

Q1. Carbon dioxide gas (1.00 mol) at 373 K occupies 536 mL at 50.0 atmosphere pressure. What is the calculated value of the pressure using

(i) Ideal gas equation

(ii) Van der Waals equation?

[Van der Waals constants for carbon dioxide:  $a = 3.61 \text{ L}^2 \text{ atm mol}^{-2}$ ;  $b = 0.0428 \text{ L mol}^{-1}$ ,  
 $R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$ .]

Calculate the % deviation of each value from that observed.

(i) Using the Ideal Gas Equation

$$V = 0.536 \text{ L}$$

$$n = 1.00 \text{ mol}$$

$$T = 373 \text{ K}$$

$$PV = nRT$$

$$P = \frac{nRT}{V} = 1.00 \times 0.0821 \times 373 / 0.536$$

$$= 57.1 \text{ atm}$$

$$\text{Actual pressure} = 50.0 \text{ atm}$$

$$\% \text{ deviation} = (7.1 / 50) \times 100 = 14.2 \%$$

(ii) Using Van der Waals equation.

$$(P + an^2/V^2)(V - nb) = nRT$$

$$(P + 3.61 \times (1.00/0.536)^2)(0.536 - 1.00 \times 0.0428) = 1.00 \times 0.0821 \times 373$$

$$(P + 12.57)(0.493) = 30.62$$

$$P + 12.57 = 62.12$$

$$P = 49.6 \text{ atm}$$

$$\% \text{ deviation} = (0.4 / 50) \times 100 = 0.8\%$$

Q2. The values of  $T_c$  and  $P_c$  for  $N_2$  are 126K and 34 atm; for  $C_2H_6$  they are 305 and 48 atm respectively,

- (i) Which gas has the smaller van der Waals constant “b” ?
- (ii) Which has the smaller “a” value ?
- (iii) Which has the larger “ $V_c$ ” value ?
- (iv) Which should show the most nearly ideal behaviour at  $25^0C$  and 10 atm ?

(i)  $N_2$

(ii)  $N_2$

$$\bar{V}_c = 3b \quad P_c = \frac{a}{27b^2} \quad T_c = \frac{8a}{27bR}$$

(iii)  $C_2H_6$

(iv)  $N_2$

**Q2. Predict which of the substances: NH<sub>3</sub>, N<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, Cl<sub>2</sub>, CCl<sub>4</sub> has**

- (i) the smallest van der Waals "a" constant
- (ii) the largest "b" constant.

(i) N<sub>2</sub>

The value of the Van der Waals constant, a, of a given gaseous substance depends on the strength of attractions between its component molecules. Molecules experiencing the weakest attractive forces will have the smallest a constant while those with the strongest attractive forces will have the largest a values.

Of the molecules NH<sub>3</sub>, N<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, Cl<sub>2</sub>, CCl<sub>4</sub>, the two elements nitrogen and chlorine alone have non-polar bonds between their component atoms. This results in weaker attractions between molecules, so N<sub>2</sub> and Cl<sub>2</sub> will have the smallest a values. The remaining molecules all have polar bonds between their component atoms and in the case of NH<sub>3</sub>, hydrogen bonds between molecules. These are factors that lead to increased a constants. As the N<sub>2</sub> molecule is smaller than the Cl<sub>2</sub> molecule and therefore has less electrons present, the attractive forces between N<sub>2</sub> molecules will be weaker than those between Cl<sub>2</sub> molecules and N<sub>2</sub> will have the smallest a constant.

(ii) CCl<sub>4</sub>

The value of the Van der Waals b constant is merely the actual volume of a mole of the molecules and this can be deduced by comparing the volumes of the molecules in the list. Small molecular volume results in small b values and a large molecular volume corresponds to a large b constant. From the compound in the list, CCl<sub>4</sub> is the largest and so it will have the greatest b constant.

Q3. (i) Using Van der Waals equation, calculate the temperature of 20.0 mole of helium in a 10.0 litre cylinder at 120 atmosphere pressure. [vdw constants for helium:  $a = 0.0341 \text{ L}^2 \text{ mol}^{-2}$ ;  $b = 0.0237 \text{ L mol}^{-1}$ ,  $R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$ ]  
(ii) Compare this value with the temperature calculated from the ideal gas equation.

(i) Using the Van der Waals equation:

Substituting in

$$(P + an^2/V^2)(V - nb) = nRT,$$

$$P = 120 \text{ atm}$$

$$n = 20.0 \text{ mol}$$

$$V = 10.0 \text{ L}$$

$$(120 + 0.0341 \times (20.0/10.0)^2)(10.0 - 20.0 \times 0.0237) = 20.0 \times 0.0821 \times T$$

$$(120 + 0.1364)(10.0 - 0.5) = 1.64 \times T$$

$$T = 696 \text{ K}$$

(ii) Using the Ideal Gas Equation:

Substituting in

$$PV = nRT,$$

$$120 \times 10.0 = 20.0 \times 0.0821 \times T$$

$$T = 1200/1.642$$

$$= 731 \text{ K}$$

# L3

## A REDUCED EQUATION OF STATE

$$\left(P + \frac{a}{V^2}\right)(\bar{V} - b) = RT \quad \bar{V}_c = 3b \quad P_c = \frac{a}{27b^2} \quad T_c = \frac{8a}{27bR}$$



$$\left(P_R + \frac{3}{\bar{V}_R^2}\right)\left(\bar{V}_R - \frac{1}{3}\right) = \frac{8}{3}T_R \quad P_R = \frac{P}{P_c} \quad \bar{V}_R = \frac{\bar{V}}{\bar{V}_c} \quad T_R = \frac{T}{T_c}$$

universal equation for all gases

reduced quantities

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The law of corresponding states

rewrite Van der waals eqn so that does not contain any const. (a, b).

$$\Pi = \frac{P}{P_c}, \quad \theta = \frac{T_c}{T}, \quad \phi = \frac{\bar{V}_m}{\bar{V}_c}$$

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

$$\Rightarrow \left(\Pi P_c + \frac{a}{\phi^2 \bar{V}_c^2}\right)(\phi \bar{V}_c - b) = R \theta T_c$$

We know,

$$P_c = \frac{a}{27b^2}, \quad b = 3b, \quad T_c = \frac{8a}{27bR}$$

$$\Rightarrow \left(\Pi + \frac{a}{27b^2} + \frac{a}{\phi^2 (3b)^2}\right)(\phi \bar{V}_c - b) = R \theta \left(\frac{8a}{27b}\right)$$

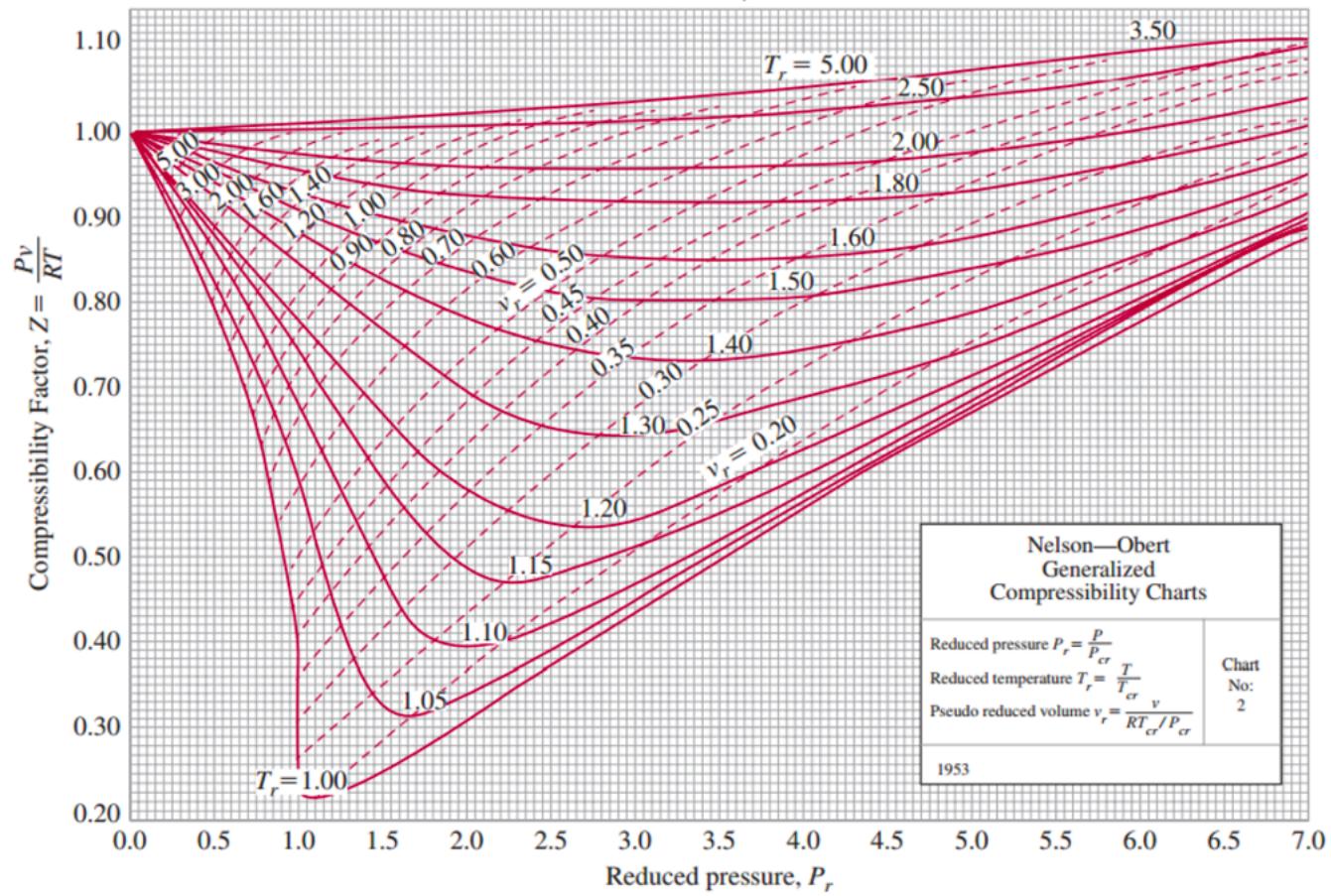
$$\Rightarrow \left(\frac{\Pi}{27} + \frac{1}{9\phi^2}\right)(3\phi - 1) = \theta \frac{8}{27}$$

$$\Rightarrow \left(\Pi + 3\phi^2\right)(3\phi - 1) = 8\theta$$

Reduced eqn of state.

OR TWO GASES DON'T HAVE SAME REDUCED PRESSURE AND REDUCED TEMPERATURE THEY WILL HAVE SAME REDUCED VOLUME

(b)  $0 < P_r < 7$



Q4. A closed, rigid tank filled with water vapor, initially at 20 MPa, 520°C, is cooled until its temperature reaches 400°C.

Using the compressibility chart, determine

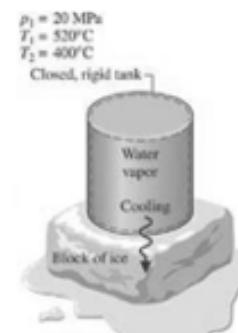
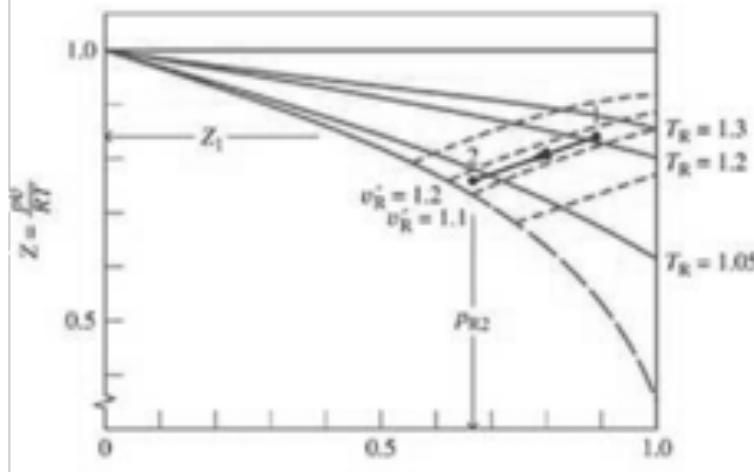
(a) the specific volume of the water vapor in m<sup>3</sup>/kg at the initial state.

(b) the pressure in MPa at the final state.

[ R = 8314 N. m/kmol. K ]

Look up the critical temperature  $T_c$  and critical pressure  $p_c$  of water:

| Substance | Chemical Formula | M (kg/kmol) | $T_c$ (K) | $p_c$ (bar) | $Z_c = \frac{\mu_c v_c}{R T_c}$ |
|-----------|------------------|-------------|-----------|-------------|---------------------------------|
| Water     | H <sub>2</sub> O | 18.02       | 647.3     | 220.9       | 0.233                           |



- Q4. A closed, rigid tank filled with water vapor, initially at 20 MPa, 520°C, is cooled until its temperature reaches 400°C. Using the compressibility chart, determine
- the specific volume of the water vapor in m<sup>3</sup>/kg at the initial state.
  - the pressure in MPa at the final state.
- [ R = 8314 N. m/kmol. K ]

$$p_{R1} = 20/22.09 = 0.91, T_{R1} = (520 + 273.15)/647.3 = 1.23$$

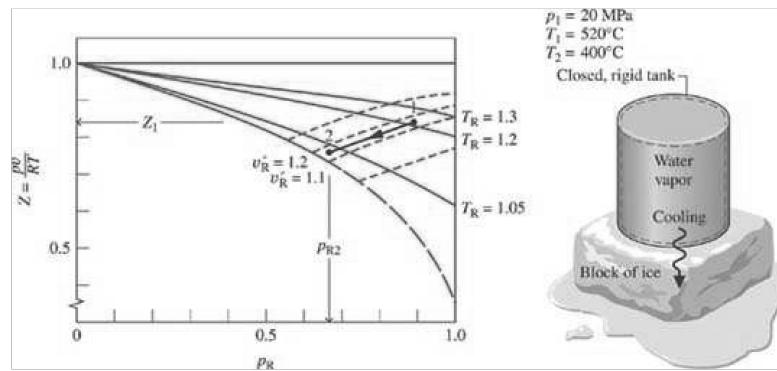


Figure E3.4-2 Generalized Compressibility Chart

With these values for the reduced pressure and reduced temperature, the value of Z from Figure E3.4-2 is approximately 0.83

$$Z = \frac{p\bar{v}}{\bar{R}T} = \frac{pMv}{\bar{R}T} \Rightarrow v_1 = Z_1 \frac{\bar{R}T_1}{Mp_1}$$

$$\therefore v_1 = 0.83 \left( \frac{8314 \text{ N} \cdot \text{m}/\text{kmol} \cdot \text{K}}{18.02 \text{ kg}/\text{kmol}} \right) \left( \frac{793.15 \text{ K}}{20 \times 10^6 \text{ N}/\text{m}^2} \right) = 0.0152 \text{ m}^3/\text{kg}$$

Look up the critical temperature  $T_c$  and critical pressure  $p_c$  of water:

| Substance | Chemical Formula | $M$ (kg/kmol) | $T_c$ (K) | $p_c$ (bar) | $Z_c = \frac{\mu_c v_c}{R T_c}$ |
|-----------|------------------|---------------|-----------|-------------|---------------------------------|
| Water     | H <sub>2</sub> O | 18.02         | 647.3     | 220.9       | 0.233                           |

Since both mass and volume remain constant, the water vapor cools at constant specific volume and thus at reduced specific volume

$$v'_R = \frac{vp_c}{RT_c} = \frac{(0.0152 \text{ m}^3/\text{kg})(22.09 \times 10^6 \text{ N}/\text{m}^2)}{\left( \frac{8314 \text{ N} \cdot \text{m}}{18.02 \text{ kg} \cdot \text{K}} \right)(647.3 \text{ K})} = 1.12$$

The reduced temperature at the final state is  $T_{R2} = (400 + 273.15)/647.3 = 1.04$

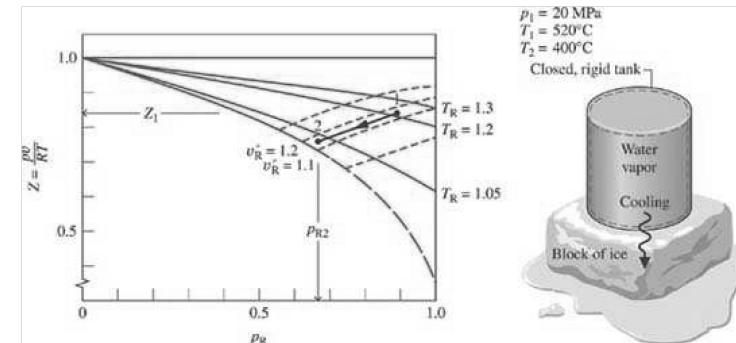


Figure E3.4-2 Generalized Compressibility Chart

Locating the point on the compressibility chart where  $v'_R = 1.12$  and  $T_R = 1.04$ , the corresponding value for  $p_{R2}$  is about 0.69. The final pressure is then

$$p_2 = p_c(p_{R2}) = (22.09 \text{ MPa})(0.69) = 15.24 \text{ MPa}$$

## L2: Home Work: Derive the following

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

$$= \frac{3\bar{V}_R}{3\bar{V}_R - 1} - \frac{9}{8\bar{V}_R T_R}$$

for vdW equation of state

Derive "Z" as a function of any Two variables (Try)....

$$\frac{P_c \bar{V}_c}{RT_c} = \frac{1}{R} \left( \frac{a}{27b^2} \right) (3b) \left( \frac{27bR}{8a} \right) = 0.375!$$

there is an apparent correspondence between different "real" gases that is entirely independent of the van der Waals equation of state

Lecture 2, Slide 13

$$Z = \frac{\bar{V}}{RT}$$

$$P_R = \frac{P}{P_c}, \quad \bar{V}_R = \frac{\bar{V}}{V_c}, \quad T_R = \frac{T}{T_c}$$

$$\therefore Z = \frac{(P_R P_c) \times (\bar{V}_R \bar{V}_c)}{R \cdot (T_R T_c)}$$

$$= \frac{P_R \bar{V}_R \times (P_c \bar{V}_c)}{T_R \cdot R T_c}$$

$$= \frac{P_R \bar{V}_R \times \left(\frac{3}{8}\right)}{P_R} \xrightarrow{\text{vdw}} \textcircled{1}$$

NOTE:  $\frac{3}{8} = \frac{3}{\bar{V}_R^2}$

$$\Rightarrow \left( P_R + \frac{3}{\bar{V}_R^2} \right) \left( \bar{V}_R - \frac{1}{3} \right) = \frac{8}{3} T_R$$

$$\Rightarrow \left( P_R + \frac{3}{\bar{V}_R^2} \right) (3\bar{V}_R - 1) = 8 T_R$$

$$\therefore P_R = \frac{8 T_R}{(3\bar{V}_R - 1)} - \frac{3}{\bar{V}_R^2}$$

$$\textcircled{1} Z = \left[ \frac{8 T_R}{(3\bar{V}_R - 1)} - \frac{3}{\bar{V}_R^2} \right] \times \frac{\bar{V}_R \times 3}{T_R \cdot 8}$$

$$Z = \left[ \frac{3\bar{V}_R}{(3\bar{V}_R - 1)} - \frac{9}{8 T_R \bar{V}_R} \right]$$

## L3

Through manipulation of the two virial expansions, one can also show that  $\rightarrow B_{2V}(T) = RTB_{2P}(T)$

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Prove  $B_{2V}(T) = RTB_{2P}(T)$

$\frac{PV}{RT} = 1 + \frac{B_{2V}(T)}{V} + \frac{B_{3V}(T)}{V^2} + \dots \quad \text{--- (1)}$

$\frac{PV}{RT} = 1 + B_{2P}(T)P + B_{3P}(T)P^2 + \dots \quad \text{--- (2)}$

~~From eqn (1)~~  
 $P = \frac{RT}{V} \left( 1 + \frac{B_{2V}(T)}{P} + \frac{B_{3V}(T)}{P^2} + \dots \right) \quad \text{--- (3)}$

~~Substitute (3) into (2)~~  
 $\frac{PV}{RT} = 1 + B_{2P}(T) \left[ \frac{RT}{V} \left( 1 + \frac{B_{2V}(T)}{P} + \frac{B_{3V}(T)}{P^2} + \dots \right) \right] + B_{3P}(T) \left[ \frac{RT}{V} \left( 1 + \frac{B_{2V}(T)}{P} + \frac{B_{3V}(T)}{P^2} + \dots \right) \right]^2 \quad \text{--- (4)}$

equate (1) & (4)

~~$B_{2P}(T)$~~   $B_{2V}(T) = RTB_{2P}(T)$

$B_{3V}(T) = ?$



# Next: Introduction to thermodynamics