

1.10 Partial Pressures and Kp

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

$$p_1 = x_1 P$$

mole fraction

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

For a 3 part mixture

$$x_1 = \frac{y_1}{y_1 + y_2 + y_3}$$

Example : A mixture contains 0.2 moles N₂, 0.5 moles O₂ and 1.2 moles of CO₂. If the total pressure is 3kPa. What are the partial pressures of the 3 gases?

$$\begin{aligned} \text{Total moles of gas} &= 0.5 + 1.2 + 0.2 \\ &= 1.9 \end{aligned}$$

$$\begin{aligned} \text{mole fraction of N}_2 &= 0.2/1.9 \\ &= 0.105 \end{aligned}$$

$$\begin{aligned} \text{mole fraction of O}_2 &= 0.5/1.9 \\ &= 0.263 \end{aligned}$$

$$\begin{aligned} \text{mole fraction of CO}_2 &= 1.2/1.9 \\ &= 0.632 \end{aligned}$$

$$\begin{aligned} \text{Partial pressure of N}_2 &= 0.105 \times 3 \\ &= 0.315 \end{aligned}$$

$$\begin{aligned} \text{Partial pressure of O}_2 &= 0.263 \times 3 \\ &= 0.789 \end{aligned}$$

$$\begin{aligned} \text{Partial pressure of CO}_2 &= 0.632 \times 3 \\ &= 1.896 \end{aligned}$$

Writing an expression for K_p



$$K_p = \frac{p^2 \text{NH}_3}{p \text{N}_2 p^3 \text{H}_2}$$

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

$$\begin{aligned} K_p &= \frac{p^2 \text{NH}_3(\text{g})}{p \text{N}_2(\text{g}) p^3 \text{H}_2(\text{g})} & \text{Unit} &= \frac{\text{kPa}^2}{\text{kPa} \text{kPa}^3} \\ & & \text{Unit} &= \frac{1}{\text{kPa}^2} \\ & & \text{Unit} &= \text{kPa}^{-2} \end{aligned}$$

Cancel out units

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 kPa².

It is important therefore to write an equation when quoting values of K_p.

Example

For the following equilibrium
$$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$$

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. If the total pressure is 2kPa what is 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 = $0.2 \times 1.0 = 0.2$ moles reacted.
Using the balanced equation 3×0.2 moles of H_2 must have reacted and 2×0.2 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 = $3.0 - 0.20 \times 3 = 2.40$

moles of product at equilibrium = initial moles + moles formed

moles of ammonia at equilibrium = $0 + (0.2 \times 2) = 0.4$

	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	0.222×2 = 0.444	0.667×2 = 1.33	0.111×2 = 0.222

Finally put concentrations into K_p expression

$$K_p = \frac{p^2 \text{NH}_3(\text{g})}{p \text{N}_2(\text{g}) p^3 \text{H}_2(\text{g})}$$

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

Heterogeneous equilibria for K_p

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



$$K_p = p \text{CO}_2$$

Unit kPa

Effect of changing conditions on value of Kc or Kp

The larger the Kc the greater the amount of products.
If Kc is small we say the equilibrium favours the reactants

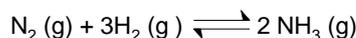
Kc and Kp only change with temperature.

It does not change if pressure or concentration is altered.
A catalyst also has no effect on Kc or Kp

Effect of Temperature on position of equilibrium and Kc

Both the **position of equilibrium** and the value of **Kc or Kp will change** if temperature is altered

In this equilibrium which is exothermic in the forward direction

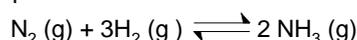


If temperature is increased the reaction will shift to oppose the change and move in the backwards endothermic direction. The position of equilibrium shifts left. The value of Kc gets smaller as there are fewer products.

Effect of Pressure on position of equilibrium and Kp

The position of equilibrium will change if pressure is altered but the value of **Kp stays constant** as Kp only varies with temperature

In this equilibrium which has fewer moles of gas on the product side



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 Kp stays the same though as only temperature changes the value of Kp.

Increasing pressure does not change Kp.
The increased pressure increases the pressure terms on bottom of Kp 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 Kp expression therefore increases and the bottom decreases until the original value of Kp is restored

$$K_p = \frac{p^2 \text{NH}_3}{p \text{N}_2 p^3 \text{H}_2}$$

$$K_p = \frac{x^2 \text{NH}_3 \cdot P^2}{x \text{N}_2 \cdot P \cdot x^3 \text{H}_2 \cdot P^3}$$

$$K_p = \frac{x^2 \text{NH}_3 \cdot P^2}{x \text{N}_2 \cdot x^3 \text{H}_2 \cdot P^4}$$

Where P is total pressure and x mole fraction