Chapters from Chemistry 6

Dynamic equilibrium. Reaction kinetics. Chemical equilibrium. Guldberg-Waage Law. Le Chatelier´s principle.

6.1. Dynamic equilibrium

When a dynamic process reaches a steady state in which opposing changes occur at identical rates and no further net changes takes place, **dynamic equilibrium** exists for the system.

Some times we include heat in an equilibrium expression . For example, the certain amount of heat of vaporization is needed to change a liquid into its vapor. The same amount of heat is released when the vapor condenses.

$$\text{water (l) + heat} \leftrightarrow \text{water (g)}$$

Any change that consumes heat, like evaporation, is said **endothermic**. The opposite term is **exothermic**. The condensation of steam to liquid water, or the condensation of any vapor, is an exothermic change.

Forward and reverse reaction in dynamic equilibrium.

Dynamic equilibrium can be shifted. When an equilibrium is established, no net change occurs spontaneously, but this doesn´t mean that we cannot cause a change.
We add heat to the water in an equilibrium system, the rate of evaporation increases. For a time the system will not be in a equilibrium because forvard rate is now greater than the reverse. The equilibrium was upset. When we stop now adding of heat but yet we maintain the temperature of the closed system at a constant but higher value, the rate at which vapor molecules return to the liquid will increase. The two opposing rates of evaporation and condensation will become the same again. Both will be faster than at the lower temperature, but when both are equally fast there is no other net change → dynamic equilibrium.
A disturbance to an equilibrium is called a **stress**.

Shifts in equilibria can be predicted by **Le Chatelier´s Principle** : If a system in equilibrium is upset by a stress, the system shifts in whichever direction most directly absorbs the stress and restores equilibrium.
Provided that the applied stress hasn´t been overwhelming, equilibrium will be restored.

A change of reaction conditions (concentration, temperature, pressure) cause stress - upsets the equilibrium of a system (viz given above).
An equilibrium law exists for every chemical equilibrium.
One of the major facts about our Word is that all chemici systems tend toward equilibrium. We have spoken about equilibria in liquid-vapor system, and heterogeneous systems. Now we speak about equilibria in homogeneous systems. Guldburg and Waage discovered a relationship concerning the molar concentrations of the species in a chemical equilibrium **- equilibrium law** for the system.

A change of concentration : Increasing of concentration of reactants will cause the shift to the right (products)

A change of pressure : (in the gaseous states) Increasing of pressure will cause the shift in direction of smaller amount of particles.

A change of temperature : Increasing of temperature will cause the shift in direction of endothermic reaction.

$$CO + 2H_2 \leftrightarrow CH_3OH \ (Q_m > 0)$$

An equilibrium is shifted to the right when we increase concentration of reactants, or decrease concentration of products, increase temperature or increase of pressure.

6.2. Le Chateliers' principle

Equilibrium. In a chemical equilibrium, the opposing reactions take place at identical rates. Not all weak acids are equally weak. It is necessary to find number for each weak acid for comparison of acid strengths. It will be the equilibrium constant . Guldburg and Waage discovered how the molar concentrations of species at equilibrium interact. When the reaction can be described by equation :

$$aA \ + \ bB \ \rightarrow cC \ + \ dD$$
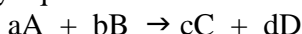
We know that at equilibrium the rates of the forward and reverse reactions are equal. They (G-W) ensured the relation of the molar concentrations of reactants and products to equilibrium law :

$$K_{eq} = [C]^c \ [D]^d \ / \ [A]^a \ [B]^b$$

K_{eq} = equilibrium constant

Shifting of equilibrium. Generally, any equilibrium can be shifted in response to a disturbance, like the addition or removal of heat or change of pressure (gases) or change of concentrations substrates or products. A disturbance to an equilibrium is called a stress, which causes that one of the opposing changes is faster,, at least for a while. Shifts in equilibrium can be predicted by Le Chateliers' principle.: **If a system in equilibrium is upset by a stress, the system shifts in whichever direction most directly absorbs the stress and restores equilibrium.**

The rate of the unfavored reaction will eventually catch up to the opposing reaction and both rates again become equal. It is not the identical system that existed before the stress because the actual quantities of reactants and products have changed but the equilibrium constant remains the same.

Consider the reaction :

$$CO + 2H_2 + heat \ \rightarrow \ CH_3OH \qquad [Q_m > 0 \ or \ \Delta H > 0 \ or \ endothermic \ reaction]$$
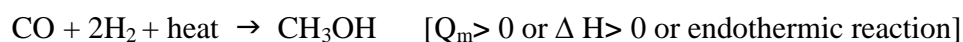
Change of concentration : the increase of concentration of reactants cause the shift in direction the formation of products.
Change of pressure : (is applied only in gaseous systems) the increase of pressure shifts the equilibrium in the direction of smaller number of particles (molecules) and in reverse.
Change of temperature : causes the shift in the direction of endothermic reaction
In given reaction the equilibrium will be shifted to the right when we increase the concentrations of reactants or decrease concentrations of products, increase the pressure or increase of temperature.

Detailed explanation of the Le Chatelier´s principle :

A) Change in reactant or product concentration
If a chemical system is at equilibrium and we add a substance (either a reactant or a product), the reaction will shift so as to reestablish equilibrium by consuming part of the added substance. Conversely, removal of a substance will result in the reaction moving in the direction that forms more of the substance. Remember that this is a change in concentration so changing the amount of a pure solid or liquid which is already in equilibrium should not make the reaction consume the additional solid or liquid. Example, if solid NaCl is already in equilibrium with a saturated solution of NaCl, adding more pure NaCl solid will not cause additional dissolving. Conversely, removal of some of the solid NaCl which is in equilibrium with a saturated solution of NaCl will not cause further crystallization of NaCl from the saturated solution.

B) Effects of volume and pressure changes
These effects are present when the two opposing reactions are of different molecularity. In solution, volume changes can be achieved by addition of solvent. Changing the volume effectively changes concentration. Adding more solvent is essentially a dilution. If the number of solute species on the reactant side is not the same as on the product side, then volume changes can cause a shift in equilibrium. Increasing the volume favors the process with lower molecularity. Increasing the volume then will cause the system to shift in the direction that increases the number of solute species. This is the same for reactions involving gases. Decreasing the volume of the container causes an equilibrium mixture of gases to shift in the direction that reduces the number of moles of gas. For gases, increasing the pressure by adding one of the gases participating in the reaction, will also disturb equilibrium (This is essentially a change in reactant or product concentration). Increasing the total pressure of a reaction vessel by adding a spectator gas does not affect equilibrium.

Remember that volume changes can only have effect if the number of solute species or gas species in the reactant side is not equal to the if the number of solute species or gas species in the product side.

C) Effect of Temperature

One can treat heat as a reactant (for an endothermic process) or a product (for an exothermic process) and the same principle used for changes in concentration of reactants or products can be used to deduce the effect of heat on an equilibrium reaction.

6.3. Reaction Kinetics

Reaction rate : is change in concentration (substrate or product) in time.

$$A \ + \ B \ \rightarrow \ products$$
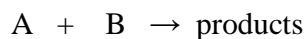
Reaction rate is directly proportional to the product of immediate concentrations of reactants. The proportional constant **k** is called the **rate constant.**

$$v_A \ = \ - d[A]/ dt \ = \ k[A][B]$$

From the Collision theory : the rate of reaction is proportional to the number of collisions occuring each second between reacting molecules. At the moment of collisions molecules must have
   a) suitable orientation of both molecules
   b) sufficient kinetic energy to overcome repulsion forces and to enable interpenetration of electron clouds
The only way to increase the collision frequency without changing the temperature of the reacting mixture is to increase the concentrations of the reactants. If the molar concentration is doubled, the frequency of all collisions must double.
Increase in temperature also increase collision frequency.

$$k \ = \ A \ e^{-E_a/RT}$$

where k is the Rate constant, E_a is Activation energy, R - universal gass constant and T is temperature

The rate constant's dependence on temperature can be explained by collision theory. This theory assumes that, for a reaction to occur, reactant molecules must collide with an energy greater than some minimum value and with the proper orientation. This minimum energy of collision required for two reactant molecules to react is called the **activation energy,** E_a.(*Activation energy is the energy required to start a chemical reaction.)*

Raising the temperature increases the fraction of molecules having very high kinetic energies. These are the ones most likely to react when they collide. The higher the temperature, the larger the fraction of molecules that can provide the activation energy needed for reaction. The rate constant, *k,* becomes larger as the temperature increases.
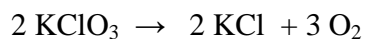
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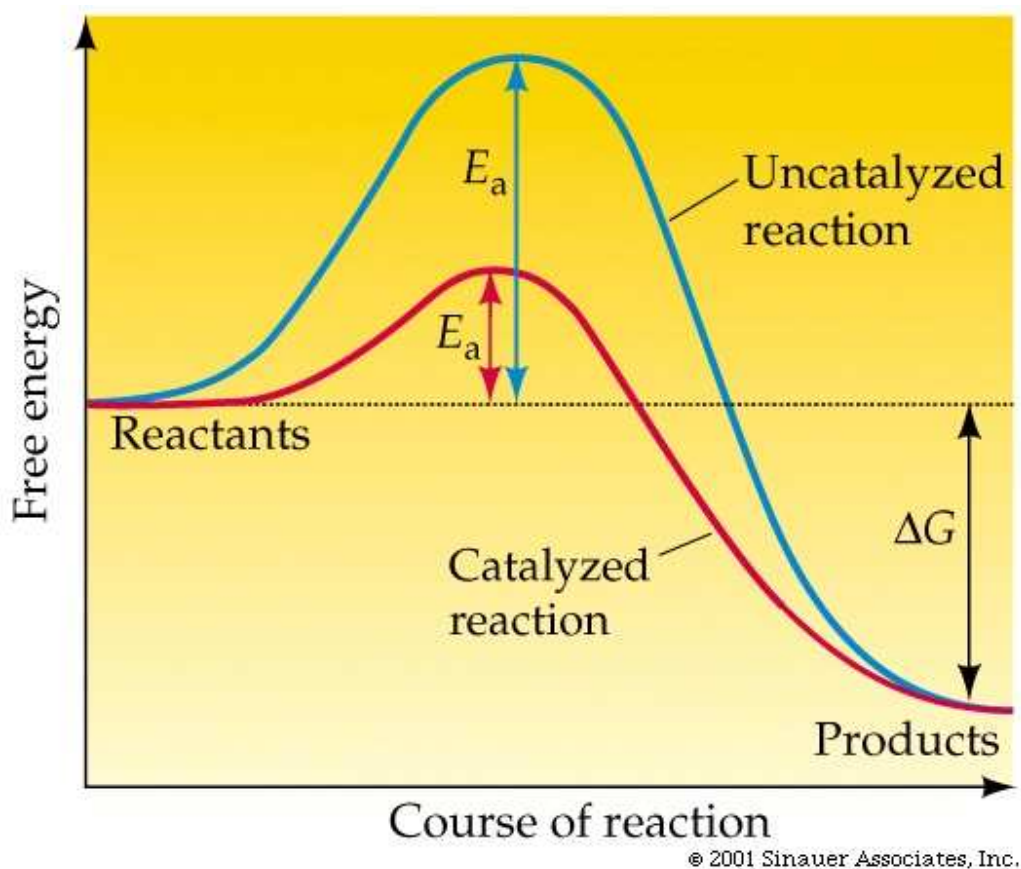
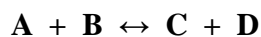### 6.4. Chemical Equilibrium. Guldberg-Waage Law.

The majority of reactions are **reversible** ones.
Irreversible reactions:
a) The product is immediately removed (formation of gas, precipitate, etc.)
b) The rate of the backward reaction is so slow as to be negligible

$$2 \, KClO_3 \; \rightarrow \; 2 \, KCl \, + 3 \, O_2$$

Equilibrium in reversible reactions

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

rate forward $= \, k_1 \, [A][B]$
rate backward $= k_2 \, [C][D]$

$$k_1 \, [A][B] = k_2 \, [C][D]$$

$$k_1/k_2 \; = \; [C][D]/[A][B] \; = \; K$$

K < 1 shift to the left
K 1 shift to the right
This law is called **Guldberg-Waage Law.**

1) The value of **K** depends on temeperature (both rate constants change in different way)
2) The catalyst cannot affect the value of **K** (speeds up both reactions the same way)
3) General validity of this equilibrium law (ionization of weak acids, hydrolysis of esters, solubility product equilibria, etc.)

For the generally stated reversible reaction

$$aA + bB + cC \ldots \rightleftharpoons pP + qQ + rR \ldots$$

the equilibrium constant is given by

$$K_c = \frac{[P]^p[Q]^q[R]^r \ldots}{[A]^a[B]^b[C]^c \ldots}$$

where **a** is the number of molecules of **A** taking part in the reaction, **b** the number of molecules of **B**, and so on.

As an example take the reaction

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

The equilibrium constant is

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

$H_2 + I_2 \rightarrow 2HI$

$2HI \rightarrow H_2 + I_2$

concentration — time — equilibrium state — [HI], [H₂, I₂]

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_(i)_ $\dfrac{k_f}{k_r} = 2 = K_{eq}$

_(ii)_ $\dfrac{k_f}{k_r} = 1 = K_{eq}$

(iii) $\dfrac{k_f}{k_r} = \tfrac{1}{2} = K_{eq}$