Unit 10

General Equilibrium

Chemical equilibrium is the condition reached, in a chemical reaction, when the concentration of reactants and products no longer change, or are constant. This condition is attained when the rates of the forward and reverse reactions are equal.

$$aA(g) + bB(g) \rightarrow cC(g) + dD(g)$$

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

K_c is the equilibrium constant in which the concentration of reactant and products are expressed in terms of molarity. K_p is the equilibrium constant in which the amounts of reactant and products are expressed in terms of partial pressures measured in atm or mm Hg.

The equilibrium constant is a number whose value reflects whether the amount of products is greater or less than the amount of reactants at equilibrium. When K is >1, the amount of products is greater than reactants; the reaction favors products. When K is <1, the amount of products is less than reactants; the reaction favors reactants.

The equilibrium constant expression is the quotient of product equilibrium concentration to reactant equilibrium concentrations as determined by the balanced chemical equation.

1. The following reaction is at equilibrium at a particular temperature

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

and the $[H_2]_{eq} = 0.012$ M, $[I_2]_{eq} = 0.15$ M and $[HI]_{eq} = 0.30$ M. Calculate the magnitude of K_c for the reaction.

Relationship of Kp to Kc:

Consider the reaction

$$A(g) + B(g) \leftrightarrow 3C(g)$$

The Kp expression for this would be:

$$Kp = \frac{P_C^{\ 3}}{P_A P_B}$$

But remember that conc. is mol/L, and if you rearange the ideal gas law:

PV = nRT

P = (n/V)RT = [conc]RT

$$Kp = \frac{\{[C]RT\}^3}{\{[A]RT\}\{[B]RT\}} = \frac{[C]^3}{[A][B]}(RT)^1 = Kc\,(RT)^1$$

This reduces to the general

$$Kp = Kc\,(RT)^{\Delta n}$$

Where Δn is the change in the # if moles of a gas. You don't memorize this formula..its given to you on your sheet, but do use it.

3. At 1100 K, $K_p = 0.25$ for the reaction: $2SO_2(g) + O_2(g) \leftrightarrow 2SO_3$
   Calculate K at this temperature.

Changing reaction form

I f the reaction is changed in anyway, the value of the equilibrium constant will change, but this changed can be determined algebraically.

Consider the following reaction

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

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = 50.$$

If the reaction is written as

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

$$K_c' = \frac{[H_2][I_2]}{[HI]^2} = \frac{1}{K_c} = \frac{1}{50} = 0.02$$

If the reaction is written as

$$\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \leftrightarrow HI(g)$$

When the coefficients in the reaction are changed, the new equilibrium constant expression becomes;

$$K_c'' = \frac{[HI]}{[H_2]^{1/2}[I_2]^{1/2}} = \sqrt{K_c} = 7.07$$

Adding equations

If two reactions are added, the resulting constant of the equation will be the products of the two equations that are added.

Consider the following reactions:

$$A \leftrightarrow B \qquad Kc_1 = \frac{[B]}{[A]}$$

$$C \leftrightarrow D \qquad Kc_2 = \frac{[D]}{[C]}$$

$$A + C \leftrightarrow D + B \qquad Kc_3 = \frac{[B][D]}{[A][C]} = Kc_1 \times Kc_2$$

4. Equilibrium constants for the following reactions have been determined at 550 °C:

$CoO(s) + H_2(g) \leftrightarrow Co(s) + H_2O(g) \qquad K_1 = 67$

$CoO(s) + CO(g) \leftrightarrow Co(s) + CO_2(g) \qquad K_2 = 490$

Calculate K (at the same temperature) for the commercially important water gas shift reaction

$H_2O(g) + CO(g) \leftrightarrow H_2(g) + CO_2(g) \qquad K_3 = ?$

5. Calculate K_c for the reaction

$$N_2(g) + O_2(g) \leftrightarrow 2NO(g)$$

if K_c for the reaction

$$\frac{1}{2} N_2(g) + \frac{1}{2} O_2(g) \leftrightarrow NO(g)$$

is 1.3×10^4.

RICE Tables:

6. 1.00 liter container holds 1.06 moles of H_2 and 1.57 moles of CO at a temperature of 162 °C. At this temperature, the following reaction occurs,

$$2H_2(g) + CO(g) \leftrightarrow CH_3OH(g)$$

After equilibrium is established, analysis shows 0.200 moles of CH_3OH in the container. Calculate the $[CO]_{eq}$, $[H_2]_{eq}$ and K_c.

2. A vessel initially has a partial pressure of NO equal to 0.526 atm and a partial pressure of Br_2 equal to 0.329 atm. At equilibrium the partial pressure of Br_2 is 0.203 atm. Calculate K_p for the reaction

$$2NO(g) + Br_2(g) \leftrightarrow 2NOBr(g)$$

7.The following reaction,

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

occurs at 298K. If 2.00 mol of HI are placed into a 1.00 liter container and permitted to react, at equilibrium it is found that 20.0 % of the HI has decomposed. Calculate K_c and K_p.

8. The equilibrium constant, K_c, for the reaction $PCl_5(g) \leftrightarrow PCl_3(g) + Cl_2(g)$

is 33.3 at 760 °C. If 0.400 mol of PCl_5 are placed in a 2.00 liter container, calculate the equilibrium concentrations of all species.

9. The equilibrium constant, K_c, for the reaction

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

is 33.3 at 760 °C. If 0.400 mol of PCl_5 and 1.0 mol of Cl_2 are placed in a 2.00 liter container, calculate the equilibrium concentrations of all species.

Le Chatelier's principle

If a chemical reaction at equilibrium is subjected to a change in conditions that displaces it from equilibrium, then the reaction proceeds toward a new equilibrium state in the direction that offsets the change in conditions.

Three factors which can affect a reaction at equilibrium

•1.Concentration of a reactant or product

When a system is at equilibrium, increasing the concentration of a reactant or product will cause the reaction to re-establish equilibrium by shifting the reaction in a direction which relieves the stress. For example, in the simulation reaction,

$$A_2(g) \quad + \quad B_2(g) \quad \text{<-->} \quad 2AB(g)$$

When the reaction is at equilibrium and the $[B_2]$ is increased the reaction proceeds from left-to-right to relieve the stress. When B_2 is added the reaction shifts in a direction to relieve the stress, by trying to decrease the amount of B_2. So the reactions proceeds from left-to-right. Similarly when the reaction is at equilibrium, addition of AB shifts the reaction from right-to-left to relieve the stress.

•2.Reaction volume or pressure

To understand the effect of volume on a reaction, consider the following reaction.

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

Assume the reaction is at equilibrium in a sealed container. If the volume of the reaction container is lowered, molecules in the container are pushed closer together and the internal pressure increases. To relieve this stress the reaction shifts in the direction to decrease the crowding of the molecules. It proceeds from right to left because the left side of the reaction has fewer gas molecules compared to the right.

If the volume is increased the reaction proceeds from left-to-right. The increase in volume means there are fewer molecules per unit volume and the reaction proceeds in a direction to increase the number of molecules per unit volume and thus maintain constant pressure.

•3.Temperature

To understand how temperature effects a reaction at equilibrium consider the equilibrium of NO_2 and N_2O_4. The reaction is endothermic;

$$\text{heat} + \underset{\text{colorless}}{N_2O_4(g)} \rightarrow \underset{\text{orange-brown}}{2NO_2(g)}$$

When the reaction is cooled the color of the sample becomes lighter, indicating more $N_2O_4(g)$ was formed. Heat is removed from the reaction system when the reaction is cooled. As the reaction is cooled it proceeds in the direction to offset the stress, in a direction to produce heat, from right to left. In general for endothermic reactions decreasing the temperature shifts the equilibrium towards the left and adding heat shifts the equilibrium to the right. It is just the opposite for exothermic reactions.

10. The reaction

$$2H_2S(g) + 3O_2(g) \;\text{<-->}\; 2H_2O(l) + 2SO_2(g)$$

has a $\Delta H = -1036$ kJ. Given the reaction is at equilibrium, predict the direction the reaction will shift when disrupted by each of the following

i) the amount of H_2O is increased

ii) the temperature of the reaction is increased

iii) the volume of the container is decreased

iv) the amount of H_2S is decreased

The non-equilibrium reaction quotient, Q

The reaction quotient for the chemical reaction,

$$aA(g) + bB(g) \;\text{<-->}\; cC(g) + dD(g)$$

is defined as,

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

The concentration used in the quotient, can be nonequilibrium concentrations. When equilibrium concentrations are used Q = K_c.

The direction the reaction will proceed to establish equilibrium depends on the comparison of the magnitudes of Q and K_c.

A guide line for predicting the direction a reaction will proceed to reach equilibrium again is as follows:

IF $Q<K_c$, the concentration of products will increase so that Q will increase
IF $Q>K_c$, the concentration of reactants will increase so that Q will decrease
IF $Q = K_c$, then no concentrations will change as the system is already at equilibrium

11. The reaction

$$NOBr(g) \leftrightarrow NO(g) + \frac{1}{2} Br_2(g)$$

has been carefully studied at 350 °C and the K_c is 0.079. Which direction will the reaction proceed to establish equilibrium under each of the following initial conditions?

i) $[NOBr]_o = 0.100$ M : $[NO]_o = 0$: $[Br_2]_o = 0$

ii) $[NOBr]_o = 0$: $[NO]_o = 0.100$ M : $[Br_2]_o = 0.100$ M

iii) $[NOBr]_o = 0.100$ M : $[NO]_o = 0.100$ M : $[Br_2]_o = 0.100$ M

iv) $[NOBr]_o = 0.200$ M : $[NO]_o = 0.0500$ M : $[Br_2]_o = 0.100$ M

12. Kc = 19.9 for the reaction: $Cl_2\,(g) + F_2\,(g) \leftrightarrow 2ClF\,(g)$
Find the equilibrium concentrations of all species if the initial concentration of $[Cl_2]$ is 0.4M, $[F_2]$ is 0.2 M, and $[ClF]$ is 7.3 M.

13. Kc = 170 at 298K for the following reaction: $2NO_2\,(g) \leftrightarrow N_2O_4\,(g)$
a) Suppose the initial concentration of NO_2 is 0.015 M and the concentration of N_2O_4 is 0.025 M. Determine the equilibrium concentrations of all species.

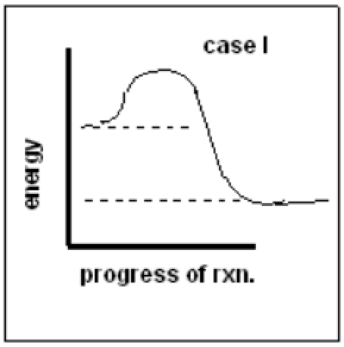
14. Kc for the decomposition of ammonium hydrogen sulfide is 1.8×10^{-4} at 298K

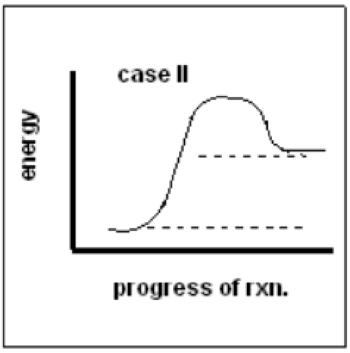
$$NH_4HS\,(s) \leftrightarrow NH_3(g) + H_2S\,(g)$$

a) When the pure salt decomposes in a flask, what are the equilibrium concentration of NH_3 and H_2S?

b) If NH_4HS is placed in a flask already containing 0.020 mol/L of NH_3 and then the system is allowed to come to equilibrium, what are the equilibrium concentrations of NH_3 and H_2S?

Relationship of Kinetics to equilibrium





Consider the following above situations:

Case I: The energy of activation of the forward reaction (the amount of energy necessary to go from reactants to the top of the hill) is much smaller than the energy of activation of the reverse reaction. This means that for the reverse reaction to happen at the same rate as the forward reaction (the condition necessary for equilibrium to occur, you must have a large concentration of products, and a much smaller concentration of reactants. Since Keq is calculated as products over reactants case I will result in a equilibrium constant larger than 1.

Case II: In this case, the activation energy of the reverse reaction is much smaller, meaning you will need more reactants to make the reactions occur at an equal rate. Since you will have more reactants at equilibrium, Keq will be less than one.

Case III: In this case the activation energies for the forward and the reverse reactions are about the same, therefore you would expect approximately equal concentrations for the two, and Keq will be close to a value of 1.

Now lets look at how equilibrium can affect the measured rate law. Consider the following mechanism:

(1) A + B <--> C equilibrium, fast

(2) C --> D slow

(3) D --> E fast

Since we know that rate law for a given mechanism is based on the slow step, the rate law expression for the above reaction would be:

rate = $k_2[C]$

But notice here that C is an intermediate and is not easily measured. To find measureable species, we need to look at the equilibrium step:

$rate_{1f} = rate_{1r}$ $\quad$ $k_{f1}[A][B] = k_{r1}[C]$ $\quad$ solving for C.

$$[C] = \frac{k_{f1}}{k_{r1}}[A][B]$$

now we can sub this back in our original rate law expression, and get a rate in terms of only A and B.

$$rate = k_2 \frac{k_{f1}}{k_{r1}}[A][B]$$

Normally all the k's are lumped into one big constant, since they are all constants themselves.

15. The formation of nitrosyl bromide, NOBr, has the following proposed mechanism:

(1)	$NO + Br_2 \Leftrightarrow NOBr_2$	fast, eq.
(2)	$NOBr_2 + NO \Rightarrow 2NOBr$	slow

Determine the Rate law!

16. The synthesis of HBr proceeds via the following steps in the gaseous state:

(1)	$Br_2 \Leftrightarrow 2Br$	fast, eq.
(2)	$Br + H_2 \Rightarrow HBr + H$	slow
(3)	$H + Br_2 \Rightarrow HBr + Br$	fast

Determine the Rate law!

17. Determine the Rate law!

(1)	A + B $\Leftrightarrow$ C	fast, eq.
(2)	C $\Rightarrow$ D	slow
(3)	D $\Rightarrow$ E	fast