

Subject: Physical Chemistry – I

Subject Code: 18K5CH09



UNIT: I

The Equilibrium Constant and Free Energy (K and ΔG°)

ΔG° Gibbs free energy change for all reactants and products in standard state.

ΔG Free energy under some other conditions.

$$\Delta G = \Delta G^\circ + RT \ln Q \quad \Rightarrow \quad \Delta G^\circ = - RT \ln K$$

At Equilibrium, $\Delta G = 0$ (no driving force)



The Equilibrium Constant and Free Energy (K and ΔG°)

$$\Delta G^\circ = -RT \ln K$$

or

$$K = e^{\frac{-\Delta G^\circ}{RT}}$$

$$\Delta G^\circ = \ominus \quad K > 1 \quad \text{Products Favored}$$

Spontaneous Reaction

$$\Delta G^\circ = \oplus \quad K < 1 \quad \text{Reactants Favored}$$

Non-Spontaneous

$$\Delta G^\circ = 0 \quad K = 1 \quad \text{Neither Products or Reactants}$$

Favored



Chemical Equilibrium

- Reactant and product concentrations remain constant
- Molecular level: rapid activity (dynamic)
- Macroscopic level: unchanging
- At equilibrium: $\text{rate}_{\text{forward}} = \text{rate}_{\text{reverse}}$
- Does not limit time



Partial Molar Quantities

- Now that we have introduced the mole fraction, X , and variable composition, we want to know how the variables of our system, e.g., V , S , change as we change composition.
 - These are partial molar quantities, usually indicated by the lower case letter.
- For example:
$$v_i = \left(\frac{\partial V}{\partial n_i} \right)_{T,P,j \neq i}$$
 - Such that
$$\sum_i n_i v_i = V$$
- This is the partial molar volume of component i . For example, the partial molar volume of O_2 dissolved in seawater.
 - This tell us how the volume of water changes for an addition of dissolved O_2 holding T , P , and the amounts of everything else constant.



Other Partial Molar Quantities

- We can also define partial molar quantities of other thermodynamic variables, such as entropy, and enthalpy.
- One partial molar quantity is particularly useful, that of the Gibbs Free Energy.



Chemical Potential

- The chemical potential is defined as *partial molar Gibbs Free Energy*:

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_{i \neq j}} \quad \text{such that} \quad \sum_{i=1}^{\infty} n_i \mu_i = G$$

- or, dividing each side by the total number of moles:
- The chemical potential tells us how the Gibbs Free Energy will vary with the number of moles, n_i , of component i holding temperature, pressure, and the number of moles of all other components constant.
- For a pure substance, the chemical potential is equal to its molar Gibbs Free Energy (also the molar Helmholtz Free Energy):



Gibbs Free Energy

- In Chapter 2, we found that the Gibbs Free Energy change of a system (and we are only interested in changes, not absolute amounts) was given by:

$$dG = VdP - SdT$$

- *(you need to memorize this equation – think about units and how free energy is minimized when entropy is maximized.)*
- We also said that for a reaction at constant temperature and pressure:

$$\Delta G_r = \Delta H_r - T\Delta S_r$$

- These equations hold for a system of fixed composition. Where composition can vary, we need to modify them to account for that variance.

Gibbs-Duhem Equation

- The Free Energy of a system (or phase) is the sum of chemical potentials of its components:

$$G = \sum_i n_i \mu_i$$

- Differentiating: $dG = \sum_i n_i d\mu_i + \sum_i \mu_i dn_i$

- Equating with the earlier equation:

$$\sum_i n_i d\mu_i + \sum_i \mu_i dn_i = VdP + SdT + \sum_i \mu_i dn_i$$

- We can rearrange this as the Gibbs-Duhem

- Equation: $VdP + SdT - \sum_i n_i d\mu_i = 0$



Chemical Equilibrium

- Reversible Reactions:

A chemical reaction in which the products can react to re-form the reactants

Chemical Equilibrium:

When the rate of the forward reaction equals the rate of the reverse reaction and the concentration of products and reactants remains unchanged



Arrows going both directions (\rightleftharpoons) indicates equilibrium in a chemical equation



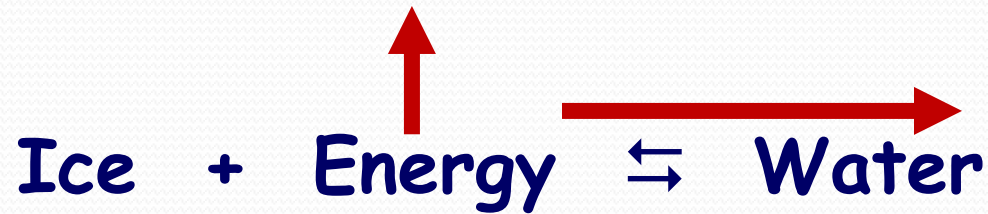
Chemical Potential in Ideal Solutions

- In terms of partial molar quantities
- For an ideal gas:
- Integrating from P° to P :
- Where P° is the pressure of pure substance in its 'standard state' and μ° is the chemical potential of i in that state. In that case, $P/P^\circ = X_i$ and:

$$\mu_{i,ideal} = \mu_i^\circ + RT \ln X_i$$

LeChatelier Example #1

A closed container of ice and water at equilibrium. The **temperature is raised**.



The equilibrium of the system shifts to the right to use up the added energy.



LeChatelier Example #2

A closed container of N_2O_4 and NO_2 at equilibrium. NO_2 is added to the container.



The equilibrium of the system shifts to the left to use up the added NO_2 .



LeChatelier Example #3

A closed container of water and its vapor at equilibrium. **Vapor is removed** from the system.



The equilibrium of the system shifts to the right to replace the vapor.



LeChatelier Example #4

A closed container of N_2O_4 and NO_2 at equilibrium. The **pressure is increased**.



The equilibrium of the system shifts to the left to lower the pressure, because there are fewer moles of gas on that side of the equation.



Law of Mass Action

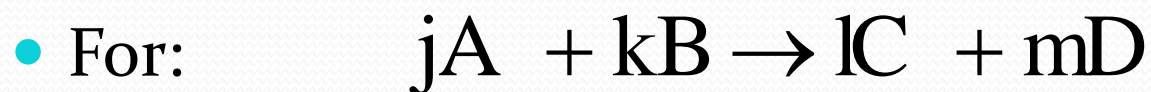
If : $\text{rate}_{\text{forward}} = \text{rate}_{\text{reverse}}$

Then : $k [\text{reactants}]^m = k [\text{products}]^n$

And : $\frac{\text{rate}_{\text{forward}}}{\text{rate}_{\text{reverse}}} = \frac{k[\text{products}]^n}{k[\text{reactants}]^m} = K$



Law of Mass Action



- Equilibrium expression:

$$K_c = \frac{[C]^l [D]^m}{[A]^j [B]^k}$$

$$k[\text{reactants}]^m = k[\text{products}]^n$$



Le Châtelier's Principle

- . . . if a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change.



Le Châtelier's Principle

- 1. Concentration
- 2. Temperature
- 3. Pressure
- 4. Volume
- 5. Catalysts*



CLAUSIUS-CLAPEYRON EQUATION

relates the latent heat (heat of transformation) of vaporization or condensation to the rate of change of vapor pressure with temperature

or, in the case of a solid-liquid transformation, it relates the latent heat of fusion or solidification to the rate of change of melting point with pressure

DERIVATION

During this process, the *Gibbs free energy* (G) of the system remains constant.

In the equilibrium system, $\Delta G = \Delta H - T\Delta S$

where H is the latent heat of vaporization, T the temperature and S the entropy of the system

Since G of the said system remains constant,

$$G_2 - G_1 = \Delta G = \Delta H - T\Delta S = 0$$

Thus,

$$\Delta H = T\Delta S$$

DERIVATION

When the transition is to a gas phase, the final volume can be many times the size of the initial volume and thus can be approximated as V_2 . Furthermore, at low pressures, the gas phase may be approximated by the ideal gas law $PV = nRT$, changing the previous equation to:

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{LP}{nRT^2}$$

DERIVATION

Since $\Delta H_{\text{vap}} = L / n$,

$$\frac{dP}{P} = \frac{dT}{T^2} \frac{\Delta H_{\text{vap}}}{R}$$

Also since ΔH_{vap} is independent of pressure and temperature and R is a constant, integrating both sides, we get

$$\ln P = - \frac{1}{T} \frac{\Delta H_{\text{vap}}}{R} + C$$

DERIVATION

If the vapor pressure was measured at two separate temperatures, we have two points on the same line.

$$\ln P_1 = - \frac{1}{T_1} \frac{\Delta H_{\text{vap}}}{R} + C$$

$$\ln P_2 = - \frac{1}{T_2} \frac{\Delta H_{\text{vap}}}{R} + C$$

Subtracting these two, we get

$$\ln P_2 - \ln P_1 = - \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

DERIVATION

Finally, we get

$$\ln \frac{P_2}{P_1} = - \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

the more commonly known form of the Clausius – Clapeyron equation

Common Applications

- Calculate the vapor pressure of a liquid at any temperature (with known vapor pressure at a given temperature and known heat of vaporization)
- Calculate the heat of a phase change
- Calculate the boiling point of a liquid at a nonstandard pressure
- Reconstruct a phase diagram
- Determine if a phase change will occur under certain circumstances



UNIT :II

CHEMICAL KINETICS

Chemical kinetics deals with the rate at which & the mechanism by which different reactions take place at different conditions

Rate of reaction

It is defined as the change in Concentration of any of the reactants in unit time.

Factors affecting the Rate

- Concentration – rate of reactions \propto Concentration
- Temperature – by temperature a rise of 10 degrees usually doubles the reaction rate
- Catalyst – Positive Catalyst increases the rate and negative catalyst decreases the rate.

Rate Law

The reaction order is the sum of the concentration term exponents in a rate law equation.



- The rate of reaction is given by the change in concentration of A as a function of time. The rate of disappearance of A is also proportional to the concentration of A.
- $-d[A]/dt \propto [A]$
- Since the rate of a reaction generally depends upon collision frequency, it stands to reason that as the concentration of A increases, the rate of reaction increases. Likewise, as the concentration of A decreases, the rate of reaction decreases. The expression for the rate of the reaction can be shown as follows:
- $\text{rate} = -d[A]/dt = k[A]$
- The proportionality between the rate and $[A]$ becomes an equal sign by the insertion of a constant (k). A **rate law** is an expression showing the relationship of the reaction rate to the concentrations of each reactant. The **specific rate constant** (k) is the proportionality constant relating the rate of the reaction to the concentrations of reactants.

* Order of reactions

A number that relates the rate of a chemical **reaction** with the concentrations of the reacting substances, the sum of all the exponents of the terms expressing concentrations of the molecules or atoms determining the rate of the **reaction**, compare **first-order reaction**, **second-order reaction**, **third-order reaction**

* Molecularity

The number of ions or molecules that take part in the rate-determining step is known as **molecularity**.

Molecularity	Order
The number of ions or molecules that take part in the rate-determining step is known as molecularity.	The sum of powers to which the reactant concentrations are raised in the rate law equation is known as the order of the reaction.
It is always a whole number	It can either be a whole number or a fraction
The molecularity of the reaction is determined by looking at the reaction mechanism	The order of the reaction is determined by the experimental methods
The molecularity of the reaction is obtained by the rate-determining step	The order of the reaction is obtained by the sum of the powers to which the reactant concentrations are raised in the rate law

Zero order reactions

- The **Differential** form of a zero order reaction can be written as:

$$\text{Rate} = -dA/dt = k[A] = k$$

Where 'Rate' refers to the rate of the reaction and 'k' is the rate constant of the reaction.

This differential form can be rearranged and integrated on both sides to get the required **Integral** form as shown below.

- $\text{Rate} = -dx/dt = kt$

Integrating on both sides, we get:

$$\int dx = \int k dt$$

$x = kt + C$ where C is the integration Constant at time $t=0$. Solving for C, we get

$x = kt$, $k = x/t$ this equation is the zero order rate equation

Examples

- Some enzyme catalysed reactions
- Thermal decomposition of HI on a gold surface
- Photochemical reaction between hydrogen and chlorine to form hydrogen chloride.

- **First order reaction**

$$k = 2.303/t \log a/(a-x) \quad H_f \quad t_{1/2} = 0.693/k$$

- **Second orders reaction**

$$k = 1/t x/a(a-x) \quad H_f \quad t_{1/2} \propto 1/a$$

$$k = 2.303/t(a-b) \log b(a-x)/a(b-x)$$

- **Third order reaction**

$$k = 1/2t x(2a-x)/a^2(a-x^2) \quad H_f \quad t_{1/2} \propto 1/a^2$$

- **Zero order reaction**

$$k = x/t \quad H_f \quad t_{1/2} \propto a$$

Pseudo first order reactions

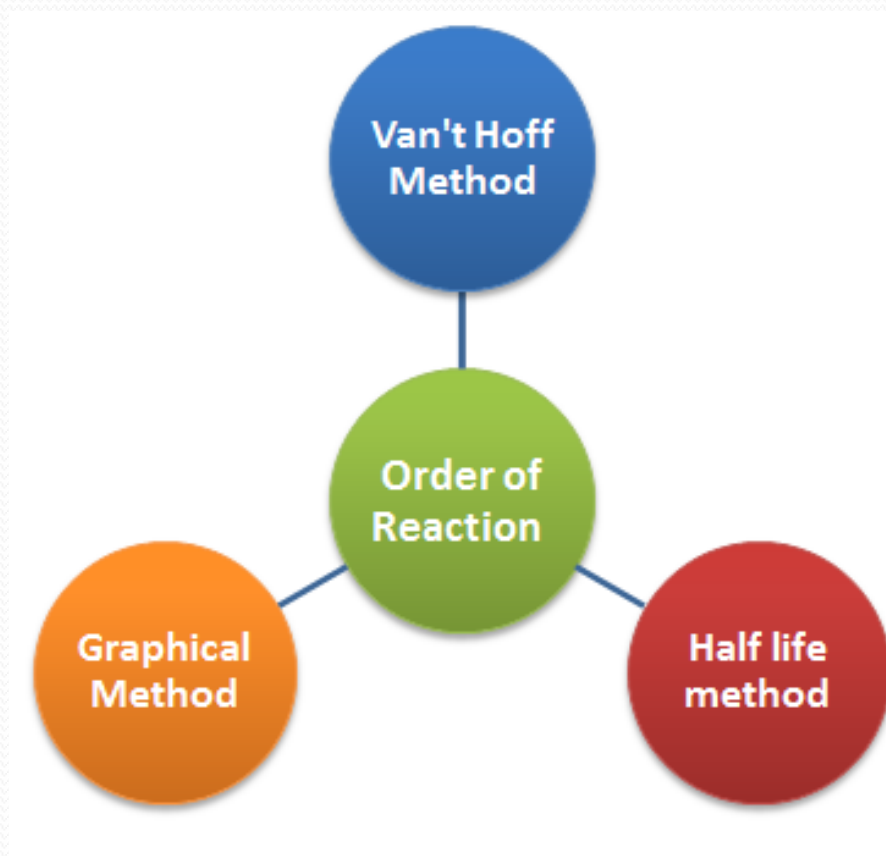
The reaction whose molecularity is two but order is one is called pseudo first order



For this reaction one molecule of $\text{CH}_3\text{COOC}_2\text{H}_5$ and one molecule of H_2O are essential for the reaction to take place so the molecularity is two but the rate depends on the concentration of ethyl acetate

Methods of determining the order of reactions

- **Methods of determining the order of reactions**



- Arrhenius Parameters

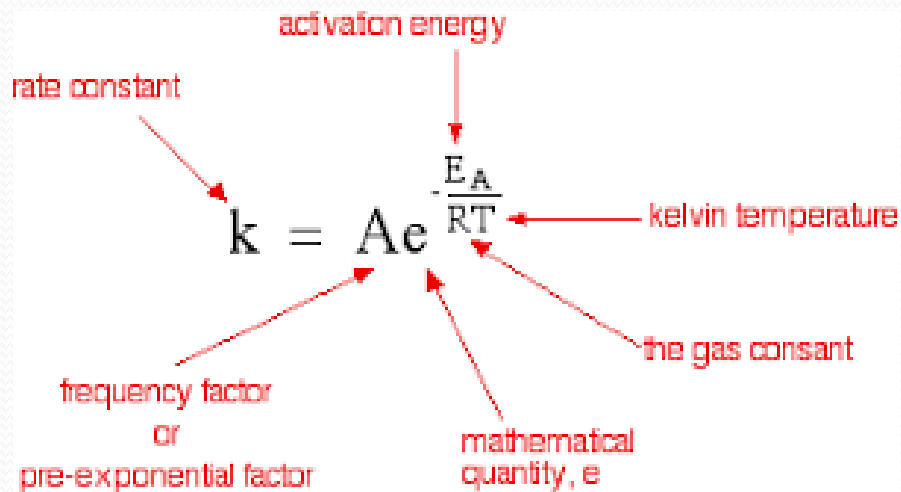
- Arrhenius equation gives the dependence of the rate constant of a chemical reaction on the absolute temperature, a empirical constant and other constants of the reaction.

$$K = Ae^{-E_a/RT} \quad \text{where}$$

- k is the rate constant (frequency of collisions resulting in a reaction), T is the absolute temperature (in kelvins), A is the pre-exponential factor, a constant for each chemical reaction, E_a is the activation energy for the reaction (in the same units as RT), R is the universal gas constant. Alternatively, the equation may be expressed as

$$K = Ae^{-E_a/k_B T} \quad \text{where}$$

- E_a is the activation energy for the reaction (in the same units as $k_B T$), k_B is the Boltzmann constant. The only difference is the energy units of E_a : the former form uses energy per mole, which is common in chemistry, while the latter form uses energy per molecule directly, which is common in physics. The different units are accounted for in using either the gas constant, R , or the Boltzmann constant, k_B , as the multiplier of temperature T .



• Simple Collision theory

- **Collision theory**, theory used to predict the rates of chemical reactions, particularly for gases. The collision theory is based on the assumption that for a reaction to occur it is necessary for the reacting species (atoms or molecules) to come together or collide with one another.
- Not all collisions, however, bring about chemical change. A collision will be effective in producing chemical change only if the species brought together possess a certain minimum value of internal energy, equal to the activation energy of the reaction. Furthermore, the colliding species must be oriented in a manner favourable to the necessary rearrangement of atoms and electrons.
- Thus, according to the collision theory, the rate at which a chemical reaction proceeds is equal to the frequency of effective collisions. Because atomic or molecular frequencies of collisions can be calculated with some degree of accuracy only for gases (by application of the kinetic theory), the application of the collision theory is limited to gas-phase reactions.

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Steady-State Approximation (SSA)



$$\frac{d[C]}{dt} = k_1[A][B] - k_{-1}[C] - k_2[C]$$

$$0 = k_1[A][B] - k_{-1}[C] - k_2[C]$$

$$k_1[A][B] = k_{-1}[C] + k_2[C]$$

$$k_1[A][B] = [C](k_{-1} + k_2)$$

$$[C] = \frac{k_1[A][B]}{k_{-1} + k_2}$$

$$\frac{d[D]}{dt} = k_2[C] = k_2 \frac{k_1[A][B]}{k_{-1} + k_2}$$

- Two general methods used to derive complex rate laws:

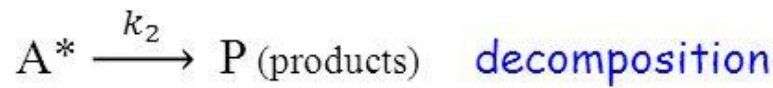
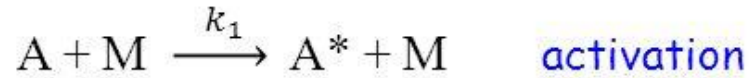
- Pre-equilibrium approximation
- Steady-state approximation

- Steady-state approximation is more commonly used, and you must be familiar with this technique!

- **Key assumption:** production of the intermediate (C) and consumption occur at the same rate, so the rate of change of [C] with respect to time is zero.

$$\frac{d[I]}{dt} = 0$$

Lindemann theory



$$k_{\text{uni}}[A] = \frac{k_2 k_1 [M][A]}{k_{-1}[M] + k_2}$$



$$k_{\text{uni}} = \frac{k_2 k_1 [M]}{k_{-1}[M] + k_2}$$

$$\text{Low pressure limit: } k_{-1}[M] \ll k_2 \Rightarrow [M] \ll \frac{k_2}{k_{-1}} \Rightarrow k_{\text{uni}} = k_1 [M] \quad \text{2nd order}$$

$$\text{High pressure limit: } k_{-1}[M] \gg k_2 \Rightarrow [M] \gg \frac{k_2}{k_{-1}} \Rightarrow k_{\text{uni}} = \frac{k_2 k_1}{k_{-1}} \quad \text{1st order}$$

In accordance with experiments

Catalysis & Catalysts

Types of Catalysts & Catalytic Reactions

- The types of catalysts
 - Classification based on the its physical state, a catalyst can be
 - gas
 - liquid
 - solid
 - Classification based on the substances from which a catalyst is made
 - Inorganic (gases, metals, metal oxides, inorganic acids, bases etc.)
 - Organic (organic acids, enzymes etc.)
 - Classification based on the ways catalysts work
 - Homogeneous - both catalyst and all reactants/products are in the same phase (gas or liq)
 - Heterogeneous - reaction system involves multi-phase (catalysts + reactants/products)
 - Classification based on the catalysts' action
 - Acid-base catalysts
 - Enzymatic
 - Photocatalysis
 - Electrocatalysis, etc.

Types of Catalysis

Types	Definition	Examples
1) Homogeneous catalysis	the catalyst is present in the same phase as the reactant.	Hydrolysis of sucrose with inorganic acid.
2) Heterogeneous catalysis	the catalyst constitutes a separate phase from the reaction system	Haber's process for ammonia synthesis; contact oxidation of sulphur dioxide; Hydrogenation of alkene, aldehyde, etc.
3) Biological catalysis / enzyme catalysis	Reaction catalyzed with biological catalysts: enzyme	Hydrolysis of starch in stomach

Enzyme catalysis

- **Enzyme kinetics** is the study of the chemical reactions that are catalysed by enzymes. In enzyme kinetics, the reaction rate is measured and the effects of varying the conditions of the reaction are investigated. Studying an enzyme's kinetics in this way can reveal the catalytic mechanism of this enzyme, its role in metabolism, how its activity is controlled, and how a drug or an agonist might inhibit the enzyme.
- Enzymes are usually protein molecules that manipulate other molecules—the enzymes' substrates. These target molecules bind to an enzyme's active site and are transformed into products through a series of steps known as the enzymatic mechanism
- $E + S \rightleftharpoons ES \rightleftharpoons ES^* \rightleftharpoons EP \rightleftharpoons E + P$