# Review: Equilibrium

## I Introduction

The reaction $2Na + Cl_2 \rightarrow 2NaCl$ takes place in one direction only. It will continue until one of the reactants is used up and then it will stop. Under normal conditions none of the NaCl produced will dissociate back to Na and $Cl_2$. However, many reactions don't go to completion and are reversible. Reversible reactions make products which themselves react to give back the products – these reactions never stop.

GRAPH TO GO HERE

After time t, products are being made at the same rate as they are reacting to make reactants. Therefore the as two opposite rates are exactly equal, there is no external change – therefore the system is in **DYNAMIC EQUILIBRIUM**. Since the rate of the reverse reaction equals the rate of the forward reaction, so the concentrations remain unchanged.

## II Recognising Equilibrium in Systems

1) It can be approached from either direction
   $2CrO_4^{-2} + 2H_3O^+ \leftrightarrow Cr_2O_7^{2-} + 3H_2O$
   yellow orange
2) Closed system
3) Concentrations remain constant
4) Macroscopic properties constant
5) Microscopic properties continuous

Homogeneous Equilibria: systems in which all of the reactants and products are in the same state
Heterogeneous Equilibria: some of the reactants are products are in different states

## The Effect of Changing the Equilibrium of a System

Because equilibrium systems are dynamic, i.e. forward and reverse reactions going on all the time, and then when conditions are changed, the system will respond and change itself.

**Le Châtelier** – If a constraint is applied to a system at equilibrium, the system will react in such a way as to oppose the applied constraint

Equilibrium position is used to describe qualitatively whether reactants or products are more plentiful, i.e. in the system of equilibrium position lies to the left .: reactants predominate; or to the right .: products predominate.

## I Changing Concentrations

Adding a reactant – therefore increasing the concentration of nitrogen, the reaction will favour the forward reaction until equilibrium is re-established

$$N_2 + 3H_2 \leftrightarrow 2NH_3$$

GRAPH TO GO HERE

Addition of reactants or removal of products → favours the forward reaction
Addition of products or removal of reactants → favours the reverse reaction

### II Increasing the Pressure on the System

$$N_2 + 3H_2 \leftrightarrow 2NH_3$$

Increasing the pressure favours reaction with fewer molecules
Decreasing the pressure favours reaction with more molecules

If there is the same number of molecules on both sides of the equations then no change occurs; pressure has no effect.

### III Effect of Temperature

Increase in temperature will favour the equilibrium in the endothermic reaction (so absorbing heat).

Decrease in temperature will shift the position if equilibrium in the exothermic direction (so releasing heat and increasing the temperature).

$$\overset{\text{Exo (increase temp)} \rightarrow}{\underset{\leftarrow \text{ Endo (decrease temp)}}{N_2 + 3H_2 \leftrightarrow 2NH_3}} \qquad \Delta H = -92.4\ \text{kJ mol}^{-1}$$

Note: in industrial plants, often moderate temperatures are used in reactions where lower temperatures favour the forward reaction. Since the rate of the reaction in these is generally much lower, thus to compensate the lower rate, a compromise moderate temperature is used to facilitate a faster rate but a lower yield of products.

### IV Changes in Volume ($P \propto \frac{1}{V}$)

An increase in volume (i.e. the system wants to decrease the volume), i.e. you have effectively decreased the pressure, hence you must increase the pressure i.e. must move to side with more molecules, (thus more pressure and less volume).
NOTE: Volume changes have No Effect on a reaction with the same number of molecules on each side.
Also a change in volume changes the concentration, and hence the rate of the reaction.

### V Adding a Noble Gas

No effect

### VI Catalyst

Has no effect on both the forward and reverse reaction.
It changes the time taken for the system to attain equilibrium, but does not alter the proportions of reactants and products in the equilibrium mixture.

### VII Industrial Application of Le Châtelier's Principle

| | | |
|---|---|---|
| Haber Process (iron catalyst) | $N_2 + 3H_2 \leftrightarrow 2NH_3$ | $\Delta H = -192\ \text{kJ mol}^{-1}$ |
| Contact Process (NO catalyst) | $2SO_2 + O_2 \leftrightarrow 2SO_3$ | $\Delta H = -98\ \text{kJ mol}^{-1}$ |

Equilibrium position is used to describe qualitative whether the reactants or products are more plentiful in the system. Equilibrium position lies to the LEFT ← i.e. the reactants predominate or to the RIGHT → products predominate.

Note : Haber process is an example of heterogeneous catalysis, recall: mechanism for catalysis.
Contact process is an example of homogeneous catalysis.

## The Equilibrium Law

- Relates the concentrations of reactants and products
- States that for any system at equilibrium, there is a numerical relationship between the concentrations of products raised to the power of their stoichiometric numbers, and the concentrations of the reactants, raised to the power of their stoichiometric numbers. This is called the Equilibrium constant $K_c$.

$$K_c = \frac{[products]}{[reac\tan ts]}$$

*example* :

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

- For heterogeneous equilibria, pure solid or pure liquid – their concentrations remain constant.
- For example:
  - $CaCO_{3(g)} \leftrightarrow CaO_{(g)} + CO_{2(g)}$
  - $Fe_2O_{3(g)} + 3CO_{(g)} \leftrightarrow 2Fe_{(s)} + 3CO_{2(g)}$
  - $Pb^{2+} + 2I^- \leftrightarrow PbI_{2(s)}$

Reversing an equation (such as the one above) can be done as follows: $K_c = \frac{1}{K_c}$

Multiplying an equation: $K_c = (K_c)^n$

Dividing an equation: $K_c = \sqrt[n]{K_c}$

### I Significance of the Numerical Value of the Equilibrium Constant

Indicates whether there are more reactants or products in the systems at equilibrium

If $K_c$ is:

Large → products predominate
Small → reactants predominate
Between $10^{-2}$ and $10^{2}$ → the reaction will not happen

### II Units of $K_c$

- Equilibrium constants for different systems can have different units.
- For example:

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} \Rightarrow K_c = \frac{(moldm^{-3})^2}{(moldm^{-3})(moldm^{-3})^3} \Rightarrow K_c = dm^6 mol^{-2}$$

### III Effect of Temperature on the Numerical Value of the Equilibrium Constant

- If the forward reaction is endothermic, an increase in temperature will increase $K_c$.
- If the forward reaction is exothermic, an increase in temperature will decrease $K_c$.

### IV Calculations Involving $K_c$

1) Calculation of $K_c$ from equilibrium concentrations given.
2) Calculation of $K_c$ from initial concentration and concentration of products at 1L container
3) Calculation of $K_c$ from initial concentration and concentration of products with different volume of container.
4) Calculation of equilibrium concentration, given $K_c$ and given initial concentration.
   Ex. $H_2 + I_2 \leftrightarrow 2HI$ $K_c = 25$
   0.10 M 0.10 M
5) Calculations of equilibrium concentration given $K_c$ is very, very small and the initial concentration, (make assumption …)
6) Reaction Quotient vs. reaction at equilibrium? If not, in which direction?

**Relationship of Gibbs Free Energy to $K_c$**

$\Delta G = -RT \ln K_c$ large $K_c$ means reaction is spontaneous