

## Chapter 1- New Exercises and Solutions.

**E1.2(c)** A perfect gas undergoes isothermal compression, which reduces its volume by  $3.08 \text{ dm}^3$ . The final pressure and volume of the gas are  $6.42 \text{ bar}$  and  $5.38 \text{ dm}^3$ , respectively. Calculate the original pressure of the gas in (a) bar, (b) atm.

**E1.2(c)** Boyle's law [1.6] in the form  $p_f V_f = p_i V_i$  can be solved for either initial or final pressure, hence

$$p_i = \frac{V_f}{V_i} \times p_f$$

$$V_f = 5.38 \text{ dm}^3, \quad V_i = 5.38 \text{ dm}^3 + 3.08 \text{ dm}^3 = 8.46 \text{ dm}^3, \quad p_f = 6.42 \text{ bar}$$

Therefore,

$$\text{(a)} \quad p_i = \left( \frac{5.38 \text{ dm}^3}{8.46 \text{ dm}^3} \right) \times (6.42 \text{ bar}) = \boxed{4.08 \text{ bar}}$$

$$\text{(b)} \quad \text{Since } 1 \text{ atm} = 1.013 \text{ bar}, \quad p_i = (4.08 \text{ bar}) \times \left( \frac{1 \text{ atm}}{1.013 \text{ bar}} \right) = \boxed{4.03 \text{ atm}}$$

**E1.3(c)** A car tyre (i.e. an automobile tire) was inflated to a pressure of  $30 \text{ lb in}^{-2}$  ( $1.00 \text{ atm} = 14.7 \text{ lb in}^{-2}$ ) on a winter's day when the temperature was  $0^\circ\text{F}$ . What pressure will be found, assuming no leaks have occurred and that the volume is constant, on a subsequent hot summer's day when the temperature is  $95^\circ\text{F}$ ? What complications should be taken into account in practice?

**E1.3(c)** The perfect gas law,  $pV = nRT$  [1.8], can be rearranged to  $\frac{p}{T} = \frac{nR}{V} = \text{constant}$ , if  $n$  and  $V$  are

constant. Hence,  $\frac{p_f}{T_f} = \frac{p_i}{T_i}$  or, solving for  $p_f$ ,  $p_f = \frac{T_f}{T_i} \times p_i$

Internal pressure = pump pressure + atmospheric pressure

$$p_i = 30 \text{ lb in}^{-2} + 14.7 \text{ lb in}^{-2} = 44.7 \text{ lb in}^{-2}, \quad T_i = 255 \text{ K}(0^\circ\text{F}), \quad T_f = 308 \text{ K}(95^\circ\text{F})$$

$$p_f = \frac{308 \text{ K}}{255 \text{ K}} \times 44.7 \text{ lb in}^{-2} = 54.0 \text{ lb in}^{-2}$$

$$\text{Therefore, } p(\text{pump}) = 54.0 \text{ lb in}^{-2} - 14.7 \text{ lb in}^{-2} = \boxed{39 \text{ lb in}^{-2}}$$

Complications are those factors that destroy the constancy of  $V$  or  $n$ , such as the change in volume of the tyre, the change in rigidity of the material from which it is made, and loss of pressure by leaks and diffusion.

**E1.5(c)** What pressure difference must be generated along a vertical single stage water pump tube to extract water from a well  $5.0 \text{ m}$  deep?

**E1.5(c)** Identifying  $p_{\text{ex}}$  in the equation  $p = p_{\text{ex}} + \rho gh$  [1.3] as the pressure at the top of the tube and  $p$  as the atmospheric pressure on the liquid, the pressure difference is

$$p - p_{\text{ex}} = \rho gh = (1.0 \times 10^3 \text{ kg m}^{-3}) \times (9.81 \text{ m s}^{-2}) \times (5.0 \text{ m})$$

$$= \boxed{5.0 \times 10^4 \text{ Pa}} (= 0.50 \text{ atm})$$

**E1.6(c)** A manometer consists of a U-shaped tube containing a liquid. One side is connected to the apparatus and the other is open to the atmosphere. The pressure inside the apparatus is then determined from the difference in heights of the liquid. Suppose the liquid is an oil with density  $0.865 \text{ g cm}^{-3}$ , the external pressure is 750 Torr, and the open side is 15.0 cm lower than the side connected to the apparatus. What is the pressure in the apparatus?

**E1.6(c)** The pressure in the apparatus is given by

$$p = p_{\text{atm}} + \rho gh [1.3]$$

$$p_{\text{atm}} = 750 \text{ Torr} \times \left( \frac{1 \text{ atm}}{760 \text{ Torr}} \right) \times \left( \frac{1.013 \times 10^5 \text{ Pa}}{1 \text{ atm}} \right) = 0.9997 \times 10^5 \text{ Pa}$$

$$\rho gh = 0.865 \text{ g cm}^{-3} \times \left( \frac{1 \text{ kg}}{10^3 \text{ g}} \right) \times \left( \frac{10^6 \text{ cm}^3}{\text{m}^3} \right) \times 9.806 \text{ m s}^{-2} \times 0.15 \text{ m} = 1272 \text{ Pa}$$

$$p = 0.9997 \times 10^5 \text{ Pa} + 1.272 \times 10^3 \text{ Pa} = 1.012 \times 10^5 \text{ Pa} = \boxed{101 \text{ kPa}}$$

**E1.8(c)** At  $0.000^\circ\text{C}$  and 1.000 atm, the mass density of the vapour of a hydrocarbon is  $1.97 \text{ kg m}^{-3}$ . What is the molecular formula of the hydrocarbon under these conditions? What is the hydrocarbon?

**E1.8(c)** Since  $p < 1 \text{ atm}$ , the approximation that the vapour is a perfect gas is adequate. Then (as in Exercise 1.7(b)),

$$pV = nRT = \frac{m}{M} RT. \text{ Upon rearrangement,}$$

$$M = \rho \left( \frac{RT}{p} \right) = (1.97 \text{ kg m}^{-3}) \times \frac{(8.314 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1}) \times (273 \text{ K})}{1.013 \times 10^5 \text{ Pa}} = 0.0441 \text{ kg mol}^{-1} = \boxed{44.1 \text{ g mol}^{-1}}$$

The formula of the vapour is then  $\boxed{\text{C}_3\text{H}_8}$ , which is one of the propanes.

**E1.9(c)** Calculate the mass of water vapour present in a house of volume  $1000 \text{ m}^3$  that contains air at  $22^\circ\text{C}$  on a day when the relative humidity is 48 per cent indoors.

**E1.9(c)** The partial pressure of the water vapour in the house is:  $p_{\text{H}_2\text{O}} = (0.48) \times (19.827 \text{ Torr}) = 9.5 \text{ Torr}$

Assuming that the perfect gas equation [1.8] applies, with  $n = \frac{m}{M}$ ,  $pV = \frac{m}{M}RT$  or

$$m = \frac{pVM}{RT} = \frac{(9.5 \text{ Torr}) \times \left(\frac{1 \text{ atm}}{760 \text{ Torr}}\right) \times (1000 \text{ m}^3) \times \left(\frac{10^3 \text{ dm}^3}{\text{m}^3}\right) \times (18.02 \text{ g mol}^{-1})}{(0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (295 \text{ K})}$$

$$= 9.3 \times 10^3 \text{ g} = \boxed{9.3 \text{ kg}}$$

**E1.12(c)** For dry air at 1.0000 atm pressure, the densities at  $-50^\circ\text{C}$ ,  $0^\circ\text{C}$ , and  $69^\circ\text{C}$  are  $1.5826 \text{ g dm}^{-3}$ ,  $1.2929 \text{ g dm}^{-3}$ , and  $1.0322 \text{ g dm}^{-3}$ , respectively. From these data, and assuming that air obeys Charles's law, determine a value for the absolute zero of temperature in degrees Celsius.

**E1.12(c)** The easiest way to solve this exercise is to assume a sample of mass 1.000 g, then calculate the volume at each temperature, plot the volume against the Celsius temperature, and extrapolate to  $V = 0$ .

Draw up the following table

$\theta/^\circ\text{C}$	$\rho/(\text{g dm}^{-3})$	$V/(\text{dm}^3 \text{ g}^{-1})$
-50	1.5826	0.6319
0	1.2929	0.7734
69	1.0322	0.9688

Linear regression of the  $V$  versus  $\theta$  data gives a value for absolute zero close to  $-273^\circ\text{C}$ . Alternatively, one could use an equation for  $V$  as a linear function of  $\theta$ , which is Charles's law, and solve for the value of absolute zero.  $V = V_0 \times (1 + \alpha\theta)$

At absolute zero,  $V = 0$ , then  $\theta(\text{abs.zero}) = -\frac{1}{\alpha}$ . The value of  $\alpha$  can be obtained from any one of the data points (except  $\theta = 0$ ) as follows.

From  $V = V_0 \times (1 + \alpha\theta)$ ,

$$\alpha = \frac{\left(\frac{V}{V_0} - 1\right)}{\theta} = \frac{\left(\frac{0.9688}{0.7734}\right) - 1}{100^\circ\text{C}} = 0.003661(^\circ\text{C})^{-1}$$

$$-\frac{1}{\alpha} = -\frac{1}{0.003661(^\circ\text{C})^{-1}} = \boxed{-273^\circ\text{C}}$$

which is the same to within experimental error as the value obtained graphically.

**E1.13(c)** Calculate the pressure exerted by 1.0 mol  $\text{C}_6\text{H}_6$  behaving as (a) a perfect gas, (b) a van der Waals gas when it is confined under the following conditions: (i) at 373.15 K in  $22.414 \text{ dm}^3$ , (ii) at 1000 K in  $300 \text{ cm}^3$ . Use the data in Table 1.6.

**E1.13(c)** (a)  $p = \frac{nRT}{V}$  [1.8]

$$n = 1.0 \text{ mol}, \quad T = 373.15 \text{ K (i) or } 1000 \text{ K (ii)}$$

$$V = 22.414 \text{ dm}^3 \text{ (i) or } 300 \text{ cm}^3 \text{ (ii)}$$

$$(i) \quad p = \frac{(1.0 \text{ mol}) \times (8.206 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (373.15 \text{ K})}{22.414 \text{ dm}^3} = \boxed{1.37 \text{ atm}}$$

$$(ii) \quad p = \frac{(1.0 \text{ mol}) \times (8.206 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (1000 \text{ K})}{0.300 \text{ dm}^3} = \boxed{2.73 \times 10^2 \text{ atm}}$$

$$(b) \quad p = \frac{nRT}{V - nb} - \frac{an^2}{V^2} \quad [1.21a]$$

From Table 1.5,  $a = 5.507 \text{ dm}^6 \text{ atm mol}^{-2}$  and  $b = 6.51 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}$ . Therefore,

$$(i) \quad \frac{nRT}{V - nb} = \frac{(1.0 \text{ mol}) \times (8.206 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (373.15 \text{ K})}{[22.414 - (1.0) \times (6.51 \times 10^{-2})] \text{ dm}^3} = 1.37 \text{ atm}$$

$$\frac{an^2}{V^2} = \frac{(5.507 \text{ dm}^6 \text{ atm mol}^{-2}) \times (1.0 \text{ mol})^2}{(22.414 \text{ dm}^3)^2} = 1.11 \times 10^{-2} \text{ atm}$$

$$\text{and } p = 1.37 \text{ atm} - 1.11 \times 10^{-2} \text{ atm} = \boxed{1.36 \text{ atm}}$$

$$(ii) \quad \frac{nRT}{V - nb} = \frac{(1.0 \text{ mol}) \times (8.206 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (1000 \text{ K})}{(0.300 - 0.0651) \text{ dm}^3}$$

$$= 3.49 \times 10^2 \text{ atm}$$

$$\frac{an^2}{V^2} = \frac{(5.507 \text{ dm}^6 \text{ atm mol}^{-2}) \times (1.0 \text{ mol})^2}{(0.300 \text{ dm}^3)^2} = 1.83 \times 10^2 \text{ atm}$$

$$\text{and } p = 3.49 \times 10^2 \text{ atm} - 1.83 \times 10^2 \text{ atm} = \boxed{1.65 \times 10^2 \text{ atm}}$$

**Comment.** It is instructive to calculate the percentage deviation from perfect gas behaviour for (i) and (ii).

$$(i) \quad \frac{1.36 - 1.37}{1.37} \times 100\% = -0.7\%$$

$$(ii) \quad \frac{(1.65 \times 10^2) - (2.73 \times 10^2)}{2.73 \times 10^2} \times 100\% = -39.5\%$$

Deviations from perfect gas behaviour are not observed at  $p \approx 1 \text{ atm}$  except with very precise apparatus.

**E1.16(c)** Cylinders of compressed gas are typically filled to a pressure of 200 bar. For nitrogen, what would be the molar volume at this pressure and 25°C based on (a) the perfect gas equation, (b) the van der Waals equation. For nitrogen,  $a = 1.39 \text{ dm}^6 \text{ atm mol}^{-2}$ ,  $b = 0.0391 \text{ dm}^3 \text{ mol}^{-1}$ .

$$\begin{aligned} \text{E1.16(c) (a)} \quad V_m^\circ &= \frac{RT}{p} = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})}{(200 \text{ bar}) \times (10^5 \text{ Pa bar}^{-1})} \\ &= 1.24 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1} = \boxed{0.124 \text{ dm}^3 \text{ mol}^{-1}} \end{aligned}$$

(b) The van der Waals equation is a cubic equation in  $V_m$ . The most direct way of obtaining the molar volume would be to solve the cubic analytically. However, this approach is cumbersome, so we proceed as in Example 1.6. The van der Waals equation is rearranged to the cubic form

$$V_m^3 - \left(b + \frac{RT}{p}\right)V_m^2 + \left(\frac{a}{p}\right)V_m - \frac{ab}{p} = 0 \text{ or } x^3 - \left(b + \frac{RT}{p}\right)x^2 + \left(\frac{a}{p}\right)x - \frac{ab}{p} = 0$$

with  $x = V_m/(\text{dm}^3 \text{ mol}^{-1})$ .

The coefficients in the equation are evaluated as

$$b + \frac{RT}{p} = (3.91 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}) + \frac{(8.206 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}) \times (298.15 \text{ K})}{(200 \text{ bar}) \times (1.013 \text{ atm bar}^{-1})}$$

$$= (3.91 \times 10^{-2} + 0.1208) \text{ dm}^3 \text{ mol}^{-1} = 0.1599 \text{ dm}^3 \text{ mol}^{-1}$$

$$\frac{a}{p} = \frac{1.39 \text{ dm}^6 \text{ atm mol}^{-2}}{(200 \text{ bar}) \times (1.013 \text{ atm bar}^{-1})} = 6.86 \times 10^{-3} (\text{dm}^3 \text{ mol}^{-1})^2$$

$$\frac{ab}{p} = \frac{(1.39 \text{ dm}^6 \text{ atm mol}^{-2}) \times (3.91 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1})}{(200 \text{ bar}) \times (1.013 \text{ atm bar}^{-1})} = 2.68 \times 10^{-4} (\text{dm}^3 \text{ mol}^{-1})^3$$

Thus, the equation to be solved is  $x^3 - 0.1599x^2 + (6.86 \times 10^{-3})x - (2.68 \times 10^{-4}) = 0$ .

Calculators and computer software for the solution of polynomials are readily available. In this case we find

$$x = 0.122 \quad \text{or} \quad V_m = \boxed{0.122 \text{ dm}^3 \text{ mol}^{-1}}$$

The difference is about 2 percent.

**E1.18(c)** A vessel of volume  $24.4 \text{ dm}^3$  contains  $1.0 \text{ mol H}_2$  and  $2.5 \text{ mol N}_2$  at  $298.15 \text{ K}$ . Calculate (a) the mole fractions of each component, (b) their partial pressures, and (c) their total pressure.

$$\text{E1.18(c)} \quad n = n(\text{H}_2) + n(\text{N}_2) = 1.0 \text{ mol} + 2.5 \text{ mol} = 3.5 \text{ mol} \quad x_j = \frac{n_j}{n} [1.14]$$

$$\text{(a)} \quad x(\text{H}_2) = \frac{1.0 \text{ mol}}{3.5 \text{ mol}} = \boxed{0.29} \quad x(\text{N}_2) = \frac{2.5 \text{ mol}}{3.5 \text{ mol}} = \boxed{0.71}$$

(b) The perfect gas law is assumed to hold for each component individually as well as for the mixture as a whole. Hence,  $p_j = n_j \frac{RT}{V}$

$$\frac{RT}{V} = \frac{(8.206 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})}{24.4 \text{ dm}^3} = 1.00 \text{ atm mol}^{-1}$$

$$p(\text{H}_2) = (1.0 \text{ mol}) \times (1.00 \text{ atm mol}^{-1}) = \boxed{1.0 \text{ atm}}$$

$$p(\text{N}_2) = (2.5 \text{ mol}) \times (1.00 \text{ atm mol}^{-1}) = \boxed{2.5 \text{ atm}}$$

$$\text{(c)} \quad p = p(\text{H}_2) + p(\text{N}_2) [1.15] = 1.0 \text{ atm} + 2.5 \text{ atm} = \boxed{3.5 \text{ atm}}$$

**E1.19 (c)** The critical constants of carbon dioxide are  $p_c = 72.85 \text{ atm}$ ,  $V_c = 94.0 \text{ cm}^3 \text{ mol}^{-1}$ , and  $T_c = 304.2 \text{ K}$ . Calculate the van der Waals parameters of the gas and estimate the

radius of the molecules. Compare to the values in Table 1.6. What might your comparison suggest?

**E1.19(c)** Equations [1.22] are solved for  $b$  and  $a$ , respectively, and yield  $b = \frac{V_c}{3}$  and  $a = 27b^2 p_c = 3V_c^2 p_c$

Substituting the critical constants

$$b = \frac{1}{3} \times (94.0 \text{ cm}^3 \text{ mol}^{-1}) = \boxed{31.3 \text{ cm}^3 \text{ mol}^{-1}}$$

$$a = 3 \times (94.0 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1})^2 \times (72.85 \text{ atm}) = \boxed{1.93 \text{ dm}^6 \text{ atm mol}^{-2}}$$

Note that knowledge of the critical temperature,  $T_c$ , is not required.

As  $b$  is approximately the volume occupied per mole of particles

$$v_{\text{mol}} \approx \frac{b}{N_A} = \frac{31.3 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 5.20 \times 10^{-29} \text{ m}^3$$

$$\text{Then, with } v_{\text{mol}} = \frac{4}{3} \pi r^3, r \approx \left( \frac{3}{4\pi} \times (5.20 \times 10^{-29} \text{ m}^3) \right)^{1/3} = \boxed{0.23 \text{ nm}}$$

The values of  $a$  and  $b$  given in Table 1.6 differ substantially from the values calculated here. Consequently, the value of the radius of the molecule given above cannot be taken too seriously.

**E1.20(c)** Use the van der Waals parameters for carbon dioxide to calculate approximate values of (a) the Boyle temperature of the gas and (b) the radius of a  $\text{CO}_2$  molecule regarded as a sphere ( $a = 3.610 \text{ dm}^6 \text{ atm mol}^{-2}$ ,  $b = 0.0429 \text{ dm}^3 \text{ mol}^{-1}$ ).

**E1.20(c) (a)** The Boyle temperature is the temperature at which  $\lim_{V_m \rightarrow \infty} \frac{dZ}{d(1/V_m)}$  vanishes. According to the

van der Waals equation

$$Z = \frac{pV_m}{RT} = \frac{\left( \frac{RT}{V_m - b} - \frac{a}{V_m^2} \right) V_m}{RT} = \frac{V_m}{V_m - b} - \frac{a}{V_m RT}$$

$$\begin{aligned} \text{so } \frac{dZ}{d(1/V_m)} &= \left( \frac{dZ}{dV_m} \right) \times \left( \frac{dV_m}{d(1/V_m)} \right) \\ &= -V_m^2 \left( \frac{dZ}{dV_m} \right) = -V_m^2 \left( \frac{-V_m}{(V_m - b)^2} + \frac{1}{V_m - b} + \frac{a}{V_m^2 RT} \right) \\ &= \frac{V_m^2 b}{(V_m - b)^2} - \frac{a}{RT} \end{aligned}$$

In the limit of large molar volume, we have

$$\lim_{V_m \rightarrow \infty} \frac{dZ}{d(1/V_m)} = b - \frac{a}{RT} = 0 \quad \text{so} \quad \frac{a}{RT} = b$$

$$\text{and } T = \frac{a}{Rb} = \frac{(3.610 \text{ dm}^6 \text{ atm mol}^{-2})}{(0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (0.0429 \text{ dm}^3 \text{ mol}^{-1})} = \boxed{1025 \text{ K}}$$

**(b)** By interpreting  $b$  as the excluded volume of a mole of spherical molecules, we can obtain an estimate of molecular size. The centres of spherical particles are excluded from a sphere whose radius is the diameter of those spherical particles (i.e. twice their radius); the Avogadro constant times the volume is the molar excluded volume  $b$ .

$$b = N_A \left( \frac{4\pi(2r)^3}{3} \right) \quad \text{so} \quad r = \frac{1}{2} \left( \frac{3b}{4\pi N_A} \right)^{1/3}$$

$$r = \frac{1}{2} \left( \frac{3(0.0429 \text{ dm}^3 \text{ mol}^{-1})}{4\pi(6.022 \times 10^{23} \text{ mol}^{-1})} \right)^{1/3} = 1.286 \times 10^{-9} \text{ dm} = 1.29 \times 10^{-10} \text{ m} = \boxed{0.129 \text{ nm}}$$

**E1.22(c)** A certain gas obeys the van der Waals equation with  $a = 0.580 \text{ m}^6 \text{ Pa mol}^{-2}$ . Its volume is found to be  $3.50 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}$  at 273 K and 5.0 MPa. From this information calculate the van der Waals constant  $b$ . What is the compression factor for this gas at the prevailing temperature and pressure?

**E1.22(c)** The van der Waals equation [1.21b] is solved for  $b$ , which yields

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

Substituting the data

$$b = 3.50 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1} - \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (273 \text{ K})}{\left\{ (5.0 \times 10^6 \text{ Pa}) + \left( \frac{0.580 \text{ m}^6 \text{ Pa mol}^{-2}}{(3.50 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1})^2} \right) \right\}}$$

$$= \boxed{1.17 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}}$$

$$Z = \frac{pV_m}{RT} [1.17] = \frac{(5.0 \times 10^6 \text{ Pa}) \times (3.50 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (273 \text{ K})} = \boxed{0.77}$$

**Comment.** The definition of  $Z$  involves the actual pressure, volume, and temperature and does not depend upon the equation of state used to relate these variables.