

## Gases Tutorial 2

### Partial Pressures

A gas sample contains the following amounts of three gases:

$$\text{H}_{2(\text{g})} : 3.00 \text{ g}$$

$$\text{Cl}_{2(\text{g})} : 20.0 \text{ g}$$

$$\text{Kr}_{(\text{g})} : 30.0 \text{ g}$$

The sample is contained in a 20.0 L container at 50° C. Find the partial pressures of each gas.

$$n(\text{H}_{2(\text{g})}) = 3.00 \text{ g} / 2.01 \text{ g/mol} = 1.49 \text{ mol}$$

$$n(\text{Cl}_{2(\text{g})}) = 20.0 \text{ g} / 71.1 \text{ g/mol} = 0.28 \text{ mol}$$

$$n(\text{Kr}_{(\text{g})}) = 30.0 \text{ g} / 83.80 \text{ g/mol} = 0.358 \text{ mol}$$

$$n_{\text{total}} = 1.49 + 0.28 + 0.358 = 2.13 \text{ mol}$$

$$X_{\text{H}_2} = n_{\text{H}_2} / n_{\text{total}} = 1.49 / 2.13 = 0.70$$

$$X_{\text{Cl}_2} = n_{\text{Cl}_2} / n_{\text{total}} = 0.28 / 2.13 = 0.13$$

$$X_{\text{Kr}} = n_{\text{Kr}} / n_{\text{total}} = 0.358 / 2.13 = 0.17 \text{ (note that the mole fractions sum to 1.00)}$$

$$p_{\text{total}} = n_{\text{total}}RT/V = 2.13 \text{ mol} (8.314 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1} \times 323 \text{ K}) / 0.020 \text{ m}^3 = 285997 \text{ Pa}$$

$$p_{\text{H}_2} = p_{\text{total}} X_{\text{H}_2} = 286000 \text{ Pa} (0.70) = 200,200 \text{ Pa}$$

$$p_{\text{Cl}_2} = p_{\text{total}} X_{\text{Cl}_2} = 286000 \text{ Pa} (0.13) = 37,200 \text{ Pa}$$

$$p_{\text{Kr}} = p_{\text{total}} X_{\text{Kr}} = 286000 \text{ Pa} (0.17) = 48,600 \text{ Pa}$$

$$\text{note that } p_{\text{H}_2} + p_{\text{Cl}_2} + p_{\text{Kr}} = 200,200 + 37,200 + 48,600 = 286,000 \text{ Pa} = p_{\text{total}}$$

### Gas Density

e.g. To identify the contents of an unlabelled cylinder of gas, a sample was weighed and found to have a density of 5.380 g/L at 15° C and 736 Torr. What is the molecular weight of the gas?

Here,  $p = 736/760 = 0.968 \text{ atm}$  ( $\times 101325 \text{ Pa/atm} = 98125 \text{ Pa}$ );  $T = 15^\circ \text{ C} = 288 \text{ K}$ ; assume  $V = 1 \text{ L} = 0.001 \text{ m}^3$

$$n = pV/RT = 98125 \text{ Pa} (0.001 \text{ m}^3) / (8.314 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1} \times 288 \text{ K}) = 0.0410 \text{ mol}$$

$$\text{MW} = 5.380 \text{ g} / 0.0410 \text{ mol} = 131 \text{ g/mol (probably Xe gas!)}$$

e.g. What is the density of ammonia (NH<sub>3</sub>) at 100° C and 2 bar pressure?

$$\text{density} = pM/RT = 2 \times 10^5 \text{ Pa} (0.017 \text{ kg/mol}) / ((8.314 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1} \times 373 \text{ K})) = 1.10 \text{ kg m}^{-3} = 1.10 \text{ g L}^{-1}$$

## Kinetic Molecular Theory, Effusion, Diffusion

e.g. Calculate the average velocity of gaseous Hg atoms at 500°C.

$$v = [3RT/MW]^{1/2}$$

At 500°C (773 K), the average velocity will be  $v = [3(8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times (273+500)\text{K}) / 0.2006 \text{ kg mol}^{-1}]^{1/2} = 310.0 \text{ m/s}$

Repeat for He atoms at 500°C.

At 500°C (773 K), the average velocity will be  $v = [3(8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times (273+500)\text{K}) / 0.004 \text{ kg mol}^{-1}]^{1/2} = 2,195 \text{ m/s}$

Now calculate the average kinetic energies of Hg and He atoms at 500°C:

$$KE = 1/2 mv^2$$

$m(\text{Hg}) = 200.6 \text{ g/mol} / N_{\text{Av}} \text{ mol}^{-1} = 3.33 \times 10^{-22} \text{ g} = 3.33 \times 10^{-25} \text{ kg}$  (per atom)  
 $KE = 1/2 (3.33 \times 10^{-25} \text{ kg})(310.0 \text{ m/s})^2 = 3.20 \times 10^{-20} \text{ kg m}^2 \text{ s}^{-2} = 3.20 \times 10^{-20} \text{ J}$  (per atom)

$m(\text{He}) = 4.00 \text{ g/mol} / N_{\text{Av}} \text{ mol}^{-1} = 6.64 \times 10^{-24} \text{ g} = 6.64 \times 10^{-27} \text{ kg}$  (per atom)  
 $KE = 1/2 (6.64 \times 10^{-27} \text{ kg})(2195 \text{ m/s})^2 = 3.20 \times 10^{-20} \text{ kg m}^2 \text{ s}^{-2} = 3.20 \times 10^{-20} \text{ J}$  (per atom)

Note that the speeds are different (because of the different masses), but that the kinetic energies are the same (because of the identical temperature in each case).

e.g. Is it easier to separate the oxygen isotopes  $^{12}\text{C}$  and  $^{16}\text{C}$  by diffusion using  $\text{CO}_2$  or  $\text{CO}$ ?

This is an application of Graham's Law. The easier separation process will have a ratio of diffusion rates that is larger than the other. Thus, fewer diffusion stages would be required.

For the isotopes at the dioxides, we have:

$$\text{rate}(^{12}\text{CO}_2) / \text{rate}(^{16}\text{CO}_2) = [MW(^{16}\text{CO}_2) / MW(^{12}\text{CO}_2)]^{1/2} = [48.0 / 44.0]^{1/2} = 1.044$$

$$\text{rate}(^{12}\text{CO}) / \text{rate}(^{16}\text{CO}) = [MW(^{16}\text{CO}) / MW(^{12}\text{CO})]^{1/2} = [32.0 / 28.0]^{1/2} = 1.069$$

Thus, separation of the monoxides would be easier. Still easier to separate would be the methanes of the two carbon isotopes:

$$\text{rate}(^{12}\text{CH}_4) / \text{rate}(^{16}\text{CH}_4) = [MW(^{16}\text{CH}_4) / MW(^{12}\text{CH}_4)]^{1/2} = [20.0 / 16.0]^{1/2} = 1.118$$

## The van der Waals equation

Remember why this equation is important - it takes into account the actual volumes of the gas molecules, and the fact that gas molecules do interact (generally by forces of attraction).

$$P = (nRT)/(v-nb) - a(n/V)^2$$

e.g. given the same number of moles of  $\text{H}_2\text{O}_{(g)}$  and  $\text{CO}_{2(g)}$  both at the same T and V, which will have the larger pressure?

$b(\text{H}_2\text{O}) \approx b(\text{CO}_2)$ , since both molecules are about the same size.

However, water is a polar molecule, and so we expect  $a(\text{H}_2\text{O}) > a(\text{CO}_2)$ . Thus,  $p(\text{H}_2\text{O}) < p(\text{CO}_2)$ .

e.g. calculate the pressure exerted by 50 mol of  $\text{He}_{(g)}$  in a 2.0 L vessel at 25°C using the ideal gas law and using the van der Waals equation. Compare to the pressure exerted by the same amount of Ar under the same conditions.

For He,  $p(\text{ideal}) = nRT/V = 50 \text{ mol } (8.314 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1})(25 + 273)\text{K} / 0.002 \text{ m}^3 = 6.19 \times 10^7 \text{ Pa} = 619 \text{ bar}$

The van der Waals constants for  $\text{He}_{(g)}$  are  $a = 0.0341 \text{ L}^2 \text{ mol}^{-2} \text{ atm}$ ,  $b = 0.0237 \text{ L mol}^{-1}$ .

$$\begin{aligned} p(\text{vdW})(\text{He}_{(g)}) &= (nRT)/(v-nb) - a(n/V)^2 \\ &= (50(0.082 \text{ L atm K}^{-1} \text{ mol}^{-1})(298 \text{ K})/(2.0 \text{ L} - 50 \text{ mol } (0.0237 \text{ L mol}^{-1})) - 0.0341 \text{ L}^2 \text{ mol}^{-2} \text{ atm}(50 \text{ mol}/2 \text{ L})^2 \\ &= 1499 \text{ atm} - 21 \text{ atm} \\ &= 1478 \text{ atm} \\ &\times 1.01325 = 1,498 \text{ bar} \end{aligned}$$

For Ar,  $p(\text{ideal}) = nRT/V = 50 \text{ mol } (8.314 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1})(25 + 273)\text{K} / 0.002 \text{ m}^3 = 6.19 \times 10^7 \text{ Pa} = 619 \text{ bar}$ , i.e. same as for He because both are assumed to be ideal (no interactions among the molecules and the molecules have zero volume).

The van der Waals constants for Ar are  $a = 1.345 \text{ L}^2 \text{ mol}^{-2} \text{ atm}$ ,  $b = 0.03219 \text{ L mol}^{-1}$ .

$$\begin{aligned} p(\text{vdW})(\text{Ar}_{(g)}) &= (nRT)/(v-nb) - a(n/V)^2 \\ &= (50(0.082)(298)/(2.0 - 50(0.03219)) - 1.345(50/2)^2 \\ &= 3128 - 840 \\ &= 2288 \text{ atm} \\ &\times 1.01325 = 2,318 \text{ bar} \end{aligned}$$

Why is the vdW pressure for Ar so much larger than that for He? The  $a$  term for Ar is larger, which would make the pressure smaller. However, the  $b$  term (size of the atom) is also larger for Ar, making the pressure larger than that of He. In this case, the effect of molecular size is greater than that of intermolecular interactions.