QUESTION 1 (*15 marks*)

Hydrogen (H_2) and Argon (Ar) are two gases that are sometimes combined to generate mixtures used in welding applications. The molar mass of H_2 is 2.0 g/mol, and the molar mass of argon is 39.95 g/mol. Answer the questions below assuming that hydrogen, argon, and their mixtures all act as ideal gases under the conditions specified.

(a) Identify the gas (H_2 or Ar) which you think would have the lower speed at 100°C and 1 atm, and calculate the root mean square speed (in m/s) of that gas under these conditions.

It would be ARGON as it has a larger molar mass

2

$$\sqrt{\overline{C^2}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{(3)\left(8314\ \frac{kg\ m^2}{kmol\ s^2 K}\right)(373.15K)}{39.95\ kg/kmol}} = \boxed{482.7\ m/s}$$

(b) What is the mean separation distance (in angstroms) between argon molecules at 100°C and 1 atm?

2

$$\delta = \left(\frac{kT}{P}\right)^{1/3} = \left(\frac{(1.3805\times10^{-23}\ J/K)(373.15K)}{(1\ atm)(101325\ Pa/atm)}\right)^{1/3} = 3.7\times10^{-9}m$$

$$(3.7\times10^{-9}m)\left(\frac{1\ \text{Å}}{10^{-10}m}\right) = \boxed{37\ \text{Å}}$$

(c) Determine the ratio of the mean free path length of H_2 at 100°C to the mean free path length 200°C within a rigid container.

let condition 1 = 100°C and condition 2 = 200°C

2

For condition 1: $\lambda_1 = \frac{kT_1}{\pi\sigma^2 P_1\sqrt{2}} = \frac{kT_1}{\pi\sigma^2 \frac{n_1RT_1}{v_1}\sqrt{2}} = \frac{kv_1}{\pi\sigma^2 n_1 R\sqrt{2}}$ EQN 1

similarly for condition 2: $\lambda_2 = \frac{kv_2}{\pi\sigma^2 n_2 R\sqrt{2}}$ EQN 2.

divide EQN 1 by EQN 2

$$\frac{\lambda_1}{\lambda_2} = \frac{k\,v_1 / \cancel{\pi\sigma^2} n_1 \cancel{R\sqrt{2}}}{\cancel{k}\,v_2 / \cancel{\pi\sigma^2} n_2 \cancel{R\sqrt{2}}} = \frac{v_1}{v_2}\frac{n_2}{n_1}$$

Since $v_1 = v_2$ (rigid vessel) and $n_1 = n_2$ $\frac{\lambda_1}{\lambda_2} = \boxed{1}$

QUESTION 1 ***Contd.***

(d) 180 mol of argon and 20 mol of hydrogen are placed into a variable volume container where the pressure is always maintained constant at 1.2 atm. The initial temperature of the mixture is 100°C.

(i) Calculate the average molar mass (in kg/kmol) of the mixture.

1

$$M_{Avg} = y_1 M_1 + y_2 M_2 = \left(\frac{180\text{ mol}}{200\text{ mol}}\right)\left(39.95\,\frac{\text{kg}}{\text{Kmol}}\right) + \left(\frac{20\text{ mol}}{200\text{ mol}}\right)\left(2\text{ kg/kmol}\right) = \boxed{36.155\text{ kg/kmol}}$$

(ii) Calculate the density (in kg/m^3) of the gas mixture

2

$$Pv = nRT$$
$$P = \frac{n}{v}RT$$
$$PM = \frac{Mn}{v}RT$$
$$PM = \rho RT$$

$$\therefore \rho = \frac{PM}{RT} = \frac{(1.2\text{ atm})(36.155\text{ kg/kmol})}{\left(0.08205\,\frac{\text{atm m}^3}{\text{kmol K}}\right)(373.15\text{ K})} = \boxed{1.417\text{ kg/m}^3}$$

(iii) Calculate the total kinetic energy (in kJ) possessed by all of the Ar molecules in the mixture at 100°C.

3

Kinetic energy of one Argon atom $= \bar{E}_K = \frac{3}{2}kT = \frac{3}{2}\left(1.3805\times10^{-23}\text{ J/K}\right)(373.15\text{ K}) = 7.73\times10^{-21}\text{ J}$

Total number of Argon atoms $= (180\text{ mol})\left(6.022\times10^{23}\text{ atoms/mol}\right) = 1.08396\times10^{26}\text{ atoms}$

$\therefore$ Total kinetic energy $= \left(7.73\times10^{-21}\text{ J/atom}\right)\left(1.08396\times10^{26}\text{ atoms}\right) = 837901\text{ J} = \boxed{837.9\text{ kJ}}$

(iv) Calculate the energy required (in J) to raise the temperature of the mixture by 1.0 K.

Variable volume container → P is constant → ∴ use C_p value $= \frac{5}{2}R$

2

$$Q = nC_p\Delta T = (200\text{ mol})\left(\tfrac{5}{2}\right)\left(8.314\text{ J/mol K}\right)(1\text{ K}) = \boxed{4157\text{ J}}$$

(v) Determine the partial pressure (in kPa) of argon after exactly half of the gas mixture has been removed from the vessel.

1

Pressure remains constant in vessel

$$\therefore P_{Argon} = y_i P = (0.9)(1.2\text{ atm})\left(101.325\,\frac{\text{kPa}}{\text{atm}}\right) = \boxed{109.4\text{ kPa}}$$

Question 2 (*10 Marks*)

You are planning an experiment in which you will have a gas mixture in a 12 L rigid vessel at a pressure of 20 atm. The mixture will be composed of 1 mol of ethane (C_2H_6), 5 mol of hydrogen (H_2) and 4 mol of water (H_2O). Information about these gases are shown in the table.

Species	**T_C (K)**	**P_C (atm)**	**a (atm (m^3/kmol)^2)**	**b (m^3/kmol)**
C_2H_6	305	48		0.0652
H_2	33	13	0.24	
H_2O	647	218	5.45	

(a) Calculate the van der Waals parameter 'a' (in atm (m^3/kmol)^2) for pure C_2H_6

2

$$a = \frac{27}{64}\frac{R^2 T_c^2}{P_c} = \frac{27}{64}\frac{(0.08205 \text{ atm m}^3/\text{kmol}\cdot\text{K})^2 (305\text{K})^2}{(48\text{atm})}$$

$$a = \boxed{5.504 \text{ atm } (\text{m}^3/\text{kmol})^2}$$

(b) Calculate the van der Waals parameter 'b' (in m^3/kmol) for pure H_2 and pure H_20.

2 H_2 :

$$b = \frac{RT_c}{8P_c} = \frac{\left(0.08205 \frac{\text{atm m}^3}{\text{kmol K}}\right)(33\text{ K})}{8\,(13\text{ atm})} = \boxed{0.026 \text{ m}^3/\text{kmol}}$$

H_2O :

$$b = \frac{RT_c}{8P_c} = \frac{\left(0.08205 \frac{\text{atm m}^3}{\text{kmol K}}\right)(647\text{ K})}{(8)\,(218\text{ atm})} = \boxed{0.030 \text{ m}^3/\text{kmol}}$$

QUESTION 1 ***Contd.***

(c) Use the mixing rules method to determine the values of $\bar{a}$ (in atm (m^3/kmol)^2) and $\bar{b}$ (in m^3/kmol) for the mixture.

$y_{ethane} = 0.1 \qquad y_{H_2} = 0.5 \qquad y_{H_2O} = 0.4$

3

$$\bar{a} = \left[\left(y_{ethane}\sqrt{a_{ethane}}\right) + \left(y_{H_2}\right)\sqrt{a_{H_2}}\right) + \left(\left(y_{H_2O}\right)\sqrt{a_{H_2O}}\right)\right]^2$$

$$= \left[(0.1)\left(5.504\ \mathrm{atm}\left(\frac{m^3}{kmol}\right)^2\right)^{1/2} + (0.5)\left(0.24\ \mathrm{atm}\left(\frac{m^3}{kmol}\right)^2\right)^{1/2} + (0.4)\left(5.45\ \mathrm{atm}\left(\frac{m^3}{kmol}\right)^2\right)^{1/2}\right]^2$$

$$= \boxed{2\ \mathrm{atm}\cdot(m^3/kmol)^2}$$

$$\bar{b} = (0.1)\left(0.0652\frac{m^3}{kmol}\right) + (0.5)\left(0.026\frac{m^3}{kmol}\right) + (0.4)\left(0.030\frac{m^3}{kmol}\right) = \boxed{0.0315\ m^3/kmol}$$

(d) Using the van der Waals equation of state, calculate the temperature (in °C) of this mixture at equilibrium.

3

$$P = \left[\frac{RT}{V_m - \bar{b}}\right] - \frac{\bar{a}}{V_m^2}$$

$$T = \frac{\left(P + \bar{a}/V_m^2\right)\left(V_m - \bar{b}\right)}{R}.$$

$$V_m = \frac{v}{n} = \frac{(12\,L)(1\,m^3/1000\,L)}{(10\,mol)(1\,kmol/1000\,mol)} = 1.2\ m^3/kmol.$$

$$\therefore T = \frac{\left(20\ \mathrm{atm} + \frac{2\ \mathrm{atm}(m^3/kmol)^2}{\left(1.2\,(m^3/kmol)\right)^2]^2}\right)\left(1.2\ m^3/kmol - 0.0315\ m^3/kmol\right)}{0.08205\ \frac{\mathrm{atm}\ m^3}{kmol\ K}}$$

$$T = 313.30\ K \longrightarrow \boxed{40.15\ ^\circ C}$$

Question 3 ***(14 Marks)***

You are given information about three different gases in the table on the right. Note that methane has an acentricity of $\omega = 0.008$

Gas	T_C (K)	P_C (atm)	Molar mass (kg/kmol)
Methane	190.6	45.4	16
Ethane	305.4	48.2	30
Ethylene	282.4	49.7	28

PART A: 685 kg of methane gas is heated to a temperature of 304.94 K and is maintained at a pressure of 36.32 atm in a closed rigid container.

(a) Determine the molar volume (in m^3/kmol) of methane under the specified conditions using the ideal gas law.

1 $$V_m = \frac{RT}{P} = \frac{\left(0.08205 \frac{atm\ m^3}{kmol\ K}\right)(304.94K)}{36.32\ atm} = \boxed{0.689\ m^3/kmol}$$

↳ this is $V_{m,ideal}$

(b) Determine the molar volume (in m^3/kmol) of the methane under the specified conditions using the generalized compressibility chart.

3 $$\left.\begin{array}{l} T_R = \frac{T}{T_c} = \frac{304.94K}{190.6K} = 1.6 \\ P_R = \frac{P}{P_c} = \frac{36.32\ atm}{45.4\ atm} = 0.8 \end{array}\right\} Z \approx 0.96$$

$$V_m = Z(V_{m,ideal}) = (0.96)(0.689\ m^3/kmol) = \boxed{0.661\ m^3/kmol}$$

(c) Determine the molar volume (in m^3/kmol) of the methane under the specified conditions using Pitzer-Curl tables.

2 ~~All~~ At the T_R and P_R found above $Z^{(0)} = 0.944$ $Z^{(1)} = 0.07$

$$Z = Z^{(0)} + \omega Z^{(1)} = (0.944) + (0.008)(0.07) = 0.94456$$

$$\therefore V_m = Z(V_{m,ideal}) = (0.94456)(0.689\ m^3/kmol) = \boxed{0.651\ m^3/kmol}$$

(d) Determine the volume (in m^3) of the container from the molar volume obtained in part (c)

1 $$V = (V_m)(m)/M = \frac{(0.651\ m^3/kmol)(685\ kg)}{16\ kg/kmol} = \boxed{27.86\ m^3}$$

Question 3 *Contd.*

PART B: A rigid container of volume 0.04 m^3 contains a gas mixture composed of methane (30 mol%), ethane (20 mol%), and ethylene (50 mol%) at 48.11 atm and 285.4 K.

(e) Estimate the value of the compressibility factor (Z) from the generalized compressibility chart for this mixture.

5

$$T_{pc} = \sum y_i T_{ci} = (0.3)(190.6K) + (0.2)(305.4K) + (0.5)(282.4K) = 259.46\,K$$

$$P_{pc} = \sum y_i P_{ci} = (0.3)(45.4\,atm) + (0.2)(48.2\,atm) + (0.5)(49.7\,atm) = 48.11\,atm.$$

$$\left.\begin{aligned} T_{PR} &= \frac{T}{T_{pc}} = \frac{285.4K}{259.46K} = 1.1 \\ P_{PR} &= \frac{P}{P_{pc}} = \frac{48.11\,atm}{48.11\,atm} = 1.0 \end{aligned}\right] \quad Z \simeq 0.7$$

(f) Determine the mass (in kg) of gas mixture in the vessel

2

$$n = \frac{PV}{ZRT} = \frac{(48.11\,atm)(0.04\,m^3)}{(0.7)\left(0.08205\,\frac{atm\,m^3}{kmol\,K}\right)(285.4K)}$$

$$n = 0.1174\,kmol$$

$$M_{Avg} = (0.3)(16\,kg/kmol) + (0.2)(30\,kg/kmol) + (0.5)(28\,kg/kmol)$$
$$= 24.8\,kg/kmol.$$

$$\therefore\ mass = n M_{Avg} = (0.1174\,kmol)(24.8\,kg/kmol) = \boxed{2.91\,kg}$$

Question 4 (*16 Marks*)

You are asked to work with a mixture of n-butane (Component 1) and n-pentane (Component 2). The molecules of these two substances are very similar in size and shape. You are told that at 290 K, the vapour pressure of n-butane is 187 kPa and the vapour pressure of n-pentane is 500 kPa

1 **(a)** Estimate the bubble point pressure (in kPa) at 290 K of a binary liquid mixture composed of 20 mol% n-butane with the remainder being n-pentane.

$$P = \Sigma x_i P_{V_i} = (0.2)(187\,kPa) + (0.8)(500\,kPa) = 437.4\,kPa$$

2 **(b)** The liquid mixture in part (a) is set to its bubble point pressure at 290 K. Determine composition (in mol fraction) of the vapor phase in equilibrium with the liquid phase.

$$y_1 = \frac{P_{V_1} x_1}{P} = \frac{(0.2)(187\,kPa)}{437.4\,kPa} = \boxed{0.0855} \text{ mol fraction n-butane}$$

$$\therefore y_2 = 1 - y_1 = 1 - 0.0855 = \boxed{0.9145} \text{ mol fraction n-pentane}$$

3 **(c)** The pressure of the mixture described in part (a) is now decreased to 400 kPa while maintaining a temperature of 290 K. Under these new conditions, the mixture exists as a liquid in equilibrium with a vapour. Determine the composition (in mol %) of each phase present at this new equilibrium.

$$P = P_{V_1} x_1 + P_{V_2} x_2 = P_{V_1} x_1 + P_{V_2}(1 - x_1) = P_{V_1} x_1 + P_{V_2} - P_{V_2} x_1$$

$$x_1 = \left(\frac{P - P_{V_2}}{P_{V_1} - P_{V_2}}\right) = \frac{400\,kPa - 500\,kPa}{187\,kPa - 500\,kPa} = \boxed{0.319}$$

↳ 31.9 mol% butane

$$x_2 = 1 - 0.319 = \boxed{0.681} \rightarrow 68.1 \text{ mol\% n-pentane.}$$

$$\therefore y_1 = \frac{P_{V_1} x_1}{P} = \frac{(187\,kPa)(0.319)}{400\,kPa} = 0.149 \rightarrow 14.9 \text{ mol\%}$$

$$y_2 = 1 - 0.149 = 0.851 \rightarrow 85.1 \text{ mol\%}.$$

Question 4 ***Contd.***

(d) What is the dew point pressure (in kPa) at 290 K of a binary vapour containing 20 mol% n-butane?

2

$$x_1 + x_2 = 1$$

$$\frac{y_1 P}{P_{v_1}} + \frac{y_2 P}{P_{v_2}} = 1$$

$$\therefore P = \frac{1}{\left(\frac{y_1}{P_{v_1}}\right) + \left(\frac{y_2}{P_{v_2}}\right)} = \frac{1}{\left(\frac{0.2}{187\ kPa}\right) + \left(\frac{0.8}{500\ kPa}\right)} = \boxed{374.6\ kPa}$$

(e) You are now told that the normal boiling point of n-butane is -1°C, and that the vapor pressure of ~~n-butane~~ n-pentane is 1216.6 kPa at 320 K.

(i) Estimate the heat of vaporization (in kJ/kmol) of n-butane (*Do not use Trouton's rule*)

2

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_v}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{101.325\ kPa}{187\ kPa}\right) = \frac{\Delta H_v}{8.314\ kJ/kmol \cdot K}\left(\frac{1}{290K} - \frac{1}{272.15K}\right)$$

$$\boxed{\Delta H_v = 22526\ kJ/kmol}$$

(ii) Calculate the amount of much heat energy (in kJ) that will need be supplied to convert 1 kmol of liquid n-butane at 250 K to vapor at 280 K at a constant pressure of 1 atm in a closed variable-volume container? Assume the heat capacity of liquid butane is 132 kJ/kmol K and for butane vapour is 99 kJ/kmol K.

2

$$Q = n\,C_{p_L}(T_b - T_1) + n\,\Delta H_v + n\,C_{p_v}(T_2 - T_b)$$

$$Q = (1 kmol)\left(132 \frac{kJ}{kmol \cdot K}\right)(272.15 K - 250 K) + (1 kmol)\left(22526\ kJ/kmol\right)$$

$$+ (1 kmol)\left(99 \frac{kJ}{kmol\ K}\right)(280 K - 272.15 K)$$

$$\boxed{Q = 26227\ kJ}$$

Question 4 ***Contd.***

(iii) Determine the composition (in mol%) of a liquid in equilibrium with a vapour at 320 K if the vapour contains 50 mol% butane.

4

First we need the vapor pressure of n-butane at 320 K (call this P_v)

$$\ln\left(\frac{P_v}{P_{v_1}}\right) = \frac{\Delta H_v}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)$$

$$\ln\left(\frac{P_v}{101.325\ \text{kPa}}\right) = \frac{22\,526\ \text{kJ/kmol}}{8.314\ \text{kJ/kmol K}}\left(\frac{1}{272.15\text{K}} - \frac{1}{320\text{K}}\right)$$

$$P_v = 448.98\ \text{kPa}$$

Second, we need to find the system pressure (P)

$$P = \frac{1}{(y_1/P_{v_1}) + (y_2/P_{v_2})}$$

$$= \frac{1}{(0.5/448.98\ \text{kPa}) + (0.5/1216.6\ \text{kPa})}$$

$$= 655.9\ \text{kPa}.$$

Since the system pressure is also the bubble point pressure

$$P = P_{v_1} x_1 + P_{v_2} x_2$$

$$x_1 = \frac{P - P_{v_2}}{P_{v_1} - P_{v_2}}$$

$$x_1 = \frac{655.9\ \text{kPa} - 1216.6\ \text{kPa}}{448.98\ \text{kPa} - 1216.6\ \text{kPa}} = 0.73$$

$$\therefore x_2 = 1 - 0.73 = 0.27$$

$$\boxed{\therefore \text{Composition is 73 mol\% n-butane and 27 mol\% n-pentane}}$$