

Example (From Fall 1993 final)

A spherical vessel, 5 m in diameter, is used for storing *n*-butane (C_4H_{10}) at 200°C and 1.0 MPa. Estimate the molar volume and the mass of *n*-butane in the vessel using the following methods.

- (a) The ideal gas law.
- (b) The generalized compressibility chart method.
- (c) Pitzer and Curl method
- (d) The van der Waals equation of state.

$$\text{Volume} = \frac{1}{6} \pi D^3 = \frac{3.14 \times 5^3}{6} = 65.417 \text{ m}^3$$

$$T = 473.14 \text{ K}$$

$$P = 1,000,000 \text{ Pa}$$

$$M = 58 \text{ kg/kmol}$$

$$(a) \ n = \frac{PV}{RT} = \frac{1000000 \times 65.417}{8314 \times 473.15} = 16.63 \text{ kmol}$$

$$\text{Molar volume} = 65.417/16.63 = 3.933 \text{ m}^3/\text{kmol}$$

$$\text{Mass} = 16.63 \times 58 = 965 \text{ kg}$$

(b) To use the generalized compressibility chart, we need to calculate the reduced pressure and temperature and that requires the critical properties of *n*-butane. From Table B-2,

$$T_c = 425.2 \text{ K}$$

$$P_c = 37.5 \text{ atm} = 3800 \text{ kPa}, z_c = 0.274$$

$$T_r = 473.15/425.2 = 1.11$$

$$P_r = 1,000 \text{ kPa}/3800 \text{ kPa} = 0.26$$

From the compressibility chart, $z = 0.93$

$$n = \frac{PV}{zRT} = \frac{1000000 \times 65.417}{0.93 \times 8314 \times 473.15} = 17.88$$

$$\text{Molar volume} = 65.417/17.88 = 3.659 \text{ m}^3/\text{kmol}$$

$$\text{Mass} = 17.88 \times 58 = 1037 \text{ kg}$$

(c) For the Pitzer and Curl method we need to look up the acentricity factor from table C-1 and C-2 on page 392 and 393.

$$\omega = 0.193$$

The values of $z^{(0)}$ and $z^{(1)}$ are obtained from table C-1, at $T_r = 1.11$ and $P_r = 0.26$

$$z^{(0)} = 0.95$$

$$z^{(1)} = 0.002$$

$$z = z^{(0)} + z^{(1)} = 0.95 + 0.002 = 0.952$$

$$n = \frac{PV}{zRT} = \frac{1000000 \times 65.417}{0.952 \times 8314 \times 473.15} = 17.47$$

$$\text{Molar volume} = 65.417/17.47 = 3.745 \text{ m}^3/\text{kmol}$$

$$\text{Mass} = 17.47 \times 58 = 1013 \text{ kg}$$

(d) To use the van der Waal's equation of state we need the values of a and b. These can be calculated from the critical properties.

$$a = \frac{27R^2T_c^2}{64P_c} = \frac{27 \times (8314)^2 \times 425.2^2}{64 \times 3,800,000} = 1,386,000 (\text{m}^3 / \text{kmol})^2$$

$$b = \frac{RT_c}{8P_c} = \frac{8314 \times 425.2}{8 \times 3,800,000} = 0.116 \text{ m}^3 / \text{kmol}$$

The van der Waal's equation can be written as:

$$P = \frac{RT}{v_m - b} - \frac{a}{v_m^2}$$

At the given conditions,

$$1,000,000 = \frac{8314 \times 473.15}{v_m - 0.116} - \frac{1,386,000}{v_m^2}, \text{ or}$$

$$1 = \frac{3.93}{v_m - 0.116} - \frac{1.386}{v_m^2}$$

This equation can be solved by trial and error.

v_m	3.66	3.70	3.68
R.H.S.	1.005	0.995	1.0003

$$\text{Molar volume} = 3.68 \text{ m}^3/\text{kmol}$$

$$\text{Number of moles} = 65.417/3.68 = 17.78$$

$$\text{Mass} = 58 \times 17.78 = 1031 \text{ kg}$$

6.8 Real Gas Mixtures:

Real gas mixtures have properties that are different from the individual constituents. The reasons for this are not difficult to see. The deviations from spherical shape, the intermolecular forces, the volume of molecules etc. are different for different components. The intermolecular attraction between two dissimilar molecules may be very different compared to attraction between molecules of same type.

Basically three methods can be used for correlating the P-V-T properties of real gas mixtures.

1. Pseudo-critical point method
2. Application of Dalton's & Amagat's Laws
3. The mixing Rule method

We will only look at the pseudo critical point method. You can read about the other methods in your book.

6.8.1 The Pseudo-Critical Point Method

In this method we combine the critical properties of individual components to come up with values of T_c , P_c for the mixture as a whole. Then we use the principle of corresponding states. The mixture properties are used to represent the mixture as a fictitious (not real) pure fluid having the same critical properties. The tricky part is in combining the individual component properties to find the mixture properties. Different techniques have been developed by different people. The simplest and also the most commonly used is Kay's method.

Kay's Method (1936) (applicable in 50 - 300 atm range)

The following formulae are used

$$P_{pc} = \sum y_i P_{ci} = y_1 P_{c1} + y_2 P_{c2} + \dots + y_N P_{cN}$$

And

$$T_{pc} = \sum y_i T_{ci} = y_1 T_{c1} + y_2 T_{c2} + \dots + y_N T_{cN}$$

Where,

P_{pc} = the pseudo-critical pressure

T_{pc} = the pseudo-critical temperature

y_i = mole fraction of the i^{th} component

Once the pseudo-critical pressure and pseudo-critical temperature have been calculated, the mixture compressibility can be read from generalized compressibility

charts. If the Pitzer-Curl acentricity factor method is to be used, instead of the generalized compressibility charts, then a molar average acentricity factor is calculated in the same way as pseudo-critical pressure and pseudo-critical temperature.

$$\omega_{pc} = \sum y_i \omega_i = y_1 \omega_1 + y_2 \omega_2 + \dots + y_N \omega_N$$

And then the value of mixture compressibility is calculated using,

$$Z_m = Z^{(0)}(T_{rpc}, P_{rpc}) + w_{pc} Z^{(1)}(T_{rpc}, P_{rpc})$$

Example Problem (Fall 2000 Final):

A gas storage tank is filled with a gas mixture containing 802 kg methane, 1,100.25 kg CO₂, and 751.75 kg ethane. The temperature and pressure in the tank are 25 °C and 7.25 MPa respectively. The critical properties of these components are listed below.

Component	Molar Mass kg/kmol	T _c K	P _c atm	ω
Methane	16.04	190.6	45.4	0.008
CO ₂	44.01	304.2	72.8	0.225
Ethane	30.07	305.4	48.2	0.098

Calculate the volume of the tank using:

- The ideal gas law.
- The pseudo critical point method with the generalized compressibility chart.
- The Pitzer and Curl Method

Solution:

(a) Moles of methane = 802 kg/(16.04 kg/kmol) = **50 kmol**

Moles of CO₂ = 1100.25 kg/(44.01 kg/kmol) = **25 kmol**

Moles of ethane = 751.75 kg/(30.07 kg/kmol) = **25 kmol**

→ Total number of moles = **100 kmol**

Using the ideal gas law

$$v = \frac{nRT}{P} = \frac{100 \text{ kmol} * 8314 \text{ J / kmol K} * 298.15 \text{ K}}{7,250,000 \text{ Pa}} = 34.2 \text{ m}^3$$

(b) The first step is the calculation of pseudo-critical properties. Mole fractions of individual components are obtained by dividing their number of moles by the total number of moles.

Component	x _i	T _{ci} K	x _i T _{ci}	P _{ci} atm	x _i P _{ci}	ω _i	x _i ω _i
CH ₄	.5	190.6	95.3	45.4	22.7	0.008	0.004
CO ₂	.25	304.2	76.05	72.8	18.2	0.225	0.056
C ₂ H ₆	.25	305.4	76.35	48.2	12.1	0.098	0.025
Summations			247.7		53		0.085

$$T_{pc} = \mathbf{247.7\ K}; \quad P_{pc} = \mathbf{53\ atm}; \quad \omega_{pc} = \mathbf{0.085}$$

$$T_r = 298.15/247.15 = \mathbf{1.2}$$

$$P_r = 7,250,000/(53 * 101325) = \mathbf{1.34}$$

$$Z \text{ (from chart)} = \mathbf{0.72}$$

$$v = \frac{nZRT}{P} = \frac{100\ kmol * 0.72 * 8314\ J / kmol\ K * 298.15\ K}{7,250,000\ Pa} = 24.6\ m^3$$

(c) Pitzer and Curl method

At $T_r = 1.2$ and $P_r = 1.34$, values of $Z^{(0)}$ and $Z^{(1)}$ are: $Z^{(0)} = \mathbf{0.85}$

$$Z^{(1)} = \mathbf{0.1}$$

$$\rightarrow Z = 0.85 + 0.085 * 0.1 = \mathbf{0.86}$$

$$v = \frac{nZRT}{P} = \frac{100\ kmol * 0.86 * 8314\ J / kmol\ K * 298.15\ K}{7,250,000\ Pa} = 29.4\ m^3$$