Chapter Three

Gases, Vapors, Liquids, and Solids

- ☒ **Property** is meaning any measurable characteristic of a substance, such as **pressure**, **volume**, or **temperature**, or a characteristic that can be calculated or deduced, such as internal energy.
- ☒ **State and Equilibrium** A system will possess a unique set of properties, such as temperature, pressure, density, and so on, at a given time, and thus is said to be in a particular state. A change in the state of the system results in a change in at least one of its properties.
- ☒ By **equilibrium** we mean a state in which there is no tendency toward spontaneous change. When a system is in equilibrium with another system, or the surroundings, it will not change its state unless the other system, or the surroundings, also changes.
- ☒ A **phase** is defined as a completely homogeneous and uniform state of matter. Liquid water would be a phase; ice would be another phase. Two immiscible liquids in the same container, such as mercury and water, would represent two different phases because the liquids have different properties.

3.1 Ideal Gas Law Calculations

The Ideal Gas Law

Under conditions such that the average distance between the molecules in a substance is great enough to neglect the effect of the intermolecular forces and the volume of the molecules themselves, a gas can be termed an **ideal gas**. More properly, an ideal gas is an imaginary gas that obeys exactly the following relationship

$$pV = nRT \qquad (1)$$

Where p = absolute pressure of the gas

V = total volume occupied by the gas

n = number of moles of the gas

R = ideal gas constant in appropriate units

T = absolute temperature of the gas

Sometimes the ideal gas law is written as

$$p\hat{V} = RT \qquad (1a)$$

Where $\hat{V}$ is the specific volume (volume per mole or mass) of the gas.

Table 1 Common Standard Conditions for the Ideal Gas

System	T	P	$\hat{V}$
SI	273.15K	101.325 kPa	22.415 m^3/kg mol
Universal scientific	0.0°C	760 mm Hg	22.415 liters/g mol
Natural gas industry	60.0°F (15.0°C)	14.696 psia (101.325 kPa)	379.4 ft^3/lb mol
American engineering	32°F	1 atm	359.05 ft^3/lb mol

Example 1

Calculate the volume, in cubic meters, occupied by 40 kg of CO_2 at standard conditions.

Solution

Basis: 40 kg of CO_2

40 kg CO_2	**1 kg mol CO_2**	**22.42 m^3 CO_2**	**= 20.4 m^3 CO_2 atS.C.**
	44 kg CO_2	**1 kg mol CO_2**	

Example 2

Find the value for the universal gas constant ***R*** for the following combinations of units: For 1 g mol of ideal gas when the pressure is in atm, the volume in cm^3, and the temperature in K.

Solution

At standard conditions we will use the approximate values

$$p = 1 \text{ atm}$$
$$\hat{V} = 22{,}415 \text{ cm}^3/\text{g mol}$$
$$T = 273.15\text{K}$$

$$R = \frac{p\hat{V}}{T} = \frac{1 \text{ atm}}{273.15 \text{ K}} \Bigg| \frac{22{,}415 \text{ cm}^3}{1 \text{ g mol}} = 82.06 \frac{(\text{cm}^3)(\text{atm})}{(\text{K})(\text{g mol})}$$

In many processes going from an initial state to a final state, you can use the ratio of ideal gas law in the respective states and eliminate *R* as follows (the subscript 1 designates the initial state, and the subscript 2 designates the final state)

$$\frac{p_1V_1}{p_2V_2} = \frac{n_1RT_1}{n_2RT_2}$$

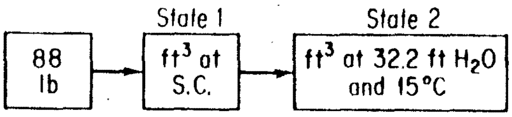
or

$$\left(\frac{p_1}{p_2}\right)\left(\frac{V_1}{V_2}\right) = \left(\frac{n_1}{n_2}\right)\left(\frac{T_1}{T_2}\right) \tag{2}$$

Example 3

Calculate the volume occupied by 88 lb of $\mathbf{CO_2}$ at a pressure of 32.2 ft of water and at 15°C

Solution



The final volume can be calculated via Equation 13.2 in which both **R** and $\mathbf{n_1/n_2}$ cancel out:

$$V_2 = V_1\left(\frac{p_1}{p_2}\right)\left(\frac{T_2}{T_1}\right)$$

Assume that the pressure is absolute pressure.

At S.C. (state 1)	*At state 2*
$p = 33.91$ ft H_2O	$p = 32.2$ ft H_2O
$T = 273$ K	$T = 273 + 15 = 288$ K

Basis: 88 lb of CO_2

$$\underbrace{\begin{array}{l|l|l}
88\ \text{lb}\ CO_2 & & 359\ \text{ft}^3 \\
\hline
 & 44\ \text{lb}\ CO_2 & 1\ \text{lb mol} \\
 & 1\ \text{lb mol}\ CO_2 &
\end{array}}_{\text{Calculation of } V_1}
\begin{array}{l|l}
288 & 33.91 \\
\hline
273 & 32.2 \\
 &
\end{array} = \begin{array}{l}798\ \text{ft}^3\ CO_2 \\ \text{at } 32.2\ \text{ft}\ H_2O \text{ and } 15°C\end{array}$$

Another solution

The same results can be obtained by using Eq. 1

$$R = \frac{p\hat{V}}{T}$$

At S.C.,

$p = 33.91$ ft H_2O $\quad V = 359$ ft^3/lb mol $\quad T = 273$K

$$R = \frac{33.91}{} \left| \frac{359}{273} \right. = 44.59\ \frac{(\text{ft } H_2O)(\text{ft}^3)}{(\text{lb mol})(\text{K})}$$

Basis: 88 lb of CO_2

$$V = \frac{nRT}{p} = \begin{array}{c|c|c}
88\ \text{lb}\ CO_2 & 44.59\ (\text{ft}\ H_2O)(\text{ft}^3) & 288\ \text{K} \\
\hline
44\ \text{lb}\ CO_2 & (\text{lb mol})(\text{K}) & 32.2\ \text{ft}\ H_2O \\
\text{lb mol}\ CO_2 & &
\end{array}$$

$= 798$ ft^3 CO_2 at 32.2 ft H_2O and 15°C

The Gas Density

The **density of a gas** is defined as the mass per unit volume and can be expressed in kilograms per cubic meter, pounds per cubic foot, grams per liter, or other units

Example 4

What is the density of N_2 at 27°C and 100 kPa in SI units?

Solution

Basis: 1 m^3 of N_2 at 27°C and 100 kPa

$$\begin{array}{c|c|c|c|c} 1\ \text{m}^3 & 273\ \text{K} & 100\ \text{kPa} & 1\ \text{kg mol} & 28\ \text{kg} \\ \hline & 300\ \text{K} & 101.3\ \text{kPa} & 22.4\ \text{m}^3 & 1\ \text{kg mol} \end{array} = 1.123\ \text{kg}$$

density = 1.123 kg/m^3 of N_2 at 27°C (300 K) and 100 kPa

The Gas Specific Gravity

The **specific gravity of a gas** is usually defined as the ratio of the density of the gas at a desired temperature and pressure to that of air (or any specified reference gas) at a certain temperature and pressure.

Example 5

What is the specific gravity of N_2 at 80°F and 745 mm Hg compared to air at 80°F and 745 mm Hg?

Solution

Basis: 1 ft^3 of air at 80°F and 745 mm Hg

$$\begin{array}{c|c|c|c|c} 1 & 492 & 745 & & 29 \\ \hline & 540 & 760 & 359 & \end{array} = 0.0721\ \text{lb/ft}^3 \text{ at } 80°\text{F and } 745\ \text{mm Hg}$$

Basis: 1 ft^3 of N_2 at 80°F and 745 mm Hg

$$\begin{array}{c|c|c|c|c} 1 & 492 & 745 & & 28 \\ \hline & 540 & 760 & 359 & \end{array} = 0.0697\ \text{lb/ft}^3 \text{ at } 80°\text{F and } 745\ \text{mm Hg}$$

$$(\text{sp. gr.})_{N_2} = \frac{0.0697}{0.0721} = 0.967\ \frac{\text{lb } N_2/\text{ft}^3 \text{ at } 80°\text{F, } 745\ \text{mm Hg}}{\text{lb air/ft}^3 \text{ air at } 80°\text{F, } 745\ \text{mm Hg}}$$

Note: for gases at the same temperature and pressure, the specific gravity is just the ratio of the respective **molecular weights**. Let A be one gas and B be another.

$$p\hat{V} = RT \qquad \text{or} \qquad p\frac{1}{\rho} = RT$$

Thus $$sp.gr. = \frac{\rho_A}{\rho_B} = \left(\frac{p_A}{p_B}\right)\left(\frac{mol.wt.A}{mol.wt.B}\right)\left(\frac{T_B}{T_A}\right) \qquad (3)$$

Ideal Gas Mixtures and Partial Pressure

The **partial pressure** of gas; i defined by **Dalton**, p_i, namely the pressure that would be exerted by a single component in a gaseous mixture if it existed by itself in the same volume as occupied by the mixture and at the same temperature of the mixture is

$$p_i V_{total} = n_i R T_{total} \qquad (4)$$

Where p_i is the partial pressure of component i. If you divide Eq. (4) by Eq. (1), you find that

$$\frac{p_i V_{total}}{p_{total} V_{total}} = \frac{n_i R T_{total}}{n_{total} R T_{total}}$$

or

$$p_i = p_{total}\frac{n_i}{n_{total}} = p_{total}.y_i \qquad (5)$$

Where y_i is the mole fraction of component i. Can you show that Dalton's law of the summation of partial pressures is true using Eq. 13.5?

$$p_1 + p_2 + \ldots + p_n = p_t \qquad \ldots 3.6 \qquad (6)$$

Although you cannot measure the partial pressure directly with an instrument, you can calculate the value from Eqs. 5 and/or 6.

Example 6

A flue gas analyzes 14.0% CO_2, 6.0% O_2, and 80.0% N_2. It is at 400°F and 765.0 mm Hg pressure. Calculate the partial pressure of each component.

Solution

Use Eq, (13.5) $p_i = p_t\, y_i$

Basis: 1.00 kg (or lb) mol flue gas

Component	*kg (or lb) mol*	*p (mm Hg)*
CO_2	0.140	107.1
O_2	0.060	45.9
N_2	0.800	612.0
Total	1.000	765.0

On the basis of 1.00 mole of flue gas, the mole fraction y of each component, when multiplied by the total pressure, gives the partial pressure of that component.

Real Gas Relationships

- ☒ We have said that at **room temperature and pressure** many gases can be assumed to act as **ideal gases**.
- ☒ However, for some gases under normal conditions, and for most gases under conditions of **high pressure**, values of the gas properties that you might obtain using the ideal gas law would be at wide variance with the experimental evidence. . You might wonder exactly how the behavior of **real gases** compares with that calculated from the **ideal gas laws**.
- ☒ In Fig. 3.2 you can see how the ($p\ \hat{V}$)product of several gases **deviates** from that predicted by the **ideal gas** laws as the **pressure increases** substantially. Thus it is clear that we need some way of computing **the *p-V-T* properties** of a gas that is **not ideal, i.e. the real gas**.

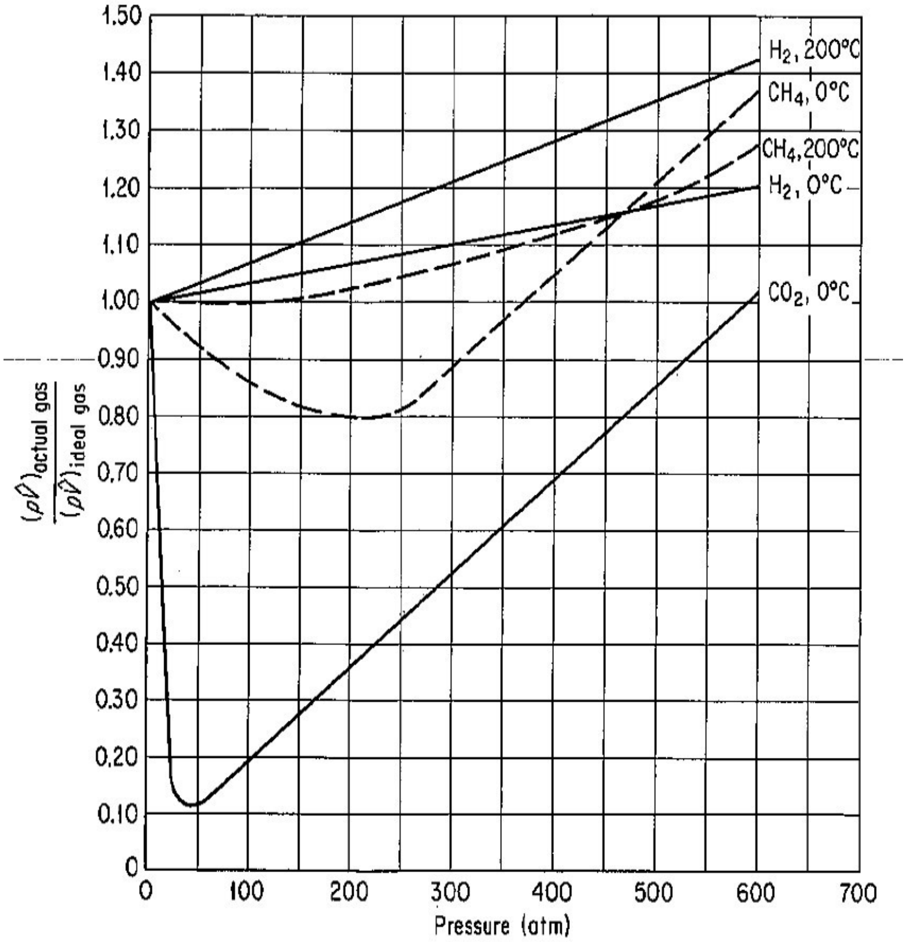


Figure 1 Deviation of real gases from the ideal gas law at high pressures.

Three methods of getting or predicting real gas properties in lieu of having experimental data:

1. Compressibility charts
2. Equations of state
3. Estimated properties

Critical State, Reduced Parameters, and Compressibility

- The critical state for the gas-liquid transition is the set of physical conditions at which the density and other properties of the liquid and vapor become identical.
- The **law of corresponding states** expresses the idea that in the **critical state** all substances should behave alike.
- Refer to Figure 2 in which the states of water are illustrated. As the temperature increases, the density of the liquid and vapor approach each other until finally at 374.14 °C, the values are the same.

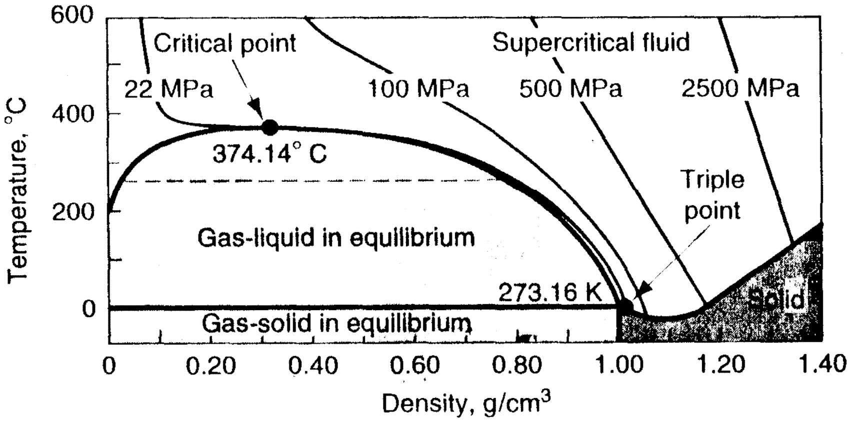


Figure 2 The regions of existence of solid, liquid, gaseous, and supercritical water. At the triple point solid, liquid, and gas are all in equilibrium.

- A **supercritical fluid**, that is, a compound in a state above the critical point, combines some of the properties of both gases and liquids.
- Another set of terms with which you should immediately become familiar are the **reduced parameters**. These are **corrected, or normalized**, conditions of temperature, pressure, and volume and are expressed mathematically as

$$T_r = \frac{T}{T_c}$$

$$p_r = \frac{p}{p_c}$$

$$V_r = \frac{V}{V_c}$$

Compressibility Factor (*z*)

One common way is to modify the ideal gas law by inserting an adjustable coefficient *z*, the compressibility factor, a factor that compensates for the **nonideality** of the gas. Thus, the **ideal gas law** becomes a **real gas law**, a generalized equation of state.

$$pV = znRT \qquad (7)$$

- Figure 3 shows the **generalized compressibility charts** or ***z* – factor chart** prepared by Nelson and Obert. These charts are based on 30 gases.

Figure 3 (e) is a unique chart that, by having several parameters plotted simultaneously on it, helps you avoid trial-and-error solutions or graphical solutions of **real gas problems**. One of these helpful parameters is the ideal reduced volume defined as

$$V_{r_i} = \frac{\hat{V}}{\hat{V}_{c_i}}$$

V_{c_i} the ideal critical volume (not the experimental value of the critical volume), or

$$\hat{V}_{c_i} = \frac{RT_c}{p_c}$$

Both V_{r_i} and $\hat{V}_{c_i}$ are easy to calculate since T_c and p_c are presumed known.

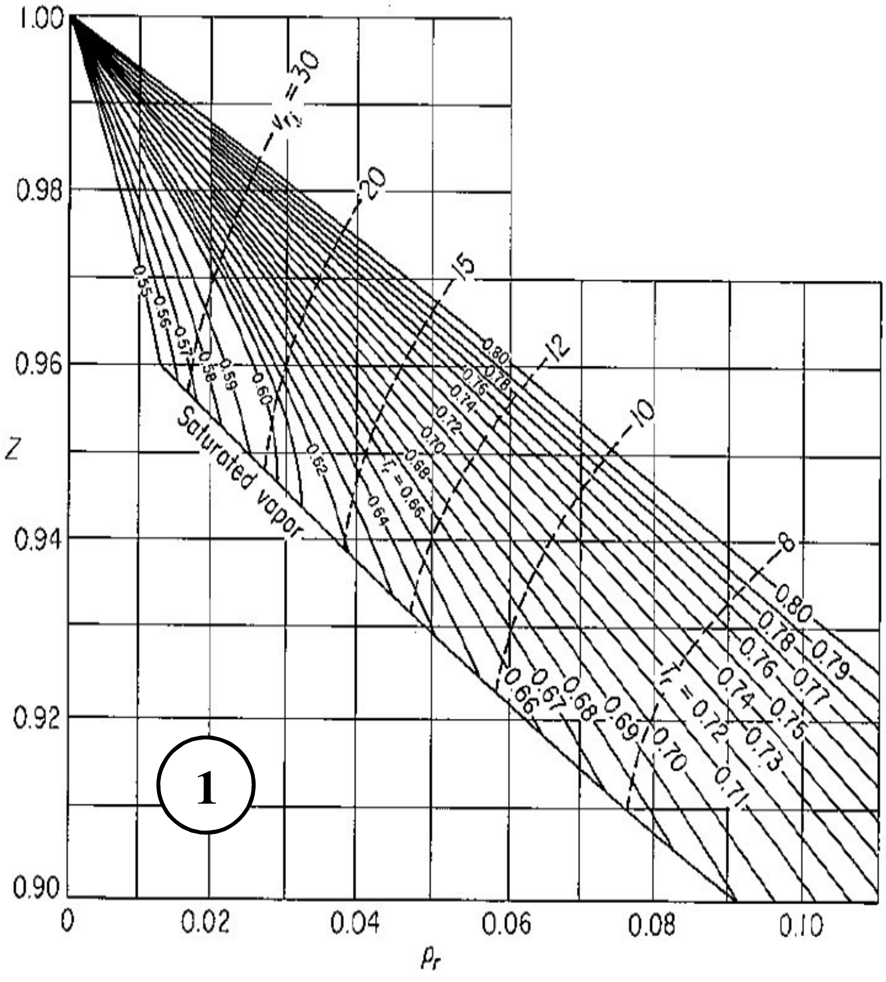


Figure 3(a) Generalized Compressibility Chart, Very Low Reduced Pressure.

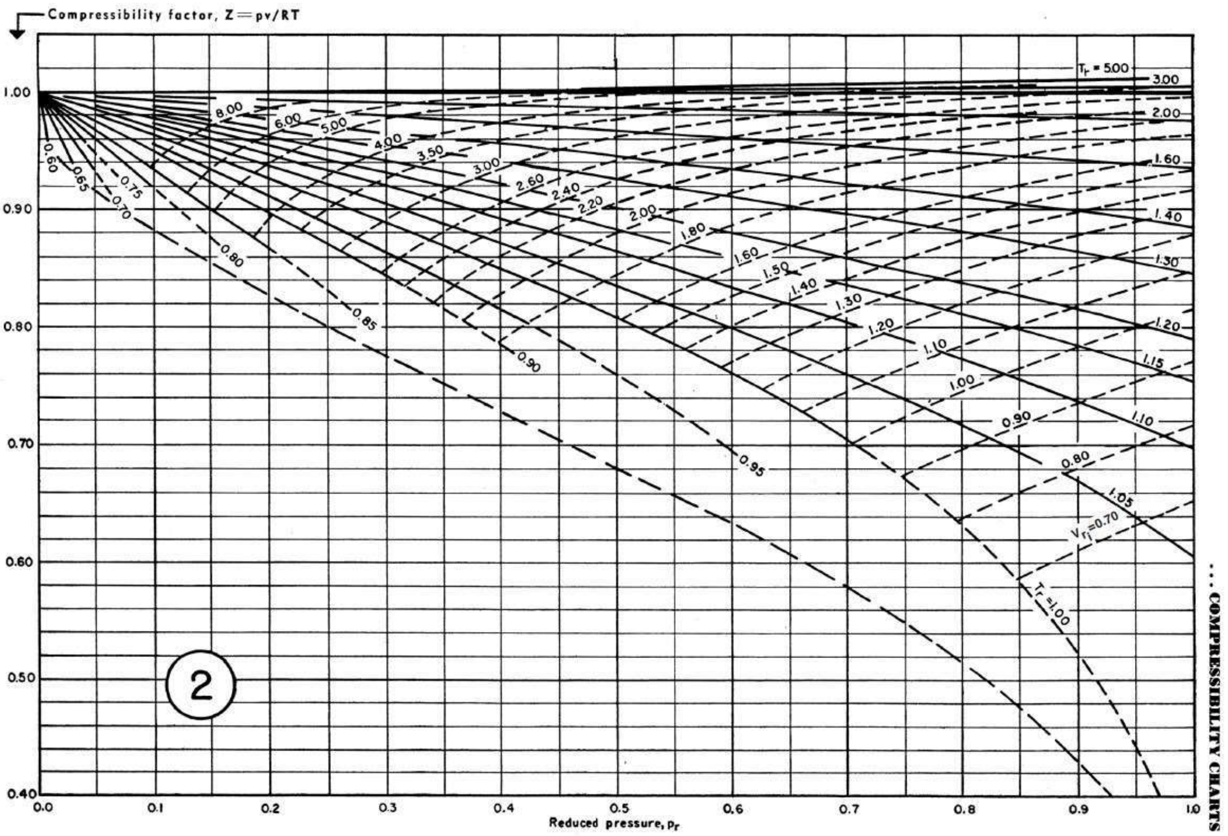


Figure 3(b) Generalized Compressibility Chart, Low Pressure.

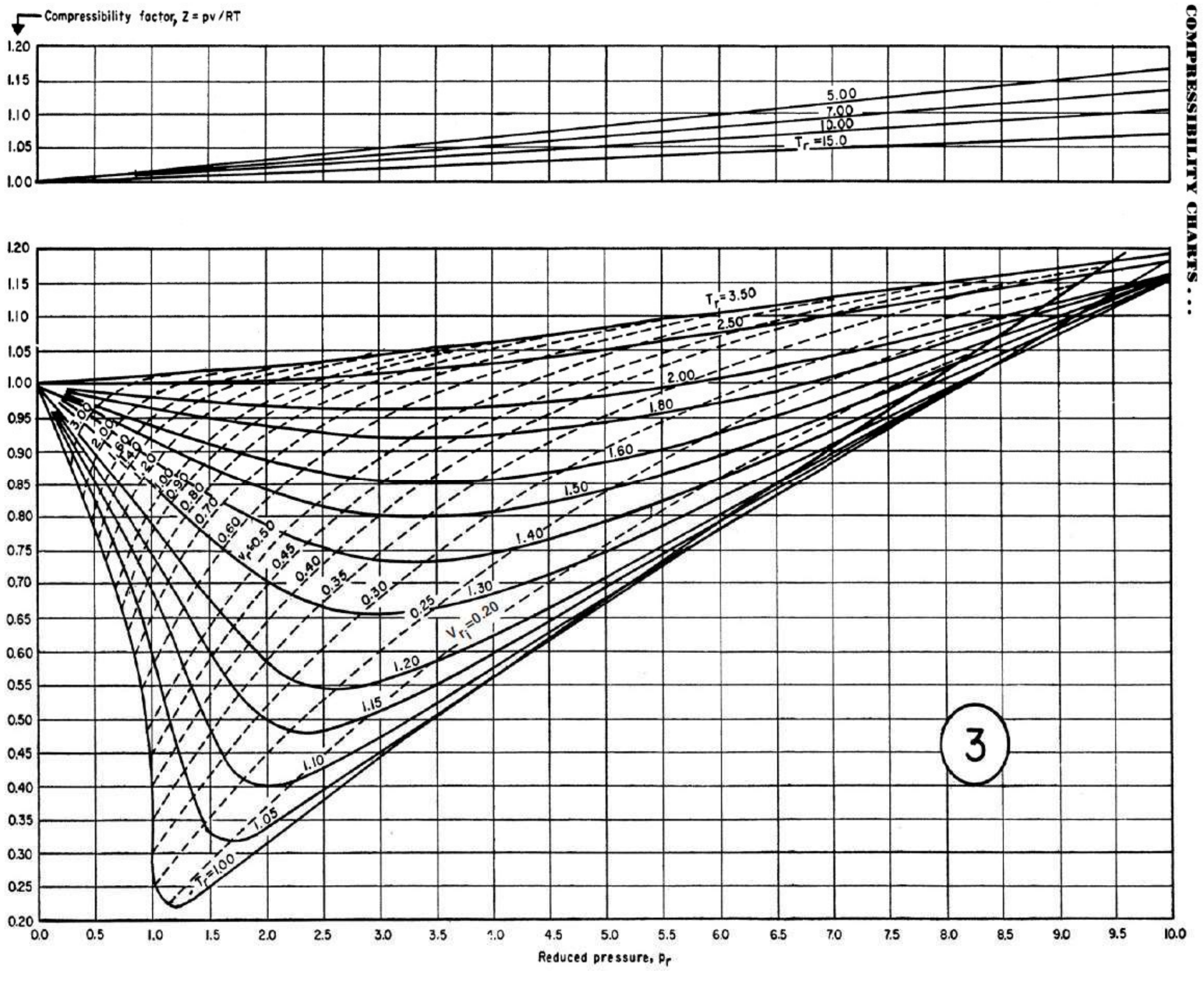


Figure 3(c) Generalized Compressibility Chart, Medium Pressure**.**

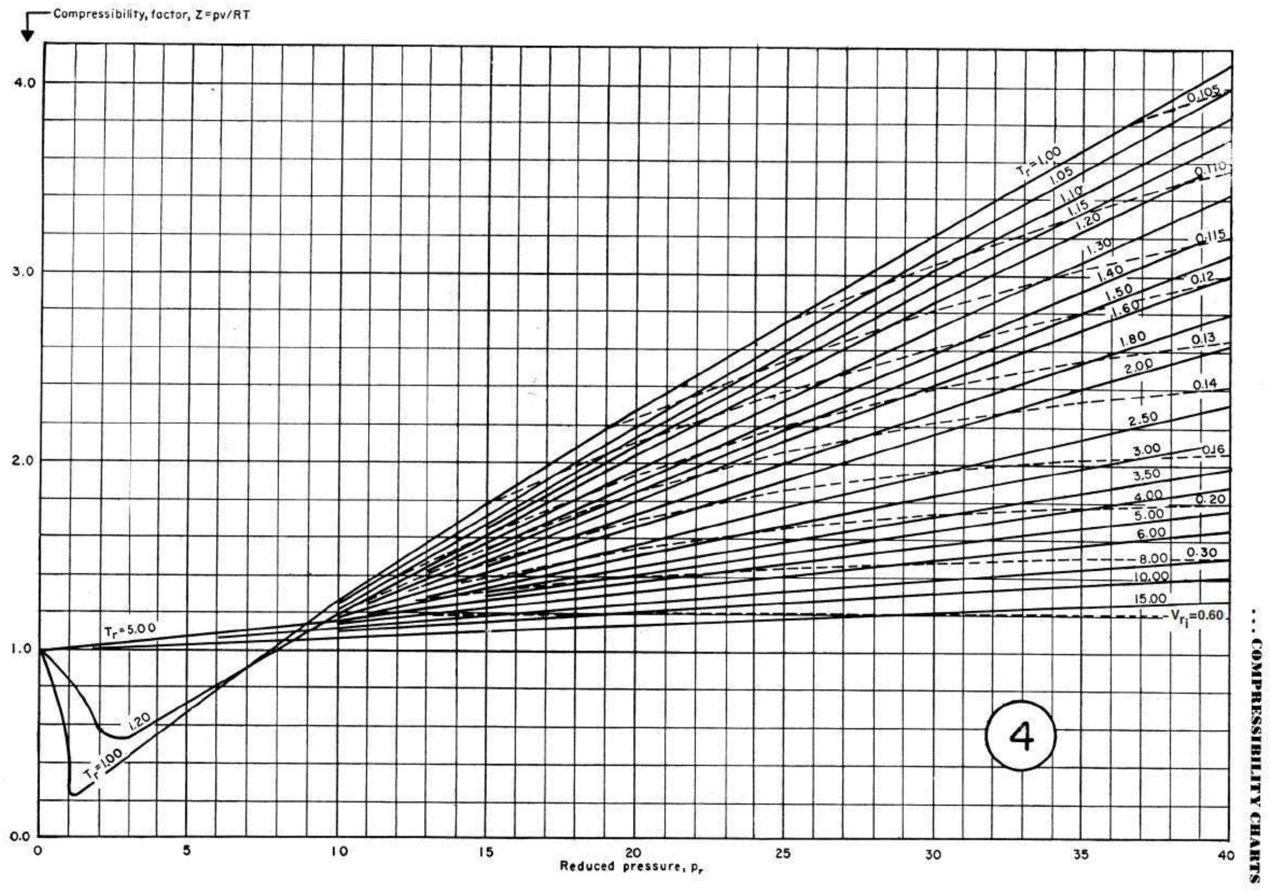


Figure 3(d) Generalized Compressibility Chart, High Pressure.

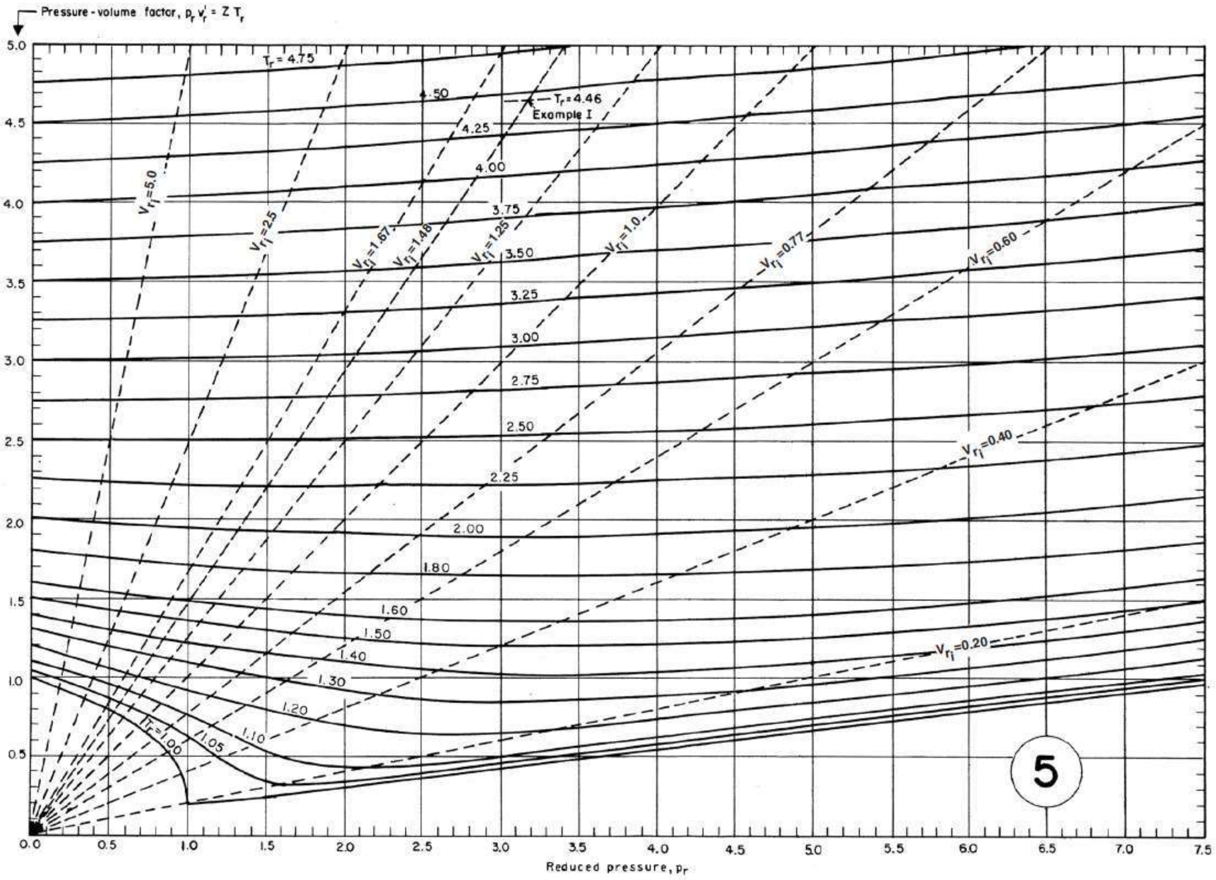


Figure 3 (e) Generalized Compressibility Chart, with Special Scales.

Note

The value **$z = 1$** represents **ideality**, and the value **$z = 0.27$** is the compressibility factor at the **critical point**.

Example 7

In spreading liquid ammonia fertilizer, the charges for the amount of NH_3 are based on the time involved plus the pounds of NH_3 injected into the soil. After the liquid has been spread, there is still some ammonia left in the source tank (volume = 120 ft^3), but in the form of a gas. Suppose that your weight tally, which is obtained by difference, shows a net weight of 125 lb of NH_3 left in the tank as a gas at 292 psig. Because the tank is sitting in the sun, the temperature in the tank is 125°F. Your boss complains that his calculations show that the specific volume of the gas is 1.20 ft^3/lb and hence that there are only 100 lb of NH_3 in the tank. Could he be correct? See Figure E 3.7.

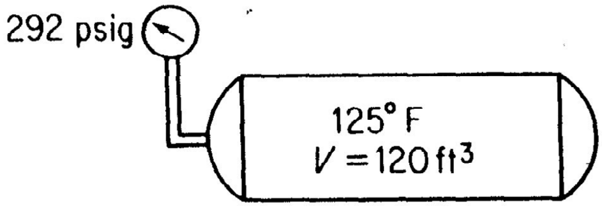


Figure E 3.7

Solution

Apparently, your boss used the ideal gas law in getting his figure of 1.20 ft^3/lb of NH_3 gas:

$$R = 10.73 \frac{(\text{psia})(\text{ft}^3)}{(\text{lb mol})(°\text{R})} \qquad p = 292 + 14.7 = 306.7 \text{ psia}$$

$$T = 125°\text{F} + 460 = 585°\text{R} \qquad n = \frac{1 \text{ lb}}{17 \text{ lb/lb mol}}$$

$$\hat{V} = \frac{RT}{p} = \frac{\frac{1}{17}(10.73)(585)}{306.7} = 1.20 \text{ ft}^3/\text{lb}$$

However, he should have used the **compressibility factor**, because NH_3 does not behave as an **ideal gas** under the observed conditions of **temperature and pressure**. Let us again compute the mass of gas in the tank this time using

$$pV = znRT$$

From Appendix D:

$$T_c = 405.5K \simeq 729.9R$$

$$p_c = 111.3 \text{ atm} \simeq 1636 \text{ psia}$$

Then, since z is a function of T_r and p_r,

$$T_r = \frac{T}{T_c} = \frac{585° \text{R}}{729.9° \text{R}} = 0.801$$

$$p_r = \frac{p}{p_c} = \frac{306.7 \text{ psia}}{1636 \text{ psia}} = 0.187$$

From the Nelson and Obert chart, Fig. 13.3 (b), you can read z = 0.855. Now $\hat{V}$ can be calculated as

$$\hat{V} = \frac{1.20 \text{ ft}^3 \text{ ideal}}{\text{lb}} \Big| \frac{0.855}{1} = 1.03 \text{ ft}^3/\text{lb NH}_3$$

$$\frac{1 \text{ lb NH}_3}{1.03 \text{ ft}^3} \Big| \frac{120 \text{ ft}^3}{} = 117 \text{ lb NH}_3$$

Note : Certainly 117 lb is a more realistic figure than 100 lb, and it is easily possible to be in error by 8 lb if the residual weight of NH_3 in the tank is determined by difference. As a matter of interest you might look up the specific volume of NH_3 at the conditions in the tank in a handbook. You would find that $\hat{V}$ = 0.973 ft^3/lb, and hence the compressibility factor calculation yielded a volume with an error of only about 4%.

Example 13.8

Liquid oxygen is used in the steel industry, in the chemical industry, in hospitals, as rocket fuel, and for wastewater treatment as well as many other applications. In a hospital a tank of 0.0284-m^3 volume is filled with 3.500 kg of liquid O_2 that vaporized at -25°C. Will the pressure in the tank exceed the safety limit of the tank (10^4 kPa)?

Solution

Basis: 3.500 kg O_2

We know from Appendix D that

$$T_c = 154.4 \text{ K}$$

$$p_c = 49.7 \text{ atm} \rightarrow 5{,}035 \text{ kPa}$$

$$\hat{V}\ (molal\ volume) = \frac{0.0284\ \text{m}^3}{3.500\ \text{kg}}\left|\frac{32\ \text{kg}}{1\ \text{kg mol}}\right. = 0.260\ \text{m}^3/\text{kg mol}$$

Note that the *molal volume must* be used in calculating V_{r_i} Since $\hat{V}_{c_i}$ is a volume per mole.

$$\hat{V}_{c_i} = \frac{RT_c}{p_c} = \frac{8.313\ (\text{m}^3)\ (\text{kPa})}{(\text{kg mol})(\text{K})}\left|\frac{154.4\ \text{K}}{5,035\ \text{kPa}}\right. = 0.255\frac{\text{m}^3}{\text{kg mol}}$$

Then

$$V_{r_i} = \frac{\hat{V}}{\hat{V}_{c_i}} = \frac{0.260}{0.255} = 1.02$$

Now we know two parameters, V_{r_i} and,

$$T_r = \frac{248\ \text{K}}{154.4\ \text{K}} = 1.61$$

From the Nelson and Obert chart [Fig. 3 (e)],

$$p_r = 1.43$$

Then

$$p = p_r p_c$$
$$= 1.43\ (5,035) = 7200\ \text{kPa}$$

The pressure of 100 atm will not be exceeded. Even at room temperature the pressure will be less than 10^4 kPa.

13.2.2 Equations of State

- Equations of state relate the ***p**-V-T* properties of a pure substance (or mixtures) by theoretical or empirical relations.
- The simplest example of an equation of state is the ideal gas law itself. Table 13.2 lists a few of the commonly used equations of state (from among the hundreds that have been proposed) that involve two or more coefficients.

TABLE 3.2 Equations of State (for 1 Mole)*

Van der Waals:

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

$$a = \left(\frac{27}{64}\right)\frac{R^2T_c^2}{P_c}$$

$$b = \left(\frac{1}{8}\right)\frac{RT_c}{P_c}$$

Dieterici:

$$p = \frac{RT}{\hat{V} - b} e^{-a/\hat{V}RT}$$

Berthelot:

$$p = \frac{RT}{\hat{V} - b} - \frac{a}{T\hat{V}^2}$$

Redlich-Kwong:

$$\left[p + \frac{a}{T^{1/2}\hat{V}(\hat{V} + b)}\right](\hat{V} - b) = RT$$

$$a = 0.4278\frac{R^2T_c^{2.5}}{p_c}$$

$$b = 0.0867\frac{RT_c}{p_c}$$

Kammerlingh-Onnes:

$$p\hat{V} = RT\left(1 + \frac{B}{\hat{V}} + \frac{C}{\hat{V}^2} + \cdots\right)$$

Holborn:

$$p\hat{V} = RT(1 + B'p + C'p^2 + \cdots)$$

Beattie-Bridgeman:

$$p\hat{V} = RT + \frac{\beta}{\hat{V}} + \frac{\gamma}{\hat{V}^2} + \frac{\delta}{\hat{V}^3}$$

$$\beta = RTB_0 - A_0 - \frac{Rc}{T^2}$$

$$\gamma = -RTB_0b + aA_0 - \frac{RB_0c}{T^2}$$

$$\delta = \frac{RB_0bc}{T^2}$$

Benedict-Webb-Rubin:

$$p\hat{V} = RT + \frac{\beta}{\hat{V}} + \frac{\sigma}{\hat{V}^2} + \frac{\eta}{\hat{V}^4} + \frac{w}{\hat{V}^5}$$

$$\beta = RTB_0 - A_0 - \frac{C_0}{T^2}$$

$$\sigma = bRT - a + \frac{c}{T^2}\exp\left(-\frac{\gamma}{\hat{V}^2}\right)$$

$$\eta = c\gamma\exp\left(-\frac{\gamma}{\hat{V}^2}\right)$$

$$w = a\alpha$$

Peng-Robinson:

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

$$a = 0.45724\left(\frac{R^2T_c^2}{p_c}\right)$$

$$b = 0.07780\left(\frac{RT_c}{p_c}\right)$$

$$\alpha = [1 + \kappa(1 - T_r^{1/2})]^2$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

ω = acentric factor (see p. 275)

- **Van der Waals equation** can easily be solved explicitly for **(p)** as follows:

$$p = \frac{nRT}{V - nb} - \frac{n^2a}{V^2}$$

However, if you want to solve for V (or n), you can see that the equation becomes cubic in V (or n):

$$f(V) = V^3 - \left(nb + \frac{nRT}{p}\right)V^2 + \frac{n^2a}{p}V - \frac{n^3ab}{p} = 0$$

And can have multiple roots. We want a positive real root. **Computer programs** can solve nonlinear equations and can be used to solve for **V** if you have a reasonable **initial guess** for **V**, say from the ideal gas law.

Example 13.9

A cylinder 0.150 m^3 in volume containing 22.7 kg of propane C_3H_8 stands in the hot sun. A pressure gauge shows that the pressure is 4790 kPa gauge. What is the temperature of the propane in the cylinder? Use van der Waals equation.

Solution

Basis: 22.7 kg of propane

The van der Waals constants obtained from any suitable handbook

$$a = 9.24 \times 10^6 \text{ atm}\left(\frac{\text{cm}^3}{\text{g mol}}\right)^2$$

$$b = 90.7\,\frac{\text{cm}^3}{\text{g mol}}$$

$$p + \left(\frac{n^2a}{V^2}\right)(V - nb) = nRT$$

All the additional information you need is as follows:

$$p = \frac{(4790 + 101)\text{kPa}}{} \left| \frac{1 \text{ atm}}{101.3 \text{ kPa}} \right. = 48.3 \text{ atm abs}$$

$$R \text{ in the proper units is} = \frac{82.06(\text{cm}^3)(\text{atm})}{(\text{g mol})(\text{K})}$$

$$n = \frac{22.7}{44 \text{ kg/kg mol}} = 0.516 \text{ kg mol propane}$$

$$\left[48.3 + \frac{(0.516\times10^3)^2(9.24\times10^6)}{(0.150\times10^6)^2}\right]\left[0.150\times10^6 - (0.516\times10^3)(90.7)\right] = (0.516\times10^3)(82.06)(T_K)$$

$$T = 384 \text{ K}$$

3.2.3 Gaseous Mixtures

In **Kay's method**, **pseudocritical** values for mixtures of gases are calculated on the assumption that each component in the mixture contributes to the pseudocritical value in the same proportion as the number of moles of that component. Thus the pseudocritical values are computed as follows:

$$p'_c = p_{c_A}y_A + p_{c_B}y_B + \cdots \qquad (8a)$$

$$T'_c = T_{c_A}y_A + T_{c_B}y_B + \cdots \qquad (8b)$$

Where p'_c = pseudocritical pressure and T_c = pseudocritical temperature. (It has also been found convenient in some problems to calculate similarly a weighted pseudo-ideal-critical volume V'_{ci}.)

Then the respective pseudo-reduced values are

$$p'_r = \frac{p}{p'_c}$$

$$T'_r = \frac{T}{T'_c}$$

Example 10

A gaseous mixture has the following composition (in mole percent):

Methane, CH_4	20
Ethylene, C_2H_4	30
Nitrogen, N_2	50

at 90 atm pressure and 100°C. Compare the volume per mole as computed by the methods of:

(a) the perfect gas law

(b) the pseudoreduced technique (Kay's method)

Solution

Basis: 1 g mol of gas mixture

Additional data needed are:

Component	T_c (K)	p_c (atm)
CH_4	191	45.8
C_2H_4	283	50.5
N_2	126	33.5

$$R = 82.06\frac{(\text{cm}^3)(\text{atm})}{(\text{g mol})(\text{K})}$$

(a) Perfect gas law:

$$\hat{V} = \frac{RT}{p} = \frac{1(82.06)(373)}{90} = 340 \text{ cm}^3 \text{ at } 90 \text{ atm and } 373 \text{ K}$$

(b) According to Kay's method, we first calculate the pseudocritical values for the mixture

$$p_c' = p_{c_A}y_A + p_{c_B}y_B + p_{c_C}y_C = (45.8)(0.2) + (50.5)(0.3) + (33.5)(0.5)$$

$$= 41.2 \text{ atm}$$

$$T_c' = T_{c_A}y_A + T_{c_B}y_B + T_{c_C}y_C = (191)(0.2) + (283)(0.3) + (126)(0.5)$$

$$= 186 \text{ K}$$

Then we calculate the pseudo-reduced values for the mixture

$$p_r' = \frac{p}{p_c'} = \frac{90}{41.2} = 2.18, \qquad T_r' = \frac{T}{T_c'} = \frac{373}{186} = 2.01$$

With the aid of these two parameters we can find from **Figure 13.3(c)** $z = 0.965$. Thus

$$\hat{V} = \frac{zRT}{p} = \frac{0.965(1)(82.06)(373)}{90} = 328 \text{ cm}^3 \text{ at } 90 \text{ atm and } 373 \text{ K}$$

Note

In instances in which the temperature or pressure of a gas mixture is unknown, to avoid a trial – and – error solution using the generalized compressibility charts, you can compute the pseudocritical ideal volume and a **pseudoreduced ideal reduced** volume V_{ri} thus

$$\hat{V}'_{c_i} = \frac{RT'_c}{p'_c} \qquad \text{and} \qquad V'_{r_i} = \frac{\hat{V}}{\hat{V}'_{c_i}}$$

$\hat{V}'_{r_i}$ can be used in lieu of p'_r or T'_r in the compressibility charts.

Vapor Pressure and Liquids

☒ The terms **vapor** and **gas** are used very loosely. From now on, the word **vapor** will be reserved to describe a gas below its critical point in a process in which the phase change is of primary interest, while the word **gas** or **noncondensable gas** will be used to describe a gas above the critical point or a gas in a process in which it cannot condense.

☒ If the vapor and liquid of a pure component are in **equilibrium**, then the **equilibrium pressure is called the vapor pressure** (see Figure 13.4).

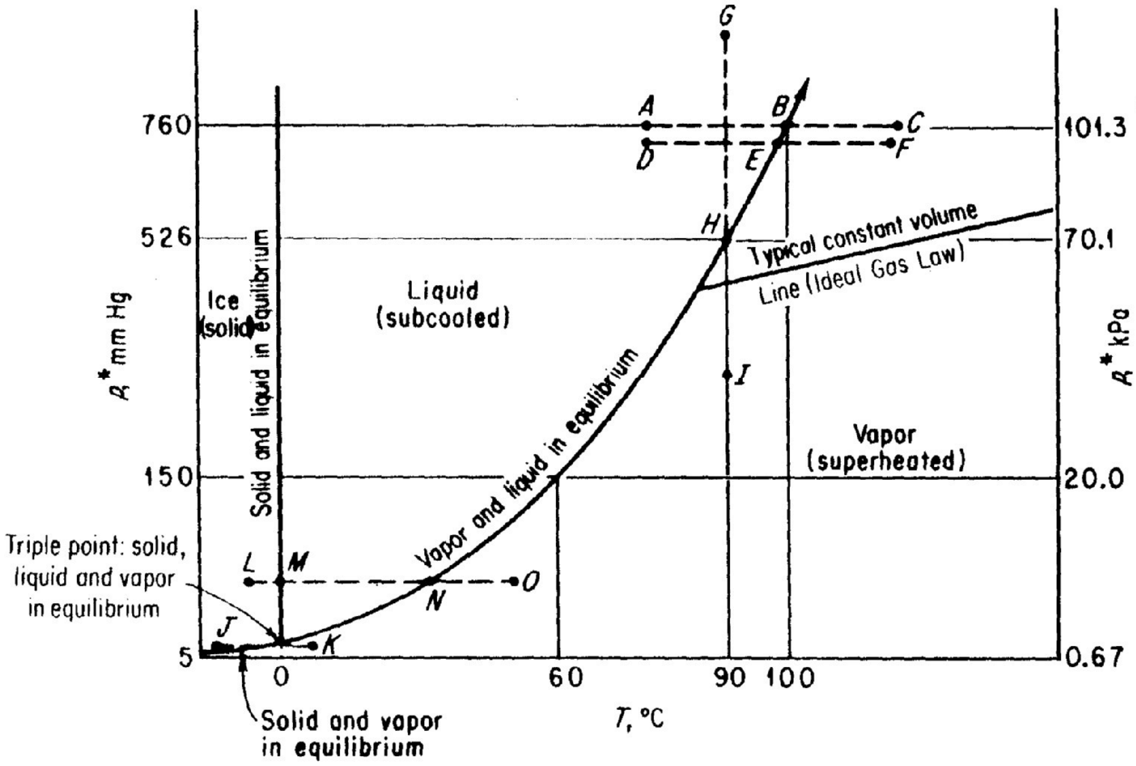


Figure 13.4 Vapor-pressure curve for water.

- Any substance has an infinite number of **boiling points**, but by custom we say the **"normal" boiling point** is the temperature at which boiling takes place under a pressure of 1 atm (101.3 kPa, 760 mm Hg). (see Figure 13.5)

- When the solid passes directly into the vapor phase without first melting to become a liquid (line J-K as opposed to line L-M-N-O in Figure 13.4) it is said to **sublime**.

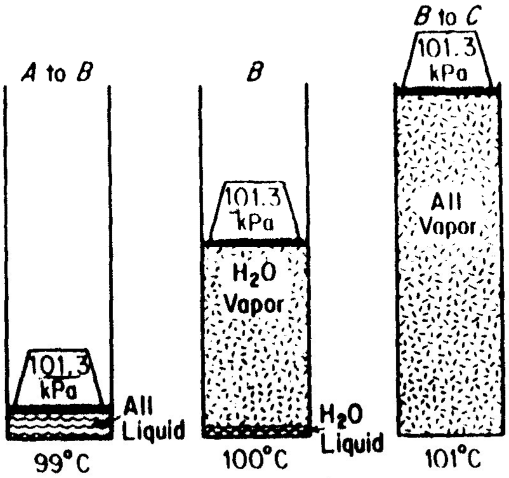


Figure13.5 Transformation of liquid water into vapor at constant pressure. The 101.3 kPa exerted by the piston includes the force of the atmosphere above the piston.

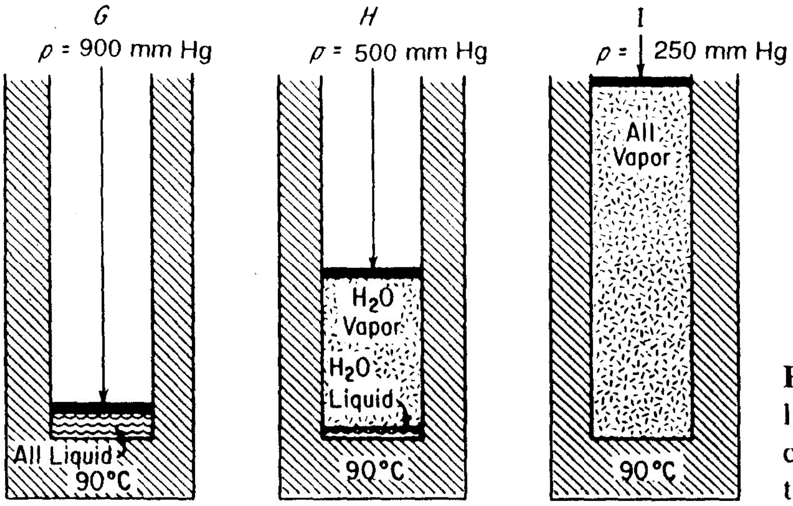


Figure13.6 Transformation of liquid water into water vapor at a constant temperature by changing the imposed pressure.

- Another new term you will find used frequently is the word **quality**. A wet vapor consists of saturated vapor and saturated liquid in equilibrium. The **mass fraction of vapor** is known as the **quality** (*x*).

Change of Vapor Pressure with Temperature

You can see from Figure 13.4 that the function of p^* versus T is not a linear Function (except as an approximation over a very small temperature range).

We will use the **Antoine equation** — it has sufficient accuracy for our needs:

$$\ln p^* = A - \frac{B}{C+T} \tag{9}$$

Where $A,\ B,\ C$ = constants different for each substance T = temperature, K

Example 11

Calculate the vapor pressure of benzene at 50°C using the Antoine Equation. Also estimate the normal boiling point of benzene (the vapor pressure at 1 atm).

Solution

Antoine Equation $\ln(p^*) = A - \dfrac{B}{C+T}$

From Appendix G in the text the coefficients are
Benzene: $A = 15.9008$ $T = K$
$B = 2788.51$ $p^* = \text{mmHg}$
$C = -52.36$

a. Vapor Pressure of benzene at 50°C

$$\ln(p^*) = 15.9008 - \frac{2788.51}{-52.36 + (50 + 273)}$$

$$p^* = \mathbf{270\ mmHg\ abs}$$

b. At the boiling point the vapor pressure is 1 atm (760 mmHg abs.)

$$\ln(760) = 15.9008 - \frac{2788.51}{-52.36 + T}$$

Solving, $T =$ **353.3K**

Liquid Properties

Often making density a linear function of temperature that is independent of pressure provides sufficiently accurate predictions

$$\rho = \rho_0 - \beta(T - T_0) \qquad (10)$$

Where ρ_0 and β are constants and ρ is the density of the liquid. Most liquids can be considered to be incompressible, that is, their density is independent of pressure.

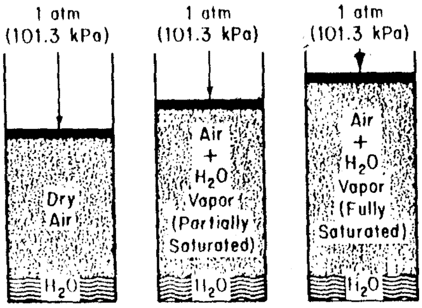
For compounds with like **molecular structures**, such as hydrocarbons of similar molecular weight, called **ideal liquids**, the density of a liquid mixture can be approximated by assuming that the weighted specific volumes are additive:

$$\hat{V}_{\text{average}} = x_1\hat{V}_1 + x_2\hat{V}_2 + \cdots x_n\hat{V}_n = \sum_{i=1}^{n} x_i\hat{V}_i \qquad (11)$$

Where **n** is the number of components in the mixture. For **nonideal liquids** or solids dissolved in liquids, experimental data or estimation techniques described in many of the references, as the specific volumes are not additive.

Saturation

Figure below shows that the **volume** of the **air** plus the **water vapor increases** until the air is **saturated** with water vapor, after which stage the volume remains constant.



Evaporation of water at constant pressure and temperature of 65°C

Assuming that the ideal gas law applies to both air and water vapor with excellent precision, we can say that the following relations hold **at saturation***:*

$$\frac{p_{\text{air}}V}{p_{H_2O}V} = \frac{n_{\text{air}}RT}{n_{H_2O}RT}$$

or

$$\frac{p_{\text{air}}}{p_{H_2O}} = \frac{n_{\text{air}}}{n_{H_2O}} = \frac{p_{\text{air}}}{p_{\text{total}} - p_{\text{air}}}$$

in a volume V at temperature T.

Example 12

What is the minimum number of cubic meters of dry air al 20°C and 100 kpa necessary to evaporate 6.0 kg of ethyl alcohol if the total pressure remains constant al 100 kpa and the temperature remains 20°C? Assume that the air is blown through the alcohol to evaporate it in such a way that the exit pressure of the air alcohol mixture is at 100 kPa. (Given: p^*_{alcohol} at 20°C = 5.93 kPa, mol. wt. ethyl alcohol = 46.07).

Solution

See Figure E13.12. Assume that the process is isothermal.

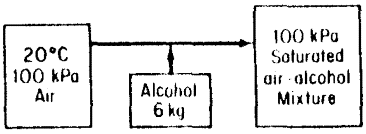


Figure E13.12

Basis: 6 kg of alcohol

$$\frac{p^*_{\text{alcohol}}}{p_{\text{air}}} = \frac{n_{\text{alcohol}}}{n_{\text{air}}}$$

$$p_{\text{air}} = p_{\text{total}} - p^*_{\text{alcohol}} = (100 - 5.93)\ \text{kPa} = 94.07\ \text{kPa}$$

$$\frac{6.0\ \text{kg alcohol}}{} \left| \frac{1\ \text{kg mol alcohol}}{46.07\ \text{kg alcohol}} \right| \frac{94.07\ \text{kg mol air}}{5.93\ \text{kg mol alcohol}} = 2.07\ \text{kg mol air}$$

$$V_{\text{air}} = \frac{2.07\ \text{kg mol air}}{} \left| \frac{8.314\ (\text{kPa})(\text{m}^3)}{(\text{kg mol})(\text{K})} \right| \frac{293\ \text{K}}{100\ \text{kPa}} = 50.3\ \text{m}^3 \text{ at } 20°\text{C and } 100\ \text{kPa}$$

- **Another way** to view this problem is to say that the final volume contains

V m^3 of alcohol at 5.93 kPa and 20°C

V m^3 of air at 94.07 kPa and 20°C

V m^3 of air plus alcohol at 100 kPa and 20°C

Thus, the volume could be calculated from the information about the alcohol

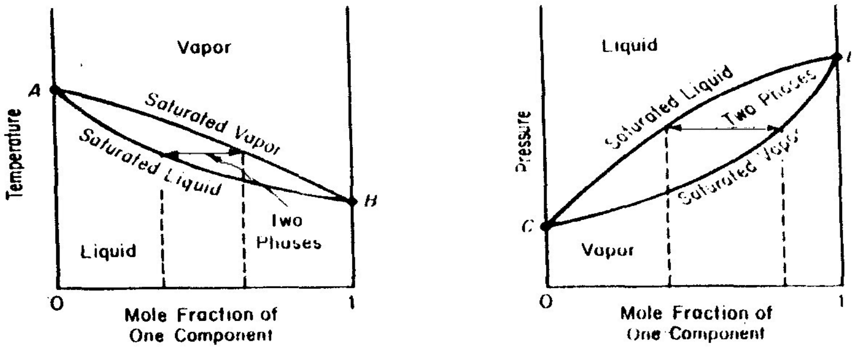
$$V_{\text{alcohol}} = \frac{\left(\frac{6}{46.07}\right) \Big| \; 8.314 \; \Big| \; 293}{\Big| \qquad \Big| \; 5.93} = 53.5\ \text{m}^3 \text{ at } 20°\text{C and } 5.93\ \text{kPa}$$

$$= V_{\text{air}} \text{ at } 94.07\ \text{kPa and } 20°\text{C}$$

$$V_{\text{air}} = \frac{53.5\ \text{m}^3 \; \Big| \; 94.07}{\Big| \; 100} = 50.3\ \text{m}^3 \text{ at } 100\ \text{kPa and } 20°\text{C}$$

Vapor-Liquid Equilibria for Multicomponent Systems

In two-phase **vapor-liquid mixture at equilibrium**, a component in one phase is in equilibrium with the same component in the other phase. The equilibrium relationship depends on the temperature, pressure, and composition of the mixture. **Figure 13.7** illustrates two cases, one at constant pressure and the other at constant temperature.



(a) Constant Pressure (b) Constant Temperature

Figure 13.17 Vapor-liquid equilibrium for a binary mixture. The dashed lines show the equilibrium compositions.

Henry's law. Used primarily for a component whose mole fraction approaches **zero**, such as a dilute gas dissolved in as liquid:

$$p_i = H_i\, x_i \qquad (12)$$

Where p_i is the pressure in the gas phase of the dilute component at equilibrium at some temperature, and H_i is the Henry's law constant. Note that in the limit where $x_i \equiv 0$, $p_i \equiv 0$. Values of H can be found in several handbooks.

Note that

$$y_i = \frac{p_i}{p_{tot}} = \frac{H_i x_i}{p_{tot}}$$

And since Hi, is roughly independent of p_{tot}, the higher the total pressure, the larger x_i.

Raoult's law. Used primarily for a component whose **mole fraction** approaches **unity** or for solutions of components quite similar in chemical nature, such as straight chain hydrocarbons. Let the subscript $\boldsymbol{i}$ denote the component, $\boldsymbol{p_i}$ be the partial pressure of component $\boldsymbol{i}$ in the gas phase, $\boldsymbol{y_i}$ be the gas-phase mole fraction, and $\boldsymbol{x_i}$ be the liquid-phase mole fraction. Then:

Note that in the limit where $x_i \equiv 1$, $p_i \equiv p_i^*$.

$$p_i = p_i^* x_i \tag{13}$$

Note that in the limit where $x_i \equiv 1$, $p_i \equiv p_i^*$.

Equilibrium constant K_i is defined using Eq. (13.13) as follows by assuming that **Dalton's law** applies to the gas phase ($p_i = p_t\, y_i$):

$$K_i = \frac{y_i}{x_i} = \frac{p_i^*}{p_{tot}} \tag{14}$$

Equation (14) gives reasonable estimates of K_i values at **low pressures** for components well below their critical temperatures, but yields values **too large** for components above their **critical temperatures**, at **high pressures**, and/or for polar compounds.

Bubble Point Temperature

Bubble point: The temperature at which a liquid just **starts to vaporize** (**See Figure 13.4**).

- To calculate **the bubble point temperature** (given the total pressure and liquid composition), you can write Eq. (13.14) as $y_i = K_i x_i$ and you know that $\sum y_i = 1$ in the vapor phase.

$$1 = \sum_{i=1}^{n} K_i x_i \tag{15}$$

In which the K's are functions of solely the temperature and $\boldsymbol{n}$ is the number of components. For an ideal solution:

$$p_{tot} = \sum_{i=1}^{n} p_i^* x_i \tag{16}$$

And you might use **Anionie's equation** for p_i^*. Once the bubble point temperature is determined, the vapor composition can be calculated from

$$y_i = \frac{p_i^* x_i}{p_{tot}} \tag{17}$$

Dew Point Temperature

Dew Point: The temperature, at which the vapor just begins to condense at specified pressure, namely temperature values along the vapor pressure curve (**See Figure 13.4**).

- To calculate the **dew point temperature** (given the total pressure and vapor composition), you can write Eq. (13.14) as $x_i = y_i / K_i$ and you know $\sum x_i = 1$ in the liquid phase. Consequently, you want to solve the equation

$$1 = \sum_{i=1}^{n} \frac{y_i}{K_i} \qquad (18)$$

In which the *K*'s are function of temperature as explained for the bubble point temperature calculation. For an ideal solution,

$$1 = p_{tot} \sum_{i=1}^{n} \frac{y_i}{p_i^*} \qquad (19)$$

Example 13

A gas containing nitrogen, benzene, and toluene is in equilibrium with 40 mole% benzene and 60 mole% toluene liquid mixtures at 100 °C and 10 atm. Estimate the gas phase composition (mole fractions) using Raoult's law.

Antoine equation constants	A	B	C	Pressure (mm Hg) Temperature (K)
Benzene	15.9008	2788.51	- 52.36	
Toluene	16.0137	3096.52	- 53.67	

Solution

$$\ln p^* = A - \frac{B}{C+T} \Rightarrow p_B^* = \mathrm{Exp}\left[15.9008 - \frac{2788.51}{-52.36+373}\right] = 1344.9\,\mathrm{mm\,Hg}$$

$$p_T^* = \mathrm{Exp}\left[16.0137 - \frac{3096.52}{-53.67+373}\right] = 553.8\,\mathrm{mm\,Hg}$$

Raoult's law $p_i = p_i^* x_i$, and $p_i = y_i\, p_T$

$$y_B\, p_T = x_B\, p_B^* \Rightarrow y_B = \frac{0.4 \times 1344.9}{(10)(760)} = 0.071$$

$$y_T = \frac{0.6 \times 553.8}{(10)(760)} = 0.044, \quad y_{N_2} = 1 - 0.071 - 0.044 = 0.885$$

Example 14

Air and liquid water are contained at equilibrium in a closed chamber at 75° C and 760 mm Hg. Calculate the molar composition of the gas phase. p^*_{H2O} (75° C) = 289 mm Hg

Solution

Since the gas and liquid are in equilibrium, the air must be saturated with water vapor (if it was not, more water would evaporate), so that **Raoult's law may be applied**:

$$y_{H_2O} = p^*_{H_2O}(75°\mathrm{C})/P$$

$$y_{H_2O} = \frac{289\text{ mm Hg}}{760\text{ mm Hg}} = \boxed{0.380\ \frac{\text{mol } H_2O}{\text{mol}}}$$

$$y_{\text{dry air}} = 1 - y_{H_2O} = \boxed{0.620\ \frac{\text{mol dry air}}{\text{mol}}}$$

Example 15

Use either Raoult's law or Henry's law to solve the following problems.

1. A gas containing 1.00 mole% ethane is in contact with water at 20.0° C and 20.0 atm. Estimate the mole fraction of dissolved ethane.
2. An **equimolar** liquid mixture of benzene (B) and toluene (T) is in equilibrium with its vapor at 30.0° C. What are the system pressure and the composition of the vapor?

(Henry's law constant for ethane in water at 20°C as 2.63 x 10^4 atm/mole fraction)

Solution

1. Hydrocarbons normally are relatively insoluble in water, so that the solution of ethane is probably extremely dilute. Let us therefore apply Henry's law.

$$x_{C_2H_6} = \frac{y_{C_2H_6}P}{H_{C_2H_6}} = \frac{(0.0100)(20.0\text{ atm})}{2.63\times10^4\text{ atm/mole fraction}} = \boxed{7.60\times10^{-6}\ \frac{\text{mol } C_2H_6}{\text{mol}}}$$

2. Since benzene and toluene are structurally similar compounds, we may apply Raoult's law.

$$\ln p^* = A - \frac{B}{C+T}$$

$$= 6.906 - \frac{1211}{T+220.8} \xRightarrow{T = 30°\text{C}} p_B^* = 119\text{ mm Hg}$$

$$= 6.9533 - \frac{1343.9}{T+219.38} \xRightarrow{T = 30°\text{C}} p_T^* = 36.7\text{ mm Hg}$$

$$p_B = x_B p_B^* = (0.500)(119\text{ mm Hg}) = 59.5\text{ mm Hg}$$

$$p_T = x_T p_T^* = (0.500)(36.7\text{ mm Hg}) = 18.35\text{ mm Hg}$$

$$P = p_B + p_T = \boxed{77.9\text{ mm Hg}}$$

$$y_B = p_B/P = \boxed{0.764\text{ mole benzene/mole}}$$

$$y_T = p_T/P = \boxed{0.236\text{ mole toluene/mole}}$$

Gibb's phase rule

The rule can be applied only to systems in **equilibrium**.

$$F = C - P + 2 \qquad (20)$$

Where

F = number of degrees of freedom (i.e., the number of independent properties that have to be specified to determine all the intensive properties of each phase of the system of interest).

C = number of components in the system.

P = number of phases that can exist in the system; a phase is a homogeneous quantity of material such as a gas, a pure liquid, a solution, or a homogeneous solid.

Example 16

Calculate the number of degrees of freedom (how many additional intensive variables must be specified to fix the system) from the phase rule for the following materials at equilibrium:

(a) Pure liquid benzene.
(b) A mixture of ice and water only.
(c) A mixture of liquid benzene, benzene vapor, and helium gas.
(d) A mixture of salt and water designed to achieve a specific vapor pressure.

What variables might be specified in each case? **Solution**

$$F = C - P + 2$$

(a) $C = 1$, $P = 1$, hence $F = 1 - 1 + 2 = 2$. The temperature and pressure might be specified in the range in which benzene remains a liquid.
(b) $C = 1$, $P = 2$, hence $F = 1 - 2 + 2 = 1$. Once either the temperature or the pressure is specified, the other intensive variables are fixed.
(c) $C = 2$, $P = 2$, hence $F = 2 - 2 + 2 = 2$. A pair from temperature, pressure, or mole fraction can be specified.
(d) $C = 2$, $P = 2$, hence $F = 2 - 2 + 2 = 2$. Since a particular pressure is to be achieved, you would adjust the salt concentration and the temperature of the solution.

Note in (a) and (b) it would be unlikely that a vapor phase would not exist in practice, increasing ***P*** by 1 and reducing ***F*** by one.

Problems

1. Calculate the volume in ft^3 of 10 lb mol of an ideal gas at 68°F and 30 psia.
2. A steel cylinder of volume 2 m^3 contains methane gas (CH_4) at 50°C and 250 kPa absolute. How many kilograms of methane are in the cylinder?
3. What is the value of the ideal gas constant R to use if the pressure is to be expressed in atm, the temperature in Kelvin, the volume in cubic feet, and the quantity of material in pound moles?
4. Twenty-two kilograms per hour of CH_4 are flowing in a gas pipeline at 30°C and 920 mm Hg. What is the volumetric flow rate of the CH_4 in m^3 per hour?
5. What is the density of a gas that has a molecular weight of 0.123 kg/kg mol at 300 K and 1000 kPa?
6. What is the specific gravity of CH_4 at 70°F and 2 atm compared to air at S.C.?
7. A gas has the following composition at 120°F and 13.8 psia.

Component	Mol %
N_2	2
CH_4	79
C_2H_6	19

(a) What is the partial pressure of each component?
(b) What is the volume fraction of each component?

8. (a) If the C_2H_6 were removed from the gas in problem 7, what would be the subsequent pressure in the vessel?

   (b) What would be the subsequent partial pressure of the N_2?

9. What is the ideal critical volume? What is the advantage of using V_{ci}?

10. A carbon dioxide fire extinguisher has a volume of 40 L and is to be charged to a pressure of 20 atm at a storage temperature of 20°C. Determine the mass in kilograms of CO_2 at 1 atm.

11. Calculate the pressure of 4 g mol CO_2 contained in a 6.25×10^{-3} m^3 fire extinguisher at 25°C.

12. You measure that 0.00220 lb mol of a certain gas occupies a volume of 0.95 ft^3 at 1 atm and 32°F. If the equation of state for this gas is $pV = nRT(1 + bp)$, where b is a constant, find the volume at 2 atm and 71°F.

13. Calculate the temperature of 2 g mol of a gas using van der Waals' equation with $a = 1.35 * 10^{-6}$ m^6(atm)(g mol^{-2}), $b = 0.0322 * 10^{-3}$ (m^3)(g mol^{-1}) if the pressure is 100 kPa and the volume is 0.0515 m^3.

14. Calculate the pressure of 10 kg mol of ethane in a 4.86 m^3 vessel at 300 K using two equations of state: (a) ideal gas and (b) Soave-Redlich-Kwong. Compare with your answer the observed value of 34.0 atm.

15. One pound mole of a mixture containing 0.400 lb mol of N_2 and 0.600 lb mol C_2H_4 at 50°C occupies a volume of 1.44 ft^3. What is the pressure in the vessel? Compute your answer by Kay's method.

16. Use the Antoine equation to calculate the vapor pressure of ethanol at 50°C, and compare with the experimental value (Experimental $p^* = 219.9$ mm Hg)

17. What does the term "saturated gas" mean?

18. If a container with a volumetric ratio of air to liquid water of 5 is heated to 60°C and equilibrium is reached, will there still be liquid water present? at 125°C?

19. A mixture of air and benzene contains 10 mole% benzene at 43°C and 105 kPa pressure. At what temperature does the first liquid form? What is the liquid?

20. The dew point of water in atmospheric air is 82°F. What is the mole fraction of water vapor in the air if the barometric pressure is 750 mm Hg?

21. Ten pounds of $KClO_3$ is completely decomposed and the oxygen evolved collected over water at 80°F. The barometer reads 29.7 in. Hg. What weight of saturated oxygen is obtained?

22. If a gas is saturated with water vapor, describe the state of the water vapor and the air if it is:

    (a) Heated at constant pressure.

    (b) Cooled at constant pressure.

    (c) Expanded at constant temperature.

    (d) Compressed at constant temperature.

23. Calculate (a) the pressure at the dew point for the following mixture at 100 °F and (b) the liquid composition.

Component	**Mole fraction**	**K values at psia of**		
		190	**200**	**210**
C_2H_6	0.218	3.22	3.07	2.92
C_3H_8	0.665	1.005	0.973	0.92
i-C_4H_{10}	0.1073	0.45	0.43	0.41
n- C_4H_{10}	0.0097	0.315	0.305	0.295
Total	1			

24. Is the critical point a single phase? If not, what phases are present? Repeat for the triple point (for water).

25. A vessel contains air: N_2 (g), O_2 (g), and Ar (g).

(a) How many phases, components, and degrees of freedom are there according to the phase rule?

(b) Repeat for a vessel one-third filled with liquid ethanol and two-thirds filled with N_2 plus ethanol vapor.

Answers:

1. 1883 ft^3
2. 2.98 kg
3. 1.32
4. 28.3 m^3/hr
5. 0.0493 kg/m^3
6. 1.02 (lb CH_4/ft^3 at 70 °F and 2 atm)/ (lb air/ ft^3 at S.C.)
7. N_2, 0.28 psia; CH_4, 10.9 psia; C_2H_6, 2.62 psia
8. (a) 11.12 psia at 2 ft^3 and 120°F; (b) 0.28 psia at 2 ft^3 and 120°F
9. $V_{ci} = R\,T_c/P_c$. It can be used to calculate V_{ri}, which is a parameter on the Nelson and Obert charts.
10. 1.65 kg
11. 14.9 atm
12. $V = 0.60\ ft^3$
13. 314 K
14. (a) 50.7 atm; (b) 34.0 atm
15. 262 atm
16. predicted 220.9 mm Hg
17. The partial pressure of the vapor equals the vapor pressure of the gas. Liquid and vapor are in equilibrium.
18. Yes; yes
19. 21°C; benzene
20. 0.0373
21. 4.00 lb

22. (a) Both gas; (b) some liquid water, residual is gas; (c) both gas; (d) some liquid water, residual is gas.
23. 190 psia; $C_2H_6 = 0.0677$, $C_3H_8 = 0.66$, i-$C_4H_{10} = 0.2415$, n- $C_4H_{10} = 0.0308$.
24. No, gas and liquid in equilibrium. The triple point in the $p - T$ projection in actually a line on the $p - V - T$ surface. The pressure and temperature are fixed but the volume is not fixed.
25. (a) $C = 3$, $P = 1$, $F = 4$; (b) $C = 2$, $P = 2$, $F = 2$