

## A Review of the Essence of Stability Constants in the Thermodynamic Assessments of Chemical Compounds

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### ABSTRACT

**Background:** This treatise discusses the following topics:

- Chemical compounds
- Factors affecting stability of chemical compounds
- Stability constants
- The significance of stability constants vis-a-vis equilibrium constant,  $K_{eq}$

The different forms of stability constant are reviewed and the thermodynamic assessment of stability constant is explained.

**Method:** The approach involved the review from reputable authors and writers, of the topics that are associated with stability constant and the generalization is remarked following the thermodynamic assessment of the stability constant of chemical compounds.

**Findings:** The thermodynamic analysis of stability constant of chemical compounds and of reactions shows that reactions proceed in the direction of decreasing Gibbs free energy,  $G$ , where the standard reaction Gibbs free energy,  $\Delta_r G^\circ = \Delta_f G^\circ(B) - \Delta_f G^\circ(A)$ , defines the formation of the pure substance B, from the pure substance A, at its standard state.

**Conclusion:**  $RT \ln K = -\Delta_r G^\circ$  is the link between thermodynamic data and the equilibrium constant (stability constant),  $K$ . When  $\Delta_r G^\circ > 0$ ,  $K < 1$  and at equilibrium the partial pressure of A exceeds that of B. This means that the reactant A is favored in the equilibrium. When  $\Delta_r G^\circ < 0$ ,  $K > 1$  and at the equilibrium the partial pressure of B exceeds that of A. The product B is favored in the equilibrium. The equation is an exact thermodynamic relation. The equilibrium constant,  $K$ , when expressed in terms of activities, is called a thermodynamic equilibrium constant.

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### Introduction

Chemistry is the study of matter and its changes into many products under various conditions. Matter is any substance that has mass and takes up space. An element is a basic unadulterated simple item that cannot be decomposed further and from which all forms of compounds are built. However, the smallest particle of an element that exists is called an atom. An element is a substance composed of only one kind of atom. Thus, matter is made up of various combinations of the simple forms of elements called the chemical substance. In a wider scale, the chemical combination of different elements forms a compound. The substances around us are combinations of elements i.e., compounds rather than single elements [1]. A compound is a substance that contains more than one element in a definite ratio. Water is a compound that contains two elements of hydrogen and an element of oxygen ( $H_2O$ ). The

common table salt (i.e., Sodium Chloride) is a compound too. It contains one sodium atom for each chlorine atom,  $NaCl$ . Some compounds show specific combination of atoms. These compounds are classified as either organic or inorganic. For ease of carriage in science, with respect to Chemistry, combinations of either same elements, as in Oxygen,  $O_2$  or different elements, such as in Water, both are referred to as the molecule, i.e., a molecule of Oxygen and a molecule of Water respectively. Thus, a molecule may be either a compound of same elements (Oxygen) or a compound of different elements (Water). Note: Students are often confused by this simple usage of these terms for convenience. On the other hand, an ion is either a charged element or a charged molecule - this charge can be positive or negative that are called a cation and an anion respectively. Compounds are classified as molecular if they consist of molecules and as ionic if they consist of ions. A compound can be changed into a different substance by chemical reactions which may involve interactions with other substances. In this process, bonds between atoms may be broken and/or new bonds formed [2]. [Chemical compound - Wikipedia]

## Chemical Compounds

There are four major types of compounds - these compounds are distinguished by how the constituent atoms are bonded together. They are:

- molecular compounds, held together by covalent bonds
- ionic compounds, held together by ionic bonds
- intermetallic compounds, held together by metallic bonds
- coordination complexes, held together by coordinate covalent bonds

Non-stoichiometric crystals form a marginal case that could be given special considerations. [Chemical compound - Wikipedia] The chemical formula of a compound is a statement of its composition in terms of the chemical symbols of the elements present. The molecular compound shows how many atoms of each type of element present in the molecule. A covalent bond described as a molecular bond involves the sharing of electrons between two atoms. It occurs between atoms of elements that fall close to each other on the Periodic Table of elements. Elements that fall close to each other on the Periodic Table have both similar electronegativities and affinity for electrons. Since neither element has a stronger affinity to donate or gain electrons, it causes the elements to share electrons, thereby both elements have a more stable octet. Chemical compounds are unique because they established chemical structures that are held together in a defined spatial arrangement by chemical bonds. Chemical compounds could be molecular compounds held together by covalent bond, salts held together by ionic bonds, intermetallic compounds held together by metallic bonds, or the subset of chemical complexes that are held together by coordinate covalent bonds. The chemical formula of a compound is a statement of its composition in terms of the chemical symbols of the elements present [1]. [Chemical compound - Wikipedia]

## Factor Affecting Stability of Chemical Compounds

In Chemistry, chemical stability could be described by the thermodynamic stability of the chemical system. Thermodynamic stability occurs when a system is in its lowest energy state or in chemical equilibrium with its environment. Chemical systems undergo changes in the phase of matter or a set of chemical reactions. Generally, a chemical substance is stable if it is not reactive in the environment or during normal use, it retains its useful properties on the timescale of its expected usefulness. The usefulness is retained in the presence of air, moisture, heat and under the expected conditions of application. A material is said to be unstable if it corrodes, decomposes, polymerizes, burns or explodes under the conditions of anticipated use or normal environmental conditions. [Chemical stability - Wikipedia] Chemical stability is important in the comprehensive assessment of pharmaceutical properties, activity and selectivity during drug discovery. As recorded in [Chemical stability - Wikipedia], some of the questions that are considered in the formation of stable compounds are: "will an active ingredient be stable under the influence of heat? Is the product stable in water? How can the viscosity of the compound be influenced? What kind of container should the preparation be dispensed in? What kind of storage condition should be needed? What should this compound look like? Stability could be defined as the extent to which a product retains the same properties and characteristics that it had when it was produced throughout its shelf life. [THE PCCA BLOG | Factors That Affect the Stability of Compounded M (pccarx.com)] The general stability of a compound is made up of five different types, namely: chemical, physical, microbiological, therapeutic and toxicological stabilities. Chemical stability means that each

active pharmaceutical ingredient (API) maintains its chemical integrity and potency. Physical stability means that properties like appearance, solubility, ability to be suspended and particle size are maintained. Microbiological stability means that microbial growth is avoided. Therapeutic stability ensures that the therapeutic effect does not change. Toxicological stability means that there is no significant increase in toxicity. These five stability issues are considered during release inspections.

## Stability Constants

A stability constant, often referred to as either formation constant or binding constant, is the thermodynamic equilibrium constant for the formation of a complex from its reactants in solution. It is a measure of the strength of the interaction between the reactants to form the complex product(s). [stability constant - Search (bing.com)] Stability constant may refer to: [Stability constant - Wikipedia]

- Equilibrium constant
- Acid dissociation constant
- Stability constants of complexes

There are also thermodynamic and kinetic stability constants. Thermodynamic stability constant describes the transformation energy from reactants to products as described by change of the Gibb's free energy ( $\Delta G$ ) for the reaction at equilibrium. This paper limits its scope on the thermodynamic stability constant. Also, in Coordination Chemistry, stability constant is considered either as formation constant or binding constant. This is the same as equilibrium constant for the formation of a complex in solution. It is a measure of the strength of the interaction between the reagents that come together to form the complex. The stability constant gives the information needed to calculate the concentrations of the complexes in solution. The applications of stability constant are observed in Chemistry, Biology, Medicine, such as in pharmaceutical products, etc. [Stability constants of complexes - Wikipedia]

## Thermodynamic Analysis of Equilibrium Constant

Thermodynamic stability describes the energetics associated with equilibrium constant for any reactions at equilibrium. [Stability Constants | Definition, Examples, Diagrams (toppr.com)] The thermodynamic analysis of equilibrium constant is as illustrated below.

The First law of thermodynamics states mathematically that:

$$dq = dE + dw \quad (1)$$

(q = Heat energy, E = Internal energy, w = work done)

$$dq = dE + PdV \text{ (i.e., for only chemical work at constant pressure, P)} \quad (2)$$

The Second law of thermodynamics states that:

$$dq_{rev}/T = dS_{rev} \quad (3)$$

(T = Temperature in Kelvin, S = Entropy)

From equation (3),

$$dq_{rev} = TdS_{rev} \quad (4)$$

Combining equations (1) & (4) shows that:

$$TdS_{rev} = dE + dw \quad (5)$$

OR

$$dE = TdS - PdV \quad (6)$$

Also from First law,

$$d_{sp} = dE + PdV \quad (7)$$

$$H^p = E + PV \quad \text{(By definition)} \quad (8)$$

(H = Enthalpy, P = Pressure and V = Volume)

The total differentiation of equation (8) gives:

$$dH = dE + PdV + VdP \quad (9)$$

But  
 $dE = TdS - PdV$  (6)

$\therefore$   
 $dH = TdS - PdV + PdV + VdP$  (10)

$dH = TdS + VdP$  (11)

From equation (11),  
 $H = H(S, P)$  (12)

The differentiation of equation (12) gives:

$$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP$$
 (13)

Comparing the coefficients of equations (11) & (13) gives:

$$\left(\frac{\partial H}{\partial S}\right)_P = T$$
 (14)

$$\left(\frac{\partial H}{\partial P}\right)_S = V$$
 (15)

Integration of equation (14) after rearrangement gives:

$$\int dH = \int TdS + \text{constant}$$
 (16)

Assigning the integration Constant, G in equation (16) and re-substituting gives:

$$H = TS + G$$
 (17)

$$G = H - TS$$
 (18)

G is the Gibb's free energy [3].

### Gibb's Free Energy Change of a Reaction

The standard state of a pure solid or liquid is taken as the solid or liquid at 1 atm. pressure and 273K temperature [1].

Consider the hypothetical reaction



If the activities as defined by:  $a_A$  and  $a_B$  are for the reactants A and B;  $a_C$  and  $a_D$  are for the products C and D, the free energy of each of these substances is assumed to be one mole. [1]

The Gibb's free energy expression becomes:

$$G_A = G_A^0 + RT \ln a_A$$
 (20)

$$G_B = G_B^0 + RT \ln a_B$$
 (21)

$$G_C = G_C^0 + RT \ln a_C$$
 (22)

$$G_D = G_D^0 + RT \ln a_D$$
 (23)

$$\Delta G_{rxn} = (cG_C + dG_D) - (aG_A + bG_B)$$
 (24)

$$= (cG_C^0 + cRT \ln a_C + dG_D^0 + dRT \ln a_D) - (aG_A^0 + aRT \ln a_A + bG_B^0 + bRT \ln a_B)$$
 (25)

$$= (cG_C^0 + dG_D^0) - (aG_A^0 + bG_B^0) + RT \ln \frac{a_C^c \times a_D^d}{a_A^a \times a_B^b}$$
 (26)

$$\Delta G = \Delta G^0 + RT \ln \frac{a_C^c \times a_D^d}{a_A^a \times a_B^b}$$
 (27)

The value of the Gibb's free energy is used to determine the feasibility of a chemical reaction.

From the equation:

$$G = H - T\Delta S$$
 (18)

When,  $\Delta G > 0$  at all temperatures, the reaction is not feasible.

$\Delta G < 0$  at all temperatures, the reaction is feasible.

The value of  $\Delta G$  depends on the magnitude of  $\Delta S$  and  $\Delta H$  at constant temperature. At high temperature, the magnitude of  $T\Delta S > \Delta H$ , then,  $\Delta G$  is negative and the reaction is feasible. At low temperature, the magnitude of  $T\Delta S < \Delta H$ .  $\Delta G$  is positive and the system is not feasible. If at low temperature,  $\Delta H$  and  $\Delta S$  are small such that  $\Delta H = T\Delta S$ .

Then,  $\Delta G = 0$  and the reaction is in equilibrium and reversible.

### Brief History

[As adapted from Atkins P, Jones L: Chemistry Molecules, Matter and Change. New York: Sumanas, Inc., and W. H. Freeman and Company; Third Edition 1997]

The Elements: Thinkers and philosophers have considered the structure of matter since ancient times. The ancient Greeks developed the concept of elements as fundamental substances from which all forms of matter are built. Four types of matter were identified, namely earth, air, fire, and water. These four elements were believed to produce all other substances when combined in the right proportions. This concept of element is consistent with the current belief. There are more than one hundred chemical elements which in various combinations make up all the matter on earth. The ancient Greeks analyzed what would happen if matter is continuously cut into smaller pieces. Would there be a point at which the pieces would no longer have the same properties as the whole? Matter is not continuous. It consists of tiny particles. The smallest particle of an element that exists is called an atom. The first convincing argument for atoms was made in 1807 by the English school teacher and chemist John Dalton. Each element has a name and a unique chemical symbol.

The next question that was considered was where the elements come from? All the elements in the universe except hydrogen and most of the helium were made in the stars. Seconds after the universe came into being with the Big Bang, the only element present were hydrogen and helium. After millions of years, as the universe cooled, the atoms of hydrogen and helium collected together in large clouds under the influence of gravity. These clouds gradually became hotter and hotter as they contracted and in due course they burst into incandescence as stars. Within the stars, intense heat caused atoms of hydrogen to smash together, merge, and become atoms of other elements. When two protons and one or two neutrons merge together, the outcome is an atom of helium ( $Z = 2$ ,  $A = 3$  or  $4$ ). When a third proton and more neutrons join, the atom of lithium ( $Z = 3$ ,  $A = 6$  or  $7$ ) is formed etc. This merging released more heat which generated starlight.

Many million years after a star was formed and it began to cool, its outer layer might collapse, like a falling roof into its exhausted core. This mighty starquake produced such great shock waves that the star shrugged off its outer layers and sent them into space in a huge explosion called a supernova. Six of such explosions were detected in the galaxy in the past 1000 years. The most recent explosion was in 1987. The shock of explosion raised the temperature in the star, making it even brighter than before. The Crab nebula, produced by the supernova of 1054, was visible in broad daylight for three weeks. At a high temperature, the heavy atoms collided violently enough to merge and become heavier

atoms. The heavy elements found on Earth, including uranium and gold, were made in this way. The Debris of exploding stars collected together under the influence of gravity and gave rise to a new generation of stars. However, not all the debris collected in a single central body, some collected into smaller bodies that go into orbit around the star. These bodies are the planets and one of them is the earth. All matter on earth was formed in this way in long-dead stars. All the elements other than hydrogen and most of helium, from which everything is made, were formed inside a star. The human flesh is stardust. According to current ideas, hydrogen and helium were formed in the Big Bang. The heavier elements were made inside stars and then scattered throughout space [1].

### Chemical Equilibrium

Chemical reactions like the formation and disintegration of compounds move towards a dynamic equilibrium. Thermodynamics gives a guide on the condition and direction of chemical reactions, to achieve economic yield. The direction of spontaneous change at constant temperature and pressure is towards lower values of the Gibbs energy G. The spontaneity of a reaction is determined by calculating the Gibb's energy [G] of the mixture at various compositions [4]. The minimum in [G] occurs at the composition corresponding to equilibrium. Consider the hypothetical reaction:



Suppose an infinitesimal amount,  $d\varepsilon$ , of A turns into B, then, let:

- change in amount of A present:  $dn_A = -d\varepsilon$  (29)

- change in amount of B present:  $dn_B = +d\varepsilon$  (30)

The extent of reaction,  $\varepsilon$ , is a measure of the progress of the reaction.

Assigning the Conditions:

$$\text{pure A} \Rightarrow \varepsilon = 0 \quad (31)$$

When  $\varepsilon = 1 \text{ mol} \Rightarrow 1 \text{ mol}$  of A has been destroyed and 1 mol of B has been formed.

When the reaction advances by  $d\varepsilon$ , the change in composition of the reaction mixture results in a change in the Gibb's free energy of the system. The change  $d\dot{G}$  is expressed in terms of the chemical potentials (i.e., the partial molar Gibbs energies,  $\dot{G}$ ) of the species in the mixture[3]. At constant temperature and pressure,

$$d\dot{G} = \mu_A dn_A + \mu_B dn_B \quad (32)$$

$$= -\mu_A d\varepsilon + \mu_B d\varepsilon \quad (33)$$

Rearranging the equation gives:

$$\left(\frac{\partial \dot{G}}{\partial \varepsilon}\right)_{P,T} = \mu_B - \mu_A \quad (34)$$

Equation (34) gives the slope of a graph of the Gibbs energy plotted against the extent of reaction. Chemical potentials change with composition, therefore, the slope of the graph of  $\dot{G}$  against  $\varepsilon$ , equation (34) changes as the reaction proceeds. The reaction proceeds in the direction of decreasing  $\dot{G}$ ; if at some stage,  $\mu_A > \mu_B$ , then the reaction  $A \rightarrow B$  is spontaneous. If  $\mu_A < \mu_B$ , then the reverse reaction  $A \leftarrow B$  is spontaneous. When  $\mu_A = \mu_B$ , the slope of the graph is zero. This condition occurs at the minimum of the chemical equilibrium.

At  $\mu_A = \mu_B$ ; neither  $A \rightarrow B$  nor  $A \leftarrow B$  is spontaneous. (35)

The reaction Gibbs energy ( $\Delta_r G$ ) for the reaction  $A \rightarrow B$  is the change in [ $\dot{G}$ ] when 1 mol A forms 1 mol B at a fixed composition of the reaction mixture. It is defined as the slope of the graph of the Gibbs energy plotted against the extent of reaction.

Thus: 
$$\Delta_r G = \left(\frac{\partial \dot{G}}{\partial \varepsilon}\right)_{P,T} \quad (36)$$

$\Delta_r$  signifies a derivative of the slope of  $\dot{G}$  with respect to  $\varepsilon$ .

Thus: 
$$d\dot{G} = \Delta_r G \times d\varepsilon \quad (37)$$

Assuming  $\varepsilon = 1 \text{ mol}$ ,

then,

$$\Delta \dot{G} = \Delta_r G \times 1 \text{ mol} \quad (38)$$

for the reaction  $A \rightarrow B$

$$\partial \dot{G} / \partial \varepsilon = \mu_B - \mu_A \quad (34)$$

For the equilibrium, at constant temperature and pressure;

$$\Delta_r G = 0 \quad (39)$$

Equation (39) states that the slope of the graph of the Gibb's energy plotted against the extent of reaction is zero when products are formed from reactants at the equilibrium composition of the reaction mixture [4]. The standard molar reaction Gibb's energy, is given as:

$$\Delta_r G^0 = \mu_B^0 - \mu_A^0 \quad (40)$$

Equation (40) gives the difference between the molar Gibb's energy of pure B in its standard state and the molar Gibb's energy of pure A in its standard state. Also, the difference in the standard molar Gibb's energies of the products and reactants is equal to the difference in their standard Gibb's energies of formation [4]. Thus:

$$\Delta_r G^0 = \Delta_f G^0(B) - \Delta_f G^0(A) \quad (41)$$

The spontaneity of a reaction is defined as:

If  $\Delta_r G < 0$ , then the reaction  $A \rightarrow B$  is spontaneous.

If  $\Delta_r G > 0$ , then the reverse reaction  $A \leftarrow B$  is spontaneous.

Reactions for which  $\Delta_r G < 0$  are called exergonic reactions (from the Greek words for work-producing). The name signifies that because they are spontaneous, they are used to drive other processes such as other reactions, or are used to do non-expansion work. Reaction for which  $\Delta_r G > 0$  are called endergonic reactions (signifying work consuming). They are spontaneous in the reverse direction. Reactions at equilibrium are neither exergonic or endergonic [3].

The composition of reactions at equilibrium

Consider the reaction: 
$$A \rightarrow B \quad (42)$$

Suppose A and B are perfect gases,

$$\Delta_r G = \{\mu_B^0 + RT \ln\left(\frac{P_B}{P^0}\right)\} - \{\mu_A^0 + RT \ln\left(\frac{P_A}{P^0}\right)\} \quad (43)$$

$$= \Delta_r G^0 + RT \ln\left(\frac{P_B}{P_A}\right) \quad (44)$$

If the ratio of partial pressures at ordinary condition is denoted Q, Then,

$$\Delta_r G = \Delta_r G^0 + RT \ln Q \quad (45)$$

$$\left( Q = \frac{P_B}{P_A} \right) \quad (46)$$

At equilibrium,  $\Delta_r G = 0$  and  $Q = K$

Equation (45) rearranges to:

$$RT \ln K = -\Delta_r G^0 \quad (47)$$

Equation (47) is the link between thermodynamic data and the equilibrium constant (stability constant),  $K$ .

When  $\Delta_r G^0 > 0$ ,  $K < 1$  and at equilibrium the partial pressure of A exceeds that of B. This means that the reactant A is favored in the equilibrium. When  $\Delta_r G^0 < 0$ ,  $K > 1$  and at the equilibrium the partial pressure of B exceeds that of A. The product B is favored in the equilibrium.

The General Case of a Reaction

Consider also the hypothetical chemical reaction  
 $2A + 3B \rightarrow C + 2D$  (48)

$$0 = \sum_j v_j \mu_j \quad (49)$$

(where  $v_A = -2$ ,  $v_B = -3$ ,  $v_C = +1$  and  $v_D = +2$ )

When the reaction advances by  $d\varepsilon$ , the amounts of reactants and products change as follows:

$$dn_A = -2d\varepsilon; \quad dn_B = -3d\varepsilon; \quad dn_C = +d\varepsilon; \quad dn_D = +2d\varepsilon \quad (50)$$

$$\text{In general, } dn_j = v_j d\varepsilon \quad (51)$$

At constant temperature and pressure, the change in the Gibbs energy becomes:

$$d\hat{G} = \mu_A dn_A + \mu_B dn_B + \mu_C dn_C + \mu_D dn_D \quad (52)$$

$$= (-2\mu_A - 3\mu_B + \mu_C + 2\mu_D)d\varepsilon \quad (53)$$

The reaction Gibbs energy, the slope of  $\hat{G}$  as  $\varepsilon$  changes is:

$$\Delta_r G = \left( \frac{\partial \hat{G}}{\partial \varepsilon} \right)_{P, T} = -2\mu_A - 3\mu_B + \mu_C + 2\mu_D \quad (54)$$

$$\text{Thus } \Delta_r G = \sum_j v_j \mu_j \quad (55)$$

The chemical potential is expressed in terms of activities by using

$$\mu_j = \mu_j^0 + RT \ln a_j \quad (56)$$

(where  $a_j$  is interpreted as a fugacity if J is a gas; specifically,  $a_j = f_j/P^0$ ) At the ordinary reaction condition where:

$$\Delta_r G = \Delta_r G^0 + RT \ln Q \quad (45)$$

$$\Delta_r G^0 = -2\mu_A^0 - 3\mu_B^0 + \mu_C^0 + 2\mu_D^0 \quad (46)$$

Thus

$$\Delta_r G^0 = \sum_j v_j \mu_j^0 \quad (47)$$

The reaction quotient Q is given as:

$$Q = \frac{a_C \times a_D^2}{a_A^2 \times a_B^3} \quad (48)$$

At equilibrium,  $\Delta_r G = 0$  and  $Q = K$

$$RT \ln K = -\Delta_r G^0 \quad (49)$$

The equation is an exact thermodynamic relation. The equilibrium constant,  $K$ , expressed in equation (49), in terms of activities, is called a thermodynamic equilibrium constant.

### The Response of Equilibria to Conditions

There are namely: the response of equilibria to pressure and the response of equilibria to temperature.

#### Response of Equilibria to Pressure

The equilibrium constant depends on the value of  $\Delta_r G^0$  which is defined at a single standard pressure. The value of  $\Delta_r G^0$  and therefore of  $K$ , is a constant, independent of the pressure at which the equilibrium is established. [[http://en.wikipedia.org/wiki/Equilibrium\\_constant](http://en.wikipedia.org/wiki/Equilibrium_constant)]

$$\text{Thus, } \left( \frac{\partial K}{\partial P} \right)_T = 0 \quad (50)$$

Pressure is applied to a system in two ways, namely:

- Pressure is applied by injecting an inert gas into the reaction system. If the gases are perfect, this addition keeps all the partial pressures gases unchanged. The addition of an inert gas maintains the molar concentration of the original gases unchanged. The gases continue to occupy the same volume. Pressurization by the addition of an inert gas has no effect on the equilibrium composition of the system.
- The pressure of the system may be increased by physical composition, by confining the gases to a smaller volume. Following this, the values of the partial pressures are changed. The molar concentrations are modified because the volume the gases occupy is reduced.

Consider the perfect gas equilibrium;



The equilibrium constant,  $K$ , is given as:

$$K = \frac{P_B^2}{P_A} \times P^0 \quad (52)$$

The right-hand side of the equation remains constant only if an increase in  $P_A$  cancels an increase in the square of  $P_B$ . This increase in  $P_A$  compared to  $P_B$  will occur if the equilibrium composition shifts in favor of A at the expense of B. The number of A molecules will increase as the volume of the container is decreased and its partial pressure will rise rapidly. This condition is in agreement with the principle proposed by Henri Le Chatelier[1]. Le Chatelier's principle states that "A system at equilibrium, when subjected to a disturbance, responds in a way that tends to minimize the effects of the disturbance."

**Response of Equilibria to Temperature:** Le Chatelier's principle predicts that a system at equilibrium will tend to shift in the endothermic direction if the temperature is raised, for then energy is absorbed as heat [1,8]. Also, an equilibrium is expected to shift in the exothermic direction if the temperature is lowered, for then, the reduction in temperature is opposed[1]. Using the van't Hoff equation:

$$\frac{d \ln K}{dT} = \Delta_r H^0 / RT^2 \quad (53)$$

Equation (53) shows that  $d\ln K/dT < 0$  (i.e.,  $dK/dT < 0$ ) for a reaction that is exothermic under standard conditions ( $\Delta_r H^0 < 0$ ). A negative slope means that  $\ln K$  and therefore  $K$ , decreases as the temperature rises. Therefore, as stated above, in the case of an exothermic reaction the equilibrium shifts away from products. The opposite occurs in the case of endothermic reactions. The equilibrium constant could be calculated at a temperature,  $T_2$  in terms of its value  $K_1$  at another temperature  $T_1$ .

Integrating the equation (53) gives:

$$\int_{\ln K_1}^{\ln K_2} d\ln K = \Delta_r H^0/R \int_{1/T_1}^{1/T_2} dT \quad (55)$$

$$\therefore \ln K_2 = \ln K_1 - \Delta_r H^0/R (1/T_2 - 1/T_1) \quad (56)$$

In summary:

$$\Delta_r G^0 = -RT \ln K \quad (49)$$

Thermodynamic data are listed for processes at 298K.  $RT = 2.48 \text{ KJmol}^{-1}$  at 298K. Equilibrium constants are often calculated at that temperature too. [[1,3,8]

### Equilibrium constant

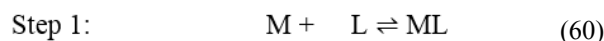
**Cumulative and stepwise equilibrium constants:** A cumulative (overall constant),  $\beta$ , is the constant for the formation of a complex from reagents. [[http://en.wikipedia.org/wiki/Equilibrium\\_constant](http://en.wikipedia.org/wiki/Equilibrium_constant), [http://en.wikipedia.org/wiki/Acid\\_dissociation\\_constant](http://en.wikipedia.org/wiki/Acid_dissociation_constant)] The cumulative constant for the formation of  $ML_2$  is given by:



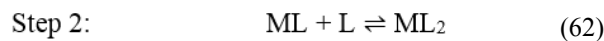
$$\text{Thus; } [ML_2] = \beta_1 [M][L]^2 \quad (58)$$

$$\beta_1 = [ML_2]/[M][L]^2 \quad (59)$$

The stepwise constants,  $K_1$  and  $K_2$  refer to the formation of the complexes one step at a time.



$$K_1 = \frac{[ML]}{[M][L]} \quad (61)$$



$$K_2 = \frac{[ML_2]}{[ML][L]} \quad (63)$$

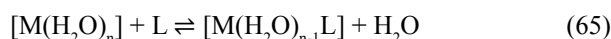
$$\text{It follows that; } \beta_1 = K_1 K_2 \quad (64)$$

A cumulative constant is expressed as the product of stepwise constant. The two kinds of complex are:

- Compounds formed by the interaction of a metal ion with a ligand.
- Supramolecular complexes: Examples are host-guest complexes and complexes of anions. [[http://en.wikipedia.org/wiki/Acid\\_dissociation\\_constant](http://en.wikipedia.org/wiki/Acid_dissociation_constant)] Supramolecular complexes are held together by hydrogen bonding, hydrophobia forces, van der Waals forces,  $\pi$ - $\pi$  interactions, and electrostatic effects or non-covalent bonding.

The formation of a complex between a metal ion M, and a ligand, L, is a substitution reaction. [<http://goldbook.iupac.org/St06785>.

html] In aqueous solutions, metal ions are present as aqua-ions. The reaction for the formation of the first complex is written as:



The equilibrium constant for this reaction is given by:

$$\beta^1 = [M(H_2O)_{n-1}L][H_2O]/[M(H_2O)_n][L] \quad (66)$$

Removing the terms that are constants gives

$$\beta^1 = [M(H_2O)_{n-1}L]/[M(H_2O)_n][L] \quad (67)$$

**Competition Method:** Stepwise constant is used in the determination of stability values outside the normal range for a given method. Examples are EDTA complexes of many metals which are outside the range for the potentiometric method. The stability constants for these complexes are determined by competition with a weaker ligand. [[http://en.wikipedia.org/wiki/Stability\\_constants\\_of\\_complexes](http://en.wikipedia.org/wiki/Stability_constants_of_complexes)]



$$[ML^1] = K[ML][L^1]/[L] \quad (69)$$

**Association and Dissociation Constants:** In Organic Chemistry and Biochemistry, pKa values are used for acid dissociation equilibria. [[http://en.wikipedia.org/wiki/Acid\\_dissociation\\_constant](http://en.wikipedia.org/wiki/Acid_dissociation_constant)]

$$\text{Thus: } pK_a = -\log K_{\text{diss}} = \log(1/K_{\text{diss}}) \quad (70)$$

$K_{\text{diss}}$  is a stepwise acid dissociation constant. The base association constant  $pK_b$ , is used for bases. For any given acid or base, the two constants are related by:

$$pK_a + pK_b = pK_w \quad (71)$$

Stability constant for metal complexes and binding constant for host-guest complexes are generally expressed as association constants. When considering equilibria such as:



It is customary to use association constants for both ML and HL. [[http://en.wikipedia.org/wiki/Stability\\_constants\\_of\\_complexes](http://en.wikipedia.org/wiki/Stability_constants_of_complexes)] Also, in generalized computer programs dealing with equilibrium constants, it is a general practice to use cumulative constants rather than stepwise constants, and to omit ionic charges from equilibrium expressions. [[http://en.wikipedia.org/wiki/Stability\\_constants\\_of\\_complexes](http://en.wikipedia.org/wiki/Stability_constants_of_complexes)] If nitrilotriacetic acid,  $N(CH_2CO_2H)_3$  is designated as  $H_3L$  and forms complexes ML and  $MHL$  with a metal ion M, the following expressions would apply for the dissociation constants. Thus;



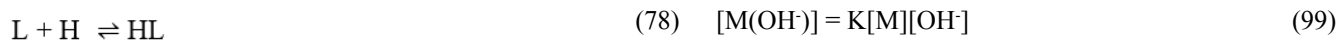
$$pK_1 = -\log\left(\frac{[H_2L][H]}{[H_3L]}\right) \quad (73)$$



$$pK_2 = -\log\left(\frac{[HL][H]}{[H_2L]}\right) \quad (75)$$



$$pK_3 = -\log\left(\frac{[L][H]}{[HL]}\right) \quad (77)$$



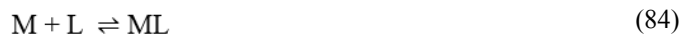
$$\log \beta = \log \left( \frac{[HL]}{[L][H]} \right) = pK_3 \quad (79)$$



$$\log \beta = \log \left( \frac{[H_2L]}{[L][H]^2} \right) = pK_3 + pK_2 \quad (81)$$



$$\log \beta = \log \left( \frac{[H_3L]}{[L][H]^3} \right) = pK_3 + pK_2 + pK_1 \quad (83)$$



$$\text{Log} \beta = \log \left( \frac{[ML]}{[M][L]} \right) \quad (85)$$



$$\text{Log} \beta = \log \left( \frac{[MLH]}{[M][L][H]} \right) \quad (87)$$

**Micro-Constants:** When two or more sites in an asymmetrical molecule are involved in an equilibrium reaction, there are more than one possible equilibrium constants. For example, the molecule L-dopa has two non-equivalent hydroxyl groups which may be deprotonated. [http://en.wikipedia.org/wiki/Stability\_constants\_of\_complexes] Denoting L-Dopa as LH<sub>2</sub>, different species may be formed. The first protonation constants are:

$$[L^+H] = K_1[L][H] \quad (88)$$

$$[L^2H] = K_2[L][H] \quad (89)$$

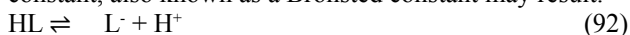
The concentration of LH is the sum of the concentrations of the two micro-species. Therefore, the equilibrium constant for the reaction, the micro-constant, is the sum of the micro-constants:  
 $K = K_1 + K_2 \quad (90)$

A macro-constant is equal to the sum of all the micro-constant and the occupancy of each site is proportional to the micro-constants.

**pH Consideration (Bronsted Constants):** pH is defined in terms of the activity of the hydrogen ion.

$$pH = -\log_{10} \{H^+\} \quad (91)$$

pH is measured by means of a glass electrode; a mixed equilibrium constant, also known as a Bronsted constant may result.



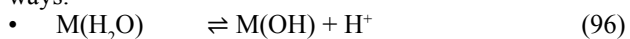
$$pK = -\log \left( \frac{[L][H]}{[HL]} \right) \quad (93)$$

**Hydrolysis Constant:** In aqueous solution the concentrations of the hydroxide ion is related to the concentration of the hydrogen ion by:

$$K_w = [H][OH] \quad (94)$$

$$[OH] = K_w [H]^{-1} \quad (95)$$

The first step in metal ion hydrolysis is expressed in two different ways.



$$[M(OH)] = \beta[M(H_2O)][H^+] \quad (97)$$



**Conditional Constants:** They are also known as apparent constants. They are concentration quotients which are not true equilibrium constants but are derived from them. An example is where pH is fixed at a particular value (buffered). In the case of iron (III) interacting with EDTA, a conditional constant is defined by:

$$K_{\text{cond}} = \frac{[\text{Total Fe bound to EDTA}]}{[\text{Total Fe not bound to EDTA}] \times [\text{Total EDTA not bound to Fe}]} \quad (100)$$

This conditional constant will change with pH. It has a maximum at a certain pH where the ligand sequesters the metal most effectively.

**Acid Dissociation Constant:** An acid dissociation constant, K<sub>a</sub> also known as acid constant or acid ionization constant is a quantitative measure of the strength of an acid in solution. [5,6] It is the equilibrium constant for a chemical reaction known as dissociation in the context of acid-base reactions. [http://www.acadsoft.co.uk/] The equilibrium is written as:



(HA is a generic acid that dissociates by splitting into A<sup>-</sup>, known as the conjugate base of the acid and the hydrogen ion or proton, H<sup>+</sup>, which, in the case of aqueous solution, exists as a solvated hydronium ion. The dissociation constant is written as a quotient of the equilibrium concentration (in mol/L).

$$\text{Thus: } K_a = \frac{a_{A^-} a_{H^+}}{a_{HA}} = \frac{[A^-][H^+]}{[HA]} \quad (102)$$

The logarithmic measure of the acid dissociation constant is used in practice. The acid dissociation constant for an acid is a direct consequence of the underlying thermodynamics of the dissociation reaction.

**Gas Phase Equilibria:** For equilibria in a gas phase, fugacity, f, is used in place of activity. Fugacity has the dimension of pressure. It is divided by a standard pressure, usually 1 bar, in order to produce a dimensionless quantity, f/p<sup>std</sup>. An equilibrium constant is expressed in terms of the dimensionless quantity. [5,6] Example of the equilibrium reaction analysis is given as:



$$f_{NO_2}/P = K(f_{NO_2}/P)^2 \quad (104)$$

Fugacity is related to partial pressure, p, by a dimensionless fugacity coefficient, φ.

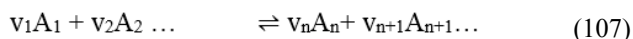
$$f = \phi p \quad (105)$$

$$\text{Thus: } K = \frac{(\phi_{N_2O_4} P_{N_2O_4}/P)}{(\phi_{NO_2} P_{NO_2}/P)^2} \quad (106)$$

**Derivation of Stability Constant from Gibb's Free energy (A Case of a Large System):** Thermodynamic potentials are related to any two variables plus the composition of the system. [1,3,4] For a system of variable composition such as liquid solutions or heterogeneous system containing two or more phases, the thermodynamic potentials depend on temperature, pressure, and the composition of the system. In a binary system, the thermodynamic potentials depend on T, P, and two compositions represented by n<sub>1</sub>, and n<sub>2</sub>. The mathematical definition of the

equilibrium constant is derived directly from the Gibb's Free Energy of the system, along with the Law of Mass Action.  $\mu$  is the chemical potential. By definition,  $\mu$  is the change in the Gibb's free energy per mole of the substances added in the system. It is analogous to temperature and pressure.[1] [[http://en.wikipedia.org/wiki/Equilibrium\\_constant](http://en.wikipedia.org/wiki/Equilibrium_constant)] Also,  $\mu$  is the "driving force" of a chemical reaction. It prompts the tendency of a substance to diffuse from one phase into another.  $n$  is the number of molecules in the system,  $S$  is the entropy of the system,  $T$  is the temperature,  $V$  is the volume and  $P$  is the pressure.

For any chemical reaction,



$$v_1A_1 + v_2A_2 \dots + v_nA_n = 0 \quad (108)$$

$$\sum_j v_j A_j = 0 \quad (109)$$

$$dG = \sum_j \mu dn_j - SdT + VdP \quad (110)$$

Assuming constant pressure and temperature,

$$dP = 0, \quad (111)$$

$$dT = 0, \quad (112)$$

$$dG = \sum_j \mu dn_j \quad (113)$$

$$dn_j = v_j dn \quad (114)$$

$$dG = (\sum_j v_j \mu_j) dn \quad (115)$$

At equilibrium conditions,

$$dG = 0 \quad (116)$$

$$dG = \sum_j v_j \mu_j = 0 \quad (117)$$

$$\text{Thus: } \mu_j = T(\ln n_j - \ln c_j) \quad (118)$$

$n_j$  is the moles of the species  $j$  and  $c_j$  is a constant dependent on the temperature but not on the concentration.

$$\sum_j v_j \ln n_j = \sum_j v_j \ln c_j \quad (119)$$

$$\sum_j \ln n_j^{v_j} = \sum_j \ln c_j^{v_j} \quad (120)$$

$$\sum_j \ln c_j^{v_j} = \ln \pi_j c_j^{v_j} \equiv \ln K(T) \quad (121)$$

$K(T)$  is the equilibrium constant.

$$\ln \prod_j n_j^{v_j} = \ln K(T) \quad (122)$$

$$\prod_j n_j^{v_j} = K(T) \quad (123)$$

$$K(T) = \{A_n\}^{v_n} \{A_{n+1}\}^{v_{n+1}} \dots / \{A_1\}^{v_1} \{A_2\}^{v_2} \dots \quad (124)$$

## Conclusion

Thermodynamic assessment is used in the study of the equilibrium constant of chemical reactions.  $RT \ln K = -\Delta_r G^0$  defines the equilibrium constant,  $K$ , within the limit given as:

- $\Delta_r G^0 > 0$ ,  $K < 1$  and at equilibrium the partial pressure of A exceeds that of B. This means that the reactant A is favored in the equilibrium.
- $\Delta_r G^0 < 0$ ,  $K > 1$  and at the equilibrium the partial pressure of B exceeds that of A. The product B is favored in the equilibrium. The equation is an exact thermodynamic relation.

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