Chemical Equilibrium

by

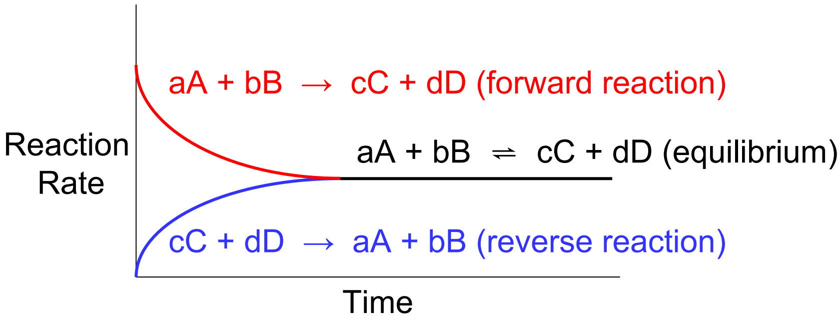
Professor Bice Martincigh

Equilibrium

- involves reversible reactions
- Some reactions appear to go only in one direction – are said to go to completion.
- indicated by $\rightleftharpoons$
- All reactions are theoretically reversible but in some cases the reverse reaction is so slight or takes place so slowly that the reaction is considered irreversible.

Homogeneous Equilibria

$$aA + bB \rightleftharpoons cC + dD$$



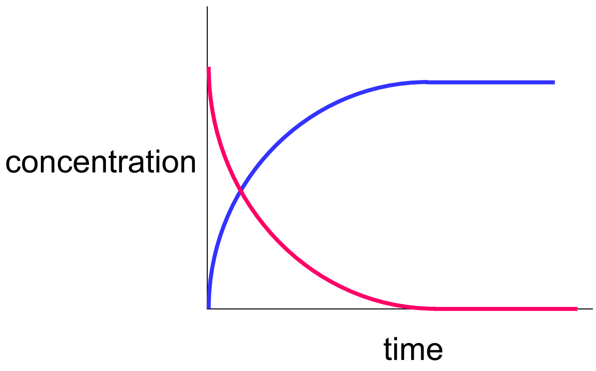
At equilibrium:

- rate (forward reaction) = rate (reverse reaction)
- overall composition of reaction mixture does not change
- individual molecules go on reacting

  dynamic equilibrium

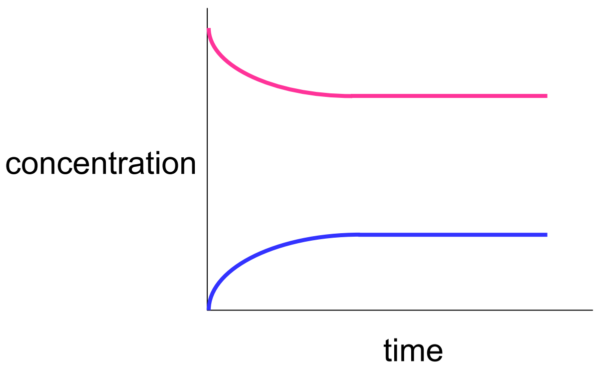
  As long as the temperature and pressure remain constant and nothing is added to or taken from the mixture, the equilibrium state remains unchanged.

$$aA + bB \rightarrow cC + dD$$



Reaction goes to ______________.

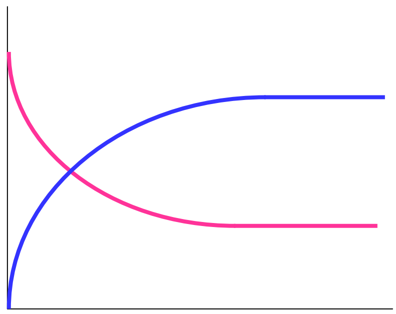
$$aA + bB \rightleftharpoons cC + dD$$



reactant molecules > product molecules

____

$$aA + bB \rightleftharpoons cC + dD$$



reactant molecules < product molecules
forward reaction favourable,

$$aA + bB \rightleftharpoons cC + dD$$

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

$K_c \equiv$ equilibrium constant

[ ] ≡ molarity **at** equilibrium

K does vary with temperature

K > 1 _______ favoured, _______ reaction favoured

K < 1 _______ favoured, _______ reaction favoured

Interpreting the equilibrium constant

If K_c for a reaction,

$$aA + bB \rightleftharpoons cC + dD$$

is large, the equilibrium mixture is mostly ________. If K_c is small, the equilibrium mixture is mostly ________. When K_c is around 1, the equilibrium mixture contains appreciable amounts of both reactants and products.

Example

For the reaction

$$SO_2(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$$

$$K_c = \frac{[SO_3]}{[SO_2][O_2]^{1/2}} = 25.0 \text{ at } 600\ ^\circ C$$

Calculate the value of K_c for each of the following reactions, at the same temperature:

- $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
- $SO_3(g) \rightleftharpoons SO_2(g) + \tfrac{1}{2}O_2(g)$

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

$$K_c = \frac{[CH_4][H_2O]}{[CO][H_2]^3}$$

	Starting Conc.	Equil. Conc.	K_c
Exp I	0.1000 M CO 0.3000 M H_2	0.0613 M CO 0.1839 M H_2 0.0387 M CH_4 0.0387 M H_2O	3.93

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

$$K_c = \frac{[CH_4][H_2O]}{[CO][H_2]^3}$$

	Starting Conc.	Equil. Conc.	K_c
Exp II	0.2000 M CO 0.3000 M H_2	0.1522 M CO 0.1566 M H_2 0.0478 M CH_4 0.0478 M H_2O	3.91

$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

$$K_c = \frac{[CH_4][H_2O]}{[CO][H_2]^3}$$

	Starting Conc.	Equil. Conc.	K_c
Exp III	0.1000 M CH_4	0.0613 M CO	
	0.1000 M H_2O	0.1839 M H_2	3.93
		0.0387 M CH_4	
		0.0387 M H_2O	

$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

When 1.000 mol CO and 3.000 mol H_2 are placed in a 10.00 dm^3 vessel at 1200 K and allowed to come to equilibrium, the mixture is found to contain 0.387 mol H_2O.

What is the molar composition of the equilibrium mixture? That is, how many moles of each substance are present?

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

Starting

Change

Equil.

CO =

H_2 =

CH_4 =

Reaction Quotient, Q_c

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

Takes the same form as K_c but is written for reactions **not** at equilibrium.

Predicting the direction of reaction

- $Q > K$ to establish equilibrium ________ reaction is favoured
- $Q < K$ to establish equilibrium ________ reaction is favoured
- $Q = K$ ____________

Example

A 50.0 dm^3 reaction vessel contains 1.00 mol N_2, 3.00 mol H_2, and 0.500 mol NH_3. Will more ammonia, NH_3, be formed or will it dissociate when the mixture goes to equilibrium at 400 °C? The equation is

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

K_c is 0.500 at 400 °C.

Equilibrium constant, K_p

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

- This is a gas phase reaction and we can use partial pressures instead of concentration, i.e. K_p.

partial pressure $\propto$ [ ]

$$P_A = \frac{n_A}{V_A}RT$$

$$= [A]RT$$

$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$

$$K_c = \frac{[PCl_5]}{[PCl_3][Cl_2]} = 9.7 \times 10^{-4}$$

$$K_p = \frac{P_{PCl5}}{P_{PCl_3}P_{Cl_2}} = 1.2 \times 10^{-5}$$

$$K_p = K_c(RT)^{\Delta n}$$

Δn = (moles of gaseous products) – (moles of gaseous reactants)

Heterogeneous Equilibria

$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

$K_c = -$ or $K_p = -$

- As long as some solid is present (no matter how much), equilibrium is reached in the same way.
- The equilibrium law for a heterogeneous reaction is written **without** concentration terms for **pure** solids or liquids.

Homogeneous Equilibria in Solution

alcohol + acid $\rightleftharpoons$ ester + water

$$C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

$$K_c = -$$

When water is a reactant or product but is **not** present in excess as the solvent, its concentration must be included in the equilibrium constant expression.

Reactions in dilute aqueous solution

Here water is the solvent and is in great excess:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$K_c = -$$

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

$$K_c = -$$

Factors that influence equilibria

- Le Chatelier's Principle

  If a system at equilibrium is subjected to a stress, the system will react in a way that tends to relieve the stress.

- Two factors cause the equilibrium to shift:
  - concentration
  - temperature

Changing the amounts of products or reactants

- Can be changed either by changing the amount of a particular substance or the volume that it is contained in.
- Changing the volume causes a change in pressure.

Adding or removing a reactant or product

The reaction shifts in a direction that will partially remove a substance that has been added or partially replace a substance that has been removed.

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

Remove water?

Original equi.	0.613	1.839	0.387	0.387
Remove H_2O	0.613	1.839	0.387	0
New Equil.	0.491	1.473	0.509	0.122

Equilibrium shifts to the ______ (_________ direction). K_c does not change.

Changing the volume

Reducing the volume of a gaseous reaction mixture shifts the equilibrium in whichever direction will, if possible, decrease the number of molecules of gas.

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

- Reduce the volume at constant T
- Equilibrium shifts to the ______ to decrease the moles of gas and reduce the pressure.

$$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$$

- Increase the pressure by decreasing the volume
- Shifts to the _____ (_________ reaction)
- Solids and liquids are incompressible and not much affected by pressure changes.

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

- Does not respond to pressure changes.

Changing the temperature

- Increasing the temperature shifts an equilibrium in a direction that produces an endothermic change (which absorbs heat).

Increasing temperature

- Exothermic reaction

  $A + B \rightleftharpoons C + D + \text{heat}$

- Endothermic reaction

  $A + B + \text{heat} \rightleftharpoons C + D$

K changes with temperature

- If the forward reaction in an equilibrium is exothermic, raising the temperature causes the equilibrium constant to become smaller.
- The opposite change in K occurs if the forward reaction is endothermic.

Agents that do not affect the position of equilibrium

- catalyst
  - affects both the forward and reverse reactions equally and does not affect the position of the equilibrium
  - causes no change in the value of K or in the concentrations at equilibrium
- adding an inert gas at constant volume

Example

Consider the reaction:

$$4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Cl_2(g);$$

$$\Delta H = 28 \text{ kJ}$$

Describe what happens to the composition of the equilibrium mixture and to K_c with each of the following changes to the system at equilibrium:

(a) Addition of oxygen gas

(b) An increase in temperature

(c) Reduction of the volume of the reaction container

(d) Addition of a catalyst

(e) Removal of HCl(g) from the reaction vessel.

Calculating equilibrium concentrations

- Consider the reaction

  $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$.

  Suppose you start with 1.00 mol each of carbon monoxide and water in a 50.0 dm^3 vessel. How many moles of each substance are in the equilibrium mixture at 1000 °C? The equilibrium constant K_c at this temperature is 0.58.

Example

- Suppose that in the preceding example 0.060 mol each of CO and H_2O are mixed with 0.100 mol each of CO_2 and H_2. What will the concentrations of all the substances be when the mixture reaches equilibrium at the same temperature?

Example

- Consider the reaction

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

Suppose 1.00 mol H_2 and 2.00 mol I_2 are placed in a 1.00 dm^3 vessel. How many moles of substances are in the gaseous mixture when it comes to equilibrium at 458 °C? The equilibrium constant K_c at this temperature is 49.7.