The University of Jordan
Faculty of Engineering & Technology
Chemical Engineering Department

Chemical Engineering Principles
(0905211)

Single Phase Systems

Dr.-Ing. Zayed Al-Hamamre

Content

- Introduction
- Solid and liquid densities
- Ideal gas
    - Ideal gas equation of state
    - Ideal gas mixtures
- Real (Non-ideal) gases
    - Critical temperature and pressure
    - Virial equations of state
    - Cubic Equations of state
- compressibility factor equation of state
    - compressibility factor tables and charts
    - The law of corresponding states

Introduction

The following methods can be used to determine a physical property of a process material:

i. Look It Up
  - Perry's Chemical Engineers' Handbook, nth Edition, R. H. Perry and D. W. Green, Eds.McGraw-Hill, New York, 1997.
  - CRC Handbook of Chemistry and Physics, 79th Edition, D. Lide, Ed., Chemical Rubber Company, Boca Raton, FL, 1998

ii. Estimate It
  - Interpolation or extrapolation
  - Using Correlations, available in
    Bruce E. Poling, John M. Prausnitz, John P. O'Connell, The Properties of Gases and Liquids, 5th Edition, McGraw-Hill, New York, 2004

ii. Measure It

Solid and liquid densities

Solid and liquid densities are independent of temperature.

Changes in pressure do not cause significant changes in densities (incompressible)

Perry's Chemical Engineers' Handbook

The Properties of Gases and Liquids

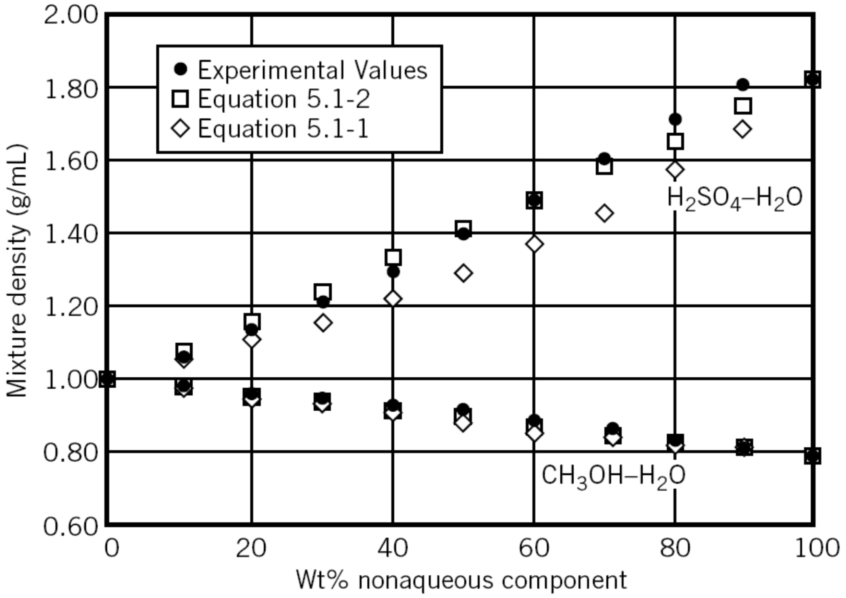
To estimate the density if a mixture,

i. Assume volume additivity

$$\frac{1}{\bar{\rho}} = \sum_{i=1}^{n} \frac{x_i}{\rho_i} \qquad (5.1\text{-}1)$$

ii. Assuming average the pure-component densities

$$\bar{\rho} = \sum_{i=1}^{n} x_i \rho_i \qquad (5.1\text{-}2)$$



Experimental and estimated mixture densities. Experimental values from Perry's Chemical Engineers' Handbook, p. 2-107 for sulfuric acid-water and p. 2-111 for methanol-water, both at 20℃.

Example

Determine the density in g/cm^3 of a 50 wt% aqueous solution of H_2SO4 at 20°C, both by (1) looking up a tabulated value and (2) assuming volume additivity of the solution components

The Ideal Gas Equation of State

The ideal gas equation of state (relation between state variables) can be derived from the kinetic theory of gases by assuming that

i. Gas molecules have a negligible volume,

ii. Exert no forces on one another, and

iii. Collide elastically with the walls of their container

$$PV = nRT \qquad P\dot{V} = \dot{n}RT$$

P = *absolute* pressure of a gas

$V(\dot{V})$ = volume (volumetric flow rate) of the gas

$n(\dot{n})$ = number of moles (molar flow rate) of the gas

R = the *gas constant,* whose value depends on the units of P, V, n, and T

T = *absolute* temperature of the gas

The equation valid at high temperatures and low pressures.

The gas constant

$8.314\ \text{m}^3\cdot\text{Pa/(mol}\cdot\text{K)}$

$0.08206\ \text{L}\cdot\text{atm/(mol}\cdot\text{K)}$

$10.73\ \text{ft}^3\cdot\text{psia/(lb-mole}\cdot{}^\circ\text{R)}$

$8.314\ \text{J/(mol}\cdot\text{K)}$

$1.987\ \text{cal/(mol}\cdot\text{K)}$

Relative error

$$\epsilon = \frac{X_{\text{ideal}} - X_{\text{true}}}{X_{\text{true}}} \times 100\%$$

$$|\epsilon| < 1\% \text{ if } \hat{V}_{\text{ideal}} = \frac{RT}{P} > 5\ \text{L/mol}\ (80\ \text{ft}^3/\text{lb-mole}) \qquad \text{(diatomic gases)}$$

$$> 20\ \text{L/mol}\ (320\ \text{ft}^3/\text{lb-mole}) \qquad \text{(other gases)}$$

$\hat{V}_{\text{ideal}}$: the ideal specific molar volume

Example

One hundred grams of nitrogen is stored in a container at 23°C and 3.00 psig.

1. Assuming ideal gas behavior, calculate the container volume in liters.
2. Verify that the ideal gas equation of state is a good approximation for the given conditions

---

Density of ideal gas

$$PV = nRT \qquad \text{Where} \qquad n = \frac{m}{M.wt}$$

$$P = \frac{m}{V * M.wt}RT \quad \Rightarrow \quad P = \frac{\rho}{M.wt}RT$$

$$\Rightarrow \quad \rho = \frac{P * M.wt}{RT}$$

For ideal gas mixture

$$\rho = \frac{P\bar{M}}{RT}$$

Where

$$\bar{M} = \sum y_i M_i$$

Standard Temperature and Pressure

For an ideal gas at any P and T $\quad PV = nRT$

At specified reference temperature T_s and pressure P_s (referred to as standard temperature and pressure, or STP)

$$P_s\hat{V}_s = RT_s$$

$$\Rightarrow \quad \frac{PV}{\boxed{P_s\hat{V}_s}} = n\frac{T}{\boxed{T_s}}$$

Known values

Determine V for a given value of n or vice versa without the need for need a value for R.

$$\Rightarrow \quad \frac{P\dot{V}}{P_s\hat{V}_s} = \dot{n}\frac{T}{T_s}$$

Table 5.2-1 Standard Conditions for Gases

System	T_s	P_s	V_s	n_s
SI	273 K	1 atm		1 mol
CGS	273 K	1 atm		1 mol
American Engineering	492°R	1 atm		1 lb-mole

Standard Cubic Meters (or SCM) is often used to denote m^3(STP).

Standard Cubic Feet (or SCF) denotes ft^3(STP).

A volumetric flow rate of 18.2 SCMH means 18.2 m^3/h at 0°C and 1 atm.

$$273\text{ K, }1\text{ atm} \Rightarrow \hat{V} = 0.022415\text{ m}^3 = 22.415\text{ liters}$$

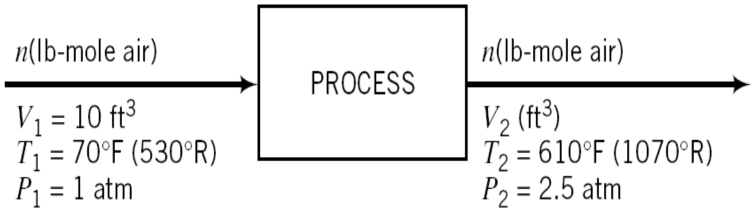
$$32^\circ\text{F, }1\text{ atm} \Rightarrow \hat{V} = 359.05\text{ ft}^3$$

Example

Butane (C_4H_{10}) at 360°C and 3.0 atm absolute flows into a reactor at a rate of 1100 kg/h. Calculate the volumetric flow rate of this stream using conversion from standard conditions.

Example

Ten cubic feet of air at 70°F and 1.00 atm is heated to 610°F and compressed to 2.50 atm. What volume does the gas occupy in its final state?



Example

The flow rate of a methane stream at 285°F and 1.30 atm is measured with an orifice meter. The calibration chart for the meter indicates that the flow rate is 3.95 X10^5 SCFH. Calculate the molar flow rate and the true volumetric flow rate of the stream.

Example

A cylinder contains 1.0 ft^3 of oxygen at 70 F and 200 psig. What will be the volume of this gas in a balloon at 90 F and 4.0 in H_2O above atmospheric? The barometer reads 29.92 in Hg

---

Ideal Gas Mixtures

A mixture of ideal gases is itself an ideal gas,

- Suppose you have a mixture of gases, each is ideal, i.e. the mixture is ideal gas mixture, then

$$PV = n_T RT$$

For species A, B and C in the mixture,

$$n_T = n_A + n_B + n_C$$

$$\rightarrow \quad n_T = y_A n_T + y_B n_T + y_C n_T$$

since each component *i* represent an ideal gas $P_i V = n_i RT$

$$\frac{P_i}{P} = \frac{n_i}{n_T} = y_i \quad \rightarrow \quad P_i = y_i P$$

P_i: the pressure that would be exerted by n_i moles of A alone in the same total volume V at the same temperature T.

For A, B and C ideal gas mixture,

$$P = P_A + y_B + P_C$$

Dalton's Law

$$\rightarrow \quad P = y_A P + y_B P + y_C P$$

Similar thing can be done using pure component volume

$$P v_i = n_i RT$$

$$\frac{v_i}{V} = \frac{n_i}{n_T} = y_i \quad \rightarrow \quad v_i = y_i V$$

v_A: the volume that would be occupied by n_i moles of A alone at the total pressure P and temperature T of the mixture.

For A, B and C ideal gas mixture,

$$V = v_A + v_B + v_C$$

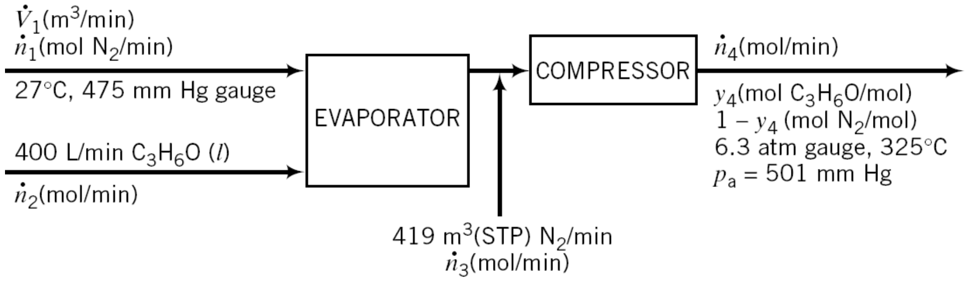
Example

Liquid acetone (C_3H_6O) is fed at a rate of 400 L/min into a heated chamber, where it evaporates into a nitrogen stream. The gas leaving the heater is diluted by another nitrogen stream flowing at a measured rate of 419 m^3(STP)/min. The combined gases are then compressed to a total pressure P = 6.3 atm gauge at a temperature of 325°C. The partial pressure of acetone in this stream is P_a = 501 mm Hg. Atmospheric pressure is 763 mm Hg.

a) What is the molar composition of the stream leaving the compressor?

b) What is the volumetric flow rate of the nitrogen entering the evaporator if the temperature and pressure of this stream are 27°C and 475 mm Hg gauge

---



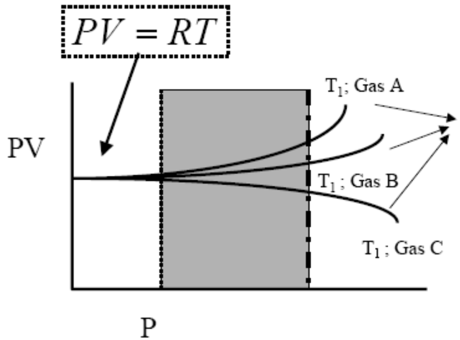
Real (Non-ideal) gases

- In the ideal gas equation of state, the calculation is independent of the species of the gas and is the same for single species and mixtures

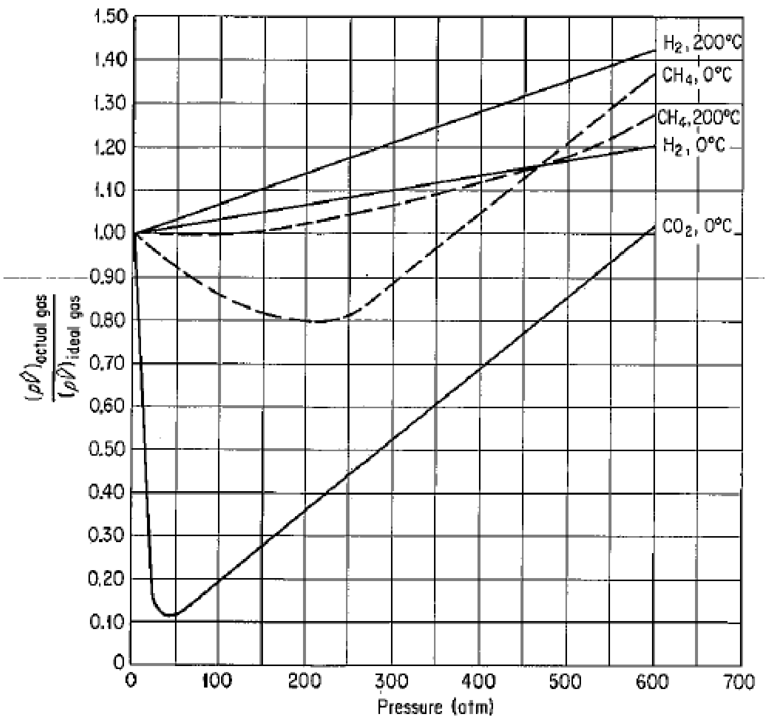
$$PV = n_T RT$$

At low temperatures and high pressures, the ideal gas equation ceases to apply.

Real gases do not obey ideal gas behavior due to intermolecular interaction and ideal gas EOS does not hold true.



VEOS add a corrective term to account nonideality due to intermolecular forces.



Deviation of real gases from the ideal gas law at high pressures.

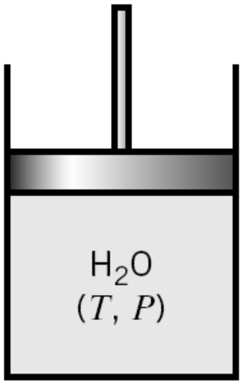
Real gases require more complex equations of state than do ideal gases:

- ○ Virial Equations of State
- ○ Cubic Equations of State
- ○ Compressibility Factor Equation

Critical Temperature and Pressure

The critical temperature of a species (T_c) is the highest temperature at which the species can coexist in two phases (liquid and vapor),

The critical pressure (P_c) is the corresponding pressure at T_C



Run	T(°C)	P_{cond}(atm)	ρ_v(kg/m^3)	ρ_l(kg/m^3)
1	25.0	0.0329	0.0234	997.0
2	100.0	1.00	0.5977	957.9
3	201.4	15.8	8.084	862.8
4	349.8	163	113.3	575.0
5	373.7	217.1	268.1	374.5
6	374.15	218.3	315.5	315.5
7	>374.15	*No condensation occurs!*		

A substance at T_c and P_c is said to be at its critical state

A substance at $T > T_c$ and $P > P_c$ is said to be at its supercritical fluid

A vapor is a gaseous species below its critical temperature, and

A gas is a species above its critical temperature

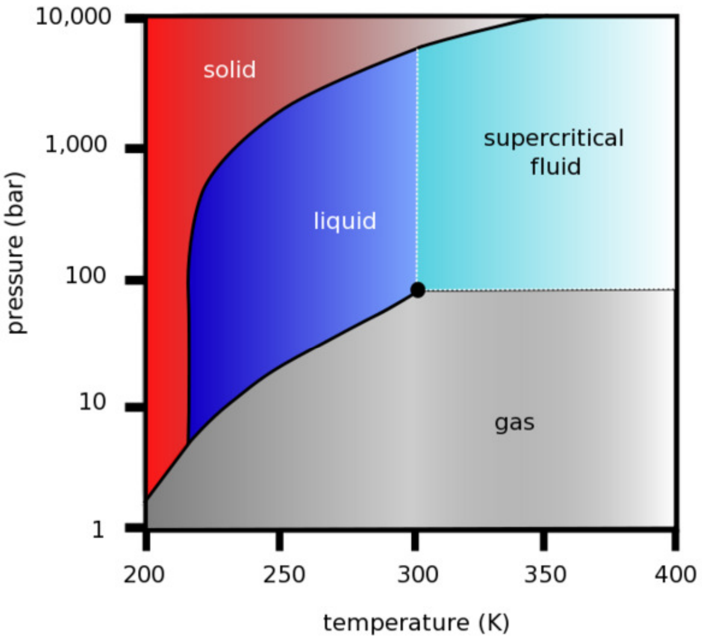
A vapor can be condensed by compressing it isothermally, or by reducing the temperature at constant pressure (cooling)

BUT

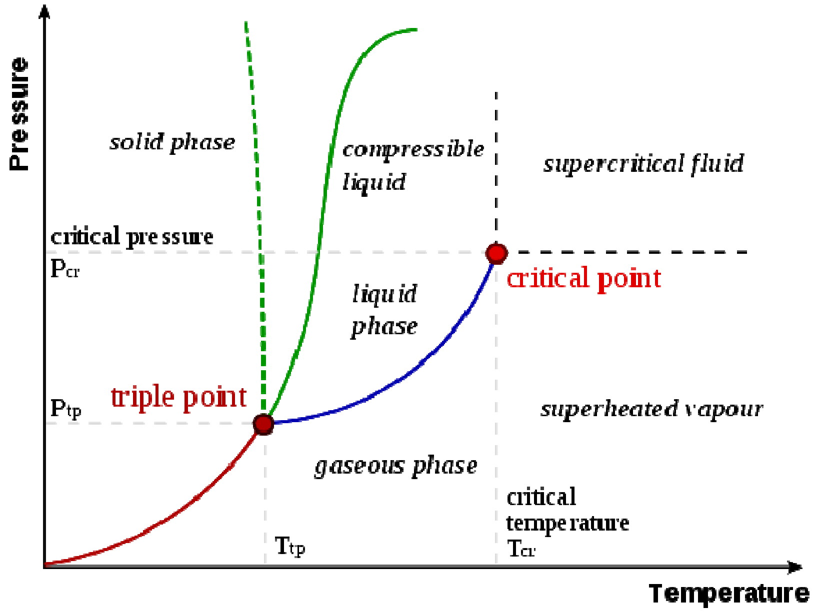
A gas can be made denser and denser by compressing it isothermally without two phase formation.

A gas can be condensed only by reducing the temperature and increasing the pressure

---



Temperature-pressure diagram (phase diagram) of CO_2



P-T diagram (phase diagram) for Water

Virial Equations of State

$$\frac{P\hat{V}}{RT} = 1 + \frac{B}{\hat{V}} + \frac{C}{\hat{V}^2} + \frac{D}{\hat{V}^3} + \cdots$$

expresses the quantity $P\hat{V}/RT$ as a power series in the inverse of specific volume in the gas region (single phase system)

where B, C, and D are functions of temperature and are known as the second, third, and fourth virial coefficients, respectively.

Since theoretical and experimental data is not readily available for viral coefficients higher than the second one, the equation is often used in truncated form.

$$\frac{P\hat{V}}{RT} = 1 + \frac{B}{\hat{V}}$$

And

$$B = \frac{RT_c}{P_c}(B_0 + \omega B_1)$$

Where

$$B_0 = 0.083 - \frac{0.422}{T_r^{1.6}}$$

$$B_1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

$$T_r = T/T_c$$

(The reduced temperature)

ω: is Pitzer acentric factor, a parameter that reflects the geometry and polarity of a molecule

Table 5.3-1 Pitzer Acentric Factors

Compound	Acentric Factor, ω
Ammonia	0.250
Argon	−0.004
Carbon dioxide	0.225
Carbon monoxide	0.049
Chlorine	0.073
Ethane	0.098
Hydrogen sulfide	0.100
Methane	0.008
Methanol	0.559
Nitrogen	0.040
Oxygen	0.021
Propane	0.152
Sulfur dioxide	0.251
Water vapor	0.344
Ethylene	0.085
Hydrogen	−0.220

SOURCE: R. C. Reid, J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids,* 4th Edition, McGraw-Hill, New York, 1986.

Example

Two gram-moles of nitrogen is placed in a three-liter tank at -150.8°C. Estimate the tank pressure using the ideal gas equation of state and then using the virial equation of state truncated after the second term. Taking the second estimate to be correct, calculate the percentage error that results from the use of the ideal gas equation at the system conditions.

Cubic Equations of State

Virial equations cannot represent thermodynamic systems where both liquid and vapor are present.

A "cubic" EoS is need to do this

Cubic Equations of State are PVT relationships when expanded, results in third-order equations for the specific volume

- Van der Waals equation of state:

$$P = \frac{RT}{\hat{V} - b} - \frac{a}{\hat{V}^2} \qquad \text{Or} \qquad p = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

Where

$$a = \frac{27R^2T_c^2}{64P_c} \qquad b = \frac{RT_c}{8P_c}$$

the term $a/\hat{V}^2$ accounts for attractive forces between molecules

and b is a correction accounting for the volume occupied by the molecules themselves

Soave-Redlich-Kwong (SRK) equation:

$$P = \frac{RT}{\hat{V} - b} - \frac{\alpha a}{\hat{V}(\hat{V} + b)}$$

Where

$$a = 0.42747\frac{(RT_c)^2}{P_c} \qquad b = 0.08664\frac{RT_c}{P_c}$$

the b term is a volume correction, while the a is a molecular interaction parameter.

$$m = 0.48508 + 1.55171\omega - 0.1561\omega^2 \qquad T_r = T/T_c$$

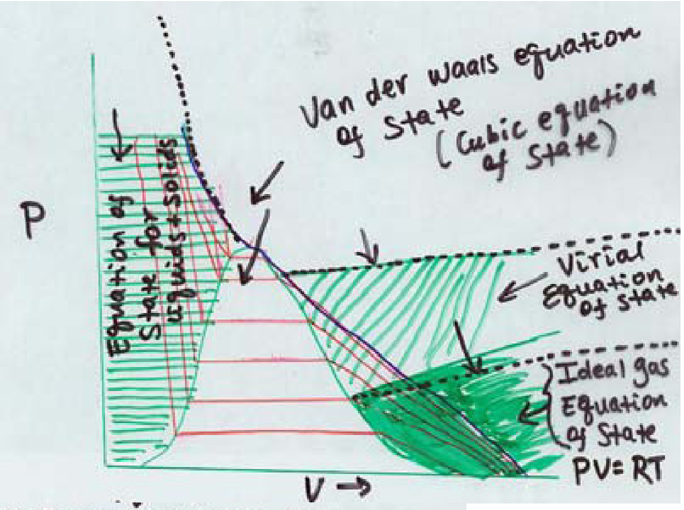
$$\alpha = \left[1 + m\left(1 - \sqrt{T_r}\right)\right]^2$$

ω: is Pitzer acentric factor, a parameter that reflects the geometry and polarity of a molecule

Solving the cubic equation typically requires an iterative ("trial-and-error") solution.

Constants for the Van der Waals and Redlich-Kwong 'Equations Calculated From the Listed Values of the Critical Constants

	van der Waals		Redlich-Kwong	
	a^* $\left[\text{atm}\left(\frac{\text{cm}^3}{\text{g mol}}\right)^2\right]$	$b^\dagger$ $\left(\frac{\text{cm}^3}{\text{g mol}}\right)$	$a^\ddagger$ $\left[(\text{atm})(\text{K})^{1/2}\left(\frac{\text{cm}^3}{\text{g mol}}\right)\right]$	$b^\dagger$ $\left(\frac{\text{cm}^3}{\text{g mol}}\right)$
Air	1.33×10^6	36.6	15.65×10^6	25.3
Ammonia	4.19×10^6	37.3	85.00×10^6	25.7
Carbon dioxide	3.60×10^6	42.8	63.81×10^6	29.7
Ethane	5.50×10^6	65.1	97.42×10^6	45.1
Ethylene	4.48×10^6	57.2	76.92×10^6	39.9
Hydrogen	0.246×10^6	26.6	1.439×10^6	18.5
Methane	2.25×10^6	42.8	31.59×10^6	29.6
Nitrogen	1.347×10^6	38.6	15.34×10^6	26.8
Oxygen	1.36×10^6	31.9	17.12×10^6	22.1
Propane	9.24×10^6	90.7	180.5×10^6	62.7
Water vapor	5.48×10^6	30.6	140.9×10^6	21.1



(1) At low Pressure, Ideal gas EOS for gases

$$\frac{P\hat{V}}{RT} = 1$$

(2) At moderate pressure, virial equation of State (in the gas region)

$$\frac{P\hat{V}}{RT} = 1 + \frac{B}{\hat{V}}$$

(3) Van der waals (Cubic) EOS for the two phase region and fluid region

$$P = \frac{RT}{\hat{V} - b} - \frac{a}{\hat{V}2}$$

(4) Liquid EOS for incompressibles ??

Example

A gas cylinder with a volume of 2.50 m contains 1.00 kmol of carbon dioxide at T = 300 K. Use the SRK equation of state to estimate the gas pressure in atm.

The specific molar volume

$$\hat{V} = \frac{V}{n} = \frac{2.5\ \text{m}^3}{1.00\ \text{kmol}}\left|\frac{10^3\ \text{L}}{1\ \text{m}^3}\right|\frac{1\ \text{kmol}}{10^3\ \text{mol}} = 2.50\frac{\textbf{liter}}{\textbf{mol}}$$

The critical properties

$$T_c = 304.2\ \text{K and } P_c = 72.9\ \text{atm.}$$

$$\omega = 0.225.$$

The constants become

$$a = 0.42747\frac{\{[0.08206\ \text{L}\cdot\text{atm/(mol}\cdot\text{K)}](304.2\ \text{K})\}^2}{72.9\ \text{atm}}$$
$$= 3.654\ \text{L}^2\cdot\text{atm/mol}^2$$

$$b = 0.08664\frac{[0.08206\ \text{L}\cdot\text{atm/(mol}\cdot\text{K)}](304.2\ \text{K})}{72.9\ \text{atm}}$$
$$= 0.02967\ \text{L/mol}$$

$$m = 0.8263$$
$$T_r = 0.986$$
$$\alpha = 1.0115$$

$$P = \frac{RT}{\hat{V} - b} - \frac{\alpha a}{\hat{V}(\hat{V} + b)}$$

$$= \frac{[0.08206\ \text{L}\cdot\text{atm/(mol}\cdot\text{K)}](300\ \text{K})}{[(2.50 - 0.02967)\text{L/mol}]} - \frac{1.0115(3.654\ \text{L}^2\cdot\text{atm/mol}^2)}{(2.50\ \text{L/mol})[(2.50 + 0.02967)\ \text{L/mol}]}$$

$$= \boxed{9.38\ \text{atm}}$$

Example

Carbon dioxide at 300 K and 6.8 atm flows at 100 kmol/h. Use the SRK equation of state to determine the volumetric flow

---

Example

A stream of propane at temperature T = 423 K and pressure P (atm) flows at a rate of 100.0 kmol/h. Use the SRK equation of state to estimate the volumetric flow rate of the stream for P = 0.7 atm, 7 atm, and 70 atm. In each case, calculate the percentage differences between the predictions of the SRK equation and the ideal gas equation of state.

Compressibility Factor Equation

The compressibility factor of a gaseous species is defined as the ratio

$$z = \frac{P\hat{V}}{RT}$$

For ideal gas z = 1, the extent to which z differs from 1 is a measure of the extent to which the gas is behaving nonideally.

The compressibility factor equation of state

$$P\hat{V} = zRT$$

$$PV = znRT \qquad P\dot{V} = z\dot{n}RT$$

The compressibility factor is a function of temperature and pressure

$$z = z(T, P)$$

Values are available in Perry's Chemical Engineers' Handbook pp. 2-140 through 2-150, for air, argon, CO_2, CO, H_2, CH_4, N_2, O_2, steam, ….. etc.

Example

Fifty cubic meters per hour of methane flows through a pipeline at 40.0 bar absolute and 300.0 K. Use the compressibility factor equation to estimate the mass flow rate in kg/h

The Law of Corresponding States and Compressibility Charts

According to the Low of Corresponding States, a few properties are the same for all gases when expressed in terms of deviation from the critical point.

The deviation from the critical point can be expressed interims of T_r (reduced temperature) and P_r (reduced pressure)

$$T_r = \frac{T}{T_c} \qquad P_r = \frac{P}{P_c}$$

Thus, a "generalized compressibility factor chart" can be used to get z once we have the reduced temperature and pressure.

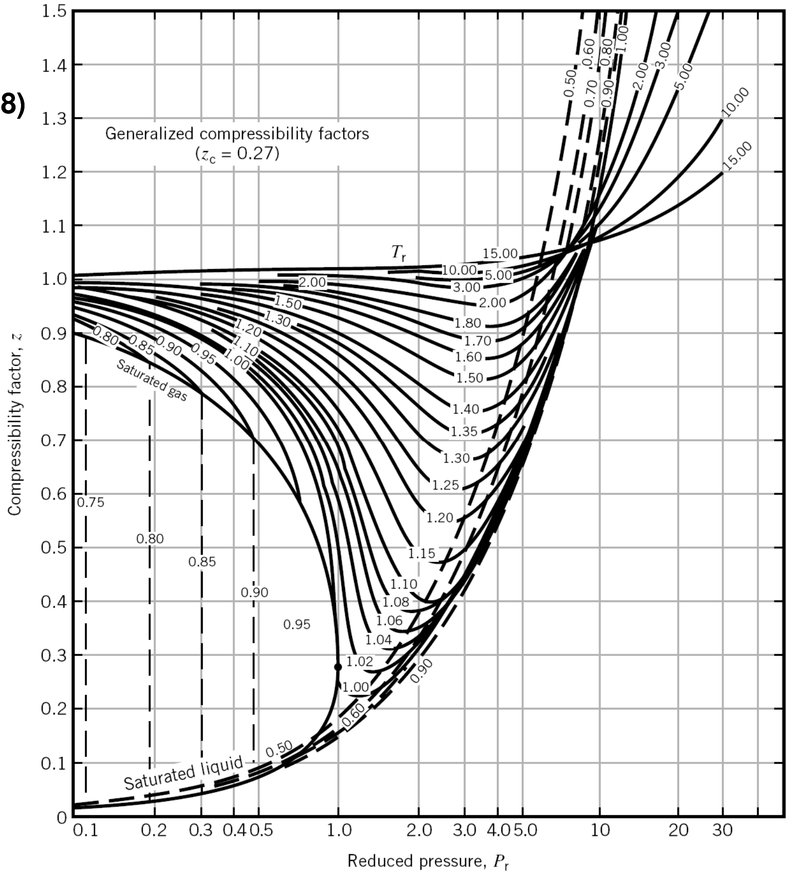
The are typically several different views of the chart, depending on the pressure range.

$$V_r^{ideal} = \frac{\hat{V}}{\hat{V}_c^{ideal}} = \frac{\hat{V}}{RT_c/P_c} = \frac{P_c\hat{V}}{RT_c}$$

Is introduced in some chart to eliminate the need for trial-and-error calculations in problems where either temperature or pressure is unknown

---

Figure 5.4-1 (p. 208)



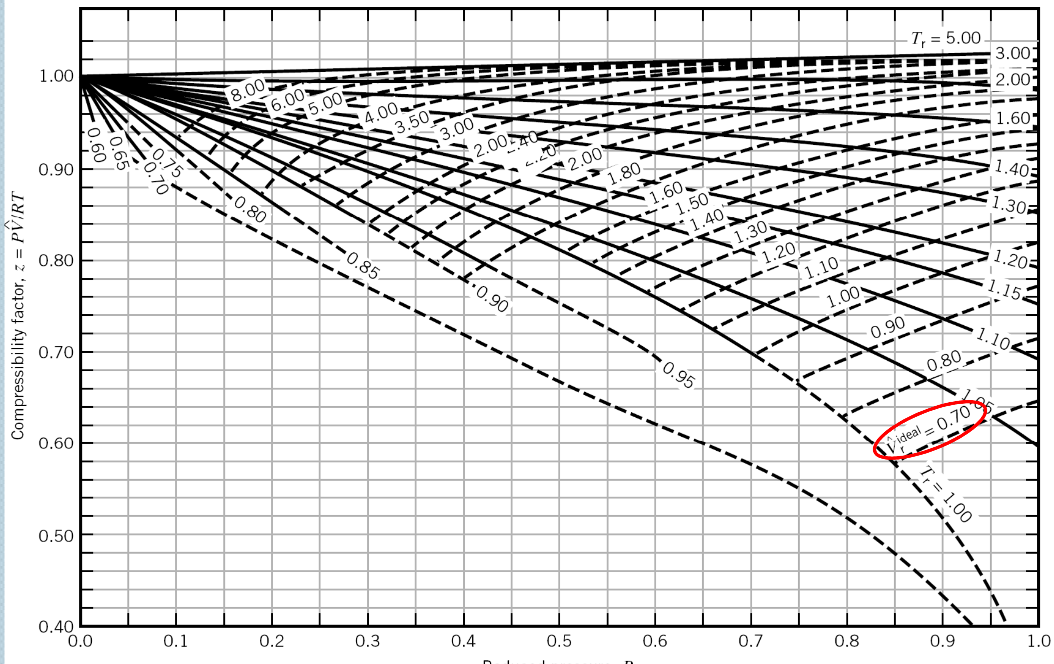


Figure 5.4-2 (p. 209)

Generalized compressibility chart, low pressures.

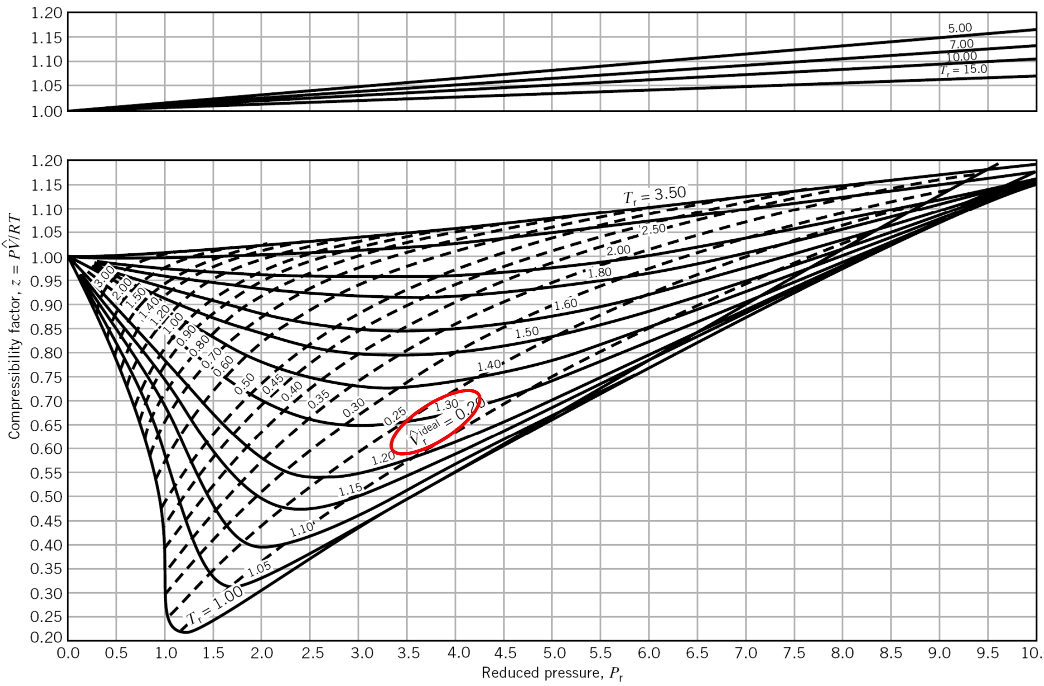


Figure 5.4-3 (p. 210)

Generalized compressibility chart, medium pressures.

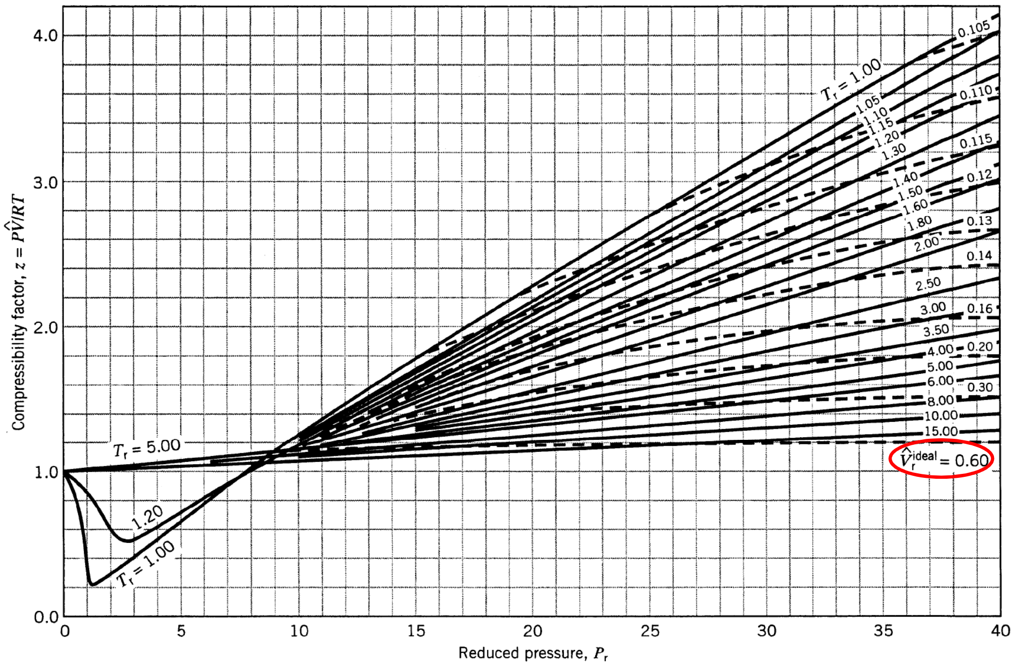
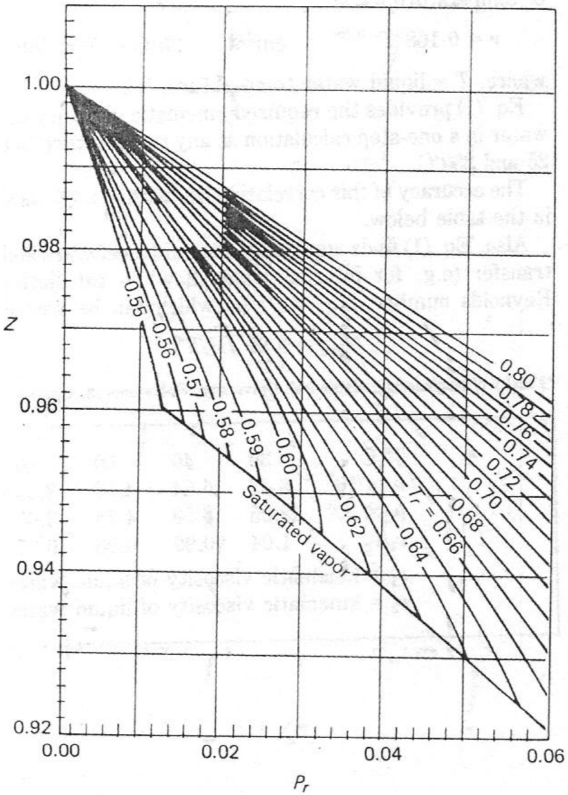
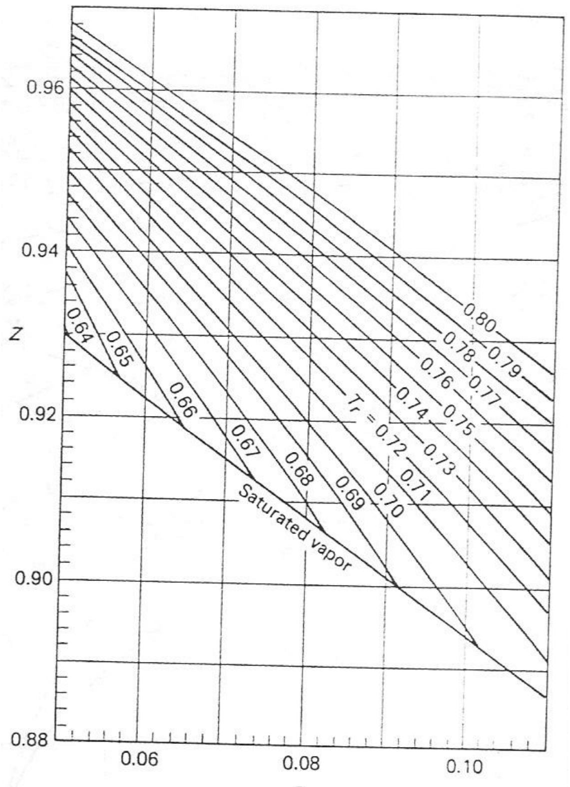


Figure 5.4-4 (p. 211)

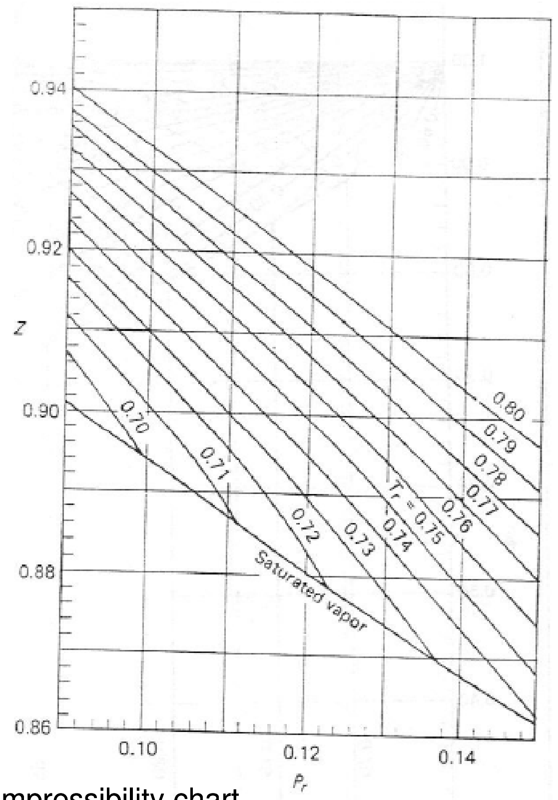
Generalized compressibility chart, high pressures.



Generalized compressibility chart

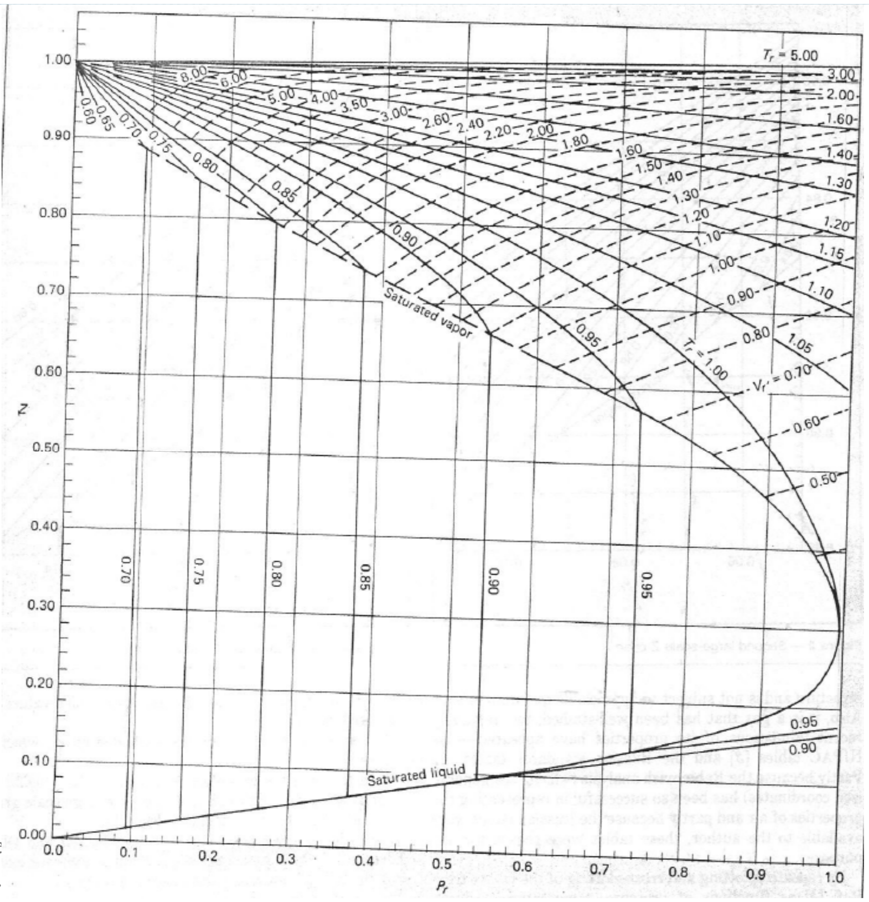


Generalized compressibility chart



Generalized compressibility chart

Generalized compressibility chart



Warning: Hydrogen and Helium are special cases. They require a correction when calculating reduced properties. Hence, determine adjusted critical constants from the empirical formulas

$$T_c^a = T_c + 8\ \mathrm{K}$$
$$P_c^a = P_c + 8\ \mathrm{atm}$$

Newton's corrections

Example

It is necessary to store 1 lbmole of methane at a temperature of 122 F and a pressure of 600 atm. What is the volume of the vessel that must be provided? Compare results using the ideal gas law and the compressibility factor equation.

Example

One hundred gram-moles of nitrogen is contained in a 5-liter vessel at -20.6℃. Estimate the pressure in the cylinder.

Real Gas Mixtures

The mixture compressibility factor, z_m, is found from the generalized compressibility factor chart using the system temperature and pressure reduced using "pseudocritical constants" given by

$$T_c' = y_A T_{cA} + y_B T_{cB} + y_C T_{cC} + \cdots$$

$$P_c' = y_A P_{cA} + y_B P_{cB} + y_C P_{cC} + \cdots$$

Kay's Rule

$$T_r' = T / T_c'$$

$$P_r' = P / P_c'$$

$$\hat{V}_r^{\text{ideal}} = \hat{V} P_c' / R T_c'$$

→

$\hat{V}$ for the mixture

$$\hat{V} = \frac{z_m R T}{P}$$

Example

300 lbs of a mixture of 10 mol% propane, 20% n-butane, and 70% n-pentane is completely vaporized in a pipestill in one hour. At the outlet, the temperature and pressure are 515 F and 600 psia. What is the volumetric flow rate at the outlet in cfm at outlet conditions.

Example

A mixture of 75% H_2 and 25% N_2 (molar basis) is contained in a tank at 800 atm and -70℃. Estimate the specific volume of the mixture in Limol using Kay's rule.