1.10 Equilibria and Kp

AS review

- Consider the reaction:

$$2SO_{2(g)} \quad + \quad O_{2(g)} \quad \rightleftharpoons \quad 2SO_{3(g)}$$

Characteristics of the dynamic equilibrium

1) The rate of the forward reaction is equal to the rate of the reverse reaction

2) The concentration of the reactants and products are unchanged under stable conditions

Le Chatelier's Principle

When a reaction at equilibrium is subject to a change in concentration, pressure or temperature, the position of the equilibrium will move to counteract the change.

1) Changing concentration – Position of equilibria shifts, K_c unchanged

$$H_{2(g)} \quad + \quad \underset{\text{Purple}}{I_{2(g)}} \quad \rightleftharpoons \quad \underset{\text{Colourless}}{2HI_{(g)}}$$

Increasing concentration:

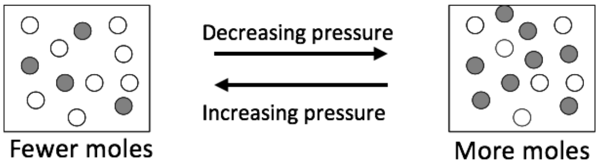
- **Adding H_2** – **increases the concentration of H_2**
- **Equilibrium** shifts to the **products**
- **To reduce the concentration** of the **H_2 – counteracting the change**
- The mixture will become less purple

Decreasing concentration:

- **Removing I_2** – **decreases the concentration of I_2**
- **Equilibrium** shifts to the **reactants**
- **To increase the concentration** of the **I_2 – counteracting the change**
- The mixture will become more purple

The equilibrium moves to oppose the change in concentration

2) Changing pressure – gases only - Position of equilibria shifts, K_c unchanged



$N_2O_4 \rightleftharpoons 2NO_2$

Colourless **Brown**

1 Mole **2 Moles**

Increasing pressure:

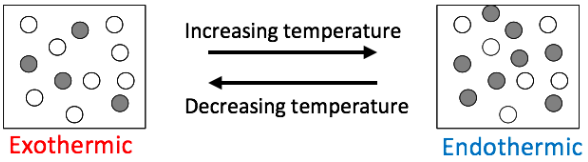
- **Equilibrium** shifts to the **reactants**
- This is the side with **fewer moles of gas**
- This will **reduce the pressure – counteracting the change**
- The mixture will become less brown

Decreasing pressure:

- **Equilibrium** shifts to the **products**
- This is the side with **more moles of gas**
- This will **increase the pressure – counteracting the change**
- The mixture will become more brown

The equilibrium moves to oppose the change in pressure

3) Changing temperature - Position of equilibria shifts, **K_c changes**



$N_2O_4 \rightleftharpoons 2NO_2$ $\Delta H = +58$ kj mol^{-1}

Colourless **Brown**

Exothermic **Endothermic**

Increasing temperature:

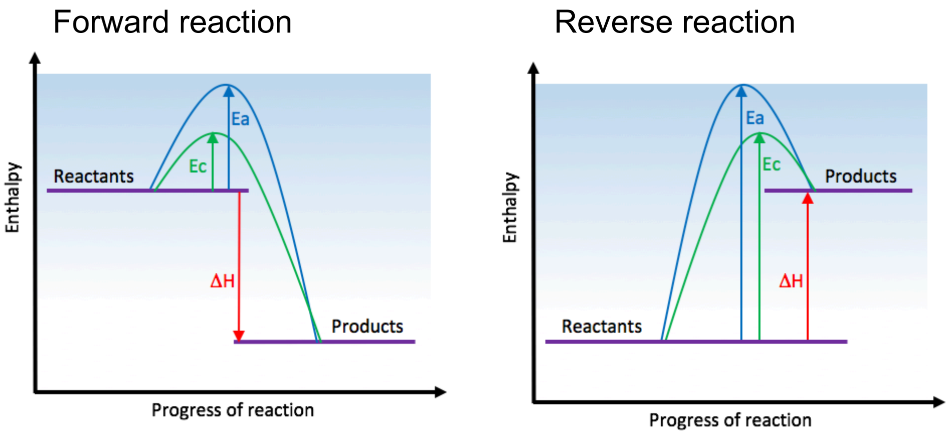
- **Equilibrium** shifts to the **products**
- As this is the **endothermic direction**
- This will **decrease temperature – counteracting the change**
- The mixture will become more brown

Decreasing temperature:

- **Equilibrium** shifts to the **reactants**
- As this is the **exothermic direction**
- This will **increase temperature – counteracting the change**
- The mixture will become less brown

The equilibrium moves to oppose the change in temperature

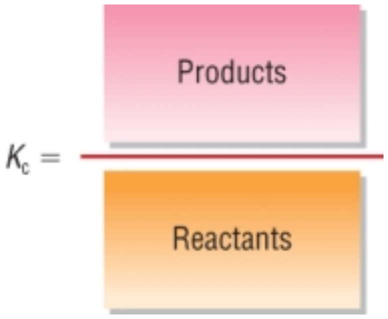
4) The effect of a catalyst on an equilibrium


Forward reaction

Reverse reaction

- A catalyst has **no effect** on the **position of the equilibrium**.
- A catalyst **speeds up the forward and reverse reaction** so it will only increase the rate at which equilibrium is achieved.

The equilibrium constant, K_c



$$K_c = \frac{[PRODUCTS]^p}{[REACTANTS]^r}$$

Writing expressions for K_c:

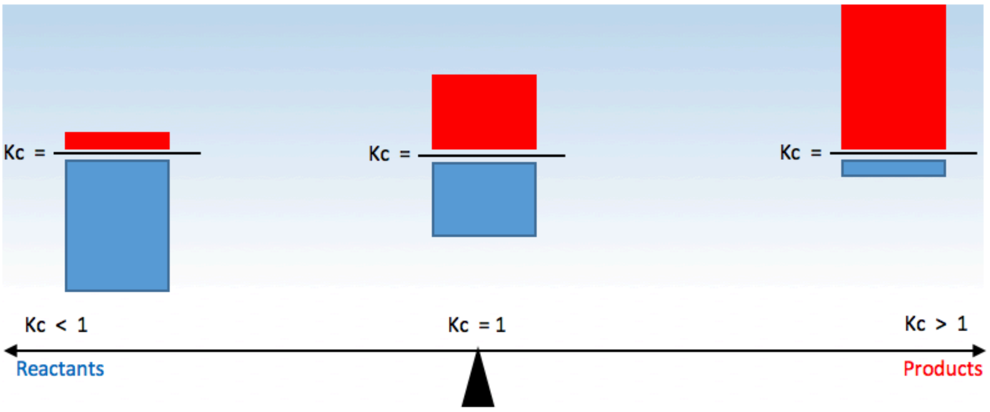
- At equilibrium the concentrations of NO_2 and N_2O_4 are constant:

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

What is the significance of a K_c

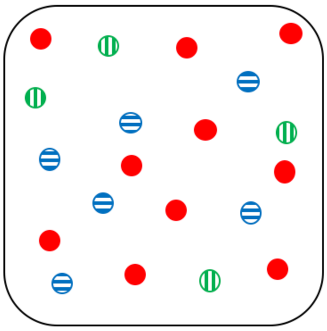
- K_c is a mathematical representation of the ratio of **products : reactants**.



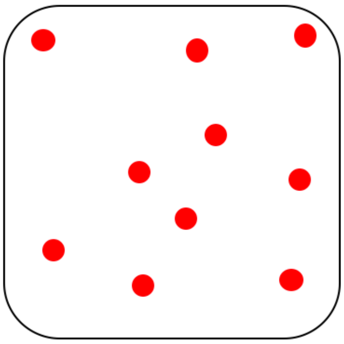
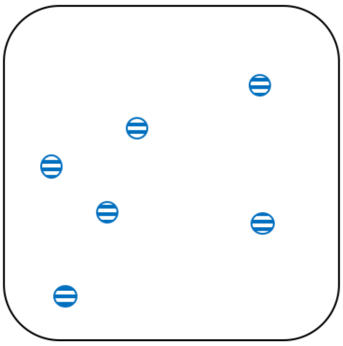
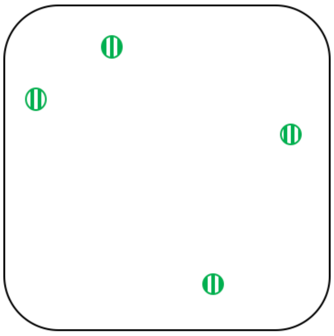
K_p and equilibria:

- K_c and K_p are both expressions to show the position of an equilibria
- c stands for an equilibrium where the individual species are measured using concentrations
- p stands for an equilibrium where the individual species are measured using partial pressures:

Imagine a mixture of gases at equilibrium with a total pressure, P_t = 100 KPa



- A total of 20 moles are responsible for the 100 KPa of pressure.
- If we separate the mixture into individual species:

		
10 / 20 th's moles of the filled red particles are responsible for a partial amount of the pressure. Partial pressure 'r', pp_r	6 / 20 th's moles of the horizontal blue striped particles are responsible for a partial amount of the pressure. Partial pressure 'b', pp_b	4 / 20 th's moles of the vertical green striped particles are responsible for a partial amount of the pressure. Partial pressure 'g', pp_g
pp_r = 50 KPa	**pp_b = 30 KPa**	**pp_g = 20 KPa**

The partial pressures, **pp**, are essentially proportional to the concentrations

The total pressure, **P_t** is equal to the sum of all of the partial pressures:

$$P_t = P_r + P_b + P_g$$

$$100 = 50 + 30 + 20$$

Writing K_p

$$Kp = \frac{\text{pp products}}{\text{pp reactants}}$$

$$Kp = \frac{pp_b \text{ x } pp_g}{pp_r}$$

- The units of K_p will depend upon the units that pressure is measured in:

Pa KPa mmHg Atm MPa

- It will also depend on the molar ratio in the equilibria equation.

Example:

$$2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)}$$

$$K_p = \frac{pp_{\text{products}}}{pp_{\text{reactants}}}$$

$$K_p = \frac{(pp\ SO_2)^2 \text{ x } pp\ O_2}{(pp\ SO_3)^2}$$

Units:

$$K_p = \frac{Pa^2 \text{ x } Pa}{Pa^2}$$

$$K_p = \frac{\cancel{Pa^2} \text{ x } Pa}{\cancel{Pa^2}}$$

$$K_p = Pa$$

Questions:

Write K_p expressions for the following equilibria, for each, work out the units

1. $N_2 + 3H_2 \rightleftharpoons 2NH_3$ Units: Pa
2. $N_2O_4 \rightleftharpoons 2NO_2$ Units: mm Hg
3. $2HI \rightleftharpoons H_2 + I_2$ Units: KPa
4. $2SO_2 + O_2 \rightleftharpoons 2SO_3$ Units: atm
5. $2A + B_2 \rightleftharpoons 2AB$ Units: MPa

The equilibrium position and K_p

1) Changing pressure – gases only - Position of equilibria shifts, **K_c unchanged**

N_2O_4	$\rightleftharpoons$	**$2NO_2$**
Colourless		**Brown**
1 Mole		**2 Moles**

Increasing pressure:

a) **Equilibrium position moves to left:**

- **Equilibrium** shifts to the **reactants**
- This is the side with **fewer moles of gas**
- This will **reduce the pressure – counteracting the change**
- The mixture will become less brown

b) **K_p is unchanged:**

$$N_2O_4 \rightleftharpoons 2NO_2$$

Equilibria shifts to LHS

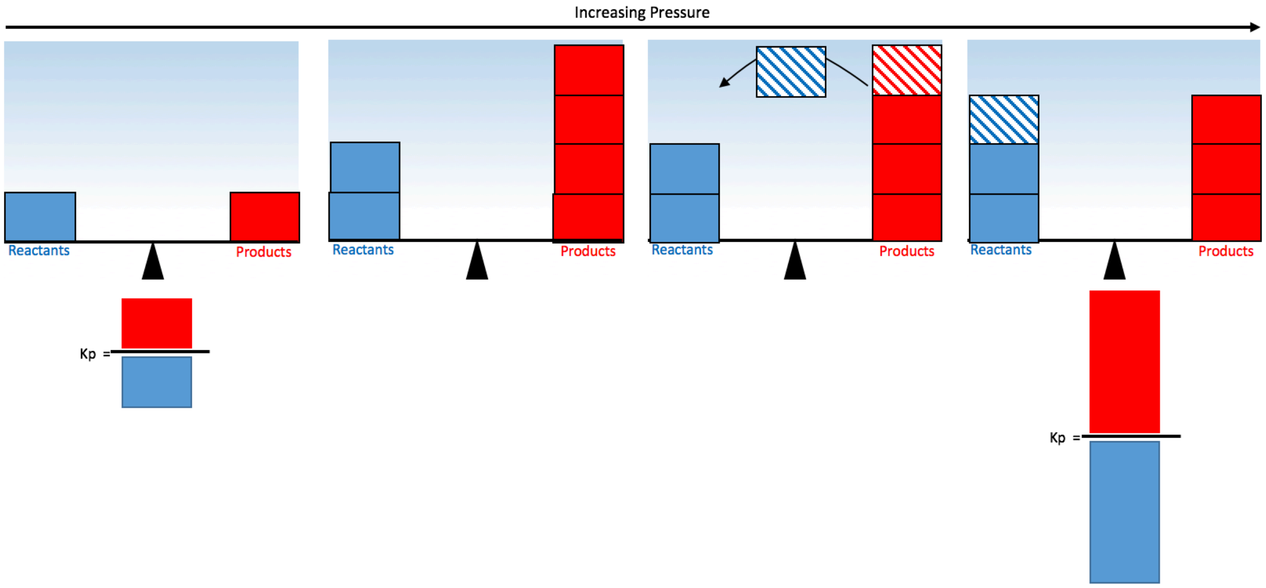
$$K_p = \frac{(pp\ NO_2)^2}{(pp\ N_2O_4)}$$

The increase in pressure also increases the partial pressure of NO_2

Partial pressure of N_2O_4 increases

This maintains K_p

- With an increase in pressure **both partial pressures increase** (smaller volume)
- Equilibrium shifts to the side with fewer moles of gas (LHS) to relieve pressure.
- This will **increase** the **partial pressure** further of the **N_2O_4**
- The partial pressure of NO_2 decreases slightly due to the shift in equilibrium. The initial increase in the partial pressures at the start outweighs this slight decrease resulting in an overall **increase partial pressure of NO_2**



Decreasing pressure:

a) **Equilibrium position moves to right:**

- **Equilibrium** shifts to the **products**
- This is the side with **more moles of gas**
- This will **increase the pressure – counteracting the change**
- The mixture will become more brown

b) **K_p is unchanged:**

$$N_2O_4 \rightleftharpoons 2NO_2$$

Equilibria shifts to RHS

$$K_p = \frac{(pp\ NO_2)^2}{(pp\ N_2O_4)}$$

The decrease in pressure also decreases the partial pressure of NO_2

Partial pressure of N_2O_4 decreases

This maintains K_p

- With a decrease in pressure **both partial pressures decrease** (larger volume)
- Equilibrium shifts to the side with more moles of gas (RHS) to increase pressure.
- This will **decrease** the **partial pressure** further of the **N_2O_4**
- The partial pressure of NO_2 increases slightly due to the shift in equilibrium. The initial decrease in the partial pressures at the start outweighs this slight increase resulting in an overall **decrease partial pressure of NO_2**

2) Changing temperature - Position of equilibria shifts, K_c changes

$$N_2O_4 \rightleftharpoons 2NO_2 \qquad \Delta H = +58 \text{ kj mol}^{-1}$$

Colourless **Brown**

Exothermic **Endothermic**

Increasing temperature:

a) Equilibrium shifts to the **right hand side**

- As this is the **endothermic direction**
- This will **decrease temperature – counteracting the change**
- The mixture will become more brown

b) K_p is increases:

$$N_2O_4 \rightleftharpoons 2NO_2$$

Equilibria shifts to RHS

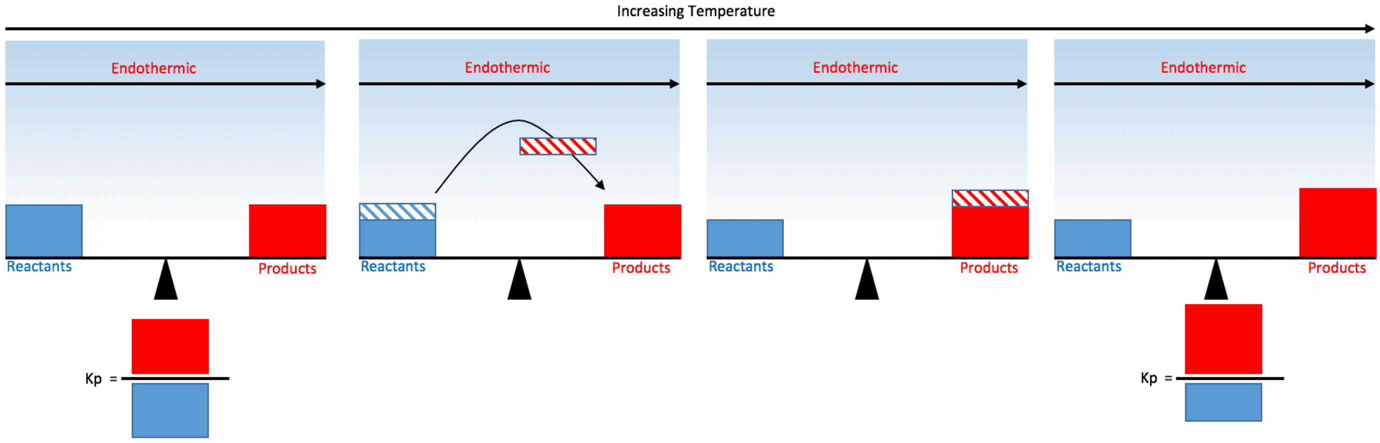
$$K_p = \frac{(pp_{NO_2})^2}{(pp_{N_2O_4})}$$

This increases the partial pressure of NO_2

This decreases the partial pressure of N_2O_4

K_p Increases

- As equilibria shifts to the products, **pp NO_2 increases**
- As equilibria shifts to the products, **pp N_2O_4 decreases**
- Products increase / reactants decrease, therefore **Kp increases**



Decreasing temperature:

a) **Equilibrium** shifts to the **reactants**

- As this is the **exothermic direction**
- This will **increase temperature – counteracting the change**
- The mixture will become less brown

b) **K_p is decreases:**

$$N_2O_4 \rightleftharpoons 2NO_2$$

Equilibria shifts to LHS

This decreases the partial pressure of NO_2

$$K_p = \frac{(pp\ NO_2)^2}{(pp\ N_2O_4)}$$

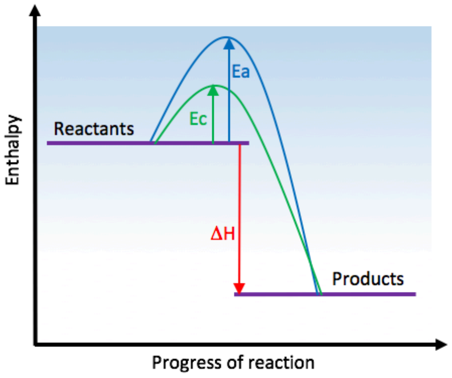
This increases the partial pressure of N_2O_4

K_p Decreases

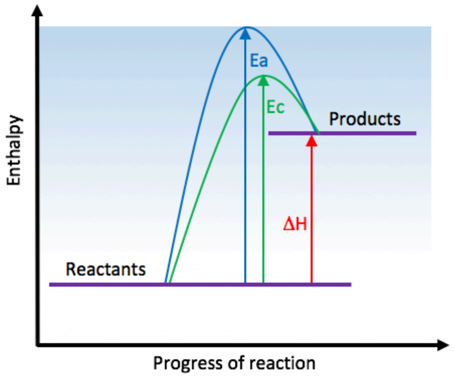
- As equilibria shifts to the products, **pp NO_2 decreases**
- As equilibria shifts to the products, **pp N_2O_4 increases**
- Products decrease / reactants increase, therefore **Kp decreases**

3) The effect of a catalyst on an equilibrium

Forward reaction



Reverse reaction



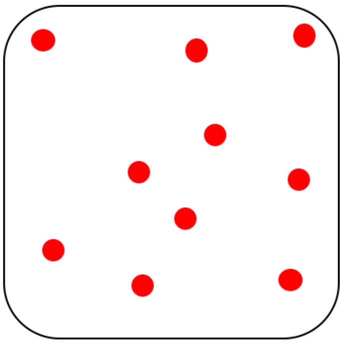
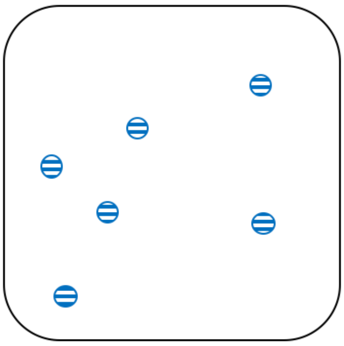
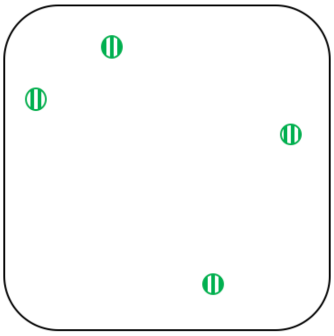
- A catalyst has **no effect** on the **position of the equilibrium**.
- A catalyst **speeds up the forward and reverse reaction <u>equally</u>** so it will only increase the rate at which equilibrium is achieved.

How are partial pressures calculated:

- Remember, each individual species exerts their own partial pressure, which, when all added together gives the total pressure.
- The partial pressure is due to the mole fraction of the total number of moles of that species present in the mixture:

Partial pressure = mole fraction x total pressure

$$\textbf{Mole fraction} = \frac{\textbf{number of moles of gas}}{\textbf{total number of moles of gas}}$$

		
Mole fraction: mf = n / n_t = 10 / 20 = 0.5 Partial pressure: pp_r = mf x P_t = 0.5 x 100 = 50	Mole fraction: mf = n / n_t = 6 / 20 = 0.3 Partial pressure: pp_b = mf x P_t = 0.3 x 100 = 30	Mole fraction: mf = n / n_t = 4 / 20 = 0.2 Partial pressure: pp_g = mf x P_t = 0.2 x 100 = 20
pp_r = 50 KPa	**pp_b = 30 KPa**	**pp_g = 20 KPa**

$$Kp = \frac{pp_b \text{ x } pp_g}{pp_r}$$

$$K_p = \frac{30 \text{ x } 20}{50}$$

K_p = 1.2 KPa

Example:

The following equilibria was found to contain 3 moles of HI, 6 moles of H_2 and 1 moles of I_2. The total pressure of the sealed vessel was 100KPa

$$2HI \rightleftharpoons H_2 + I_2$$

Moles of gas:	3	6	1
Mole fraction:	3/10	6/10	1/10
Partial pressure:	3/10 x 100	6/10 x 100	1/10 x 100
Partial pressure:	30	60	10

$$K_p = \frac{(pp\ H_2)\ \text{x}\ (pp\ I_2)}{(Pp\ \ HI)^2}$$

$$K_p = \frac{60\ \text{x}\ 10}{(30)^2}$$

$$K_p = \frac{600}{900}$$

K_p = 0.67 No units (cancel out)

Questions: Give all answers to 3SF

1) The following equilibria was found to contain 5 moles of HCl, 10 moles of H_2 and 8 moles of Cl_2. The total pressure of the sealed vessel was 50KPa

$$2HCl \rightleftharpoons H_2 + Cl_2$$

a) Write an expression for K_p

b) Calculate the mole fractions for each gas

c) Calculate the partial pressures for each gas

d) Calculate K_p for the equilibria. Include units in your answer.

Ans = 3.18

2) The following equilibria was found to contain 5 moles of NO_2 and 8 moles of N_2O_4. The total pressure of the sealed vessel was 760 mmHg

$$N_2O_4 \rightleftharpoons 2NO_2$$

Calculate K_p. Include units and show all working out clearly:

Ans = 183

3) The following equilibria was found to contain 5 moles of SO_2, 5 moles of O_2 and 8 moles of SO_3. The total pressure of the sealed vessel was 2 atm

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

Calculate K_p. Include units and show all working out clearly:

Ans = 4.59

4) An 80 dm^3 reaction vessel contains a mixture of hydrogen and oxygen with a total pressure of 300 kPa. The partial pressure of oxygen 20 kPa.

a) Calculate the partial pressure of hydrogen.

b) Calculate the mole fraction of hydrogen and oxygen.

5) The following equilibria was established. It has a K_p of 50 and the partial pressures of H_2 and I_2 are 250 and 160 respectively.

$$2HI \rightleftharpoons H_2 + I_2$$

a) Write an expression for K_p

b) Rearrange the expression and calculate the partial pressure of HI

Ans = 28.3

6) The following equilibria was established. It has a K_p of 7.48×10^{-8} kPa^{-2}. The mixture has a total pressure of 5000KPa. The partial pressures of H_2 and NH_3 are 2814 and 1250 respectively.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

Calculate the mole fraction of N_2

Ans = 0.187

Challenging:

1) 3.00 moles of $SO_{3(g)}$ are placed into an 8.00 dm^3 container and heated to 1105 K.

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$$

- At equilibrium the mixture contains 0.58 mol of $O_2(g)$.
- The total pressure of the equilibrium mixture is 3.45×10^6 Pa.
- Use this information to calculate K_p

a) Determine equilibrium moles of all gases.

b) Determine the mole fractions of each of the gases.

c) Calculate the partial pressures.

d) Write the expression for K_p.

e) Calculate K_p and state its units.

Ans = 222000

2) 9.20 g of $N_2O_4(g)$ was heated to a temperature of 340 K at a pressure of 13.3 kPa.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Once equilibrium had been reached, 70% of the $N_2O_4(g)$ had dissociated.

Use this information to calculate K_p

Ans = 51.5