Lecture 2
Solution in the gas phase

A solution in the gas phase is defined when two or more gases are mixed together

In a gaseous mixture we can define the following physical quantities:

- Total no. of moles: $n_{tot} = n_1 + n_2 + n_3 + ... + n_i = \sum_1^i n_i$
- Mole fraction: $x_i = \dfrac{n_i}{n_{tot}}$

  then $x_1 + x_2 + x_3 + ... + x_i = 1$ $\quad$ $0 < x_i \leq 1$
- Partial Volume: $V_i = x_i V_{tot}$

  e.g. the volume the gas would occupy should it be alone, keeping P and T constant
- Partial Pressure: $P_i = x_i P_{tot}$

  e.g. the fraction of pressure due to gas i

The combined gas law PV=nRT is still valid

- This law does not care about the type of molecules, provided that they are ideal
- At a given Temperature and in a given Volume the total Pressure is determined only by the number of compounds not by their nature
- Hence → $P_{tot}V_{tot}=n_{tot}RT$
- Where $P_{tot}=\Sigma_1^i P_i$ and $V_{tot}=\Sigma_1^i V_i$
- This is true whenever there is a solution, namely when the gases do not react with each other

Absolute and relative density of either a gas or a gaseous mixture/solution

- **Absolute density**: in general density is defined as the ratio between mass and volume of a given compound; for a gas we can also use the combined gas law to rearrange the formula

$$d = \frac{g}{V} = \frac{P * MW}{RT}$$

- **Relative density** of one gas with respect to a second one (P, T, V constant): this is the ratio between the densities of the two components, which indeed is equal to the ratio of their MW

$$d_r = \frac{d_1}{d_2} = \frac{MW_1}{MW_2}$$

Absolute and relative density of either a gas or a gaseous mixture/solution

- **Density of a gaseous mixture**:
  by combining the previous two definitions and what we have learned about the properties of a gaseous solution, we can derive the following formula, in which P_j is the partial pressure and MW_j is the molecula rweight of the j-th component

$$d_{mix} = \frac{\{\Sigma_1^n P_j MW_j\}}{RT} = \frac{\{P_1 MW_1 + P_2 MW_2 + \ldots + P_n MW_n\}}{RT}$$

Exercise 1

- A sample of air is made by 0.054 mol of O_2 and 0.203 mol of other gases (mostly N_2). Calculate the partial pressure of O_2 in the air, given that P= 1atm.

$P_{O2} = x_{O2} P_{tot}$

Before applying this formula, we need to calculate dioxygen mole fraction:

$$x_{O_2} = \frac{n_{O_2}}{n_{tot}} = \frac{0.054}{0.054 + 0.203} = 0.21$$

$P_{O2} = x_{O2} P_{to\ t} = 0.21 \text{ x } 1 \text{ atm} = 0.21 \text{ atm}$

Excercise 2

- Calculate the density of a gaseous solution made by methane and molecular nitrogen at 27°C, given that P_{CH4} = 0.08 atm and P_{N2}=0.1 atm.

Let's apply the formula: $$d_{mix} = \frac{\left\{\Sigma_1^n P_j MW_j\right\}}{RT}$$

T= 273+ 27 = 300 K
MW1 = 12+4 = 16 Da
MW2 = 14 +14 = 28 Da

$$d_{mix} = \frac{(16 \times 0.08) + (28 \times 0.1)}{0.082 \times 300} = 0.166\, g l^{-1}$$

Exercise 3

- A solution of methane and sulfur dioxide at 27°C and 1 atm fills up a volume of 2L. After having eliminated SO_2, methane fills up a volume of 1.4 L at 18°C and 1 atm.
Calculate the partial pressures of the gases in the solution.

$$P_i = x_i P_{tot} = \frac{(n_i Ptot)}{n_{tot}}$$

$$n_{tot} = \frac{(P_{tot} V_{tot})}{RT_1} = \frac{1\text{atm} * 2\text{L} * molK}{(0.082\text{Latm} * 300\text{K})} = 8.13\,10^{-2}\,mol$$

$$n_{CH_4} = \frac{P_{CH_4} V_{CH_4}}{RT_2} = \frac{1atm \times 1.4 l \times mol \times K}{0.082 l \times atm \times 291K} = 5.87 \times 10^{-2} mol$$

$$P_{CH_4} = \frac{n_{CH_4} P_{tot}}{n_{tot}} = \frac{5.87 \times 10^{-2} mol \times 1atm}{8.13 \times 10^{-2} mol} = 0.72 atm$$

$$P_{SO2} = P_{tot} - P_{CH4} = 1 - 0.72 = 0.28 \text{ atm}$$

Exercise 4

- Calculate the density of molecular nitrogen at 37°C and 608mmHg.

T= 273 +37 = 310K
P = 608/760 = 0.8 atm
MW= 14 +14 = 28 Da = 28 g/mol

$$d = \frac{MW * P}{RT} = \frac{28 * 0.8}{(0.082 * 310)} = 0.88\, g/l$$

Exercise 5

- An unknown gas has density= 1.8 g/L. At the same values of T and P, N_2 has density= 1.35 g/L. Which is the molecular weight of the gas?

We can calculate the relative density of gas1 with respect to N_2:

$$\frac{d_1}{d_{N2}} = \frac{MW_1}{MW_{N2}}$$

$$MW_1 = \frac{d_1 * MW_{N2}}{d_{N2}} = \frac{1.8 * 28}{1.35} = 37.33\ Da$$

Exercise 6

- Calculate P_{tot} of a gaseous mixture made by 7g of N_2, 3.84g of O_2, 14.2g of Cl_2 in a cylinder of 10L at 27°C.

$$n_{tot} = \frac{g_{N2}}{MW_{N2}} + \frac{g_{O2}}{MW_{O2}} + \frac{g_{Cl2}}{MW_{Cl2}} = \frac{7}{28} + \frac{3.84}{32} + \frac{14.2}{70.9} = 0.57\,mol$$

$$P_{tot} = \frac{n_{tot} * R * T}{V_{tot}} = \frac{0.57\text{mol} * 0.082\text{L} * atm * 300\text{K}}{(10\text{L} * mol * K)} = 1.4\,atm$$

Exercise 7

- A balloon can fly because the density of the hot air inside is smaller than that of the external air.
  At which temperature does the air reach d=1.169 g/L at 1atm? ($\langle MW_{air} \rangle$ = 28.8Da)

$$d = \frac{P * MW}{RT}$$ → hence we can derive T from this formula

$$T = \frac{(P * MW)}{(R * d)} = \frac{(1 * 28.8)}{(0.082 * 1.169)} = 300.44\mathrm{K}$$

Exercise 8

- Calculate the density of carbon dioxide in standard conditions.

Standard conditions: T=273K; P=1atm

Molar Volume = V occupied by 1 mol of gas in standard condition

V_m=22.4L; 1 mol_{CO2} = 44g

$$d = \frac{g_m}{V_m} = \frac{44\text{g}}{22.4\text{L}} = 1.96\, g/l$$

Exercise 9

- A mixture of 50% He and 50% Xe is at 100°C and 0.8 atm. Which are the partial pressures of the two gases?

50% means 50 g of compound 1 in 100 g of solution (in this case comp1 +comp2)

Let's start calculating the moles of the two gases corresponding to 50g, then we can calculate the mole fractions and finally the partial pressures

$$n_{He}=\frac{g}{MW}=\frac{50}{4}=12.5\,mol \qquad n_{Xe}=\frac{g}{MW}=\frac{50}{131.29}=0.38\,mol$$

$n_{tot} = n_{He} + n_{Xe} = 12.5+0.38 = 12.88$ mol

$$P_{He}=x_{He}*P_{tot}=\frac{n_{He}*P_{tot}}{n_{tot}}=\frac{12.5*0.8}{12.88}=0.78\text{atm}$$

$P_{Xe} = P_{tot} - P_{He} = 0.8-0.78 = 0.02$atm

Exercise 10

- The density of dioxygen is 1.43g/L in standard conditions. Which is its density at 20°C and 1.5 atm?

We have two options: either we calculate d_2 with the standard formula or we use a proportion to compare the two values

(1) $$d_2 = \frac{P_2 * MW}{RT_2} = \frac{1.5 * 32}{(0.082 * 293)} = 1.99\, g/L$$

(2) $$\frac{d_1}{d_2} = \frac{P_1 * MW}{RT_1} * \left(\frac{RT_2}{(P_2 * MW)}\right) = \frac{P_1 * T_2}{(T_1 * P_2)}$$

$$d_2 = \frac{(d_1 * T_1 * P_2)}{(P_1 * T_2)} = \frac{1.43 * 273 * 1.5}{(1 * 293)} = 1.99\, g/L$$

Exercise 11

- 4L of N_2 and 1L of O_2 (measured at standard conditions) are inserted in an empty cylinder of 8L at 27°C. Calculate the partial pressure of the two gases.

$$n_{N2}=\frac{P_1 * V_1}{RT_1}=\frac{1*4}{(0.082*273)}=0.179\,mol$$

$$n_{O2}=\frac{1*1}{(0.082*273)}=0.045\,mol$$

$n_{tot} = n_{N2} + n_{O2} = 0.179 + 0.045 = 0.224$ mol

$$P_{tot}=\frac{n_{tot}*R*T_2}{V_2}=\frac{0.224*0.082*300}{8}=0.687\,atm$$

$$P_{N2}=x_{N2}*P_{tot}=\frac{n_{N2}*P_{tot}}{n_{tot}}=\frac{0.179*0.687}{0.224}=0.55\,atm$$

$P_{O2} = P_{tot} – P_{N2} = 0.689 - 0.55 = 0.14$ atm

alternatively:

Exercise 11 -continued

- Remember the definition of partial volume:

  $$V_{N2}=x_{N2}V_{tot}$$

  hence we could have calculated the mole fraction from these data:

$$x_{N2}=\frac{V_{N2}}{V_{tot}}=\frac{4}{5}=0.8$$

$$x_{O2}=\frac{V_{O2}}{V_{tot}}=\frac{1}{5}=0.2$$

$$\frac{P_1*V_1}{T_1}=\frac{P_2*V_2}{T_2}$$

$$P_2=P_{tot}=\frac{P_1*V_1*T_2}{(T_1*V_2)}=\frac{1*5*300}{(273*8)}=0.687\,atm$$

$P_{N2} = x_{N2}P_{tot} = 0.8*0.687 = 0.55$ atm

$P_{O2} = P_{tot} – P_{N2} = 0.687 – 0.55 = 0.14$ atm