7.3 The Equilibrium Constant

Opposing Rates and the Law of Chemical Equilibrium

- The Law of Chemical Equilibrium: At equilibrium, there is a constant ratio between the concentrations of the products and the reactants in any change.
- In other words, the ratio of the forward rate and the reverse rate is a constant at a specific temperature. The ratio remains constant even if it is not at equilibrium and this well tell you which direction the reaction is going.

The Equilibrium Constant

aA + bB ↔ cC + dD

$$K_c = \frac{r_{forward}}{r_{reverse}}$$

$$r_f = k_f[A]^a[B]^b$$

$$r_r = k_r[C]^c[D]^d$$

$$at equilibrium, r_f = r_r$$

$$k_f[A]^a[B]^b = k_r[C]^c[D]^d$$

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

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

- The above equation is only used with the concentrations of products and reactants when they reach equilibrium.
- Always use moles/L for our purposes. (Other units can be used)
- Be sure to read the description of this equation on page 335.
- The textbook uses K_c however, I will have always used K_{eq} so we don't get confused if I make a mistake, $K_c = K_{eq}$.
- The equilibrium law expression and its associated constant, K_c, describes the behaviour of almost all gaseous and aqueous chemical equilibria. *Solids and liquids will be dealt with late in the topic of Heterogeneous Equilibria.*

The Equilibrium Constant and Temperature

- Equilibrium is dependent on temperature.
- If you change the temperature, the rate constants are changed which also changes the equilibrium constant.

Percent Reaction at Chemical Equilibrium (another bit of data that may be given to you)

- A value that is constant for a particular set of parameters.
- E.g. $H_{2(g)} + I_{2(g)} \leftrightarrow 2HI_{(g)}$ at 448°C with always react to give 78% product.
  Regardless of how much you start with, you will always end up with 78% of the reaction going to completion and the remaining 22% found as reactants.

Measuring Equilibrium Concentrations

- Equilibrium is measured experimentally using properties similar to those used in calculating rate. E.g. colour, pressure, etc.

Calculating K_c

- Always work from a balanced equation, determine the equilibrium law equation, substitute, solve. ***See examples in your text book and we will do a couple at the end of this note.***
- ICE Tables: this is the best way to solve a problem.
- The K_c value will only tell you the amount of product and reactant in a closed system. It does not tell you how fast the reaction takes place.
- It is acceptable to ignore the units for K_c.

How to solve an equilibrium problem.

a) Write the equilibrium reaction equation.
b) Write the equilibrium constant expression.
c) Identify the problem type.
   Type 1: equilibrium [reactant(s)] and [product(s)] are given, find the value of K_c.
   Type 2: K_c given; find the values of [reactant(s)] and [product(s)] at equilibrium.
d) Solve.

Solving a Type 1 Problem

- Input concentrations of solutes or gases (or partial pressure of gases) into K_c expression and calculate K_c.
- Units of all equilibrium species must be the same (usually mol/L)

Solving a Type 2 Problem

- Range from simple to difficult.
- If only one concentration missing, substitute and solve.
- If presented with unknown concentrations use ICE method. (Initial, Change, Equilibrium).
  a) Input the algebraic representations for [reactant(s)] and [product(s)] into K_c expression and solve to given value of K_c.
  b) Isolate for "x" in simple cases and re-substitute "x" into algebraic expressions for [reactant(s)] and [product(s)] to determine exact values.

- **E.g. For the reaction $NH_4CL_{(s)} \leftrightarrow NH_{3(g)} + HCl_{(g)}$, K_c is found to be 6.0×10^{-9}. What is the concentration of the products at equilibrium? Given: $K_c = [NH_3][HCl] = 6.0 \times 10^{-9}$**

	$[NH_3]$	$[HCl]$
initial	0	0
change	+x	+x
equilibrium	x	x

$K_c = [NH_3][HCl] = 6.0 \times 10^{-9} = (x)\,(x)$
$x = 7.7 \times 10^{-7}$
$\therefore$ for the above reaction with the given K_c value the concentrations of the products would each be 7.7×10^{-7} mol/L

- If both the numerator and denominator in the K_c expression are squares, solve by taking the root of both sides and isolate for "x".
- If only the numerator or the denominator in the K_c expression is a square (the other is not) solve by approximation or the quadratic equation.

- **E.g. $I_{2(g)} \leftrightarrow 2I_{(g)}$ where $K_c = 3.8 \times 10^{-5}$**
  What are the concentrations at equilibrium if you initially start with 0.200 mol/L of I_2?

	$[I_2]$	$[I]$
initial	0.200	0
change	–x	+2x
equilibrium	0.200 – x	2x

substitute: $$3.8 \times 10^{-5} = \frac{(2x)^2}{(0.200 - x)}$$

Option 1: approximation

- Use approximation rule to see if it can be solved by approximation.
- If the concentration from which "x" is being subtracted from, or to which "x" is added, must be at least 100 times larger than the value of the given K_c.
  check: $\frac{0.200}{3.8 \times 10^{-5}} = 5260$*, since it is greater than 100 you can use the approximation* $0.200 \approx (0.200 - x)$
- What does this mean? The concentration of the product is very small compared to the reactant. Very little I produced.
- You must check to see if you approximation is justified (correct) by substituting the values back into the K_c expression and ensure that the error is less than 5%.

- Solve: $3.8 \times 10^{-5} = \frac{(2x)^2}{(0.200)}$
  $x = 1.38 \times 10^{-3}$
  $[I_2] = 0.200 - x = 0.200 - 1.38 \times 10^{-3} = 0.198$ mol/L
  $[I] = 2x = 2(1.38 \times 10^{-3}) = 0.003$ mol/L

Option 2: quadratic equation

$$3.8 \times 10^{-5} = \frac{(2x)^2}{(0.200 - x)}$$

$4x^2 + 3.8 \times 10^{-5}x - 7.6 \times 10^{-6} = 0$

substitute into: $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$x = 1.38 \times 10^{-3}$

$[I_2] = 0.200 - x = 0.200 - 1.38 \times 10^{-3} = 0.198$ mol/L

$[I] = 2x = 2(1.38 \times 10^{-3}) = 0.003$ mol/L

Compare results from both methods.

Heterogeneous Equilibria

- Homogeneous equilibria: equilibria in which all entities are in the same phase.
- Heterogeneous equilibria: equilibria in which reactants and products are in more than one phase.
- E.g. $NaCl_{(s)} \leftrightarrow Na^+_{(aq)} + Cl^-_{(aq)}$
  $K_c = [Na^+_{(aq)}]\,[Cl^-_{(aq)}]$
- We ignore the material in the solid or liquid state since their concentrations do not change. The term mol/L in the case of solids and liquids is equivalent to their density, which will not change during the reaction.

Qualitatively Interpreting the Equilibrium Constant

- K>>1 products are heavily favoured and reaction nears completion.
- $K \cong 1$ concentrations of products and reactants are approximately equal at equilibrium.
- K<<1 reactants are heavily favoured and reactants do not tend to react.

Homework

- Read 7.3
- All Practice Problems
- All Section Review Problems