CHEMICAL EQUILIBRIUM

[MH5; 12.1, 12.2, 12.4, 12.5]

- Recall that at equilibrium, the rate of a reaction is equal to the rate of its reverse reaction.
- So......it is going nowhere fast; the amounts of the reactants and the products do not change.
- Every equilibrium is governed by a number which we call the **Equilibrium Constant** (denoted by $\mathbf{K_{eq}}$).
- The equilibrium constant defines the relationship between the amounts of each reactant and product in the system.

AN EXPERIMENTAL APPROACH TO EQUILIBRIUM [MH5;12.1]

- Consider the following reaction:

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

colorless gas — red - brown gas

- Initially, this is the only reaction taking place. But before long.......

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

- reaction reverses

- And soon......

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

- equilibrium is established.

- yellow gas

- Once the system attains equilibrium, the amounts of the two gases do not change; at 100 ° C, the pressures of each gas can be measured and found to be:

$P(N_2O_4) = 0.22$ atm $\qquad\qquad P(NO_2) = 1.56$ atm

- The following table (MH5: Table 12.2) outlines three different ways that this equilibrium may be approached.

Experiment	Species	P (initial)	P(equilibrium)
1	N_2O_4	1.00	0.22
	NO_2	0.00	1.56
2	N_2O_4	0.00	0.07
	NO_2	1.00	0.86
3	N_2O_4	1.00	0.42
	NO_2	1.00	2.16

- Do these experiments have anything in common ?
- It turns out that there is a relationship between the equilibrium pressures of N_2O_4 and NO_2 that is valid for all three experiments.

$$\frac{(P_{NO_2})^2}{(P_{N_2O_4})} \simeq 11$$

- for all 3 experiments

THE EQUILIBRIUM CONSTANT EXPRESSION [MH5; 12.2]

- For the reaction: $\mathbf{a\,A + b\,B \rightleftharpoons c\,C + d\,D}$

  at equilibrium $K_{eq} = \dfrac{[C]^c [D]^d}{[A]^a [B]^b}$

- [A] represents the concentration of A and K_{eq} is the **Equilibrium Constant** for the reaction at that temperature.
- Concentration is usually expressed in **Molarity** ($molL^{-1}$) for solution chemistry; for gases, values may be in $molL^{-1}$ (K_c values) or in partial pressures (K_p values).

- For the gaseous equilibrium: $\mathbf{H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)}$

  $K_p = \dfrac{(P_{HI})^2}{(P_{H_2})(P_{I_2})} = 55$ - at some temperature

- For the gaseous equilibrium: $\mathbf{N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)}$

  $K_p = \dfrac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3}$

- When all reactants and products are in the same phase (all gas phase in the above examples) we have a **homogeneous** equilibrium.
- In a **heterogeneous** equilibrium, at least one reactant or product is in a different phase: ie; gas + solid, or solid + solution etc.

- So for: $\mathbf{C(s) + O_2(g) \rightleftharpoons CO_2(g)}$

$$K_p = \frac{P_{CO_2}}{P_{O_2}}$$

SOLID

- The concentration of C(s), [C], is a constant, and is always omitted.

Points about Equilibrium Constants

1) The expression for K depends upon the chemical equation.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

$$K_p = \frac{(P_{HI})^2}{(P_{H_2})(P_{I_2})} = 55 \text{ at } 426\,^\circ C$$

2) If the equation is reversed, the K_{eq} expression is inverted - so the K values are reciprocals of one another.

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

$$K_p = \frac{(P_{H_2})(P_{I_2})}{(P_{HI})^2} = \frac{1}{55}$$

3) If the equation is halved, the K_{eq} expression becomes the square root of the original. Or if the equation is doubled, the K_{eq} expression will be squared.

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}I_2(g) \rightleftharpoons HI(g)$$

$$K_p = \frac{(P_{HI})}{(P_{H_2})^{1/2}(P_{I_2})^{1/2}} = (55)^{1/2} = \sqrt{55}$$

4) For reactions added together, the K_{eq} is the product of the K_{eq} expressions for each step.

i) $SO_2(g) + \cancel{\tfrac{1}{2}O_2}(g) \rightleftharpoons SO_3(g)$ $\qquad K_1 = 2.2$

ii) $NO_2(g) \rightleftharpoons NO(g) + \cancel{\tfrac{1}{2}O_2}(g)$ $\qquad K_2 = 4.0$

add i) and ii) to get . . .

iii) $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$

$K_3 = K_1 \times K_2 = 2.2 \times 4.0 = 8.8$

Because: $K_3 = \dfrac{(P_{SO_3})(P_{NO})}{(P_{SO_2})(P_{NO_2})}$

$$K_1 = \frac{(P_{SO_3})}{(P_{SO_2})\cancel{(P_{O_2})^{1/2}}} \qquad K_2 = \frac{(P_{NO})\cancel{(P_{O_2})^{1/2}}}{(P_{NO_2})}$$

This is sometimes called the "Rule of Multiple Equilibria".

<u>EXAMPLE of 4:</u>

Given the following equilibria:

1) $N_2\ (g) + O_2\ (g) \rightleftharpoons 2\ NO\ (g)$ $\qquad K_{c1} = 4.3 \times 10^{-25}$

2) $NO_2\ (g) \rightleftharpoons NO\ (g) + \frac{1}{2}\ O_2\ (g)$ $\qquad K_{c2} = 1.25 \times 10^{-5}$

Calculate the value of K_c for: 3) $N_2\ (g) + 2\ O_2\ (g) \rightleftharpoons 2\ NO_2\ (g)$

1) $N_2 + O_2 \rightleftharpoons \cancel{2NO}$ $\qquad K_1 = 4.3 \times 10^{-25}$

Rev 2) x 2 : $\cancel{2NO} + O_2 \rightleftharpoons 2NO_2$ $\qquad K_2^* = \dfrac{1}{(1.25 \times 10^{-5})^2}$

Add : $N_2 + 2O_2 \rightleftharpoons 2NO_2$

$$K_3 = K_1 \times K_2^* = 4.3 \times 10^{-25} \times \frac{1}{(1.25 \times 10^{-5})^2}$$

$$= \underline{2.752 \times 10^{-15}}$$

5) The magnitude of the equilibrium constant is indicative of the position of the equilibrium.......

If "K" is large (greater than 1), the equilibrium lies towards the right, or the product side.
If "K" is small (less than 1), the equilibrium lies towards the left, or the reactant side.

The Reaction Quotient, Q [MH5; 12.4]

- For any equilibrium: $aA + bB \rightleftharpoons cC + dD$

  we may write a **Reaction Quotient, "Q"**:

  $$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

  - looks just like the EQ CONSTANT

- If the concentrations (or pressures of gaseous species) of the reactants and products are known, a numerical value for Q can be calculated.
- Comparison of this numerical value for Q to the equilibrium constant, K_{eq} gives us information about the direction of the reaction and the position of the equilibrium.

- For: $H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g)$

  $$K_{eq} = \frac{(P\,HI)^2}{(P\,H_2)(P\,I_2)} = \underline{55} \quad (\text{at } 426\ ^\circ C)$$

	$H_2\,(g)$ +	$I_2\,(g)$ ⇌	$2\,HI\,(g)$	
Before:	100	100	0	kPa
After:	20	20	2(80)	If 20 is left then 80 reacted

Before: $Q = \frac{(0)^2}{(100)(100)} = 0$

Since Q < K, reaction goes forward.

After: Q = $\dfrac{(160)^2}{(20)(20)} = 64$

If Q > K, reaction goes in reverse direction.

64 > 55 ∴ reaction reverse

If Q = K, the system is at equilibrium.

LE CHATELIER'S PRINCIPLE [MH5; 12.5]

- "If a chemical system at equilibrium is disturbed by addition or removal of a reactant or product, the equilibrium will shift in a way to minimize the disturbance". $K_p = \dfrac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3}$
- Consider the equilibrium:

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

- Addition of $H_2(g)$ causes:
  - increase in amt of NH_3
  - decrease the amt of N_2

  system tries to use extra H_2
- Removal of $NH_3(g)$ causes:
  - decrease in H_2 and N_2
  - they react to form more NH_3
- Not only can addition or removal of a reagent affect the position of equilibrium, but also a **change in pressure**.......

$$\underbrace{N_2(g) + 3\ H_2(g)}_{\text{4 moles gas}} \rightleftharpoons \underbrace{2\ NH_3(g)}_{\text{2 moles gas}}$$

- If the system is compressed: (smaller volume)
  - pressure increases
  - system shift to offset inc. pressure

⇒ To RIGHT ; smaller # moles , ∴ P decreases

- If the system is expanded: (volume increases)
  - pressure decreases
  - system shifts to increase pressure

⇒ To LEFT ; greater # moles , ∴ P increases

- What about: $\underbrace{H_2(g) + I_2(g)}_{2\ mol} \rightleftharpoons \underbrace{2\ HI(g)}_{2\ mol}$

  - position of equilibrium not affected by pressure changes

- A **temperature change** also affects the position of an equilibrium.....
- The change will affect the magnitude of the equilibrium constant.
- If a reaction produces heat as it proceeds, K will decrease as the temperature increases.
- If a reaction requires heat to proceed, K will increase as the temperature increases.