\begin{aligned} V &= ZRT/P \\ &= (0.911)(82.05)(473)/(10) \\ &= 3535.6 \text{ cm}^3/(\text{g} \cdot \text{mol}) [3.536 \text{ m}^3/(\text{kg} \cdot \text{mol}) \text{ or } 56.7 \text{ ft}^3/(\text{lb} \cdot \text{mol})] \end{aligned}$$

Related Calculations: This two-constant equation of Redlich-Kwong is extensively used for engineering calculations and enjoys wide popularity. Many modifications of the Redlich-Kwong equations of state, such as those by Wilson, Barnes-King, Soave, and Peng-Robinson, have been made and are discussed in Reid et al. [1]. The constants for the equation of state may be obtained by least-squares fit of the equation to experimental P - V - T data. However, such data are often not available. When this is the case, estimate the constants on the basis of the critical properties, as shown in the example.

1-5 *P-V-T* Properties of a Gas Mixture

A gaseous mixture at 25°C (298 K) and 120 atm (12,162 kPa) contains 3% helium, 40% argon, and 57% ethylene on a mole basis. Compute the volume of the mixture per mole using the following: (a) ideal-gas law, (b) compressibility factor based on pseudoreduced conditions (Kay's method), (c) mean compressibility factor and Dalton's law, (d) van der Waal's equation and Dalton's law, and (e) van der Waal's equation based on averaged constants.

Calculation Procedure:**1. Solve the ideal-gas law for volume.**

By definition, $V = RT/P$, where V is volume per mole, T is absolute temperature, R is the gas constant, and P is pressure. Then,

$$V = [82.05 \text{ (cm}^3\text{)(atm)/(g} \cdot \text{mol)(K)}]298 \text{ K}/120 \text{ atm} = 203.8 \text{ cm}^3\text{/(g} \cdot \text{mol)}$$

2. Calculate the volume using Kay's method.

In this method, V is found from the equation $V = ZRT/P$, where Z , the compressibility factor, is calculated on the basis of pseudocritical constants that are computed as mole-fraction-weighted averages of the critical constants of the pure compounds. Thus, $T'_c = \sum Y_i T_{c,i}$ and similarly for P'_c and Z'_c , where the subscript c denotes critical, the prime denotes pseudo, the subscript i pertains to the i th component, and Y is mole fraction. Pure-component critical properties can be obtained from handbooks. The calculations can then be set out as a matrix:

Component, i	Y_i	$T_{c,i}$ (K)	$Y_i T_{c,i}$ (K)	$P_{c,i}$ (atm)	$Y_i P_{c,i}$ (atm)	$Z_{c,i}$	$Y_i Z_{c,i}$
He	0.03	5.2	0.16	2.24	0.07	0.301	0.009
A	0.40	150.7	60.28	48.00	19.20	0.291	0.116
C ₂ H ₄	0.57	283.0	161.31	50.50	28.79	0.276	0.157
$\Sigma =$	1.00		221.75		48.06		0.282

Then the reduced temperature $T_r = T/T'_c = 298/221.75 = 1.34$, and the reduced pressure $P_r = P/P'_c = 120/48.06 = 2.50$. Now $Z'_c = 0.282$. Refer to the generalized compressibility plots in Figs. 1-2 and 1-3, which pertain respectively to Z'_c values of 0.27 and 0.29. Figure 1-2 gives a Z of 0.71, and Figure 1-3 gives a Z of 0.69. By linear interpolation, then, Z for the present case is 0.70. Therefore, the mixture volume is given by

$$V = ZRT/P = (0.70)(82.05)(298)/120 = 138.8 \text{ cm}^3\text{/(g} \cdot \text{mol)}$$

3. Calculate the volume using the mean compressibility factor and Dalton's law.

Dalton's law states that the total pressure exerted by a gaseous mixture is equal to the sum of the partial pressures. In using this method, assume that the partial pressure of a

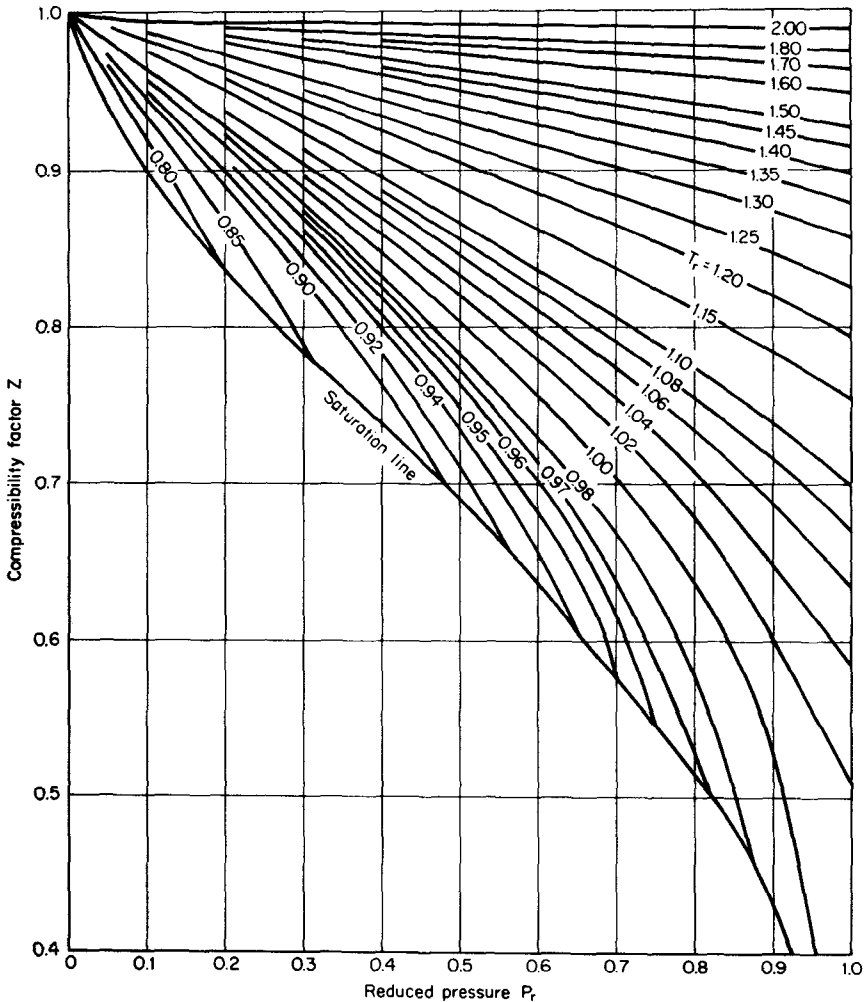


FIG. 1-1 Generalized compressibility factor; $Z_c = 0.27$; low-pressure range. (Lydersen et al., University of Wisconsin Engineering Experiment Station, 1955.)

component of a mixture is equal to the product of its mole fraction and the total pressure. Thus the method consists of calculating the partial pressure for each component, calculating the reduced pressure and reduced temperature, finding the corresponding compressibility factor for each component (from a conventional compressibility-factor chart in a handbook), and then taking the mole-fraction-weighted average of those compressibility factors and using that average value to find V . The calculations can be set out in matrix form, employing the critical properties from the matrix in step 2: