AP Chemistry
Equilibrium Notes

Consider some reaction with stoichiometric coefficients as follows:

$A + 2B \leftrightarrow 2C + D$

The reaction will proceed until there is no longer any net reactants or products being formed. This tells us nothing about the rate of the reaction (kinetics).

Back and forth reactions continue to occur at the microscopic level but macroscopically the system is in equilibrium.

Equilibrium Law:

K = Product of the concentration of products/Product of the concentrations of reactants

where K is the equilibrium constant at a particular temperature.

For concentrations expressed in molarity (M) units, the symbol is K_c

Given $aA + bB \leftrightarrow cC + dD$ then (small case letters being the coefficients of the balanced equation):

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

Values in brackets represent the concentration of that particular substance expressed in molarity units.
Note: Substances with constant concentrations (i.e. solids, pure liquids and solvents when solute < 1M) are not included in the formula since their concentrations change very little.

Example:

Write the equilibrium expressions for the following reversible reactions.

a) $4NH_{3(g)} + 5O_{2(g)} \leftrightarrow 4NO_{(g)} + 6H_2O_{(g)}$
b) $BaO_{(s)} + CO_{2(g)} \leftrightarrow BaCO_{3(s)}$

Modifying the equilibrium constant

1) Reversing the reaction $K_c = 1/K_c'$ $= K_c'^{-1}$

Reactions that are spontaneous in one direction (K_c>1) are nonspontaneous in the reverse direction.

2) Multiplying coefficients in a reaction equation by some number, z.

$K_c' = K^z$

This is useful for finding K_c values for unknown reactions using known reaction values, as we shall see.

3) Adding chemical reactions together

$K_{overall} = K_1 \times K_2 \times \ldots$

Ex.	$aA + bB \leftrightarrow cC$	K_1
	$cC + dD \leftrightarrow bB + fF$	K_2
	$aA + dD \leftrightarrow fF$	$K_{overall} = K_1 \times K_2$

Example:

Given the two reactions below, what is the equation for the addition of these two reactions, and what is the final Kc value?

$NO_{2(g)} \leftrightarrow NO_{(g)} + ½ O_{2(g)}$ $K_2 = 0.012$

$SO_{2(g)} + ½ O_{2(g)} \leftrightarrow SO_{3(g)}$ $K_1 = 20$

The **Reaction Quotient (or mass-action expression)**, Q

The reaction quotient identifies the current state of the concentrations of a reaction. When the system is in equilibrium the $Q = K_c$. The equation is set up in exactly the same manner.

Reaction progress: Comparing the Values of Q and K

If $Q<K$ then reactant → product
If $Q>K$ then product → reactant
If $Q=K$ the equilibrium is established

In order to solve an **equilibrium expression**, you must determine 1) The initial conditions of the system (M), 2) What concentration changes will take place 3) and the concentrations of the system at equilibrium. Often it is easiest to determine these values with an **equilibrium table**.

Solving equilibrium problems

If solving for unknown equilibrium concentrations

1. Set up mass-action expression
2. write reaction table
3. substitute values in expression
4. solve for x

Sometimes the quadratic formula will need to be used. Simplify perfect squares if possible
If reaction direction is not obvious, first compare Q with K
If K is small and the reactant concentration is large, then x may be ignored (5% change in concentration as a rule of thumb.)

Ex. At 400°C, $K_c = 64$ for the equilibrium

$H_{2(g)} + I_{2(g)} \leftrightarrow 2HI_{(g)}$

1.0 mole of H_2 and 2.00 moles of I_2 are introduced into an empty 0.50 L reaction vessel. Find the equilibrium concentrations of all components at 400°C

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = 64$$

Concentration	H_2	I_2	2HI
Initial	2.0M	4.0M	0
Change	-x	-x	2x
Equilibrium	2.0-x	4.0-x	2x

$Kc = (2x)^2 /((2.0-x)(4.0-x)) = 64$

Rearranging and solving the quadratic formula gives 1.9 and 4.5 mol/L of which only 1.9 mol/L is a plausible answer.

Examples:

1. 2.0 moles of I_2 and 4.0 moles of Br_2 are placed in a 2.0L reactor at 150°C, and reaction occurs until equilibrium is reached:
   $I_{2(g)} + Br_{2(g)} \leftrightarrow 2IBr_{(g)}$
   Analysis then shows that the reactor contains 3.2 moles of IBr. What is the value of the equilibrium constant K_c for the reaction?

2. At a certain temperature, the reaction
   $CO_{(g)} + Cl_{2(g)} \leftrightarrow COCl_{2(g)}$ has an equilibrium $K_c = 13.8$. Is the following mixture in equilibrium and if not, in which direction will the reaction proceed? $[CO]_o = 2.5M$, $[Cl_2]_o = 1.2M$, $[COCl_2]_o = 5.0M$

Sometimes equilibrium expressions are solved by methods of successive approximations or basic assumptions about concentrations.

In general:

A very large equilibrium constant is one where the value of K_c is at least 100 times greater than the initial concentrations.

The value of K_c is considered to be small when the equilibrium constant is less than one one-hundredth (<0.01) of the initial concentrations.

If K_c is neither very large nor very small, assumptions cannot be used and analytical solutions are then sought.

Equilibrium Constant for Gas-Phase Reactions K_p

From PV = nRT n/V = P/RT, at constant temperature where n/V = concentration

For the balanced chemical equation $aA_{(g)} + bB_{(g)} \leftrightarrow cC_{(g)}$

$K_p = P_C^{\,c}/(P_A^{\,a}\, P_B^{\,b})$

Relationship between K_p and K_c

Consider $aA_{(g)} \leftrightarrow bB_{(g)}$ $K_c = [B]^b/[A]^a$ $K_p = P_B^{\,b}/P_A^{\,a}$

$P_A = n_ART/V$ $P_B = n_BRT/V$

$K_p = (n_BRT/V)^b/(n_ART/V)^a = ((n_B/V)^b/(n_A/V)^a)\,(RT)^{b-a}$ recall n/V = molarity (M)

$\therefore$ $K_p = [B]^b(RT)^{\Delta n(gas)}/[A]^a = K_c(RT)^{\Delta n(gas)}$

Units for equilibrium constants

Normally considered to be dimensionless

Units for $K_p = (atm)^{\Delta n}$ $K_c = (M)^{\Delta n} = (mol/L)^{\Delta n}$

Examples:

At 400°C, $K_c = 64$ for the equilibrium

$$H_{2(g)} + I_{2(g)} \leftrightarrow 2HI_{(g)}$$

1.00 mol of H_2 and 2.00 mol of I_2 are introduced into an empty 0.50L reaction vessel. Find the equilibrium concentrations of all components at 400°C.

Nitrogen and oxygen can combine to form either $NO_{(g)}$ or $N_2O_{(g)}$

$$N_{2(g)} + O_{2(g)} \leftrightarrow 2NO_{(g)} \qquad K_c = 4.1x10^{-31}$$

$$N_{2(g)} + \tfrac{1}{2} O_{2(g)} \leftrightarrow N_2O_{(g)} \qquad K_c = 2.4x10^{-18}$$

Also $N_2O_{(g)}$ can react with oxygen to produce $NO_{(g)}$

$$N_2O_{(g)} + \tfrac{1}{2} O_{2(g)} \leftrightarrow 2NO_{(g)}$$

What is K_c for this reaction? What is K_p (assume 500°C)?

At 850°C, the equilibrium constant K_p for the reaction

$$C_{(s)} + CO_{2(g)} \leftrightarrow 2CO_{(g)}$$

has a value of 10.7. If the total pressure in the system at equilibrium is 1.000 atm, what is the partial pressure of carbon monoxide?

Stresses on a system: Le Châtelier's Principle

Stresses on a system can come in the form of changes in temperature, concentration, and in the case of gases, pressure. Henri Louis Le Châtelier (1850-1936) in researching flames in hopes of preventing mine explosions, observed the following:

If a change in conditions (stress) is imposed on a system at equilibrium, the equilibrium position will shift in the direction that tends to reduce that change in conditions. (Systems can be homogeneous or heterogeneous)

As an example, if a particular reaction is exothermic and heat is added to the system, the system assumes that too much product has been formed and will force the reaction back towards reactants.

Effect of Changing Concentrations

Concentration Change	Observed Effect
Increase reactant	Favors products
Decrease reactant	Favors reactants
Increase product	Favors reactants
Decrease product	Favors products

Effect of Pressure on Gaseous Reactions

Value of Δn_g	Increasing Pressure	Decreasing Pressure
Positive	Favors reactants	Favors products
Zero	No effect	No effect
Negative	Favors products	Favors reactants

Δn_g = Total moles of product – Total moles of reactant

Effect of Temperature Changes

Temperature Change	Reaction Type	Effect On Reaction	Effect On K
Increase	Exothermic	Favors reactants	Decrease
Increase	Endothermic	Favors products	Increase
Decrease	Exothermic	Favors products	Increase
Decrease	Endothermic	Favors reactants	Decrease

*** The only experimental variable that has any effect on the value of the equilibrium constant is temperature.**

Examples:

1. For the reaction at equilibrium
   $2NaHCO_{3(s)} \leftrightarrow Na_2CO_{3(s)} + H_2O_{(g)} + CO_{2(g)}$ $\Delta H^o = 128kJ$
   state the effects (increase, decrease, or no change) of the following stresses on the number of moles of sodium carbonate (Na_2CO_3) at equilibrium in a closed container. (Note that Na_2CO_3 is a solid; its concentration will remain constant, but the amount can change.)
   a. Removing $CO_{2(g)}$
   b. Adding $H_2O_{(g)}$
   c. Raising the temperature
   d. Adding $NaHCO_{3(s)}$

2. Some hydrogen and iodine are mixed at 400°C in a 1.00 liter container, and when equilibrium is established the following concentrations are present: [HI] = 0.490M, $[H_2]$ = 0.080M, and $[I_2]$ = 0.060M. If an additional 0.300 moles of HI is added, what concentrations will be present when the new equilibrium is established?

3. At 25°C the equilibrium constant, K_c, for the following reaction is $4.66x10^{-3}$. If 0.800 moles of N_2O_4 is injected into a closed 1.00 glass container at 25°C, what will the equilibrium concentrations of the two gases be? What will the concentrations be at equilibrium if the volume is suddenly halved at constant temperature? $N_2O_{4(g)} \leftrightarrow 2NO_{2(g)}$

Other Expressions Related to Equilibrium Constants

1. Solubility Product K_{sp}

The solubility product is a measure of the amount of a compound (concentration) that will dissolve in solution. This is related to the solubility rules learned earlier in the year.

Consider the equation:

$A(B)_{x\ (s)} \leftrightarrow A^{y+}_{(aq)} + xB^{z-}_{(aq)}$

The solubility product expression will be

$K_{sp} = [A^{y+}][B^{z-}]^x$ note that the solid is not part of this expression

With the **common ion effect**, the solubility of a compound can be decreased by the presence of an ion already in solution that is "common" to one of the ions in the compound under consideration. In this case, the initial concentrations of the dissolved ions must be added to the K_{sp} equation. Be mindful of simplifications where applicable, as these equations can quickly become complex as the order of the equation increases.

Solutions are considered to be **insoluble** if a saturated solution contains < .1M concentration.

2. Weak acid and weak base equilibria

a. Acid dissociation constant K_a
b. Base dissociation constant K_b

Gives the amount of dissociation for a weak acid or base. The expression is the same as the others remembering that pure liquid water is not included in the expression.

3. Formation Constants (complexation reactions)

Metal ions can react with anions and molecules to form chemical species called complexes such as in the following reaction:

$$Cu^{2+}_{(aq)} + 4NH_{3(aq)} \leftrightarrow Cu(NH_3)_4{}^{2+}_{(aq)}$$

The equilibrium expression is

$K_f = [Cu(NH_3)_4{}^{2+}]/([Cu^{2+}][NH_3]^4)$ where K_f is called the formation constant.

For the reverse reaction, the equilibrium expression is flipped and the expression is known as the dissociation constant, K_d

$K_f = 1/K_d$