Industrial Chemistry

Equilibrium Principles

Chemical Equilibrium: Qualitative Features

- Some chemical reactions are reversible and come to equilibrium.
- A dynamic state - rate of forward reaction equals rate of reverse reaction.
- Final equilibrium state is the same regardless of the direction from which it is approached.
- Le Chatelier's Principle describes the way in which a system behaves if the equilibrium is disturbed.
- Reversable reactions can be driven to completion by the use of Le Chatelier's Principle.

Chemical Equilibrium: Qualitative Features

- Position of equilibrium can be affected by:

  - Changing concentration
  - Temperature
  - Pressure

Concentration

carbon dioxide + water $\rightleftharpoons$ carbonic acid

CO_2 (g) + H_2O (l) $\rightleftharpoons$ H_2CO_3 (aq)

$\rightleftharpoons$ $2H^+$ (aq) + CO_3^{2-} (aq)

Pressure

sulfur dioxide + oxygen ⇌ sulfur trioxide

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

Temperature

hydrogen + nitrogen $\rightleftharpoons$ ammonia

$3H_2\ (g) + N_2\ (g) \rightleftharpoons 2NH_3\ (g) \quad \Delta H = -96\ kJ\ mol^{-1}$

Chemical Equilibrium: Quantitative Aspects

- There is a relationship between the concentrations of reactants and products, called the equilibrium constant, K, that is independent of the initial concentration of reactants and products.

Equilibrium Constant

For the reaction:

$aA + bB \rightleftharpoons dD + eE$

$$K = \frac{[D]^d[E]^e}{[A]^a[B]^b}$$

Hydrogen Iodide Equilibrium

$[I_2]$ (x 10^{-3} mol/L)	$[H_2]$ (x 10^{-3} mol/L)	[HI] (x 10^{-3} mol/L)	K
2.840	2.276	17.15	45.50
1.634	0.967	8.49	45.61
4.058	1.720	17.79	45.34
2.597	2.597	12.84	45.88

Reaction Quotient

- Reaction quotient, Q, has the same expression as K.

$$aA + bB \rightleftharpoons dD + eE \qquad Q = \frac{[D]^d [E]^e}{[A]^a [B]^b}$$

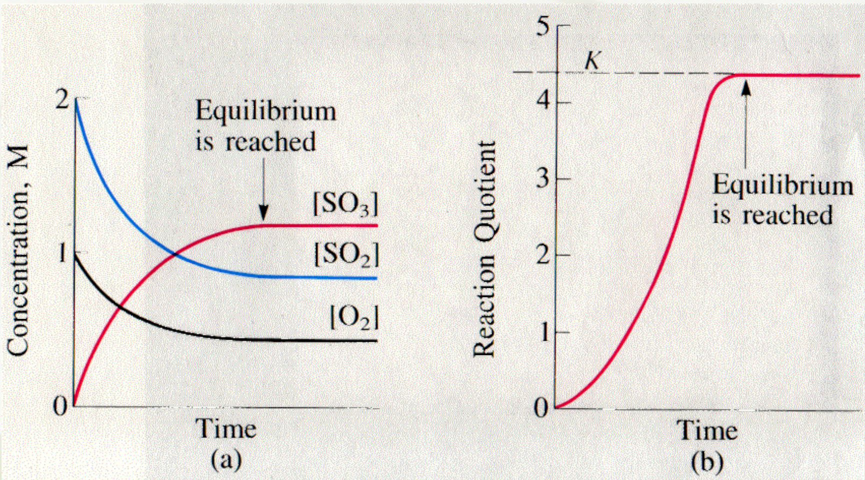
- A reaction is at equilibrium when the reaction quotient is equal to K.
- If K is different to Q then the reaction has not come to equilibrium.

Reaction Quotient

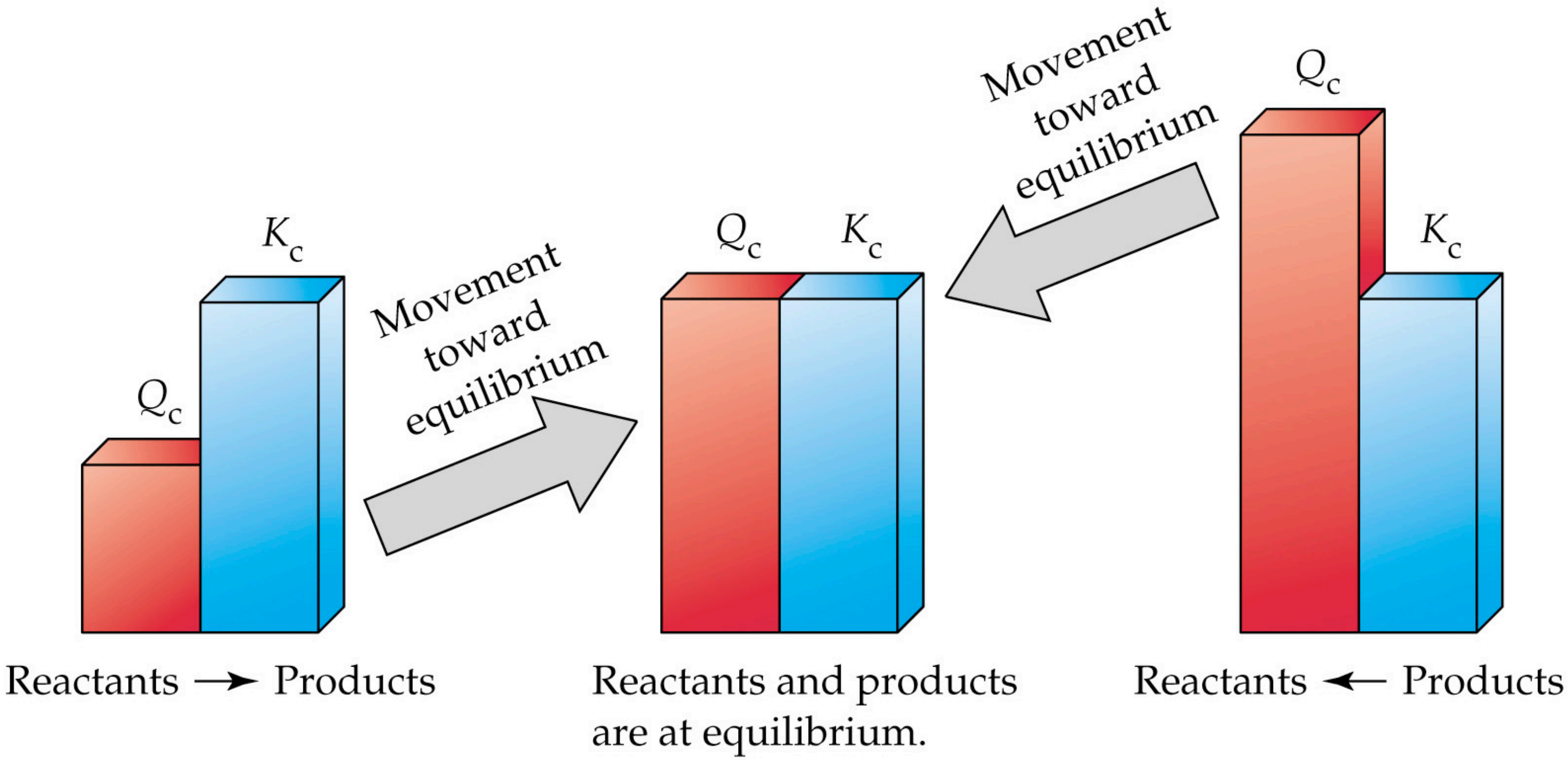
- The reaction between sulfur dioxide and oxygen

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

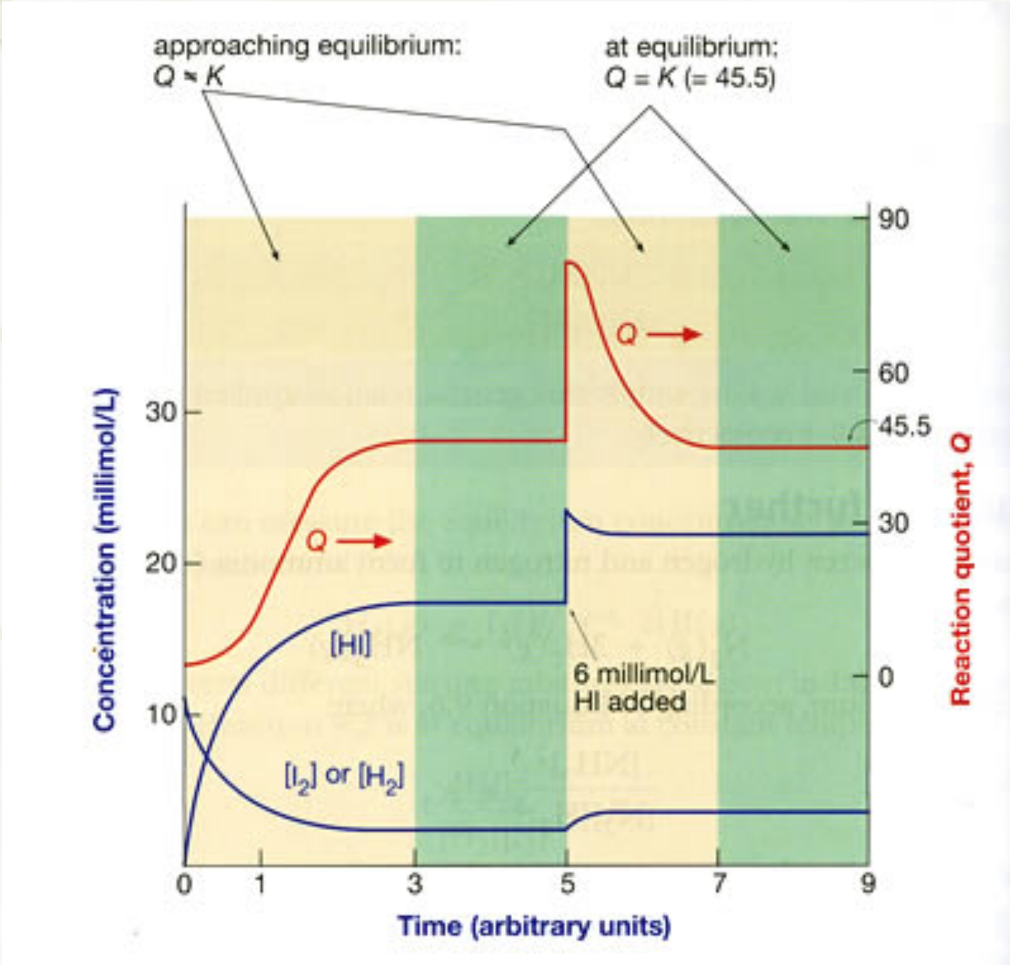
- If the initial concentration of sulfur trioxide is zero, Q starts at zero and increases to K.



Reaction Quotient



Reaction Quotient



Reaction Quotient

- At the same temperature as the quoted value for K:

  If $Q < K$, forward reaction is favoured until $Q = K$,

  If $Q > K$, reverse reaction is favoured until $Q = K$,

  If $Q = K$ the reaction is at equilibrium.

Magnitude of K

- If K is large - say greater than 10^3 - then the equilibrium lies well to the right and favours the products.
- If K is small - say less than 10^{-3} - then the equilibrium lies well to the left and favours the reactants.
- If K is between 10 and 0.1 then at equilibrium there will be an appreciable concentration of reactants and products.

Using K to Decide if a Reaction is at Equilibrium

- Dinitrogen tetroxide decomposes to nitrogen dioxide in an equilibrium reaction:

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

  If the 0.5 mol of N_2O_4 and 0.20 mol NO_2 were measured in a 500 mL flask at 100°C and the value of K was 0.48, work our whether or not the system would be at equilibrium and, if not, which direction it would proceed.

Using K to Calculate Concentration

- Phosgene decomposes according to the following equation:

  $COCl_2\ (g) \rightleftharpoons CO\ (g) + Cl_2\ (g)$

  At 1000 K, K = 0.4

  At equilibrium the concentration of carbon monoxide was 0.24 mol/L. Determine the equilibrium concentrations of chlorine and phosgene.

Equilibrium and Temperature

- The equilibrium constant, *K*, depends on temperature.
- K will be constant at the same temperature regardless of the initial concentration of reactants and products.
- Equilibrium constants are always expressed at given temperatures.

Equilibrium and Temperature

- For exothermic reactions, as the temperature increases, K decreases.
- According to Le Chatelier's Principle, the equilibrium will move towards the reactants at higher temperatures.
- The value of K must, therefore, decrease since small values for K favour the reactants.

Equilibrium and Temperature

- For endothermic reactions, as the temperature increases, K increases.
- According to Le Chatelier's Principle, the equilibrium will move towards the products at higher temperatures.
- The value of K must, therefore, increase since large values for K favour the products.

Equilibrium and Temperature

N_2O_4 (g) $\rightleftharpoons$ $2NO_2$ (g) endothermic		H_2(g) + N_2(g) $\rightleftharpoons$ $2NH_3$(g) exothermic	
Temperature (K)	**K**	**Temperature (K)**	**K**
273	5.7×10^{-4}	298	4.0×10^{8}
298	4.7×10^{-3}	500	60
373	0.48	700	0.26
500	41.4	900	5.4×10^{-3}