7.1 Equilibrium

Dynamic equilibrium

- Chemical equilibrium is **a state in which the rate of the forward reaction equals the rate of the backward reaction**
- In other words the forward and reverse reactions will continue to occur, but the concentration will stay the same
- Such a system is said to be in a state of dynamic equilibrium. Characteristics of equilibrium include:

	Feature of equilibrium state	Explanation
1	Equilibrium is dynamic	The reaction has stopped but both forward and backward reactions are still occurring at the same rate
2	Equilibrium is achieved in a closed system	A closed system prevents exchange of matter with the surroundings, so equilibrium is achieved where both reactants and products can react and recombine.
3	The concentrations of reactants and products remain constant	They are being produced and destroyed at an equal rate.
4	There is no change in macroscopic properties	Color and density do not change as these depend on the concentrations.
5	Equilibrium can be reached from either direction (products or reactants)	The reaction can be started with all reactants, all products or a mixture.

- Example: In a closed container, liquid bromine is in a dynamic equilibrium with its vapor. There will always be both liquid and gas bromine in the flask. This state is described as a dynamic equilibrium. Vaporization and condensation are both happening simultaneously in the flask. Liquid bromine is in dynamic equilibrium with bromine vapour. This can be presented as:

$$Br_2(l) \rightleftarrows Br_2(g)$$

- Dynamic equilibrium can only be established in a closed system where reactants and products cannot escape

Equilibrium Constant: K_c

- An equilibrium reaction can be represented as $aA + bB \rightleftarrows cC + dD$
- Lower case letters represent the number of moles (coefficient), the uppercase letters represent the molecule itself
- The equilibrium constant of concentration gives the ratio of concentrations of products over reactants for a reaction that is at equilibrium. The equilibrium constant expression is written as K_c and is represented as:

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

- The value of K_c represents the position of the equilibrium as equilibrium can either be near the products or reactants
    - If $K_c > 1$ then equilibrium favors the products
    - If $K_c < 1$ then equilibrium favors the reactants
- The value of K_c will remain constant as the system will adjust to keep the concentrations at equilibrium despite its environment

Le Châtelier's principle

- Le Châtelier's principle states that if a dynamic equilibrium is disturbed by changing the conditions the position of equilibrium shifts to counteract the change to re-establish an equilibrium:

Condition	Effect
Concentration	Increasing concentration shifts the equilibrium to the side with fewer moles of solute
	Decreasing concentration shifts the equilibrium to the side with more moles of solute
Pressure	Increasing pressure shifts the equilibrium to the side with fewer moles of gas
	Decreasing pressure shifts the equilibrium to the side with more moles of gas

- In order to find how temperature change affects equilibrium conditions the sign of the reaction enthalpy must be known to determine whether the reaction is exothermic or endothermic
- **Temperature is the only condition that can change the value of $\boldsymbol{K_c}$** and the position of the equilibrium

Temperature	In an exothermic reaction heat can be considered a product, so increasing the temperature will shift the equilibrium towards the reactants,
	In an endothermic heat can be considered as a reactant, so decreasing the temperature will shift the equilibrium towards the products

- A catalyst will <u>lower the activation energy an equal amount for both the forward and reverse reaction</u>
- Therefore **catalysts have no effect on the equilibrium constant**

Manipulation of K_c

Condition	Effect on $\boldsymbol{K_C}$
Inverse Reaction	$K_c' = \frac{1}{K_C} = \frac{[A]^a[B]^b}{[C]^c[D]^d}$
Multiple of a reaction	$K_c^x = \frac{[C]^{2c}[D]^{2d}}{[A]^{2a}[B]^{2b}}$
Adding two reactions	$K_c^1 \times K_c^2$

Reaction Quotient

- The reaction quotient (Q) measures the relative amounts of products and reactants present during a reaction at a particular point in time. The Q value can be compared to the Equilibrium Constant, K_c, to determine the direction of a reaction
    - If $K_C = Q$ the reaction is at equilibrium
    - If $K_C > Q$ then Q will increase and produce more products
    - If $K_C < Q$ then Q will decrease and therefore create more reactants
- The main difference between K_c and Q is that K_c describes a reaction that is at equilibrium, whereas Q describes a reaction that is not at equilibrium. To determine Q, the concentrations of the reactants and products must be known:
- A system not at equilibrium can be described as “lying to the left”, indicating that there is a greater amount of reactants or “lying to the right”, indicating that there is a greater amount of products
- As time passes and the reaction continues, the concentrations of all reaction components change and eventually reach the equilibrium concentrations. In other words, the value of Q will eventual become K_c

17.1 The equilibrium law

Equilibrium calculations

- The equilibrium law can be used either to find the value of the equilibrium constant or to find the value of an unknown equilibrium constant. The easiest approach for calculating equilibrium concentrations is to use an ICE table, which is an organized method to track which quantities are known and which need to be calculated. ICE stands for:
  - I: The initial concentration or amount
  - C: The change in concentration from the initial state to equilibrium
  - E: The equilibrium concentration

Calculating the equilibrium concentrations given K_C and initial conditions

The equilibrium constant K_C for the reaction

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

was found to be 6.78 at a specified temperature. If the initial concentrations of NO and SO_3 were both 0.03 mol dm^{-3}, what would be the equilibrium concentration of each component?

	$SO_3(g)$	+	$NO(g)$	$\rightleftharpoons$	$NO_2(g)$	+	$SO_2(g)$
Initial	0.03		0.03		0.00		0.00
Change	$-x$		$-x$		x		x
Equilibrium	$0.03 - x$		$0.03 - x$		x		x

$$K_C = \frac{[NO_2][SO_2]}{[SO_3][NO]} = \frac{x^2}{(0.03 - x)^2} = 6.78$$

Solving a quadratic gives the value of x.

- Make sure the volume of the vessel is 1. Otherwise divide the equilibrium

Gibbs free energy and Equilibrium

- Equilibrium occurs when the reaction is at a minimum value of Gibbs free energy and a maximum value of entropy
- The formula for Gibbs free energy is:

$$\Delta G^{\theta} = RT \ln K$$