## GASEOUS STATE

**PROBLEM 105** 6.0 g of He having average velocity  $4 \times 10^2 \,\mathrm{ms}^{-1}$  is mixed with 12.0 g of Ne<sup>20</sup> having the same average velocity. What is the average kinetic energy per mole in the mixture?

**PROBLEM 106** The valve of a commercial cylinder of  $N_2$  gas was left slightly open so that small amount of gas leaked into the laboratory. The leak rate was proportional to the pressure difference (internal pressure one atm). If the initial leak rate was found to be  $1~{\rm g\,s^{-1}}$  and initial pressure inside the 7.28 m<sup>3</sup> tank was 17180 kPa, what would be the pressure inside the tank after 10 days assuming temperature of the lab to be  $27^{\circ}{\rm C}$ .

**PROBLEM 107** Calculate pressure exerted by 22.0 g of  $CO_2$  in 0.5 L bulb at 300 K assuming it to be real gas with  $a = 363 \text{ kPaL}^2 \text{ mol}^{-2}$  and b = 42.67 cc/mol.

**PROBLEM 108** Molar volume of He at 10.1325 Mpa and 273 K is 0.011075 times its molar volume at 101.325 kPa. Calculate radius of He atom assuming negligible 'a'.

**PROBLEM 109** A gas mixture containing 5% by mass of butane and 95% by mass of Ar (40) is to be prepared by allowing gaseous butane to fill an evacuated 40 L cylinder at 1.0 atm and 27°C. Calculate mass of Ar that gives the desired composition and total pressure of the final mixture.

**PROBLEM 110** Cl<sub>2</sub>O<sub>7</sub> gas decomposes as:

$$Cl_2O_7 \longrightarrow Cl_2 + O_2$$

A partially decomposed gaseous mixture is allowed to effuse through a pin-hole and the gas coming out initially was analyzed. The mole fraction of the  $\rm O_2$  was found to be 0.60, determine the degree of dissociation.

**PROBLEM 111** Proportion of a lighter isotope in a gaseous mixture containing both heavier and lighter isotopes is increased by successive effusion of the gas mixture. A sample of neon gas has  $^{22}$  Ne = 90% and  $^{20}$  Ne = 10% by moles. In how many stages of successive effusion, 25% enrichment of  $^{20}$  Ne would be achieved?

- **PROBLEM 112** The density of vapour of a substance at 1.0 atm and 500 K is  $0.35 \text{ k/m}^3$ . The vapour effuses through a small hole at a rate of 1.33 times faster than oxygen under similar condition.
- (a) Determine (i) Molecular weight (ii) Molar volume (iii) Compression factor (Z) of the vapour (iv) Which forces among the gas molecules are dominating, the attractive or repulsive?
- (b) If the vapour behaves ideally at 1000 K, determine the average translational kinetic energy possessed by a molecule.
- **PROBLEM 113** Using van der Waals' equation of state, calculate the pressure correction factor for two moles of a gas confined in a four litre flask that exert a pressure of 11 atmosphere at 300 K.  $b = 0.05 \,\mathrm{L \, mol^{-1}}$ .
- **PROBLEM 114** For a van der Waals' gas Z (compressibility factor) was found to be 1.5 at 273 K and one atmosphere and  $T_B$  of the gas is 107 K. Determine value of a and b.
- **PROBLEM 115** A flask containing 2.0 moles of He gas at 1.0 atm and 300K is connected to another flask containing  $N_2(g)$  at the same temperature and pressure by a narrow tube of negligible volume. Volume of the nitrogen flask is three times volume of He-flask. Now the He-flask is placed in a thermostat at 200 K and  $N_2$ -flask in another thermostat at 400 K. Determine final pressure and final number of moles in each flask.
- **PROBLEM 116** In a spherical glass flask A of radius 1.0 m, containing 300 g  $H_2(g)$ , there was a rubber balloon B containing some  $N_2(g)$ . Inside B, there was another rubber balloon C containing some oxygen gas. At 27°C, it was found that the balloon B had radius 60 cm and of C was 30 cm. Calculate the total weight of the gas inside the flask. Now 50 g  $H_2(g)$  is further added to A, what would be the volume of B and C.
- **PROBLEM 117** A partially decomposed  $PCl_5(g)$  along with its dissociation product is subjected to diffusion study and the gases coming out initially collected in an another flask. The rate of effusion of collected gaseous mixture was found to be 0.45 times rate of effusion of pure oxygen gas. Determine the degree of dissociation of  $PCl_5(g)$  in the original sample.
- **PROBLEM 118** One mole of a monoatomic gas confined in a 22.5 litre flask at 273 K exert a pressure of 0.98 atm, whereas expected pressure was 1.0 atm has the gas behaved ideally. Determine the van der Waal's constants 'a' and 'b' and Boyle's temperature  $(T_B)$ .
- **PROBLEM 119** One litre of a gas at 300 atm and 473 K is compressed to a pressure of 600 atm and 273 K. The compressibility factors found to be 1.072 and 1.375 respectively at the initial and final states. Calculate the final volume.
- **PROBLEM 120** Calculate the van der Waal's constants for ethylene.  $T_C = 282 \text{ K}$ ,  $P_C = 50 \text{ atm.}$
- **PROBLEM 121** The second Virial coefficient of an imperfect gas is  $2 \times 10^{-2}$  (L/mol)<sup>2</sup>. Calculate the volume of a gm mole of the gas at 27°C and 5 atmosphere pressure.
- **PROBLEM 122** The van der Waal's constant 'b' of a gas is 4.42 centilitre/mol. How near can the centres of the two molecules approach each other?
- **PROBLEM 123** For carbon dioxide, critical density is 0.45 g/cc and its  $T_C = 300$  K. Determine its van der Waal's constants.

**PROBLEM 124** The Virial equation for ethane gas is given by PV = RT + BP. At 0°C, B = -0.1814 L/mol. Calculate volume of one mole of ethane at 10 atm, and 'a'.

**PROBLEM 125** An unknown gas (X) at 2.0 atmosphere and Ar (40) at 1.0 atmosphere were injected simultaneously from the two ends of a 1.0 metre long glass tube and the first collision between X and Ar occurred at a distance of 38 cm from Ar-end.Determine the molar mass of X assuming that gases were injected at same temperature and through the pin-hole of identical geometry.

**PROBLEM 126** Using van der Waals' equation of state, calculate pressure developed by 100 g of CO<sub>2</sub> contained in a volume of 5.0 litre at 40°C. Also compare this value with that calculated using ideal gas law and determine the percentage deviation from ideality. a = 3.6 atm L<sup>2</sup>mol<sup>-2</sup>, b = 44 cm<sup>3</sup>mol<sup>-1</sup>.

**PROBLEM 127** An equation of state for a non-ideal gas can be written as:  $PV_m = A + BP + CP^2$ ; where  $V_m$  is the molar volume and P is the gas pressure in atmosphere.  $B = -2.879 \times 10^{-2}$  and  $C = 14.98 \times 10^{-5}$  in litre atmosphere unit. Under the experimental condition, determine the pressure at which PV-P curve will attain minimum.

**PROBLEM 128** A modified form of van der Waal's equation of state for 1.0 mole of gas is given as:

$$\left(P + \frac{\alpha}{TV^2}\right)(V - \beta) = RT$$

Deduce expression for the first Virial coefficient (*B*) and Boyle's temperature in term of  $\alpha$  and  $\beta$  if Virial equation of state is:

$$\frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \dots$$

**PROBLEM 129** Assuming that dry air contain 79%  $N_2$  and 21%  $O_2$  by volume, calculate the density of moist air at 25°C and 1.0 atmosphere when the relative humidity is 60%. The vapour pressure of water at 25°C is 23.76 mm of Hg.

**PROBLEM 130** At what temperature, three moles of  $SO_2$  will occupy 10 litre at a pressure of 15.0 atm if it is a van der Waal's gas with a = 6.71 atm  $L^2$ mol<sup>-2</sup> and b = 56.4 cm<sup>3</sup>mol<sup>-1</sup>.

**PROBLEM 131** Pressure of He gas confined in a steel chamber drops from 4.0 to 1.0 atmosphere in 4.0 hours due to diffusion through a pin-hole in the steel chamber. If an equimolar mixture of He and methane gas at 20 atmosphere and the same temperature are confined in the same chamber, what will be the partial pressure of He and methane after 1.0 hour. Assume rate of diffusion to be linear function of gas pressure and inverse function of square root of molar masses.

**PROBLEM 132** One mole of a van der Waal's gas at 0°C and 600 atmosphere occupies 0.075 L. If  $b = 0.024 \text{ L mol}^{-1}$ , determine compressibility factor (Z) and predict the type of force dominating among the gas molecule.

**PROBLEM 133** A one litre flask containing  $NH_3(g)$  at 2.0 atmosphere and 300 K is connected to another 800 mL flask containing HCl(g) at 8.0 atmosphere and 300 K by means of a narrow tube of negligible volume and gases were allowed to react quantitatively as:

$$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s); \Delta H = -43kJ/mol$$

If heat capacity of HCl(g)  $C_V$  is  $20 \text{ JK}^{-1} \text{mol}^{-1}$ , determine final pressure inside the flask assuming negligible heat capacity of flask and negligible volume of solid  $NH_4Cl$ .

**PROBLEM 134** A long cylindrical glass tube, equipped with a porous disc at the centre, contain methane gas at 5.0 atmosphere on one side and He gas at 2.0 atmosphere on the other side of the disc as shown in the diagram below:

Disc is permeable to both gases and rate of diffusion is directly proportional to the gas pressure and inversely proportional to square root of molar masses as:

$$\begin{array}{c|c} CH_4 & He \\ 5.0 \text{ atm.} & 2.0 \text{ atm.} \end{array}$$

$$-\frac{dp}{dt} = k \frac{P}{\sqrt{M}}$$
 where, k is a constant.

If k for the diffusion of methane gas is  $2.5 \times 10^{-2}$  second<sup>-1</sup>, determine time after which pressure of methane chamber will drop to 4.0 atmospheres.

**PROBLEM 135** At a given condition of temperature, rate of change of r.m.s. of He gas is twice the rate of change of absolute temperature. Determine rms of He in the given condition.

**PROBLEM 136** 1.6 moles of ammonia gas at 300 K is taken in a 2.0 litre flask, sealed and heated to 500 K. At this temperature, ammonia is partially decomposed into N<sub>2</sub> and H<sub>2</sub> and a pressure measurement at this point gave 48.5 atmosphere. Determine number of moles of each component present at 500 K.

**PROBLEM 137** Decomposition of KClO<sub>3</sub> produces oxygen gas and KCl solid. In a typical experiment, some KClO<sub>3</sub> was decomposed and 36.00 mL oxygen gas was collected over water at 23°C. The laboratory barometer reads 751 mm and vapour pressure of water at 23°C is 21.1 mm of Hg. Find the volume of the dry oxygen at 0°C and 1.0 atmosphere.

**PROBLEM 138** A narrow tube of negligible volume connects two evacuated bulb of 1.0 litre capacity each. One bulb is placed in a 200 K thermostat bath and other in a 300 K thermostat bath and then 1.0 mole of an ideal gas is injected into the system. Find the pressure in the two flasks.

**PROBLEM 139** Isothermal compressibility ( $\kappa$ ) of a gas is defined as:

$$\kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_{T, n}$$

Determine isothermal compressibility for an ideal gas at 1.0 atmosphere.

**PROBLEM 140** What will be the temperature difference needed in a hot air balloon to lift 1.0 kg weight. Assume that the volume of balloon is 100 m<sup>3</sup>, the temperature of atmosphere is 25°C and pressure is 1.0 atmosphere. Average molar mass of air is 29 amu.

**PROBLEM 141** Using van der Waals' equation of state, find pressure at which the PV vs P curve acquires minima for 1.0 mole of oxygen gas at 0°C.  $a = 1.36 L^2$  atm mol<sup>-2</sup>, and  $b = 32 cm^3 mol^{-1}$ .

**PROBLEM 142** The van der Waals' constant 'a' is a correction factor to the ideal gas law for intermolecular force of attractions within the substance. Match the following values of 'a' ( $L^2$  atm mol<sup>-1</sup>): 0.2107, 5.464, 18.00 and 24.06 with gases benzene, toluene, Ne and steam.

**PROBLEM 143** The van der Waals' constant 'b' is a correction factor to the ideal gas law for the intrinsic volume of the molecule. Match the following values of 'b'(L mol<sup>-1</sup>): 0.017, 0.0305, 0.1154 and 0.1463, with the gases: toluene, benzene, Ne and steam.

## **Solutions**

## **GASEOUS STATE**

105. Average velocity = 
$$\sqrt{\frac{8RT}{\pi M}} = 4 \times 10^2 \Rightarrow \frac{RT}{\pi M} = 2 \times 10^4 \Rightarrow RT = 2\pi M \times 10^4$$

Total K.E. of He =  $\frac{6}{4} \times \frac{3}{2} RT = \frac{9}{4} RT = \frac{9}{4} \cdot 2\pi \times 4 \times 10^{-3} \times 10^4 = 180 \,\pi \,\text{J}$ 

Total K.E. of Ne =  $\frac{12}{20} \times \frac{3}{2} RT = \frac{9}{10} RT = \frac{9}{10} \times 2\pi \times 20 \times 10^{-3} \times 10^4 = 360 \,\pi \,\text{J}$ 

Average K.E. per mol =  $\frac{(360 + 180) \,\pi}{1.5 + 0.6} = 807.84 \,\text{J}$ 

106.  $\frac{-dP}{dt} \approx (P - 1) \Rightarrow \frac{-dP}{dt} = K (P - 1)$ 

$$\Rightarrow \frac{-dP}{P - 1} = Kdt \Rightarrow \int_{P_0}^{P} \frac{-dP}{P - 1} = K \int_{0}^{I} dt \Rightarrow \ln \frac{P_0 - 1}{P - 1} = Kt \qquad ...(i)$$

Also, 
$$\frac{d}{dt} \left(\frac{-mRt}{VM}\right) = K (P - 1)$$

$$\Rightarrow K = \frac{RT (-dm/dt)}{VM(P - 1)} = \frac{0.0821 \times 300 \times 1.0}{7.28 \times 10^3 \times 28 (171.8 - 1)} = 7 \times 10^{-7}$$

Now, 
$$\ln \frac{171.8 - 1}{P - 1} = 7 \times 10^{-7} \times 10 \times 24 \times 3600$$

Now, 
$$\ln \frac{170.8}{P - 1} = 1.83 \Rightarrow P = 94.33 \,\text{atm}.$$

107. 
$$P = \frac{nRT}{V - nb} - \frac{r^2 a}{V^2} = \frac{0.5 \times 0.082 \times 300}{0.5 - 0.5 \times 0.04267} = \frac{0.25 \times 3.63}{0.25} = 22.06 \,\text{atmosphere}$$

$$108. V - b = RT = 100(0.011075V - b) = 1.1075V - 100b \Rightarrow V = \frac{99b}{0.1075} = 921b$$

$$\Rightarrow 920 \, b = RT \Rightarrow b = 24.33 \,\text{cm}^{3} \,\text{mol}^{-1} = 4 \times \frac{4}{3} \pi \, r^{3} \times 6.023 \times 10^{23}$$

$$\Rightarrow r = 13.4 \times 10^{-9} \,\text{cm} = 134 \,\text{pm}$$

109. 
$$n \, (\text{butane}) = \frac{1 \times 40}{0.082 \times 300} = 1.626 \Rightarrow \text{Mass of butane} = 94.308 \,\text{g}$$

$$Mass \, \text{of Ar} = 94.308 \times 19 = 1791.852 \,\text{g}$$

$$n(Ar) = 44.8 \, \text{Final } P = \frac{46.426}{1.626} = 28.55 \,\text{bar}$$

110. 
$$C1_{2}O_{7} \longrightarrow C1_{2} + 3.5O_{2}$$

Now, let x be the mole fraction of  $Cl_2$  in the gaseous mixture being analyzed.

$$\Rightarrow \frac{r_{O_2}}{r_{Cl_2}} = 3.5\sqrt{\frac{71}{32}} = \frac{0.6}{x} \Rightarrow x = 0.115$$

 $\Rightarrow$  Mole fraction of Cl<sub>2</sub>O<sub>7</sub> = 0.285

Also, 
$$\frac{r_{\text{Cl}_2\text{O}_7}}{r_{\text{Cl}_2}} = \frac{1 - \alpha}{\alpha} \sqrt{\frac{71}{183}} = \frac{0.285}{0.115} \Rightarrow \alpha = \mathbf{0.2}$$

111. 
$$\left(\frac{r_1}{r_2}\right)_{n=1} = \left(\frac{N_1}{N_2}\right)_0 \left(\frac{M_2}{M_1}\right)^{n/2} = \left(\frac{N_1}{N_2}\right)_0 \implies \frac{25}{75} = \frac{10}{90} \left(\frac{22}{20}\right)^{n/2}$$
 Solving  $n = 23$ 

**112.** (a) 
$$\frac{r}{r_{\Omega_2}} = 1.33 = \sqrt{\frac{32}{M}}$$
  $M = 18$  amu.

$$V_m = \frac{18}{0.36} = 50 \text{ L}$$

$$Z = \frac{PV}{RT} = \frac{1 \times 50}{0.082 \times 500} = 1.22$$
, repulsive force is dominating.

(b) 
$$KE_T = \frac{3}{2}KT = \frac{3}{2} \times 1.38 \times 10^{-23} \times 1000 = 2.07 \times 10^{-20} \text{ J}$$

**113.** 
$$(P+K)(V-nb) = nRT \implies K = \frac{nRT}{V-nb} - P = \frac{2 \times 0.082 \times 300}{4 - 2 \times 0.05} - 11 =$$
**1.615** bar

114. 
$$Z = 1 + \frac{Pb}{RT} \implies 0.5 = \frac{Pb}{RT}$$

$$\Rightarrow b = \frac{0.5 RT}{0.5 RT} = 0.5 \times 0.082 \times 273 = 11.193$$

$$\Rightarrow b = \frac{0.5 RT}{P} = 0.5 \times 0.082 \times 273 = 11.193 \text{ L mol}^{-1}$$

Also, 
$$T_B = \frac{a}{Rb} \implies a = T_B \cdot Rb = 107 \times 0.082 \times 11.193$$

115. He N<sub>2</sub> 
$$n_{\text{He}} = \frac{1}{3} \times \frac{400}{200} = \frac{2}{3}$$

Also, 
$$n_{\text{He}} + n_{\text{N}_2} = 8 \implies n_{\text{He}} = \frac{16}{5}, \ n_{\text{N}_2} = \frac{24}{5}$$
  
Also,  $\frac{1}{300 \times 2} = \frac{P}{200 \times \frac{16}{5}} \implies P = 1.066 \text{ atm}$ 

**116.** Applying concept of uniform pressure :

$$\frac{150}{(1-0.6^3)} = \frac{n_{\text{N}_2}}{(0.6^3 - 0.3^3)} = \frac{n_{\text{O}_2}}{(0.3)^3} \implies n_{\text{N}_2} = 36.16, n_{\text{O}_2} = 5.16$$

$$W = 300 + 36.16 \times 28 + 5.16 \times 32 = 1477.6 \text{ g}$$

After adding  $50 g H_2$ :

$$\frac{175}{(1-r_B^3)} = \frac{36.16}{(r_B^3 - r_C^3)} = \frac{5.16}{r_C^3}$$

Solving,  $r_B = 57.6 \text{ cm}$  and  $r_C = 28.8 \text{ cm}$ 

**117.** 
$$\frac{r_{\text{mix}}}{r_{\text{O}_2}} = \sqrt{\frac{32}{M}} = 0.45 \implies M = 158$$

Also, 
$$\frac{r_{\text{PCl}_3}}{r_{\text{Cl}_2}} = \sqrt{\frac{71}{137.5}} = 0.72 = \frac{n_{\text{PCl}_3}}{n_{\text{Cl}_2}}$$

$$\Rightarrow 71x + 0.72x \times 137.5 + (1 - 1.72x) \times 208.5 = 158 \Rightarrow x = 0.268$$

Now, 
$$\frac{\text{PCl}_5}{1-\alpha} \rightleftharpoons \frac{\text{PCl}_3}{\alpha} + \frac{\text{Cl}_2}{\alpha}$$

$$\frac{r_{\text{PCl}_5}}{r_{\text{Cl}_5}} = \frac{1-\alpha}{\alpha} \sqrt{\frac{71}{208.5}} = \frac{0.539}{0.268} \implies \alpha = \mathbf{0.225}$$

118. 
$$\frac{n^2 a}{V^2} = 0.02$$
  $\Rightarrow a = 0.02 \times (22.5)^2 = 10.125 \text{ atm L}^2 \text{ mol}^{-2}$ 

$$V - nb = nRT \implies b = V - RT = 22.5 - 0.082 \times 273 = 114 \text{ cm}^3 \text{ mol}^{-1}$$

$$T_B = \frac{a}{Rb} = \frac{10.125}{0.082 \times 0.114} =$$
**1083.12 K**

**119.**  $300 \times 1 = n \times 1.072 \times R \times 473$ 

$$600 V = n \times 1.375 \times R \times 273 \implies V = 0.37 L$$

**120.** 
$$T_c = \frac{8a}{27Rb} = 282$$
 and  $P_c = \frac{a}{27b^2} = 50$ 

Dividing 
$$\frac{282}{50} = \frac{8a}{27Rb} \times \frac{27b^2}{a} \implies b = \frac{282R}{50 \times 8} = \mathbf{0.0578 \ L \ mol^{-1}}$$

Substituting 
$$b$$
 in  $T_c$ :  $a = \frac{282 \times 27 \times 0.082 \times 0.0578}{8} = 4.5 \text{ atm L}^2 \text{ mol}^{-2}$ 

**121.** The second Virial coefficient =  $b^2 = 2 \times 10^{-2} \implies b = 0.1414 \text{ L mol}^{-1}$ 

$$V_{\text{ideal}} = \frac{nRT}{P} = \frac{0.082 \times 300}{5} = 4.92, V_{\text{real}} = V_{\text{id}} + nb =$$
**5.0614** L

**122.** 
$$b = 4.42 \times 10^{-2} \text{ L mol}^{-1} = 44.2 \text{ cm}^3 \text{ mol}^{-1} = 4 \times \frac{4}{3} \pi r^3 \times 6.023 \times 10^{23}$$

$$\Rightarrow r = 16.36 \times 10^{-9} \text{ cm} \Rightarrow \text{Distance of closest approach} = 2r = 32.72 \times 10^{-9} \text{ cm} = 327.2 \text{ pm}$$

123. 
$$V_c = \frac{44}{0.45} = 97.77 \text{ cm}^3 \text{ mol}^{-1} \implies b = \frac{V_c}{3} = 32.6 \text{ cm}^3 \text{ mol}^{-1}$$

$$T_C = \frac{8a}{27Rh} = 300 \implies a = 2.7 \text{ atm L}^2 \text{ mol}^{-2}$$

**124.** 
$$V = \frac{RT}{P} + B = 2.058$$
 L. Also, for the given equation :

$$Z = 1 + \frac{PB}{RT} = 1 + \frac{10(-0.1814)}{0.082 \times 273} =$$
**0.918**

125.

From van der Waal's equation, for Z < 1,  $Z = 1 - \frac{a}{VRT}$ 

$$\Rightarrow \frac{a}{VRT} = 0.082 \Rightarrow a = 3.77 \text{ bar } L^2 \text{ mol}^{-2}$$

$$\frac{r_X}{r_{AB}} = \frac{62}{38} = 2\sqrt{\frac{40}{M}} \Rightarrow M = 60 \text{ amu}.$$

126. 
$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2} = \frac{100 \times 0.082 \times 313}{44 \left(5 - \frac{100}{44} \times 0.044\right)} - \left(\frac{100}{44 \times 5}\right)^2 \cdot 3.6 = 11.16 \text{ bar}$$

$$P_{id} = \frac{nRT}{V} = \frac{100}{44} \times \frac{0.082 \times 313}{5} = 11.666 \text{ bar}$$

Percentage deviation = 
$$\frac{P_{id} - P_{real}}{P_{id}} \times 100 = 4.33\%$$

**127.** At minimum in 
$$PV - P$$
 curve,  $\frac{\partial (PV)}{\partial P} = 0$ 

$$\Rightarrow B + 2CP = 0 \Rightarrow P = \frac{-B}{2C} = \frac{2.879 \times 10^{-2}}{2 \times 14.98 \times 10^{-5}} = 96 \text{ atm}$$

128. 
$$P = \frac{RT}{V - \beta} - \frac{\alpha}{TV^2} \Rightarrow \frac{PV}{RT} = \frac{V}{V - \beta} - \frac{\alpha}{RT^2V} = \left(1 - \frac{\beta}{V}\right)^{-1} - \frac{\alpha}{RT^2V}$$
$$\Rightarrow \frac{PV}{RT} = 1 + \frac{\beta}{V} + \frac{\beta^2}{V^2} + \dots - \frac{\alpha}{RT^2V} = 1 + \frac{1}{V}\left(\beta - \frac{\alpha}{RT^2}\right) + \frac{\beta^2}{V^2} + \dots$$

Comparing with Virial equation:

$$B = \beta - \frac{\alpha}{RT^2}$$
 and  $T_B = \sqrt{\frac{\alpha}{R\beta}}$ 

**129.** V. P. =  $0.6 \times 23.76 = 14.256$  mm

Moles of gas in 1.0 L dry air = 
$$\frac{1}{0.082 \times 298}$$
 = 0.0409

Moles of 
$$N_2 = 0.0409 \times 0.79 = 0.0323 \implies \text{mass of } N_2 = 0.9044 \text{ g}$$

Moles of 
$$O_2 = 0.0409 \times 0.21 = 0.0086 \implies \text{mass of } O_2 = 0.2752 \text{ g}$$

Moles of 
$$H_2O(v)$$
 in 1.0 L moist air =  $\frac{14.256}{760 \times 0.082 \times 298} = 0.76 \times 10^{-3}$ 

 $\Rightarrow$  Mass of H<sub>2</sub>O(v) = 0.0138 g

Adding masses of all the gases gives = 1.1934 g / L

130. 
$$T = \frac{1}{nR} \left[ \left( P + \frac{n^2 a}{V^2} \right) (V - nb) \right] = 623.57 \text{ K}$$

$$\frac{-dP}{dt} = \frac{KP}{\sqrt{M}} \implies \int_{P_0}^{P} \frac{-dP}{P} = \frac{K}{\sqrt{M}} \int_{0}^{t} dt$$

$$\Rightarrow \qquad \ln \left( \frac{P_0}{P} \right) = \frac{Kt}{\sqrt{M}} \implies \ln 4 = \frac{4K}{\sqrt{4}} = 2K$$

$$\ln \frac{10}{P} = \frac{K}{2} \implies P_{\text{He}} = 7.07 \text{ atm}$$
Also,
$$\ln \left( \frac{P_0}{P} \right)_{\text{He}} = \frac{Kt}{2} \quad \text{and} \quad \ln \left( \frac{P_0}{P} \right)_{\text{CH}_4} = \frac{Kt}{4}$$

$$\Rightarrow \qquad \left( \frac{P_0}{P} \right)_{\text{He}} = \left( \frac{P_0}{P} \right)_{\text{CH}_4}^{2} \implies \frac{100}{7.07} = \frac{1000}{P_{\text{CH}_4}^{2}}$$

$$\Rightarrow \qquad P_{\text{CH}_4} = 8.4 \text{ atm}$$

**132.**  $P_{\text{ideal}}$  (V - b) = RT for 1.0 mol

$$\Rightarrow$$
  $P_{\text{ideal}} = \frac{0.082 \times 273}{0.075 - 0.024} = 438.9 \Rightarrow Z = \frac{600}{438.9} = 1.367 \text{ (Repulsive force)}$ 

133. NH<sub>3</sub>(g) + HCl(g) 
$$\longrightarrow$$
 NH<sub>4</sub>Cl(s)  
Moles 0.08 0.26 0  
0 0.18 0.08  
 $\Rightarrow Q = 0.08 \times 4300 = 3440 \text{ J}$   
Also,  $Q = nC_v \Delta T \Rightarrow \Delta T = \frac{3440}{0.18 \times 20} = 955.55$   
 $T_{\text{final}} = 1255.55 \text{ K}$   
 $P_{\text{final}} = \frac{0.18 \times 0.082 \times 1255.55}{1.8} = 10.3 \text{ atmosphere}$ 

**134.** Let  $P_1$  be the pressure in methane chamber and  $P_2$  be the pressure in He chamber at any instant t. Then:

$$\frac{-dP_1}{dt} = \frac{K_1P_1}{\sqrt{16}} - \frac{K_2P_2}{\sqrt{4}} = \frac{K_1P_1}{4} - \frac{K_2P_2}{2}$$
Also, at equilibrium, 
$$\frac{-dP}{dt} = 0$$
and 
$$P_1 = P_2 = 3.7 \implies K_1 = 2K_2$$

$$\Rightarrow \frac{-dP_1}{dt} = \frac{K_1}{4} (P_1 - P_2) = \frac{K_1}{4} (2P_1 - 7) \qquad \therefore P_1 + P_2 = 7$$

$$\Rightarrow \int_{5}^{4} \frac{-dP_1}{(2P_1 - 7)} = \frac{K_1}{4} \int_{0}^{t} dt \quad \text{Solving}, \quad t = \frac{2 \ln 3}{K_1} = 87.88 \text{ second}$$

**135.** r.m.s. 
$$(s) = \sqrt{\frac{3RT}{M}} \implies \frac{ds}{dT} = \sqrt{\frac{3R}{M}} \cdot \frac{1}{2\sqrt{T}} = \frac{3R}{2MS} = 2 \implies S = \frac{3R}{4M} = 1558.87 \text{ ms}^{-1}$$

136. 
$$2NH_3 \implies N_2 + 3H_2$$
  
 $1.6 - 2x$   $x$   $3x = 1.6 + 2x$   
 $P_{\text{initial}} = \frac{1.6 \times 0.082 \times 500}{2} = 32.8$  Also,  $\frac{32.8}{48.5} = \frac{1.6}{1.6 + 2x} \implies x = 0.383$ 

$$n(NH_3) = 0.834, \quad n(N_2) = 0.383, \quad n(H_2) = 1.149$$

137. 
$$P(\text{dry oxygen}) = 729.9 \text{ mm} \Rightarrow V(\text{dry oxygen}) = \frac{729.9 \times 30}{751} = 29.15 \text{ mL}.$$

Now, applying  $\frac{PV}{T}$  = constant, V = 25.82 mL

**138.** Let x mol gas is present in cold flask and y mol in hot flask.

⇒ 
$$2x = 3y$$
 and  $x + y = 1$  Solving:  $x = \frac{3}{5}, y = \frac{2}{5}$   
 $P = \frac{3}{5} \times \frac{0.082 \times 200}{1} = 9.84$  atmosphere.

**139.** Boyle's law : PV = C (constant)

$$\Rightarrow V = \frac{C}{P} \Rightarrow \left(\frac{\partial V}{\partial P}\right)_{n,T} = \frac{-C}{P^2} = -\frac{V}{P}$$

$$\Rightarrow K = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_{n,T} = \frac{1}{P} = 1.0 \text{ atm}^{-1}$$

**140.** 
$$\Delta m = m_{\text{cold}} - m_{\text{hot}} = [n_{\text{cold}} - n_{\text{hot}}] M = \frac{PVM}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

Solving :  $\Delta T = T_2 - T_1 = 3$ 

**141.** The minimum in curve will occur at  $\frac{\partial (PV)}{\partial P} = 0$ 

Also, 
$$\frac{\partial (PV)}{\partial P} = \frac{P}{(\partial P/\partial V)} + V \qquad \dots (i)$$

for 1.0 mole, van der Waals' equation can be written as:

$$P = \frac{RT}{V - b} - \frac{a}{V^2} \qquad ...(ii)$$

$$\Rightarrow \frac{\partial P}{\partial V} = \frac{-RT}{(V - b)^2} + \frac{2a}{V^3}$$

Substituting  $\left(\frac{\partial P}{\partial V}\right)$  in Eq. (i) and equating to zero gives

$$(bRT - a)V^2 + 2abV - ab^2 = 0$$

Substituting a, b, R and T gives

$$-0.647V^{2} + 0.087V - 1.38 \times 10^{-3} = 0$$
 ...(iii)

Solving, Eq. (iii) gives

$$V = 0.0185 \text{ L mol}^{-1}$$
 and  $0.01158 \text{ L mol}^{-1}$ .

The first solution yields a negative pressure on substitution into Eq. (ii), but using V = 0.1158 gives

$$P = \frac{0.082 \times 273}{0.1158 - 0.032} - \frac{1.362}{(0.1158)^2} = 165.56 \text{ atmosphere}$$

**142.** Steam : 24.06 Benzene : 5.464 Toluene : 18.00 Neon : 0.2107

(Higher the intermolecular force of attraction, higher will be 'a')

**143.** Toluene : 0.1463 Steam : 0.0305 Benzene : 0.1154 Neon : 0.0170

(Larger the van der Waal's radius, higher will be 'b')