1.10 Partial Pressures and K_p

If a reaction contains gases an alternative equilibrium expression can be set up using the partial pressures of the gases instead of concentrations.

Partial Pressure

The partial pressure of a gas in a mixture is the pressure that the gas would have if it alone occupied the volume occupied by the whole mixture.

If a mixture of gases contains 3 different gases then the total pressure will equal the 3 partial pressure added together

$$P = p_1 + p_2 + p_3$$

partial pressure = mole fraction x total pressure
of gas 1   of gas 1

$$p_1 = x_1 \, P$$

Mole fraction

mole fraction $= \dfrac{\text{number of moles of a gas}}{\text{total number of moles of all gases}}$

For a 3 part mixture

$$x_1 = \dfrac{y1}{y_1 + y_2 + y_3}$$

Example : A mixture contains 0.2 moles N_2, 0.5 moles O_2 and 1.2 moles of CO_2. The total pressure is 3kPa. Calculate the partial pressures of the 3 gases.

Total moles of gas = 0.5 + 1.2+ 0.2
   = 1.9

mole fraction of N_2	= 0.2/1.9 =0.105
mole fraction of O_2	= 0.5/1.9 =0.263
mole fraction of CO_2	= 1.2/1.9 =0.632

Partial pressure of N_2 = 0.105 x 3 =0.315

Partial pressure of O_2 = 0.263 x 3 =0.789

Partial pressure of CO_2 = 0.632 x 3 =1.896

Writing an expression for K_p

$$N_2 \, (g) + 3H_2 \, (g) \rightleftharpoons 2 \, NH_3 \, (g)$$

$$K_p = \dfrac{p \, (NH_3)^2}{p(N_2) \; p(H_2)^3}$$

p means the partial pressure of that gas

K_p = equilibrium constant

Only include gases in the K_p expression. Ignore solids, liquids, and aqueous substances.

Working out the unit of K_p

Put the unit of pressure (kPa) into the K_p equation

$$K_p = \dfrac{p \, (NH_3)^2}{p(N_2) \; p(H_2)^3}$$

Cancel out units

$$\text{Unit} = \dfrac{kPa^2}{kPa \; kPa^3}$$

$$\text{Unit} = \dfrac{1}{kPa^2}$$

$$\text{Unit} = kPa^{-2}$$

However, if the equation is written the other way round, the value of K_p will be the inverse of above and the units will be kPa^2.
It is important therefore to write an equation when quoting values of K_p.

Be careful not to use square brackets in this expression!

Example

For the following equilibrium

$$N_2 \text{ (g)} + 3H_2 \text{ (g)} \rightleftharpoons 2 NH_3 \text{ (g)}$$

1 mole of N_2 and 3 moles of H_2 are added together and the mixture is allowed to reach equilibrium. At equilibrium 20% of the N_2 has reacted. The total pressure is 2kPa. Calculate the value of K_p

	N_2	H_2	NH_3
Initial moles	1.0	3.0	0
Equilibrium moles			

20% of the nitrogen had reacted = 0.2 x1.0 = 0.2 moles reacted. Using the balanced equation 3 x 0.2 moles of H_2 must have reacted and 2x 0.2 moles of NH_3 must have formed

Work out the moles at equilibrium for the reactants and products

moles of reactant at equilibrium = initial moles – moles reacted

moles of nitrogen at equilibrium = 1.0 – 0.2 = 0.8   moles of hydrogen at equilibrium =3.0 – 0.20 x3 = **2.40**

moles of product at equilibrium = initial moles + moles formed

moles of ammonia at equilibrium = 0 + (0.2 x 2) = 0.4

|	N_2	H_2	NH_3
Initial moles	1.0	3.0	0
Equilibrium moles	0.80	2.40	0.40
Mole fractions	0.8/3.6 =0.222	2.40/3.6 =0.667	0.40/3.6 =0.111
Partial pressure in kPa	0.222 x2 = 0.444	0.667 x2 =1.33	0.111 x2 = 0.222

Finally put concentrations into Kp expression

$$K_p = \frac{p_{(NH_3)}{}^2}{p_{(N_2)}\, p_{(H_2)}{}^3}$$

$$K_p = \frac{0.222^2}{0.444 \times 1.33^3} = 0.0469 \text{ kPa}^{-2}$$

Heterogeneous equilibria for K_p

K_p expressions only contain gaseous substances. Any substance in another state is left out.

$$CaCO_{3 \text{ (s)}} \rightleftharpoons CaO_{\text{ (s)}} + CO_{2 \text{ (g)}}$$
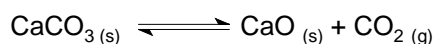
$$K_p = p\, CO_2$$

Unit kPa

Effect of changing conditions on value of K_c or K_p

The larger the K_p the greater the amount of products.
If K_p is small we say the equilibrium favours the reactants
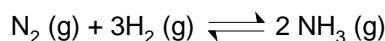
<table>
<tr><td>K_c and K_p only change with temperature.
They do not change if pressure or concentration are altered.
A catalyst also has no effect on K_c or K_p</td></tr>
</table>

Effect of temperature on position of equilibrium and K_p

<table>
<tr>
<td>Both the position of equilibrium and the value of K_c or K_p will change if temperature is altered.</td>
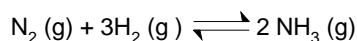<td>In this equilibrium which is exothermic in the forward direction

$$N_2 (g) + 3H_2 (g) \rightleftharpoons 2 NH_3 (g)$$
If temperature is increased the reaction will shift to oppose the change and move in the backwards endothermic direction. The position of equilibrium shifts left. The value of K_p gets smaller as there are fewer products.</td>
</tr>
</table>

Effect of pressure on position of equilibrium and K_p

<table>
<tr>
<td>The position of equilibrium will change if pressure is altered but the value of K_p stays constant as K_p only varies with temperature.</td>
<td>In this equilibrium which has fewer moles of gas on the product side
$$N_2 (g) + 3H_2 (g) \rightleftharpoons 2 NH_3 (g)$$
If pressure is increased the reaction will shift to oppose the change and move in the forward direction to the side with fewer moles of gas. The position of equilibrium shifts right. The value of K_p stays the same though as only temperature changes the value of K_p.</td>
</tr>
</table>

Increasing pressure does not change K_p.
The increased pressure increases the pressure terms on bottom of K_p expression more than the top. The system is now no longer in equilibrium so the equilibrium shifts to the right, increasing mole fractions of products and decreases the mole fractions of reactants. The top of the K_p expression therefore increases and the bottom decreases until the original value of K_p is restored.

$$K_p = \frac{p^2 NH_3}{p N_2 \; p^3 H_2}$$

$$K_p = \frac{x^2 NH_3 . P^2}{x N_2 . P \; x^3 H_2 . P^3}$$

Where P is total pressure and x mole fraction

$$K_p = \frac{x^2 NH_3 . P^2}{x N_2 \; x^3 H_2 . P^4}$$