

**KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY
COLLEGE OF ENGINEERING**

**TOPICS
IN
METALLURGICAL THERMODYNAMICS**

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DESCRIPTION OF COURSE

MPE 251: Metallurgical Thermodynamics : 3 credits

Principles of Thermodynamics; The laws of thermodynamics; thermochemistry, enthalpy and heat balances, standard state;

Chemical equilibria, entropy and equilibrium state, equilibrium constant, free energy change in chemical reactions; Chemical equilibrium and metal extraction from aqueous media (Eh-pH or Pourbaix diagrams); Chemical equilibrium and stability of metal oxides (Ellingham diagrams)

Solution Thermodynamics; gas mixtures; aqueous solutions; the structure of solutions; dilute and concentrated solutions; the activity; the Gibbs-Duhem equation; Debye -Hückle theory, solubility; complex formation; solid solutions and melts;

Phase Equilibria, fundamentals of phase diagrams;

Electrochemistry, driving force of electrochemical reactions, electrode potentials and electrochemical series, the effect of concentration on the EMF, galvanic and concentration cells, polarization and overpotential; electron activity and introduction to pE-pH diagrams.

SUGGESTED LITERATURE:

- 1) GASKELL; D. R.: Introduction to Metallurgical Thermodynamics
- 2) DEVEREUX, O. F.: Topics in Metallurgical Thermodynamics
- 3) DARKEN; L. S. and GURRY, R. W.: Physical Chemistry of Metals
- 4) MARKOWIAK, J: Physical Chemistry for Metallurgists
- 5) PERRY and CHILTON: Chemical Engineers Handbook

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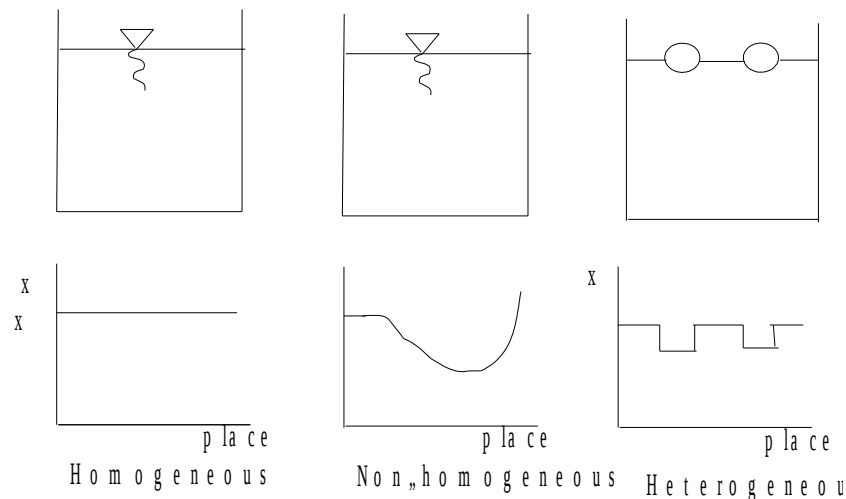
1 INTRODUCTION (BASIC CONCEPTS)

1.1 System

A system is any object, quantity of matter, region, etc., selected for study and mentally set apart from every thing else (surroundings). The system and its surroundings are separated by the boundary. The boundary serves to isolate the system from its surroundings or to provide for interaction in specific ways between the system and the surroundings.

An isolated system has no interactions of any kind, neither exchange of matter nor energy with its surroundings. When there is exchange of matter and energy the system is said to be an open system, and when there is exchange of energy but no matter, then the system is a closed system.

A homogeneous system is one in which every property of the system is constant irrespective of the coordinates of the system. In a non-homogeneous system at least one property has a continuous function with the coordinates (place). A heterogeneous system is a system in which at least one property is a discontinuous function with the coordinates.



1.2 The Equation of State

When constraints are laid upon a system, one can find a unique relationship between the thermodynamic variables, eg. for a given mass of oxygen there is a unique relationship between the pressure, volume and any other thermodynamic variable. This relationship is expressed by an empirical equation called the Equation (or Function) of State.

$$f(p, V, x) = 0 \quad \text{x is a third variable e.g. temperature}$$

The function of state describes the condition of a system as it is now, without reference to prehistory. Therefore the change of state (from state 1 \rightarrow state 2) is independent of the path, but only on the initial and final stages.

A simple example of an equation of state is the ideal gas law: $pV = nRT$

A system has an identifiable, reproducible state when its properties are fixed, or in other words the

properties of a system are fixed by its state.

1.3 Extensive and Intensive Properties

Certain properties (or variables) of a system show dependence on the size of the system and are proportional to the mass of the system. These properties are termed extensive properties. These properties are additive eg., number of moles of the system (N), the internal energy (U), the volume (V), the entropy (S), etc.

On the other hand variables such as temperature (T), pressure (P) are independent of the size or mass of the system. These properties are called intensive properties.

1.4 Equilibrium

Any change in any system can be measured by determining changes in the property of the system, e.g. by using such instruments as thermometers, pressure gauges, etc. The concept of equilibrium is central in thermodynamics. When a system is displaced from a state of equilibrium, the system undergoes a process or series of processes during which its properties change until a new equilibrium is reached. A system is in equilibrium when none of its thermodynamic properties changes with time at a measurable rate. During such a process the system may interact with its surroundings so as to interchange energy in the form of heat and work. Such changes do not continue indefinitely, but come to a state of internal equilibrium. If the changes are due to external interactions, then external, as well as internal equilibrium is reached after some time. The equilibrium state depends on the constraints (conditions) imposed on it and generally there is only one true equilibrium state for a set of constraints.

1.5 The Concept of Work

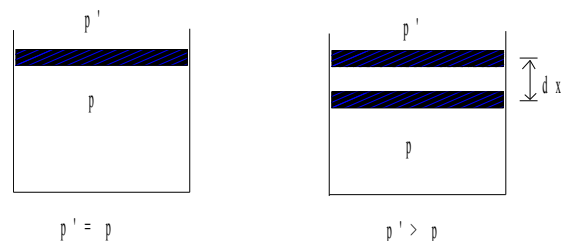
In Physics the definition of work is:

work done (δw_i) = force \times distance

ie: $\delta w_i = F_i dx_i = p_i dA_i dx_i = -p_i dV_i$

Total work done is:

$$\delta w = -p' dV$$



$$w = - \int_{V_1}^{V_2} p' dV$$

For a measurable volume, the total work done on a system is given by:

Note: δw indicates an inexact differential (that is it is not the differential of any function). In other words, it means that the integral depends on the path taken, eg. heat associated with work.

In general, if an expression, $df = M(x,y)dx + N(x,y)dy$ represents a differential of some function f , then it is called an exact differential. An inexact differential can be converted into an exact differential by multiplying by some integrating factor e.g. $2ydx + xdy$ is inexact because there is no function which satisfies the condition:

$$\left(\frac{\partial M}{\partial y} \right)_x = \left(\frac{\partial N}{\partial x} \right)_y \quad \text{However, if this expression is multiplied by } x \text{ the resultant expression becomes an exact differential.}$$

$$2xydx + x^2 dy \quad \text{becomes an exact differential of the function "x}^2\text{y"}$$

Examples of work:

1) Electrical work done in charging a capacitor is:

$$w = \int_{Q^1}^{Q^2} \mathcal{E} dq$$

where q is the charge and \mathcal{E} is the applied potential difference.

2) Work done on a point of charge (q) moving through an electrical field (E) is:

$$\delta w = F \cdot ds = qE \cdot ds = -q d\mathcal{E}$$

3) Work done in a gravitational field is:

$$-w = \int_1^2 p' dV = \frac{\int_1^2 (mg)}{A} A dh = mg \int_1^2 dh = mg \Delta h$$

1.6 Reversible and Irreversible Processes

A process is reversible if the system remains infinitesimally close to equilibrium at all times with changes taking place at near zero rates. The system thus passes through continuous sequence of equilibrium states and can be reversed in the opposite direction along the same path without any input of additional work above that for the forward process. At any point in the process any intensive property (p, T) is continuous across the boundary. An example is the expansion of gas through volume V_1 to V_2 assuming frictionless piston and that the applied pressure is the same as the pressure in the system. Reversible processes produce maximum work. Another example is tug-of-war with equal opponents.

In irreversible processes the system passes through non-equilibrium states with unbalanced forces giving the process a unique direction (eg. the flow of water to a lower level, or the flow of heat to a colder body, or the dissolution of salts, or the reaction between ammonia and hydrochloric acid). For an irreversible gas expansion the applied pressure is not the same as the pressure in the system.

Real processes have measurable rates of change, but because most real processes have their characteristics (eg. values of work, heat evolved) close to those of reversible processes, we assume reversible conditions for these processes for the purposes of calculation.

2 THE LAWS OF THERMODYNAMICS

2.1 Zeroth Law

The Concept of Temperature: The basis for empirical temperature scales is given by the so-called **Zeroth Law of Thermodynamics**, which states that: "Two bodies, each in thermal equilibrium with a third body, are in thermal equilibrium with each other. These bodies have a property in common, defined as temperature (degree of hotness)." Different temperature scales have been developed (eg. Fahrenheit, Centigrade or Celsius) but even with these scales the measured temperature depends on the thermometer used (Hg-in-glass, or thermocouple, etc.). The Kelvin scale based on the ideal gas

law, the Second Law of Thermodynamics and the Kinetic Theory, is the most accurate one and is the scale used in thermodynamic calculations.

2.2 Postulates

The **Laws of Thermodynamics** constitute varieties of observations, abstract principles which are ultimately justified by the agreement of conclusions drawn from them with experiments. To explain these observations scientifically a number of **postulates** have been advanced:

1) that there exists a form of energy, **internal energy (U)** which for systems in equilibrium state is an intrinsic, ("belonging naturally") property of the system, functionally related to the measurable coordinates which characterize the system, ie.

$$U = U(S, V, N_j) \text{ where } j = 1, 2, 3, \dots, k \text{ (for an open system).}$$

$$U = U(S, V) \text{ for a closed system}$$

In the case of work being done on an adiabatically contained body of constant potential and kinetic energy, the pertinent function which describes the state of the body is the internal energy (U).

Internal energy is a function of state and therefore any change in the internal energy is independent of the path, but only on the initial and final states. The internal energy is different from the kinetic or potential energy, which are external forms of energy.

2) that the total energy of any system and its surroundings is conserved (**First Law of Thermodynamics**). In other words, the expenditure of a given amount of work, no matter what origin, always produces the same quantity of heat.

For an isolated system the first law requires that its energy be constant. For a closed system the first law requires that energy changes in the system be exactly compensated by energy changes in its surroundings in the form of work and heat. (This law serves as the basis for the preparation of material and energy balances).

Mathematically, for a closed system of constant mass in which only the internal energy changes:

$dU = \delta Q - \delta W$ where *Q represents the heat absorbed by the system from its surroundings, and *W is work done by the system. After integration the expression becomes:

$$\Delta U = Q - W$$

For an isolated system change in internal energy is a result of "adiabatic" work done in bringing the system from initial to final equilibrium state, ie:

$$\Delta U = U_1 - U_2 = W_{ad}$$

If we consider all the different kinds of work (volume, surface, electrical, etc.) that can be done by the system then the first law can be written as:

$$dU = \delta Q - p dV + \gamma dA - \mathcal{E} dq - \dots + \sum \mu_j dN_j$$

3) There exists a property, **entropy (S)**, which for systems in equilibrium is an intrinsic property and is functionally related to the measurable coordinates of the system.

$$S=S(U, V, N_j)$$

According to Gibbs, entropy is the measure of the mixed-up-ness. It is a function of state. For reversible processes entropy change is calculated along the reversible path as:

$$dS = \frac{\delta Q_{rev}}{T} \quad \text{T is the absolute temperature, and } Q_{rev} \text{ is the heat evolved or absorbed by the system.}$$

4) The entropy change of a system and its surroundings, considered together, resulting from any real process is positive and approaches a limiting value of zero for any process that approaches reversibility (**The Second Law of Thermodynamics**)

(or "the complete conversion of heat into work is impossible without causing some effect to occur elsewhere" or " no engine, operating in cycles, can absorb heat from a reservoir at uniform temperature and convert it into an equivalent amount of work without causing some change elsewhere in the universe")

The Second Law deals with the conversion of heat into work and the law indicates that such conversion cannot be carried out to the full. For an isolated system the Law requires that the entropy increases or in the limit remains constant when the system is in equilibrium. For a closed system the Law requires that any entropy decrease in the system or its surroundings be compensated in the other part or in the limit remain constant at equilibrium.

Every substance has a finite positive entropy, but at the absolute of zero of temperature the entropy may become zero and does so in the case of a perfectly crystalline substance - **The Third Law of Thermodynamics**.

5) The macroscopic properties of a homogeneous (PVT) system in equilibrium can be expressed as functions of P, T, N only.

2.3 Mathematical formulations of thermodynamic functions

The most common systems encountered in the application of the 1st and 2nd Laws are gasses and liquids. The variables most often used are p, V, T and N (composition) and the work done in reversible processes in such systems are:

$$\delta W_{rev} = pdV$$

$$\text{For closed systems:} \quad dU = \delta Q_{rev} - \delta W_{rev} \quad \text{or} \quad dU = TdS - pdV$$

$$\text{For open systems:} \quad U = U(S, V, N_j)$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V, N_j} dS + \left(\frac{\partial U}{\partial V}\right)_{S, N_j} dV + \sum \left(\frac{\partial U}{\partial N_j}\right)_{S, V, N_i} dN_j$$

$$\text{By definition,} \quad \left(\frac{\partial U}{\partial S}\right)_{V, N_j} = T; \quad \left(\frac{\partial U}{\partial V}\right)_{S, N_j} = -p; \quad \left(\frac{\partial U}{\partial N_j}\right)_{S, V, N_i} = \mu_j$$

where μ is the chemical potential

$$\mu = f(T, P, \text{phase})$$

The chemical potential plays a vital role in phase and chemical equilibrium considerations and is generally defined as the free energy per mole of a pure substance.

The change in internal energy becomes:

$$dU = TdS - pdV + \sum \mu_j dN_j$$

This equation is known as the **Fundamental Thermodynamic Equation (Relation)** which on rearranging gives:

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\sum \mu_j}{T} dN_j$$

showing $S = f(U, V, N_j)$, which on differentiation gives:

$$dS = \left(\frac{\partial S}{\partial U} \right)_{V, N_j} dU + \left(\frac{\partial S}{\partial V} \right)_{U, N_j} dV - \sum \left(\frac{\partial S}{\partial N_j} \right)_{U, V, N_i} dN_j$$

Comparing the last two equations it is clear that:

$$\left(\frac{\partial S}{\partial U} \right)_{V, N_j} = \frac{1}{T}; \quad \left(\frac{\partial S}{\partial V} \right)_{U, N_j} = \frac{P}{T}; \quad \left(\frac{\partial S}{\partial N_j} \right)_{U, V, N_i} = \frac{-\mu_j}{T}$$

In terms of mole fractions (x), the Fundamental Thermodynamic Equation becomes:

$$dU = TdS - pdV + \sum \mu_j dx_j$$

Formulations with other thermodynamic functions include:

1) **Enthalpy (H):**

$$H = U + pV$$

$$dH = dU + pdV + Vdp$$

Substituting dU from the Fundamental Thermodynamic Equation and simplifying gives :

$$dH = TdS + Vdp + \sum \mu_j dN_j$$

from which it is evident that enthalpy is a function of the entropy, pressure and number of moles of the system, or

$$H = H(S, p, N_j)$$

(students are to find the relationship between enthalpy and pressure, temperature and the number of moles of a system, using the example shown with respect to entropy above)

2) The **Helmholtz function (A):**

$$A = U - TS$$

$$dA = dU - TdS - SdT$$

Using similar substitution from the Fundamental Thermodynamic Equation,

$$dA = -SdT - pdV + \sum \mu_j dN_j$$

$$A = A(V, T, N_j)$$

3) The **Gibbs function (G)**:

$$G = U + pV - TS = H - TS$$

With similar manipulations as above,

$$dG = Vdp - SdT + \sum \mu_j dN_j \quad G = G(p, T, N)$$

This equation shows that the Gibbs energy is a function of the pressure, temperature and the number of moles of the system.

All these energy functions are important in the study of thermochemistry, among others. For example,

(i) it is easier to calculate the enthalpy change of an isothermal, isochoric system using the expression for (dH) if the entropy, pressure and number of moles of the system are changing.

(ii) for an adiabatic, isobaric system the Helmholtz function becomes important.

(iii) the Gibbs function provides the criterion for deciding whether or not any kind of change (chemical, phase, etc) is possible,

$\Delta G < 0$, indicates a possible spontaneous change

$\Delta G = 0$, shows an equilibrium situation

$\Delta G > 0$, indicates that change is not possible, but rather the reverse change may tend to occur.

2.4 Maxwell Relations

These show the relationship between different thermodynamic expressions. These make it possible to substitute one expression for the other and make thermodynamic calculations easier.

For example, from the expression:

$$H = U + pV, \quad dH = TdS + Vdp + \sum \mu_j dN_j$$

$$\text{Also from } H = H(S, P, N_j) \quad dH = \left(\frac{\partial H}{\partial S}\right)_{p, N_j} dS + \left(\frac{\partial H}{\partial p}\right)_{S, N_j} dp + \sum \left(\frac{\partial H}{\partial N_j}\right)_{S, p, N_i} dN_j$$

$$\text{Therefore} \quad \left(\frac{\partial H}{\partial S}\right)_{p, N_j} = T; \quad \left(\frac{\partial H}{\partial p}\right)_{S, N_j} = V; \quad \left(\frac{\partial H}{\partial N_j}\right)_{S, p, N_i} = \mu_j$$

Using similar manipulations with the Helmholtz function,

$$A = A(T, V, N_j) \quad \text{and} \quad dA = -SdT - pdV + \sum \mu_j dN_j$$

$$\left(\frac{\partial A}{\partial T}\right)_{V, N_j} = -S; \quad \left(\frac{\partial A}{\partial V}\right)_{T, N_j} = -p; \quad \left(\frac{\partial A}{\partial N_j}\right)_{T, V, N_i} = \mu_j$$

$$\text{From } G = G(T, p, N_j) \quad \text{and} \quad dG = Vdp - SdT + \sum \mu_j dN_j$$

$$\left(\frac{\partial G}{\partial T}\right)_{p, N_j} = -S; \quad \left(\frac{\partial G}{\partial p}\right)_{T, N_j} = V; \quad \left(\frac{\partial G}{\partial N_j}\right)_{T, p, N_i} = \mu_j$$

Th above shows that,

$$\left(\frac{\partial U}{\partial S}\right)_{V, N_j} = \left(\frac{\partial H}{\partial P}\right)_{S, N_j}; \quad \left(\frac{\partial H}{\partial p}\right)_{S, N_j} = \left(\frac{\partial G}{\partial p}\right)_{T, N_j}; \quad \left(\frac{\partial H}{\partial T}\right)_{V, N_j} = \left(\frac{\partial G}{\partial T}\right)_{p, N_j}$$

2.5 Applications of energy functions

The energy functions are introduced as a matter of convenience. We are mostly interested in, for example, the direction of changes between phases, chemical reaction possibilities, phase equilibria, diffusion, etc., as well as to derive important relationships between properties of substances. These functions will enable us to express the equilibrium conditions for example of these changes, among others, and to work with the functions which are connected to the process under study.

2.5.1 Expressing U, S as functions of T and V

From postulate (5), at constant composition (N = constant) the molar thermodynamic properties are functions of T and P. However, sometimes it is more convenient to use T and V as the independent variables instead of T and P.

Using $U = U(T, V)$ and $S = S(T, V)$, after differentiation:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad \quad dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

By definition the molar heat capacity at constant volume (C_v) is the temperature derivative of the heat added to a mole of material at constant volume and composition and it is a property of the material and a function of T, P, and N:

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\delta Q_{rev}}{dT}\right)_V$$

From $dU = TdS - pdV$,

$$\left(\frac{\partial U}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V \quad \text{and} \quad \left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - p$$

From Maxwell relations, however,

$$\left(\frac{\partial S}{\partial V}\right)_V = \left(\frac{\partial p}{\partial T}\right)_V$$

Therefore,

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V - p \quad \text{or} \quad dU = C_v dT + [T \left(\frac{\partial p}{\partial T}\right)_V - p] dV$$

Similarly,

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_V; \quad \left(\frac{\partial S}{\partial T}\right)_V = \frac{C_v}{T}$$

and therefore

$$dS = \frac{C_v}{T} dT + \left(\frac{\partial p}{\partial T}\right)_V dV$$

2.5.2 H, S as functions of T, p

Similarly at constant N ,

$$H = H(T, p) \quad \text{and} \quad S = S(T, p)$$

Similar manipulations as above can be used to find the relationship between enthalpy (H) and temperature and pressure, and the relationship between entropy (S) and temperature and pressure (students may want to do that on their own):

$$dH = C_p dT + \left[V - T \left(\frac{\partial V}{\partial T} \right)_p \right] dp \qquad dS = \frac{C_p}{T} dT - \left(\frac{\partial V}{\partial T} \right)_p dp$$

$$C_p = f(T, p, N_i) \quad \text{and by definition} \qquad C_p = \left(\frac{\partial H}{\partial T} \right)_p = \left(\frac{\delta Q_{rev}}{dT} \right)_p$$

So we see that changes in entropy (dS), enthalpy (dH) and internal energy (dU), which are not measurable quantities can be expressed as measurable quantities. The pressure or volume dependence of molar heat capacities (C_p and C_v) are determined from PVT data. The temperature dependence is given empirically as:

$$C_p = a + bT + cT^2 + dT^3 + \dots$$

$$C_p = a + bT + cT^2 + \dots$$

As $T \rightarrow 0K$ C_p vanishes, rising to a plateau at high temperatures with discontinuities occurring at the melting and boiling points.

In a homogeneous phase at constant volume :

$$\text{Heat added to the system is given by} \qquad q = \Delta U = \int_{T_1}^{T_2} C_v dT$$

$$\text{Entropy change is,} \qquad \Delta S_v = \int_{T_1}^{T_2} \frac{C_v}{T} dT$$

At constant pressure

$$\text{Heat added to the system is given by:} \qquad q = \Delta U = \int_{T_1}^{T_2} C_p dT$$

$$\text{Entropy change is} \qquad \Delta S_p = \int_{T_1}^{T_2} \frac{C_p}{T} dT$$

At constant temperature

$$\Delta G_T = \int_{p^2}^{p^1} V dp$$

$$\Delta S_T = -R \ln \frac{p_2}{p_1}$$

$$\Delta S_T = R \ln \frac{V_2}{V_1}$$

At constant entropy (adiabatic

process)

$$\Delta U_S = -RT \ln \frac{V_2}{V_1};$$

$$\Delta H_S = RT \ln \frac{p_2}{p_1}$$

2.6 The concept of Standard States

Standard states are reference points to which energy functions can be related. Since we often consider changes in state, it would be absurd to consider "absolute values of these quantities. Usually, standard values are given at 101.3 kPa (one atmosphere) pressure and at 25°C (298.15 K). Each element in its most stable form at 25°C and 101.3 kPa is assigned a quantity of zero. The standard values are tabulated in Thermodynamic Table of Constants for substances rather than reactions.

Other applications of the First Law are found in calculations in Thermochemistry, ie. heats of reaction, combustion, neutralisation, formation, decomposition, sublimation, vaporization, bond energies, crystallization, dilution, dehydration, among others.

.....Examples of calculations in Thermochemistry

.....Material and Energy Balance calculations

3 CHEMICAL EQUILIBRIUM

Chemical equilibrium can be considered as a consequence of the Second Law of Thermodynamics. For an isolated system spontaneous, irreversible processes are accompanied by entropy increase in the system. This increase will persist so far as spontaneous changes occur, until no further spontaneous changes are possible, when the entropy increase will have reached a maximum. Then no further increase in entropy will be possible.

In this case $dS_{U,V} = 0$.

The internal energy change in such a system will be:

$$dU = TdS - TdS' - *w \quad (TdS' \text{ is a contribution from the spontaneous changes}).$$

At reversible conditions $TdS' = 0$, (ie. $dU = TdS - *w = TdS - pdV$) for a closed system. A criterion for equilibrium therefore is:

$$dU(S,V) = 0.$$

Similarly other criteria for equilibrium are:

$$dH(S,P) = 0; \quad dA(T,V) = 0$$

Another approach to chemical equilibrium is through the Gibbs free energy change. The trend of a reaction or change will always be in the direction for which change in Gibbs free energy (ΔG) is negative, and when equilibrium is reached the ΔG is zero.

Consider the general equation:

$aA + bB = cC + dD$ where a, b, c, and d are stoichiometric coefficients. A,B,C,D are the various species.

From
$$dG = Vdp - SdT + \sum \mu_j dN_j$$

the change in free energy at constant T and p is:
$$dG = \sum \mu_j dN_j$$

In an infinitely large system where finite changes occur without changes in the chemical potentials, for each mole of A consumed,

$$\Delta G = c\mu_C + d\mu_D - a\mu_A - b\mu_B$$

But
$$\mu_j = \mu_j^* + RT \ln(a_j)$$

Therefore substituting and simplifying gives:
$$\Delta G = \Delta G^o + RT \ln Q$$

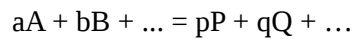
Q is the activity quotient
$$Q = \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b}$$

At equilibrium (for a closed system) $\Delta G_{T,p} = 0$, or

$$\Delta G^o = -RT \ln Q_e = -RT \ln K \quad \text{where } K \text{ is the equilibrium constant}$$

The equilibrium constant provides mathematical tool for theoretical predictions and likelihood of reactions.

In general, for the reaction:



$$\Delta G^o = -RT \ln \frac{a_P^p \cdot a_Q^q}{a_A^a \cdot a_B^b}$$

from which $\Delta G^o = -RT \ln K_a$ where K_a is the equilibrium constant expressed in terms of the activities and is a dimensionless ratio.

The above equation is termed **Reaction Isotherm Equation** or the **van't Hoff ISOTHERM**. K_a is the equilibrium constant expressed in terms of activities and is a dimensionless ratio.

$$\text{From } \Delta G = \Delta H - T\Delta S, \quad \Delta G^o = \Delta H^o - T\Delta S^o$$

Substituting into
and re-arranging

$$\Delta G^o = -RT \ln K_a$$

$$\ln K_a = -\frac{\Delta U^o}{RT} + \frac{\Delta S^o}{R}$$

This is termed as **van't Hoff ISOCHORE**

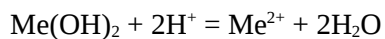
For condensed phases, K_a is expressed in terms of concentration or mole fractions, in which case $\Delta H = \Delta U$ and,

$$\ln K_c = -\frac{\Delta U^o}{RT} + \frac{\Delta S^o}{R}$$

3.1 Chemical equilibrium and metal extraction from aqueous media -

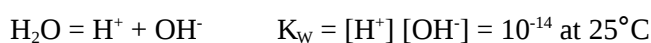
3.1.1 Application of equilibrium constant to solubility

The equilibrium solubility of a metal hydroxide in an aqueous acidic solution may be represented by the equation:



(you will see later that this equation has application in solution purification, geochemistry, environmental chemistry as well)

At the same time some of the water molecules ionize according to:



The first equation can be written as a sum of two reactions:



The equilibrium constant expression is:

$$K^* = \frac{[\text{Me}^{2+}]}{[\text{H}^{+1}]^2} = [\text{Me}^{2+}] [\text{OH}^{-1}]^2 \cdot \frac{1}{[\text{OH}^{-1}]^2 [\text{H}^{+1}]^2} = K' \frac{1}{K_w^2}$$

In general for Me(OH)_z , $K^* = K' / K_w^z$

At equilibrium,

$$\log [\text{Me}^{2+}]_e = -2\text{pH} + \log K^*$$

The equation shows that the equilibrium concentration of the metal ions, and therefore the solubility (or leachability) of the metal hydroxide depends on the pH. If the concentration of the metal ion, $[\text{Me}^{2+}]$, is less than the expected equilibrium value at a given pH (ie., $\log Q < \log K^*$) then the reaction proceeds to the right, that is dissolution occurs (or in terms of stability $[\text{Me}^{2+}]$ is more stable than Me(OH)_2). If on the other hand if metal ion concentration is more than the equilibrium value, then reaction proceeds to the left, that is precipitation of Me(OH)_2 occurs (Me(OH)_2 is more stable than $[\text{Me}^{2+}]$).

$$\log [\text{Me}^{2+}] < -2\text{pH} + \log K^* , \quad [\text{Me}^{2+}] \text{ is more stable.}$$

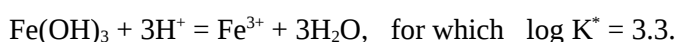
$$\log [\text{Me}^{2+}] > -2\text{pH} + \log K^* , \quad \text{Me(OH)}_2 \text{ is more stable.}$$

In graphical form, $\log [\text{Me}^{2+}] > -2\text{pH} + \log K^*$ is an equation of a straight line ($y = mx + c$), for which,

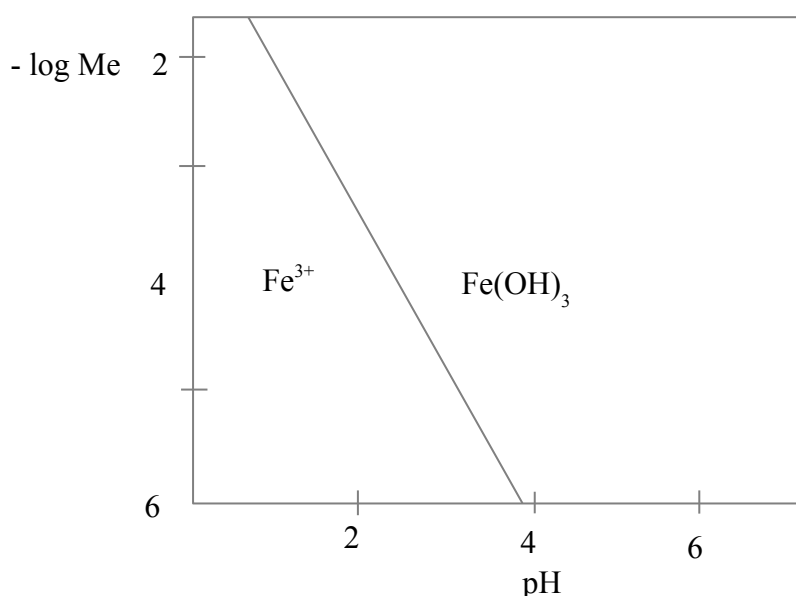
$$1) m = -2$$

$$2) \text{ at } \log [\text{Me}^{2+}] = 0, \quad \text{pH} = \frac{1}{2} \log K^*.$$

An example is the Fe(OH)_3 - H_2O system:



$$\text{Therefore: } \log [\text{Fe}^{3+}] = 3.3 - 3\text{pH}.$$

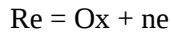


The graph of this is shown indicating the stability regions of the $[\text{Fe}^{3+}]$ and Fe(OH)_3 .

These kinds of diagrams find applications in determining the conditions for leaching, precipitation, etc.

3.1.2 Pourbaix (Eh-pH) Diagrams

Every oxidation and reduction system can be represented by the equation:



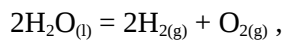
The corresponding half-cell potential is given by:

E_h is the half-cell potential relative to the H_2 -electrode. Therefore for the half-cell reaction:

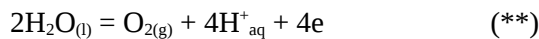
$$a\text{A} + b\text{B} = c\text{C} + d\text{D} + n\text{e}, \quad E_{h, 25^\circ\text{C}} = E^\circ + \frac{0.0592}{n} \log \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

3.1.2.1 The stability of water

The stability of water can be expressed as a function of hydrogen and oxygen partial pressures from the equilibrium constant of the equation:



giving the upper limit of water stability as the equilibrium between water and oxygen at 1 bar (atm) pressure. The stability as functions of Eh and/or pH can be obtained by rewriting the equilibrium equation between water and oxygen and/or electrons:



$$E_h = E^\circ + \frac{0.0592}{4} \log \frac{p_{\text{O}_2} [\text{H}^+]^4}{[\text{H}_2\text{O}]^2} \quad \text{or} \quad E_h = E^\circ + \frac{0.0592}{4} \log [\text{H}^+]^4 \quad (***)$$

This simplifies to:

$$E_h = E^\circ - 0.0592 \text{ pH} \quad (\text{The upper limit of water stability, } p_{\text{O}_2} = 1 \text{ bar, and the activity of pure water is 1})$$

The plot of $E_h = E^\circ - 0.0592 \text{ pH}$ is a straight line with a slope of -0.0592 Volts per pH unit, and has an intercept of E° . To obtain numerical values of E° , we can use the expression:

$$E^\circ = \frac{\Delta G^\circ}{nF}$$

Form equation (**),

$$\begin{aligned} \Delta G^\circ_{\text{r}} &= \Delta G^\circ_{\text{fO}_2} + 4 \Delta G^\circ_{\text{fH}^+} - 2 \Delta G^\circ_{\text{fH}_2\text{O}} \\ &= 0 + (4 \times 0) - (2 \times -56.69) = 113.4 \text{ kcal (....kJ)} \end{aligned}$$

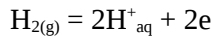
Therefore $E^\circ = (113.4) / 4 \times 23.06 = 1.23 \text{ Volts}$

Therefore $E_h = 1.23 - 0.059\text{pH}$ (see Figure)

In general equation (***) can be written as: $E_h = 1.23 + \frac{0.059}{4} \log p_{O_2} - 0.059 \text{ pH}$

or in terms of hydrogen partial pressure: $E_h = E^\circ - \frac{0.059}{2} \log p_{H_2} - 0.059 \text{ pH}$

From $2\text{H}_2\text{O}_{(l)} = 2\text{H}_{2(g)} + \text{O}_{2(g)}$



In this case $E^\circ = \frac{\Delta G_r^\circ}{nF} = 0$ $\Delta G_r^\circ = \Delta G_{\text{FH}^+}^\circ - \Delta G_{\text{FH}_2}^\circ = 0 - 0 = 0$

Therefore $E_h = - \frac{0.059}{2} \log p_{H_2} - 0.059\text{pH}$

3.1.2.2 Types of Boundaries in Eh - pH space

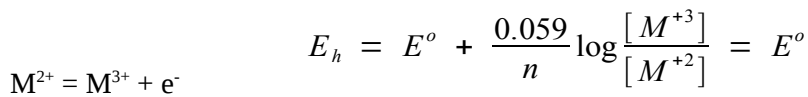
(1) For pH-dependent only



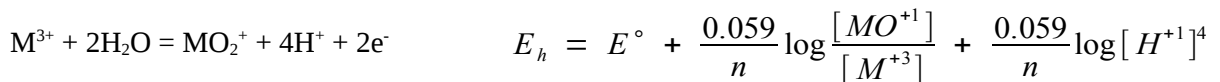
(2) For Eh-dependent only: metal to ion



(3) For Eh-dependent only: ion to ion

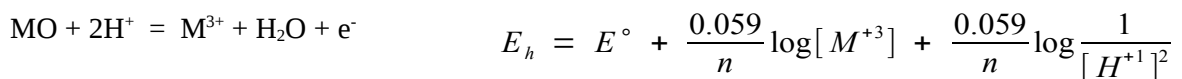


(4) For Eh-pH dependent: activities of redox species equal



$$E_h = E^\circ - 0.118 \text{ pH}$$

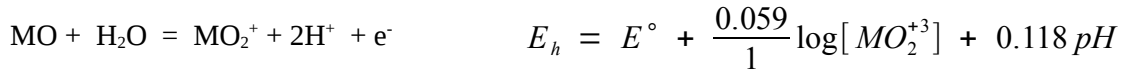
(5) For Eh-pH dependent: solid - ion redox reactions



$$E_h = E^\circ + \frac{0.059}{1} \log[M^{+3}] + 0.0295 pH$$

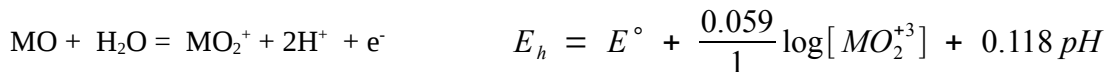
The slope of this boundary is positive since hydrogen ions appear with reactants.

(6) For Eh-pH dependent: solid - ion redox reaction



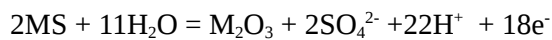
The slope of this boundary is negative since hydrogen ions appear with the products.

(7) For Eh-pH dependent: solid - ion redox reaction



(8) For Eh-pH dependent: more than one element involved in redox reactions:

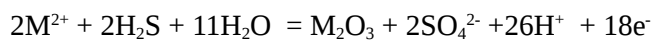
a) Oxidation of metal sulphide:



$$E_h = E^\circ + \frac{0.059}{n} \log[SO_4^{-2}]^2 + \frac{0.059}{n} \log[H^{+1}]^{22}$$

$$E_h = E^\circ + \frac{0.059}{18} \log[SO_4^{-2}] + 0.072 pH$$

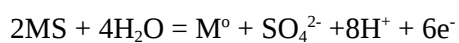
b) Oxidation of M ion and S(-II) sulphur



$$E_h = E^\circ + \frac{0.059}{n} \log \frac{[SO_4^{-2}]^2}{[M^{+2}]^2} + \frac{0.059}{n} \log[H^{+1}]^{26}$$

$$Eh = E^\circ + \frac{0.059}{18} \log \frac{[SO_4^{-2}]}{[M^{+2}]^2} - 0.085 pH$$

c) S oxidized, M reduced



$$E_h = E^\circ + \frac{0.059}{n} \log[SO_4^{-2}]^2 + \frac{0.059}{n} \log[H^{+1}]^8$$

$$E_h = E^\circ + \frac{0.059}{6} \log[SO_4^{-2}] + 0.079 pH$$

3.1.2.3 Preparation of Stability Diagrams ($Eh - pH$, $[M] - pH$, $[L] - pH$)

The stability diagrams are made up of **stability lines** and **predominant areas**. To prepare stability diagrams you need:

1. Thermodynamic data
2. Mathematical manipulations

Step 1: Write the relative stability equations using system variables (e^- , H^+ , $[M]$, H_2O). For example for M_2O/M^{2+} system, the following equation is used:

$$M_2O_{(s)} + 2H^+ = 2M^{2+} + H_2O + 2e^- \quad , \text{ for which } Q = [M^{2+}]^2 \frac{\{e^-\}^2}{[H^+]^2}$$

$$\log Q = 2 \log [M^{2+}] + 2 \log \{e^-\} - 2 \log [H^+]$$

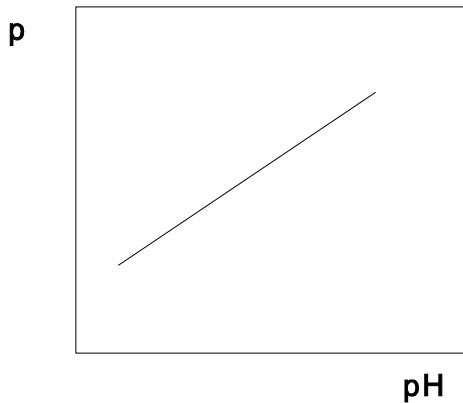
$$= 2 \log [M^{2+}] - 2 pE + 2pH$$

Step 2: Get the equation for the relative stability lines

Step 3: Plot the relative stability lines

- the reaction goes to the right if $\log K > \log Q$; $(\log K > 2 \log [M^{2+}] - 2 pE + 2pH)$

- at equilibrium, $\log K = \log Q$ $(\log K = 2 \log [M^{2+}] - 2 pE + 2pH)$



Step 4: Identify the relative stability regions

The relative stability of M_2O or M^{2+} is determined by three variables; $\{M^{2+}\}$, $\{e^-\}$, $\{H^+\}$. There are three possibilities:

(a) for $\{M^{2+}\}$ is constant, then: $pE = \{-\frac{1}{2} \log K + \frac{1}{2} \log [M^{2+}]\} + pH$

We know that the reaction proceeds to the right if:

$$\log Q \leq \log K \quad \text{or on rearranging,} \quad pE \geq \{-\frac{1}{2} \log K + \frac{1}{2} \log [M^{2+}]\} + pH$$

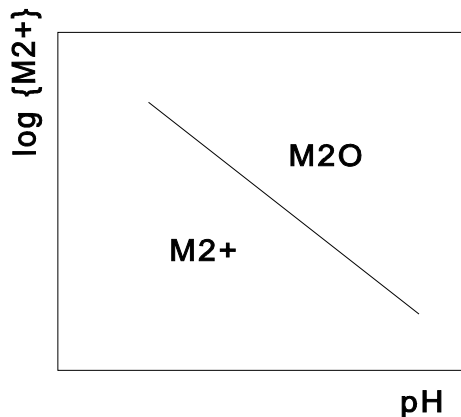
That is if $p\epsilon > k + pH$, ($k = \text{const.}$) then M^{2+} lies above the equilibrium line

(b) for $p\epsilon > k$ the reaction proceeds to the right if:

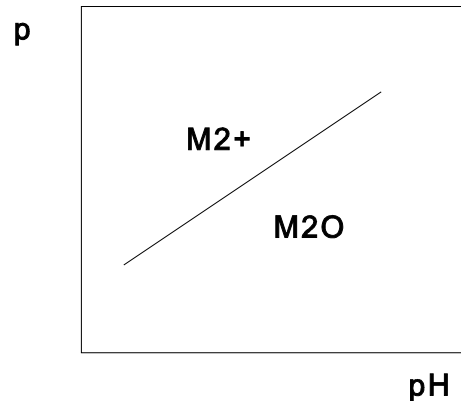
$$\log K > 2 \log [M^{2+}] - 2p\epsilon + 2pH \text{ or on rearranging,}$$

$$\log [M^{2+}] \leq [\frac{1}{2} \log K + p\epsilon] - pH \quad \text{or} \quad \log [M^{2+}] \leq k - pH$$

M_2O lies above the stability line



(i)



(ii)

(c) for $pH = \text{constant}$, $p\epsilon \geq k + \log [M^{2+}]$ the diagram is similar to that of (a)

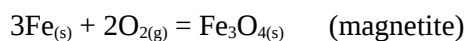
3.2 Chemical equilibrium and the stability of metal oxides in aqueous media

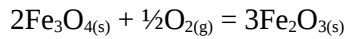
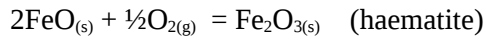
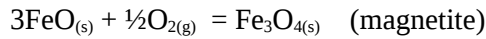
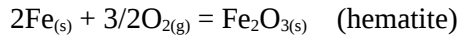
The stability relations among various metal oxides of metallurgical interest can be obtained by writing reactions in terms of the metal compounds and gaseous oxygen, including all permutations and combinations possible. Calculating the equilibrium constants and knowing that the activities of crystalline solids at standard conditions is 1, the equilibrium constant is written as a function of oxygen pressure. Calculating the standard free energy of each reaction and using,

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

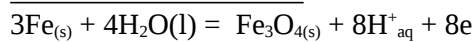
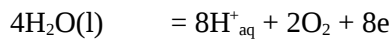
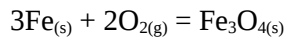
the partial O_2 pressure can be determined, and from this the relative stabilities of the oxides.

In the case of iron the following reactions could be taken into consideration:





From the above, it could be seen that the most stable iron phases are native iron, magnetite and haematite. In aqueous media, the stability relations can be converted to relations expressed as functions of E_h and pH by adding water dissociation half-cell to the reactions, eg. oxidation of Fe to magnetite:



$$E^o = \frac{\Delta G_r^o}{nF}$$

Calculating the ΔG_r^o and substituting into

gives $E^o = -0.084 \text{ V}$

$$E_h = -0.084 + \frac{0.0592}{8} \log \frac{[\text{Fe}_3\text{O}_4][\text{H}^+]^8}{[\text{Fe}]^3[\text{H}_2\text{O}]^4} \quad \text{or}$$

$$E_h = -0.084 + \frac{0.059}{8} \log [\text{H}^+]^8 \quad ; \quad Eh = -0.084 - 0.059\text{pH}$$

Similarly the oxidation of magnetite to haematite can be represented by:

$$Eh = 0.221 - 0.059\text{pH}$$

The same could be done for iron hydroxides, ions in equilibrium with iron oxides, etc., and a composite diagram could be composed showing the stability regions of the various species in the Eh-pH diagram.

(GIVE AN EXAMPLE OF THE Cu - H₂O SYSTEM)

3.3 Chemical equilibrium and the stability of metal oxides in pyrometallurgy

The relationship between the enthalpy change, ΔH (heat of reaction), entropy change, ΔS , and the free energy change ΔG .

$$\Delta G = \Delta H - T\Delta S.$$

At standard state (pure condensed phase or 1 atm. pressure for gases):

$\Delta G^0 = \Delta H^0 - T \Delta S^0$. Sometimes ΔG^0 is given as a function of temperature, T, in which case
 $\Delta G^0 = \Delta H^0 + a T \log T - \frac{1}{2} abT^2 - \frac{1}{6} cT^3 + IT$ (a, b, c, I are constants)

For reactions at equilibrium:

$$G(T, p) = O, \text{ and}$$

$$\Delta G^0 = RT \ln K \quad K: \text{equilibrium constant (so } \Delta G \text{ enables the calculation of } K \text{ and vice versa)}$$

For a metal-metal oxide system:

$$\frac{2x}{y} Me + O_2 = \frac{2}{y} Me_x O_y \quad \text{and} \quad \Delta G = - RT \ln K = - RT \ln \frac{a_{Me_x O_y}^{\frac{2}{y}}}{a_{Me}^{\frac{2x}{y}}}$$

(Note that Me and $Me_x O_y$ are assumed to be in standard state)

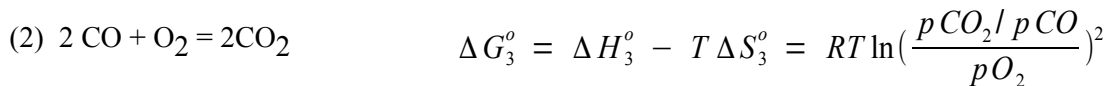
$$\text{Combining with the above equation gives:} \quad RT \ln p_{O_2} \quad \Delta G^0 = \Delta H^0 - T \Delta S^0$$

We can therefore say that with good approximation, ΔG^0 or $RT \ln p_{O_2}$ has a linear function with temperature. Plots of ΔG^0 versus T are known as Ellingham diagrams. It is also possible to regard the metal-metal oxides as being in equilibrium with a gas mixture, which in itself defines the oxygen partial pressure (eg. a mixture of CO, CO_2)

Thus for:



This is a difference of two reactions:



$$\text{so that,} \quad \Delta G_1^0 = (\Delta H_2^0 - \Delta H_3^0) - T(\Delta S_2^0 - \Delta S_3^0)$$

It is possible by these to plot $\Delta G = f(T)$ for various oxides as presented in the Ellingham diagrams. Detailed discussion of the Ellingham diagrams will be done under pyrometallurgy.

Ellingham Diagrams

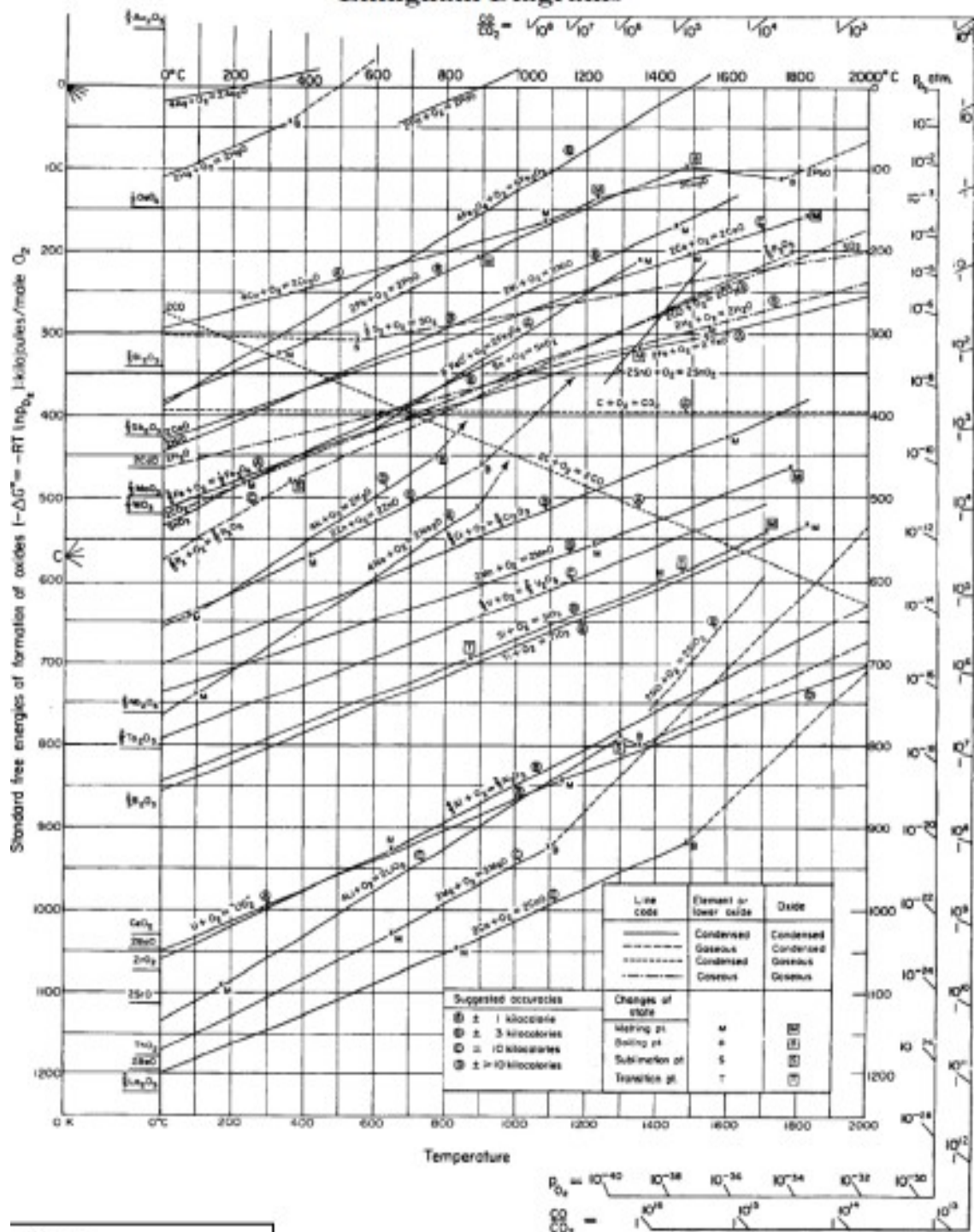


Fig. 3.1

4 COMPLEX EQUILIBRIA

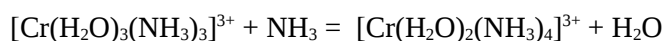
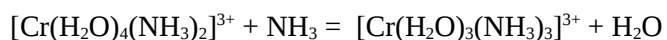
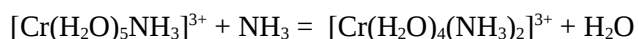
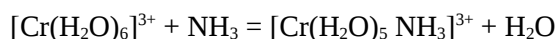
Another application of chemical equilibrium is in the formation of complexes. Metal ions in aqueous media do not exist as bare ions, but are present as complexes (coordinated compounds). In the absence of complex forming ligands, the central metal ions are surrounded with water molecules through coordination forming a kind of loose bond with the ion. These "hydrated" ions are called aquo-complexes. When other complex forming ligands are present in the solution then depending on the thermodynamics of the complex formation (or the stability of the complexes) the water molecules are replaced by the complex forming ligands.

The complex forming ligand could either be an ion (anionic ligand) or a molecule (neutral ligand) and the number of ligands that could be bonded to the central metal ion (nucleus) depends on the coordination number of the nucleus. Discussions on coordination numbers can be found in text books of inorganic chemistry. The ligands are bonded to the central metal ion by either ionic or covalent bonding.

If you consider for example the complex, $[\text{Co}(\text{NH}_3)_6]^{3+} \cdot 3\text{Cl}^-$, the ammonia molecules are needed to satisfy the coordination number (6) of the central metal ion, whilst the Cl^- ions are needed to satisfy the oxidation number (3) of the central metal ion.

4.1 Complexes with Neutral Ligands

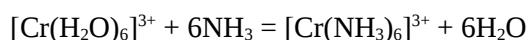
Neutral ligands are those molecules with single donor atoms, which have no charges, eg. H_2O , NH_3 . An example is the formation of Cr^{3+} amine complex:



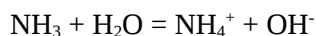
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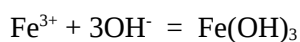
The overall complex formation reaction is:



The above represent substitution reactions (substitution of water molecules with ammonia molecules), taking place in steps, with the formation of intermediate mixed ligand complexes. For the amine complexes to be formed the concentration of ammonia in the solution must be high enough. In this case other side reactions may also take place, notably:

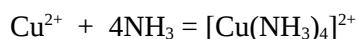


As a result, the formation of insoluble hydroxide precipitates may also occur, eg.



However, if the hydroxide is soluble and the amine complex stability is high then the formation of the

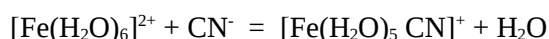
amine complex is more probable. For example, in the case of Cu^{2+} , $\text{Cu}(\text{OH})_2$ is soluble and the reaction in presence of NH_3 therefore is:



4.2 Complex formation with anionic ligands

- **acido complexes**: the ligands in this case (fluoro-, chloro- bromo-, and iodo-complexes) are slightly basic and therefore their formation depends slightly on the pH.

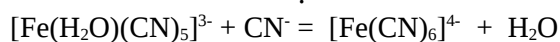
- **ciano complexes**: are formed only in neutral or basic medium, with the cyanide ion replacing the water molecules around the metal ion, eg.



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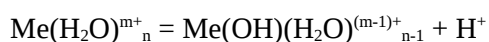
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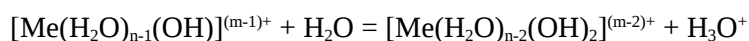


Other cianocoplexes are $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Au}(\text{CN})_2]^-$, $[\text{Ag}(\text{CN})_2]^-$, $[\text{Zn}(\text{CN})_4]^{2-}$, $[\text{Ni}(\text{CN})_4]^{2-}$. Some of these complexes can also be formed in weakly acidic solutions since their decomposition is kinetically inhibited.

-**hydroxo complexes** are formed from aquo-complexes by the deprotonation of the water molecules around the metal ion in the presence of a proton acceptor, ie:



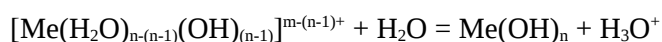
The role of the proton acceptor can be played by the water molecule since the coordinated water molecule is a stronger acid than the non-coordinated. If the pH of the solution is increased by the addition of NaOH, then all the coordinated water molecules are exchanged for OH^- ions:



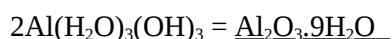
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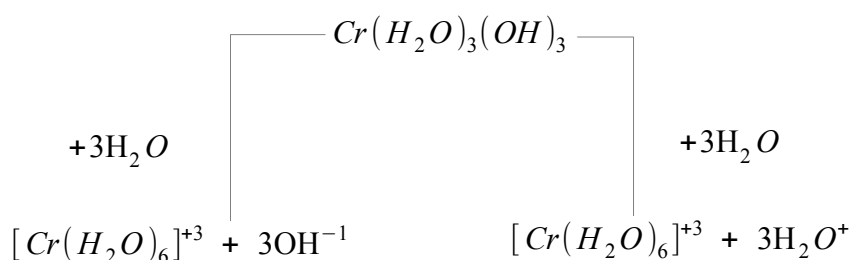
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Even though in all cases the initial and final results are known, the intermediate steps are not often the same as above. Polynuclei complexes may be formed, especially in the case of amphoteric hydroxides, eg.:



Or in the case of Cr(III), the following represents the complexation route:



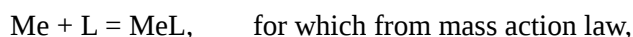
Other complexes include:

- chelate complexes**, eg. with EDTA (ethylene diamine tetraacetic acid)
- polynuclei complexes**, ie with more than one central atom taking part.
- mix ligand complexes**, eg $[PdCl_4]^{2-}$, $[PdCl_3Br]^{2-}$, $[PdCl_2Br_2]^{2-}$

4.3 Complex Stability Constants

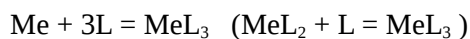
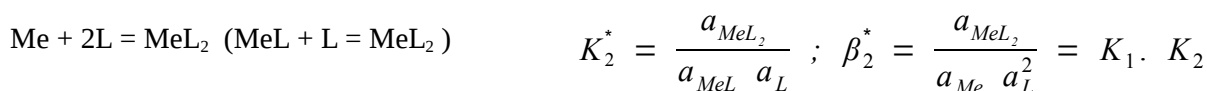
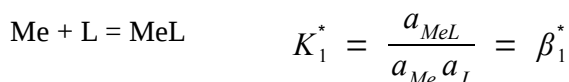
The thermodynamics of complex formation is shown through the relationship between the equilibrium complex formation constant (K) and the free energy change during the process.

Considering the equilibrium complex formation reaction between metal ion (Me) and ligand (L):

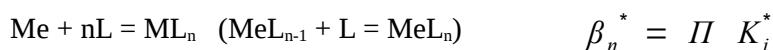


$$K = \frac{a_{MeL}}{a_{Me} a_L} \quad K \text{ is the consecutive stability constant.}$$

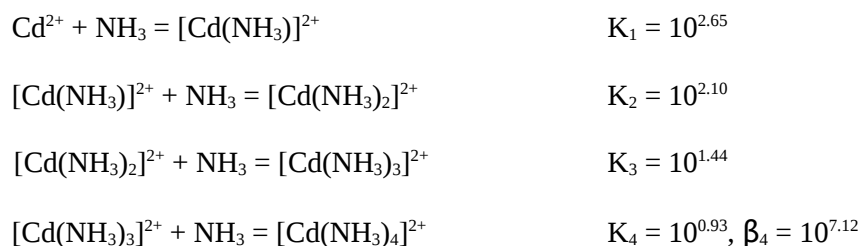
If the reaction proceeds through intermediate complexes, then:



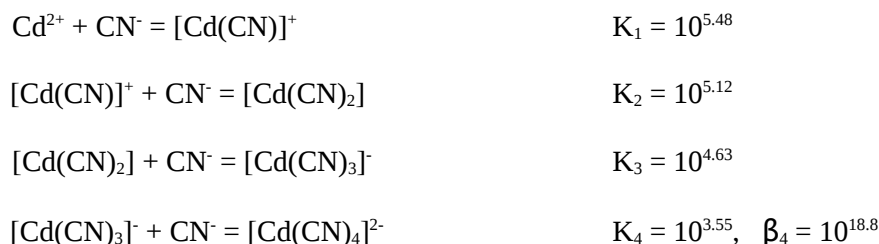
$$K_3^* = \frac{a_{MeL_3}}{a_{MeL_2} a_L} ; \beta_3^* = \frac{a_{MeL_3}}{a_{Me} a_L^3} = K_1^* \cdot K_2^* \cdot K_3^*$$



β is known as the overall stability constant. The physical understanding of the consecutive stability constant is that, in a given system containing metal ion (Me) and ligand (L), all the species from MeL ... to MeL_n exist and the amount of each species depends on the concentration of Me and L, and on the individual stability constants (K_i). For example:



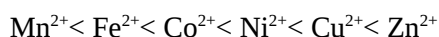
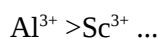
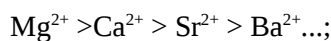
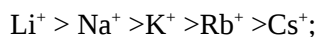
Or in the case of cyanide complex,



The above shows that in such a system MeL is first formed, and as the ligand concentration increases MeL₂ increases whilst MeL decreases, and so on.

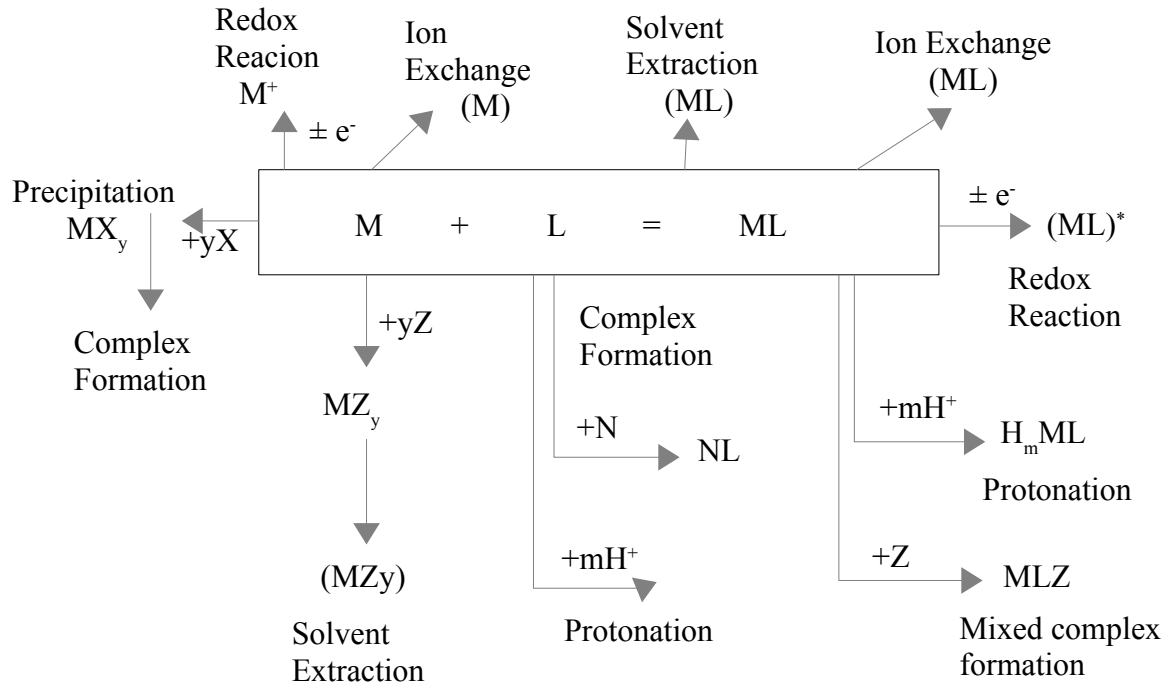
Thermodynamic Tables exist where the overall stability constants are listed for various number of complexes. Sometimes the logK is listed.

The stability of complexes for a particular metal ion depends on the size of the ion, the charge on the ion and some steric factors. Generally, complex stability constant decreases in the following order:



4.4 Complex formation in the presence of other reactions

It is possible that complex formation takes place together with other reactions. Such reactions may be acid-base, redox, precipitation or other complex formation reactions. The diagram below shows reactions that are possible. In such cases the nature of the reactions determine whether the complex formation reaction is the main or side reaction.



4.5 Complex Formation and Solubility

In some applications in the extractive metallurgy the formation of complexes is beneficial because it leads to the stability of the metal ion in solution and therefore enhances the solubility of the metal during leaching. In other applications the stability of the metal complexes could be used in selective separation of different metals from one another.

A typical example is the leaching of gold in cyanide solution. As native gold is oxidized in the presence of oxygen, the aurous ions forms a complex with the cyanide ions present in the solution:



$$E = E^\circ + \frac{RT}{nF} \ln \frac{[\text{Au}(\text{CN})_2]^{-1}}{\beta [\text{CN}]^2}$$

Combining all constants with EE and rearranging, the standard electrode potential for complex formation (E°_{comp}) is obtained:

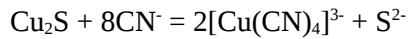
$$E^\circ_{\text{comp}} = E^\circ - \frac{RT}{nF} \ln \beta = 1.69 - 2.24 = -0.55 \text{ V}$$

Therefore,

$$E = E^\circ_{\text{comp}} + \frac{RT}{nF} \ln \frac{[\text{Au}(\text{CN})_2]}{[\text{CN}^{-1}]^2}$$

The above shows that because of complex formation the activity of the metal ion decreases leading to a shift in the electrode potential.

Another example is the change in solubility as a result of the addition of complex forming ligands into the solution:



This particular reaction is undesirable in gold cyanide leach systems because it consumes cyanide.

4.6 Speciation Diagrams

Using data from the discussions under the section on “Complex Stability Constants”, it is possible to draw speciation diagrams indicating the regions of stability of the complex species.

Let the total concentration of dissolved metal be C_M

Then $C_M = [\text{Me}] + [\text{MeL}] + \dots + [\text{MeL}_i]$

$$C_M = [\text{Me}] + \beta_1[\text{L}][\text{Me}] + \beta_2[\text{L}]^2[\text{Me}] + \beta_i[\text{L}]^i[\text{Me}]$$

$$C_M = [\text{Me}] \left\{ 1 + \sum_{i=1}^n \beta_i [\text{L}]^i \right\}$$

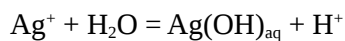
$$\alpha_o = \frac{[\text{Me}]}{C_M} = \frac{1}{1 + \sum_{i=1}^n \beta_i [\text{L}]^i} \quad \text{or} \quad \alpha_i = \beta_i [\text{L}]^i \alpha_o$$

The speciation diagram can then be drawn by plotting:

(i) α_1 vs $\log [\text{L}]$

(ii) α_1 vs pL ($-\log [\text{L}]$)

Example : the speciation diagram for Ag - OH - H₂O system



$$(\log \beta_1 = -12.0)$$



$$(\log \beta_2 = -24.0)$$

To prepare a speciation diagram (α_1 vs pH), the following expressions are used.

$$\alpha_1 = \frac{[\text{AgOH}]}{C_{\text{Ag}}} = \left(\frac{\beta_1}{[\text{H}^{+1}]} \right) \alpha_o \quad \alpha_o = \frac{[\text{Ag}^{+1}]}{C_{\text{Ag}}} = \frac{1}{1 + \frac{\beta_1}{[\text{H}^{+1}]} + \frac{\beta_2}{[\text{H}^{+1}]^2}}$$



5 PHASE EQUILIBRIA

5.1 Introduction

The knowledge of phase equilibria is important not only in the study of phase processes taking place at ordinary atmospheric conditions, but also in the study of high temperature reactions, processes involving different phases. These include high temperature and pressure solid-solid, solid-liquid, solid-gas and liquid-gas reactions, the development of products in the ceramics and glass industries, alloys and special alloys, the formation or precipitation of minerals phases, among others.

5.2 The Thermodynamic Phase Equation

The complexity in the study of such systems increases as the number of components and phases increase. It is easier in this case to first of all understand simpler multiphase, multicomponent systems and then apply the principles to the more complicated systems.

$\alpha(T, p, \mu)$
$\beta(T, p, \mu)$

Consider a one-component system involving two phases (α , β).

The two phases are in equilibrium if the following conditions are fulfilled:

$$T_{\alpha} = T_{\beta}; \quad p_{\alpha} = p_{\beta}; \quad \text{and} \quad \mu_{\alpha} = \mu_{\beta}$$

From definition, $\mu_{\alpha} = g_{\alpha}$, where g_{α} is the molar free energy.

Similarly $\mu_{\beta} = g_{\beta}$

At equilibrium and from the expression, $dG = -SdT + Vdp$,

$$dg_{\alpha} = -s_{\alpha}dT + v_{\alpha}dp = dg_{\beta} = -s_{\beta}dT + v_{\beta}dp$$

or, $(v_{\alpha} - v_{\beta})dp = (s_{\alpha} - s_{\beta})dT$

$$\frac{dp}{dT} = \frac{(s_{\alpha} - s_{\beta})}{(v_{\alpha} - v_{\beta})}$$

For isothermal transformations and at equilibrium,

$$\Delta G = 0 = \Delta H - T \Delta S \quad ; \quad \Delta g = 0 = \Delta h - T \Delta s$$

$$\Delta s = \frac{\Delta h}{T}$$

Therefore: $\frac{dp}{dT} = \frac{\Delta h}{T \Delta v}$ This is known as the **Clausius-Clayperon Equation**. This equation shows the relationship between pressure and temperature at which phases α and β exist in equilibrium. It also shows the enthalpy and volume changes that accompany such changes.

For liquid/vapour considerations the volume of a unit mass of the condensed phase is negligible as compared to that of the vapour phase, and assuming ideal conditions therefore,

$$\Delta v \simeq \frac{RT}{p}; \quad \rightarrow \quad \frac{dp}{dT} = \frac{p \Delta h}{RT^2}$$

In the form of a differential equation, $\frac{d \ln p}{d(\frac{1}{T})} = -\frac{\Delta h}{R}$

Given points such as the melting and boiling points in the system, the equations can be integrated and presented as a plot of p against T , or T against % composition.

5.3 The Phase Rule

For multicomponent multiphase systems the following conditions must be fulfilled for equilibrium to be established among the phases:

$$T_{\alpha} = T_{\beta} = T_{\gamma} = \dots \quad (P-1 \text{ equalities, } P: \text{ the no. phases})$$

$$p_{\alpha} = p_{\beta} = p_{\gamma} = \dots \quad (P-1 \text{ equalities})$$

$$\mu_{1\alpha} = \mu_{1\beta} = \mu_{1\gamma} = \dots \quad (P-1 \text{ equalities})$$

$$\vdots$$

$$\mu_{2\beta} = \mu_{2\alpha} = \mu_{2\gamma} = \dots \quad (P-1 \text{ equalities})$$

\vdots
 \vdots
 \vdots

In this type of system, there are $C+1$ variables per phase, and therefore $P(C+1)$ variables in P phases. At the same time there are $(P-1)$ equalities in chemical potential for each C component, satisfying $(P-1)(C+2)$ equations.

Therefore the **Degree of Freedom (F)** is given by:

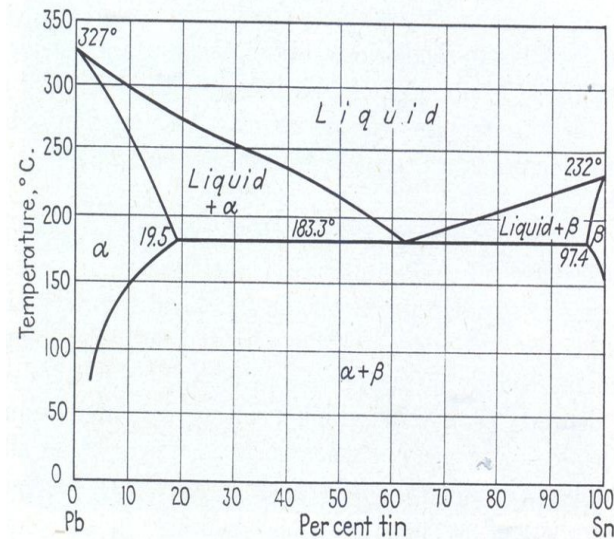
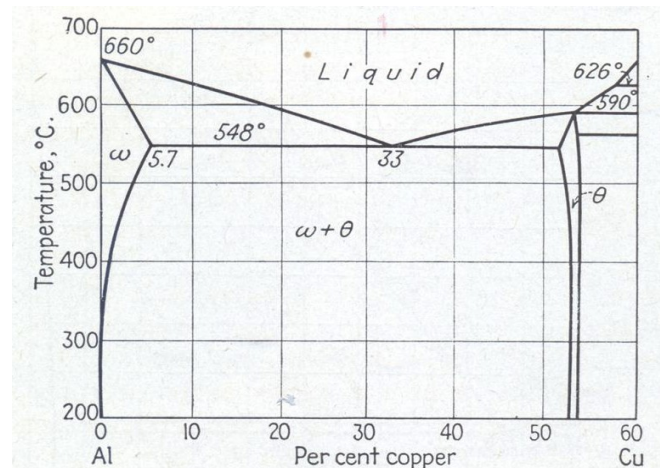
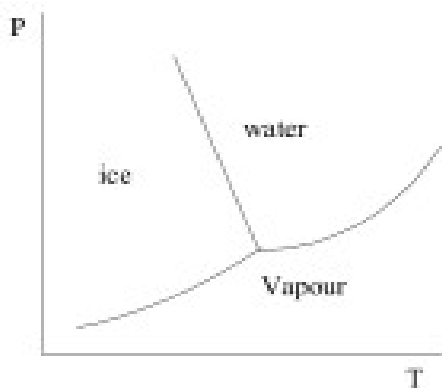
$$F = \frac{P(C+1)}{\text{(variables)}} - \frac{(P-1)(C+2)}{\text{(equalities/equations)}}$$

$$F = C - P + 2 \quad \text{This is the GIBBS Phase Rule}$$

5.4 Phase Diagrams

In a PVT system, the intensive state is established by fixing the temperature, pressure and composition of the phases in the system. In equilibrium these variables are not independent, and by fixing a limited number of them the others are automatically established. For example for a mono-component system like water, once the pressure is fixed the boiling or freezing point is automatically known.

Examples of Phase Diagrams:



6 MIXTURES, SOLUTIONS AND MELTS

6.1 General Principles

Substances often form a variety of mixtures. The components (metals, elements, compounds) often keep their individual properties. These mixtures can be homogeneous (eg. solutions) or heterogeneous. It is therefore necessary to study the relationship between the compositions structures and properties of these mixtures.

When a system is made up of a mixture of different species (eg. chemical species), one would expect the mixture property (M , thermodynamic property, eg. U , S , H , etc.) to be related to the properties (M_i) of the pure species which make up the mixtures. There are, however, no generally valid relationships. In any particular system the connection must be experimentally determined.

In a mixture or solution the constituents do not have any identifiable separate thermodynamic properties. However, it is good to think of the mixture property as being apportioned among the mixture constituents in some way. Once this appropriate procedure is adopted, the resulting property values may be treated as though they were properties of the individual constituents as they exist in the solution.

The total moles of mixture is given by:

$$n = \sum n_i$$

Then the total system property (nM) is:

$$nM = \sum (n_i \bar{M}_i)$$

where \bar{M} is the partial molar property. It denotes how the mixture property is apportioned among the mixture constituents. If the resulting molar properties are treated as properties of constituents in solution then it can be said that the total mixture property is a sum of the properties attributed to the constituents.

$$nM = \sum (n_i \bar{M}_i) \quad ; \quad M = \sum \left(\frac{n_i}{n} \bar{M}_i \right) = \sum (x_i \bar{M}_i)$$

Differentiating the above expression gives:

$$d(nM) = \sum (n_i d\bar{M}_i) + \sum \bar{M}_i dn_i$$

The molar properties can be expressed as a function of measurable quantities such as temperature, pressure and the number of moles in the system:

$$nM = f(T, p, n_i)$$

which on differentiation gives:

$$d(nM) = \left(\frac{\partial(nM)}{\partial T} \right)_{p,n} dT + \left(\frac{\partial(nM)}{\partial p} \right)_{T,n} dp + \sum \bar{M}_i dn_i$$

The expressions for $d(nM)$ are true only if:

$$\left(\frac{\partial(nM)}{\partial T} \right)_{p,n} dT + \left(\frac{\partial(nM)}{\partial p} \right)_{T,n} dp + \sum \bar{M}_i dn_i = 0 \quad \text{This is the general form of the \textbf{Gibbs-Duhem equation}}$$

or in terms of mole fractions:

$$\left(\frac{\partial(nM)}{\partial T} \right)_{p,x} dT + \left(\frac{\partial(nM)}{\partial p} \right)_{T,x} dp + \sum \bar{M}_i dx_i = 0$$

An application of the Gibbs-Duhem equation is the contribution of the various species to the overall molar free energy (chemical potential) on mixing:

$$\left(\frac{\partial(G)}{\partial T}\right)_{p,x} dT + \left(\frac{\partial(G)}{\partial p}\right)_{T,x} dp + \sum x_i d\bar{G}_i = 0$$

In other words: $-SdT + Vdp - \sum x_i d\mu_i = 0$

which at constant T and p simplifies to: $\sum x_i d\mu_i = 0$

The quantitative study of complex real solutions can be provided through the study of ideal gas mixtures.
For an ideal gas:

$pV = nRT$ where n is the number of moles of gas and R is the gas constant ($R = 8.314 \text{ J/mol.K}$).

For a mole of ideal gas in a closed system and at constant temperature:

$$dG = Vdp$$

$$dG = (RT/p)dp \text{ or } dG = RT d\ln p, \quad \text{for which}$$

$$G_2 - G_1 = RT \ln(p_2/p_1), \quad \text{giving only the change in free energy.}$$

Generally,

$$G_{(p,T)} = G^\circ_{(T)} + RT \ln p, \quad \text{where } G^\circ_{(T)} \text{ is the free energy at standard state.}$$

Similarly,

$$\mu_{(p,T)} = \mu^\circ_{(T)} + RT \ln p$$

6.2 The change in system property on mixing

Before mixing the thermodynamic property of the components is given by: $M_{(pure)} = \sum x_i M_i^*$

The mixture property is expressed as: $M_{mix} = \sum (x_i \bar{M}_i)$

The change in thermodynamic property on mixing can therefore be calculated as:

$$\Delta M_{mix} = M_{mix} - M_{pure} \quad \Delta M_{mix} = \sum x_i \bar{M}_i - \sum x_i M_i^* \quad \Delta M_{mix} = \sum x_i \bar{M}_i$$

For **ideal gas mixtures**,

$$p_i V = n_i RT \quad (\text{Dalton's Law})$$

$$p_i = x_i P, \quad \text{where } P \text{ is the total pressure } (P = \sum p_i \text{ and } n = \sum n_i)$$

$$\mu_{i(p,T)} = \mu^\circ_{i(T)} + RT \ln p_i = \mu^\circ_{i(T)} + RT \ln x_i P$$

On mixing,

$$G_{(mix)} = \sum n_i \mu_i = \sum n_i \mu_i^\circ + RT \sum n_i \ln p_i$$

Before mixing the free energy of the pure component is: $G_{(pure\ comp)} = \sum n_i \mu_i^* + RT \sum n_i \ln p_i$

The free energy change on mixing is: $\Delta G_{(mix)} = \sum n_i (\mu_i - \mu_i^*) = RT \sum n_i \ln \frac{p_i}{P_i}$

A special case is if volume is constant ($V = \text{const.}$), in this case,

$$P_1 = P_2 = P_3 = \dots = P,$$

Then: $\Delta G_{(mix)} = RT \sum n_i \ln x_i$

For a mole of gas the above equation simplifies to: $\Delta G_{(mix)} = RT \sum x_i \ln x_i$

Similarly the entropy change on mixing is: $\Delta S_{(mix)} = \frac{\Delta H_{mix}}{T} - \frac{\Delta G_{mix}}{T}$

Simplifying, $\Delta S_{mix} = -R \sum x_i \ln x_i$

For real gas mixtures

The general gas equation is not valid. In this case the equations that may be applied are the van der Waals and Virial equations, as well as the equation containing the compressibility factor ($pV = zRT$). However, to maintain simplicity we introduce a new thermodynamic constant called **fugacity (f)**, which is defined as:

$$\lim_{p \rightarrow 0} \frac{f}{p} = 1$$

So for a real gas therefore, $\mu_{(p,T)} = \mu^0_{(T)} + RT \ln f_{(p,T)}$

And for real gas mixtures, $\mu_{i(p,T)} = \mu^0_{i(T)} + RT \ln f_{i(p,T)}$

6.3 Aqueous Solutions

Leading from the discussions on gases, aqueous solutions can either be ideal or real. A simplified definition of an ideal solution is one in which the cohesive forces in the solution would be the same as those existing in the separate components of the solution.

When two substances (A & B), whose molecules are similar, form an aqueous solution the vapour pressure of the mixture is related to the vapour pressure of the pure components by the relation:

$$p_A = x_A P_A^* \quad \text{and} \quad p_B = x_B P_B^*, \quad \text{where}$$

p is the equilibrium partial pressure, P^* is the vapour pressure of pure substance and x is the mole fraction. The above relation is known as Raoult's Law, which is generally stated as:

$$p_i = x_i P_i^* \quad \text{Raoult's Law}$$

Solutions that obey Raoult's Law are said to be ideal solutions. When the Law is applied to the solubility of gases in liquid, then it becomes known as Henry's Law, which is defined as the concentration of any single molecular species in two phases in equilibrium bear a constant ratio to each other at a fixed temperature:

$$x_i = \frac{1}{P^*} p_i = k p_i$$

Henry's Law

$$H x_i = p_i$$

The above equation shows that the mole fraction of a gaseous solute is proportional to the partial pressure(p_i) of the gas above the solution. As P^* increases with temperature, the value of k decreases.

Raoult's Law is a special case of Henry's Law and it is only valid for dilute solutions. A limiting case is represented by pure solvents (molecular interactions are the same) or very similar solvent and solute cases.

(Diagrams)

6.4 Representation of Solution Concentrations

The composition of solutions are usually expressed in terms of:

- 1) molarity (M) - moles of substance per litre of solution
- 2) molality (m) - moles of substance per 1000 gram solution
- 3) mole fraction (x) - ratio of moles of a component to the total number of moles in solution.

For binary solution:

$$x_1 = \frac{n_1}{n_1 + n_2} \quad x_2 = \frac{n_2}{n_1 + n_2}$$

For binary aqueous solutions:

$$x_i = \frac{n_i}{n_i + n_{H_2O}}$$

For an M_i molar solution:

$$x_i = \frac{M_i}{M_i + \frac{(1000\rho - M_i W_i)}{18}}$$

because the number of moles of water in a litre of solution is $(1000\rho - M_i W_i)$, where W_i is the molar mass of component i.

For infinite dilution the relationship between molarity or molality and mole fraction is given by:

$$M_i = \frac{18x_i}{1000\rho} \quad ; \quad m_i = \frac{18x_i}{1000}$$

Another standard state often used in the case of liquid (molten) metals is the 1 weight percent standard state (1 wt%). This is located on the Henry's Law line at 1 wt%.

6.5 Ideal and Non-ideal Solutions

Thermodynamically, at equilibrium the chemical potentials of the components of solutions that follow Henry's Law is given by:

$$\mu_{i(l)} = \mu_{i(v)} = \mu_i^o + RT \ln p_i$$

$$\mu_{i(l)} = \mu_i^o + RT \ln k_i + RT \ln x_i = \mu_i^* + RT \ln x_i$$

μ_i^* is the standard state chemical potential in the liquid phase.

μ_i^o is the standard state chemical potential in the vapour phase

Similar to the discussions involving real gases, for real solutions we introduce another thermodynamic property called the **activity (a)**. By definition the activity (a_i) of a component in any state at temperature, T, is the ratio of the fugacity of the substance in that state to its fugacity in its standard state:

$$a_i = \frac{f_i}{f_i^o}$$

Another probably more practical definition is the "effective concentration of ions, atoms and molecules". This is introduced so that in non-ideal cases it will be possible to calculate. Activity is calculated as the product of the mole fraction (x) or concentration (c) and what is known as the activity coefficient (γ):

$$a_i = x_i \gamma_i$$

For real solutions therefore:

$$\mu_i = \mu_i^* + RT \ln a_i = \mu_i^* + RT \ln x_i + RT \ln \gamma_i$$

At equilibrium,

$$\mu_{i(\text{vap})} = \mu_i^o + RT \ln p_i = \mu_{i(\text{liq})} = \mu_i^* + RT \ln a_i$$

$$a_i = p_i \exp \frac{(\mu_i^o - \mu_i^*)}{RT}$$

On mixing ideal gases and ideal solutions, the enthalpy and volume changes are zero. The free energy and entropy changes on mixing ideal solutions are:

$$\Delta G = \sum n_i \mu_i - \sum n_i \mu_i^* = \sum n_i RT \ln x_i$$

In terms of mole fractions, $\Delta G = RT \sum x_i \ln x_i$

The entropy change on mixing is given by: $\Delta S_{\text{mix}} = \frac{\Delta H_{\text{mix}}}{T} - \frac{\Delta G_{\text{mix}}}{T} = -R \sum x_i \ln x_i$

Unlike in the case of ideal solutions, mixing real solutions is accompanied by enthalpy and volume changes. In addition the free energy change is given by:

$$\Delta G_{\text{mix}} = RT \sum x_i \ln a_i = RT \sum x_i \ln x_i + RT \sum x_i \ln \gamma_i$$

The first term represents the change due to ideal solutions and the second term represents excess free energy per mole of solution on mixing.

In general, $G = G^{\text{id}} + G^{\text{xs}}$ and $\Delta G_{\text{mix}} = \Delta G_{\text{mix}}^{\text{id}} + G^{\text{xs}}$

For any solution, $\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}}$

$$G^{\text{xs}} = \Delta G_{\text{mix}} - \Delta G_{\text{mix}}^{\text{id}} = \Delta H_{\text{mix}} - T (\Delta S_{\text{mix}} - \Delta S_{\text{mix}}^{\text{id}})$$

For binary solutions, $G^{\text{xs}} = RT (x_A \ln \gamma_A + x_B \ln \gamma_B)$

The diagrams showing the change in free energy, entropy, enthalpy and volume are given below:

diagrams

6.6 The Tangent Intercept Method

This method enables us to determine the partial molar quantities of the various thermodynamic properties (G, H, S, V, etc.,) of the components making up the solution.

6.7 Solutions of Electrolytes

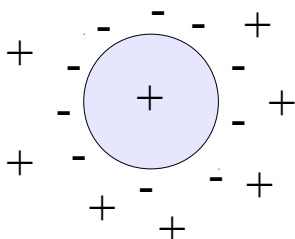
6.7.1 Basic Concepts

Electrolytic solutions are special form of solutions in which the solute exists partially or completely in the form of ions. By definition an electrolyte is any compound which in solution or fused state conducts electric current and is decomposed by it.

The behaviour of electrolytes has been studied by notable scientists including Baron C.J. von Gotthuss (who suggested that molecules of electrolytes were polar with positive and negative ends, and in an applied field line up in a chain with the molecules at the end dissociating and the free ions formed discharged at the electrodes), Classius (who proposed that energetic collisions between undissociated molecules in electrolytes maintain at equilibrium a small number of charged particles and that the particles are responsible for observed conductivity). Kohlhausch investigated extensively conductivity of electrolytic solutions. Svante A. Arrhenius compiled data available at the time and proposed the theory for the behaviour of electrolytes. Some flaws were later discovered in his proposals especially in connection with the behaviour of strong electrolytes.

P. Debye and E. Hückel provided the theory for the modern treatment of electrolytes, that is, strong electrolytes are completely dissociated into ions and that the observed deviation from ideal behaviour was due entirely to the electrical interactions of the ions in solution. The deviations are greater for more highly charged ions and in more concentrated solutions. A revised theory can be summarised as:

- 1) a solution of electrolytes contains free ions
- 2) passage of a current through a solution of an electrolyte depends on (i) the number and (ii) the speed of the ions present.
- 3) in a solution of a weak electrolyte the degree of ionisation increases with dilution until at infinite dilution there is complete ionisation.
- 4) in a solution of a strong electrolyte there is always complete ionisation but ionic interference limits the movement of the ions. This interference decreases with dilution.



Ions in solution usually have an atmosphere of opposing charges around it. Under an electric field the ions move to the opposite electrodes. However, the movement is hindered by:

- 1) the net accumulation of opposite charge behind the ion due to the asymmetric atmosphere created around the ion and exerting an electrostatic drag
- 2) frictional drag of the solvent according to Stoke's Law
- 3) the ions comprising the atmosphere around the central ion which themselves try to move in the opposite direction under the applied field (Electrophoretic effect).

According to Ohm's Law the current passing through an electrical conductor is given by: $I = \frac{V}{R}$

The resistance of an electronic conductor is given by: $R = \rho \left(\frac{l}{A} \right)$

Electrical conductivity is expressed as: $\frac{l}{\rho} = \kappa$

In the case of solutions, electrical conduction is given in terms of equivalent conductivity (Λ), which is expressed as:

$$\Lambda = \frac{\kappa}{c'}$$

where c' is concentration, eqv./cm³

6.7.2 Migration of Ions

Hittorf proposed that the amount of ions in the vicinity of an electrode changes during electrolysis and that both anions and cations migrate in the solutions to the electrodes at different speeds carrying a fraction of the current through the electrolyte. He further suggested that the fraction of current carried depends on their velocities. The fraction of total current carried by the ions species was called the **Transport number (t)**:

$$\frac{\text{Current carried by anion}}{\text{Total current}} = t_{o+} ; \quad \frac{\text{Current carried by cation}}{\text{Total current}} = t_{o-} ; \quad t_{o+} + t_{o-} = 1$$

From Kohlrausch's Law

$$t_{o+} = \lambda_{o+} \quad \text{and} \quad t_{o-} = \lambda_{o-}$$

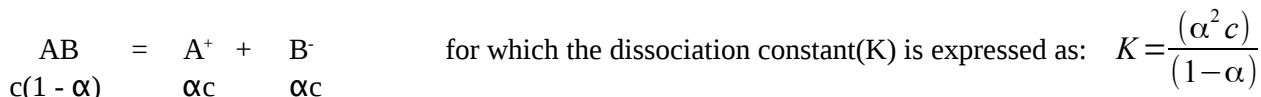
Kohlrausch's law of independent migration (mobilities) of ions states that the equivalent conductivity at infinite dilution of an electrolyte (Λ_o) is equal to the sum of the ionic mobilities of the ions produced by the electrolyte:

$$\Lambda_o = \lambda_{o+} + \lambda_{o-} \quad \text{where } \lambda \text{ is the equivalent ionic conductivity.}$$

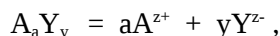
According to Arrhenius, the **degree of ionization (α)** is given by the ratio of the equivalent conductivities at a given concentration to that at infinite dilution,

$$\alpha = \frac{\Lambda}{\Lambda_o}$$

Applying mass action principle to dilution, **Ostwald** obtained the **Dilution Law**, that is, for an electrolyte (AB) dissociating in solution with a concentration of c at equilibrium:



The **mobility** (in $\text{m}^2/\text{sec.V}$) of an ion is defined as its velocity in an electric field. For an electrolyte or salt (A_aY_y) which dissociates on solution in water:



the **activity (a_2)** of the electrolyte solute is found to obey Henry's Law and the value is given by:

$a_2 = k \cdot m_2^2$ for uni-univalent electrolyte solutes and symmetrical salts in which anion and cation have the same valency, eg. NaCl, LiF, MgSO_4 , CaCO_3 , etc.

$a_2 = k \cdot m_2^3$ for ternary salts such as BaCl_2 , dissolving into three moles of ions.

$$a_2 = k \cdot m_2^{v+y} \text{ for } \text{A}_v\text{Y}_y = v\text{A}^{z+} + y\text{Y}^{z-}.$$

The value of k depends on the standard state chosen. For electrolyte solute the hypothetical state is established by the behaviour of the solution at infinite dilution,

$$a_2 = m_2^2 \quad \text{as } m_2 \text{ approaches } 0$$

At infinite dilution interaction between anions and cations vanish, and for symmetrical electrolytes,

$$m_2 = m_+ = m_- \quad \text{and therefore } a_2 = (m_+)(m_-).$$

The individual ionic activities are:

$$a_+ = m_+ \quad \text{as } m_2 \text{ approaches } 0$$

$$a_- = m_- \quad \text{as } m_2 \text{ approaches } 0$$

Therefore, $a_2 = (a_+)(a_-)$ since $m_+ = m_-$.

The mean ionic activity of a symmetrical electrolyte (a^\pm) is defined as:

$$a^\pm = (a_+ a_-)^{1/2} = a_2^{1/2}$$

The individual ionic activity coefficients are: $\gamma_+ = \frac{a_+}{m_+}$; $\gamma_- = \frac{a_-}{m_-}$ These approach 1 at infinite dilution.

The mean ionic activity coefficient is: $\gamma_\pm = (\gamma_+ \gamma_-)^{1/2} = \left(\frac{a_+ \cdot a_-}{m_+ m_-}\right)^{1/2} = \frac{a_\pm}{m_\pm} = \frac{a_2^{1/2}}{m_2}$ γ_\pm approaches 1 at infinite dilution.

For unsymmetrical electrolytes, ($A_v Y_y$) eg BaCl_2 ;

$$a_2 = km_2^{v+y}$$

$$a_2 = (a_+)^v (a_-)^y$$

$$a_\pm = [(a_+)^v (a_-)^y]^{1/(v+y)}$$

$$m_\pm = m_2 [(v)^v (y)^y]^{1/(v+y)}$$

$$\gamma_\pm = a_\pm / m_\pm = [(\gamma_+)^v (\gamma_-)^y]^{1/(v+y)}$$

Ionic Strength - is a useful generalisation for assessing the combined effects of the activities of several electrolytes in a solution of a given electrolyte. The value is given by the expression:

$$I = \frac{1}{2} \sum m_i z_i^2 \quad \text{Summation is over all ions in solution, both positive and negative.}$$

where m_i is the molality of the i^{th} ion and z is the charge on i^{th} ion.

6.7.3 Debye-Hückel Theory of Activity Coefficients

Even in very dilute solutions of electrolytes there is long-range electrostatic force between charged ions, resulting in the lowering of the activity coefficients of the ions. These effects are evaluated by the Debye-Hückel Theory. In dilute solutions Debye-Hückel expression states that the individual activity coefficient is given by:

$$-\log \gamma_i = \frac{A z_i^2 \sqrt{I}}{1 + a_i^o B \sqrt{I}} \quad \begin{array}{l} \text{where } I - \text{ionic strength} \\ z - \text{charge on the ion} \\ A, B - \text{are constants characteristic of the solvent at a} \\ \text{given temperature and pressure} \end{array}$$

a_i° - is a value which depends on the "effective diameter" of ions in solution and is determined by experiment. It is larger than values given for crystals because of solvation of ions

When ionic strength becomes very small, $-\log \gamma_i = Az_i \sqrt[2]{I}$

6.8 Solid Solutions and Melts

- Review of atomic structure
- Review of the structure of molecules
- Types of bonds in crystals
- Metallic crystals/crystals in general
- Imperfections in crystals (Lattice Defects)
 - (i) Point defects, ie. vacancies or holes from interstitial atoms, eg. H_2 in steel,
 - (ii) Line defects, ie. dislocations
 - (iii) Surface and interface defects, ie grain boundaries and crystallite boundaries.

Solid solutions are common in metallic systems (alloys) and in inorganic systems, some at elevated temperatures. Some solid solutions have been reported in the literature about organic systems as well, even though these are not common. Depending on the locations of the foreign atoms (solutes) in the crystal lattice, solid solutions can either be **substitutional** (replacement of atoms of the parent metal or solvent) or **interstitial** (atoms occupy interstitial positions in the crystal)

Two or more metals can form a homogeneous mixture in a single phase, ie. a solution. For example 10 mass% Cu in Fe forms a homogeneous alloy. But as the Cu content exceeds 10% a Cu-rich phase is also formed in addition. In all these cases the lattice parameter (d) varies as more solute is added.

Minerals are invariably solid solutions, eg. $MnCO_3$ (rhodochrosite) usually contains dissolved calcium, or Fe(II), Mg(II), or Zn(II) ions. The extent and kind of solution varies depending on the composition and crystal structure of the mineral acting as solvent. Most minerals are salts, crystalline compounds, made up of cations and anions at positions in the crystal structure. By the substitution of ions in the crystal structure solid solutions may be formed, eg. $(Fe_xMn_{1-x})CO_3$, or $Fe_{1-x}Al_xOOH$.

The extent of solution and stability of the solution depends on the similarity or otherwise of the ions (eg. in ionic radius). With increase in temperature, as the thermal motion of the ions increase and with it the effective ionic radii, and therefore the effective ionic radii of all the elements become more nearly the same. The mutual solubility of minerals become greatly enhanced, eg. KCl and NaCl are mutually soluble in all proportions above 500EC ($r_{K^+} = 1.33A^\circ$, $r_{Na^+} = 0.95A^\circ$).

As is known the activity of pure substances at standard state is 1, but that of $(Fe_xMn_{1-x})CO_3$ is not 1. For $(Fe_{0.2}Mn_{0.8})CO_3$, which might be considered as a dilute solution ($\gamma = 1$):

$$a_{MnCO_3} = x_{MnCO_3} = \frac{0.8}{0.2+0.8} = 0.8$$

Relatively few data are available on the behaviour of solid solutions and melts of geological interest. However, those studied so far behave nearly as regular solutions, for which:

$$\log \gamma_i = \frac{B}{2.303 RT} x_2^2 = B' (1 - x_1)^2$$

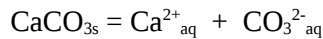
For most geological systems of interest, $0 < B' \leq \pm 5$. In most cases the activity coefficient (γ) approaches unity rapidly as the mole fraction approaches unity (1). Therefore even for solutions exhibiting large departures from ideal behaviour over much of the composition range the solvent may be considered to

behave ideally as the solution becomes dilute, especially for minor substitutions in the mineral. It is reasonably safe to assume ideal behaviour if $x_i \leq 0.9$. In the absence of the knowledge of B' no good predictions can be made if $x_i < 0.9$.

The activities of solids can be corrected as a result of compositional variations. For example:

Problem: If calcite contains 5 mole% manganese carbonate, how would the product of the activities of calcium and carbonate ions change in aqueous solution in equilibrium with calcite at 25°C.

Solution:



$$\Delta G^\circ = \Delta G^\circ_{\text{fCa}^{2+}} + \Delta G^\circ_{\text{fCO}_3^{2-}} - \Delta G^\circ_{\text{fCaCO}_3}$$

$$= -132.18 + (-126.22) - (-269.78) = 11.38$$

$$\text{But } \Delta G^\circ = -RT \log K = -1.364 \log K$$

$$11.38 = -1.364 \log ([\text{Ca}^{2+}] [\text{CO}_3^{2-}]) / [\text{CaCO}_3]$$

$$[\text{Ca}^{2+}] [\text{CO}_3^{2-}] = 10^{-8.34} \quad ([\text{CaCO}_3] = 1 \text{ for pure calcite})$$

$$\text{If } \text{Ca}_{0.95}\text{Mn}_{0.05}\text{CO}_3, \text{ then } [\text{CaCO}_3] = x_{\text{CaCO}_3} = 0.95$$

$$\text{Then } [\text{Ca}^{2+}] [\text{CO}_3^{2-}] = 10^{-8.34} \times 0.95 = 10^{-8.36}$$

7 ELECTROCHEMISTRY

7.1 Introduction

There are generally two broad categories of chemical reactions; **atom transfer reactions** and **electron transfer reactions**. In atom transfer reactions, the chemical reaction does not lead to changes in the oxidation state of the constituent atoms of the reactants. However electron transfer reactions result in the change in the oxidation state of the reactants. These reactions may occur in homogeneous or heterogeneous systems. Electrochemistry is that branch of science that deals with chemical changes that are caused by electric current and chemical reactions that are accompanied by the transfer of charges (change of oxidation state of some or all the participating atoms). Such electron transfer reactions form the basis of some important industrial processes such as electroplating, electrowinning and electrorefining, as well as some important geochemical processes that are involved in the formation of minerals or in determining the quality of groundwater. Other examples include the generation of the flow of electricity in car batteries as a result of chemical reactions in the cells, or the generation of electric current in solar cells, among others. It also helps to explain, for example the corrosion of metals.

7.2 The Energetics of Electrochemical Reactions

The thermodynamic driving force in any electrochemical reaction is related to the ease with which the change in oxidation state takes place, ie. the ease of electron transfer. The free energy decrease is a manifestation of the energetics of electron transfer. The driving force for the electron movement is the potential difference (ΔE) and the chemical reaction is driven by the thermodynamic force (ΔG).

If both electrical and chemical driving forces are involved at the same time in electrochemical reactions, then there must be some kind of relationship between these two forces. We have already learnt that for a system undergoing a reversible process at constant temperature and pressure the change (decrease) in free energy of the system equals the maximum work (other than work of expansion) done by the system. That is:

$$\Delta G (T,p) = w_{\max}$$

or in the form of a differential equation, $-dG = w_{\max}$

For example, the electrons moving in the external circuit of a galvanic cell such as a car battery, causes current to flow which is capable of doing work, such as starting a car. When an electric charge is transported across a potential difference work is done and the work done is equal to the product of the charge transported (Q , coulombs) and the electric potential difference (E). If the charge is transported reversibly, for example in a cell, then the work done is:

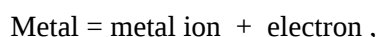
$$w_{\max} = z F E$$

where z is charge on ion,

F is Faraday's constant, 96500 C)

E is the electromotive force (EMF), which is the algebraic difference between the electrodes of a cell if no current is flowing through the cell.

If you consider the chemical reaction (cell reaction):



work is done by the system, releasing electrons to flow resulting in work being done. The free energy change for the reaction is:

$$\Delta G = \mu_{ion} - \mu_{metal} = \mu_{ion}^o - \mu_{metal}^o - RT \ln a_{ion} + RT \ln a_{metal}$$

That is:
$$E = \frac{\mu_{ion}^o - \mu_{metal}^o}{zF} - \frac{RT}{zF} \ln \frac{a_{ion}}{a_{metal}}$$

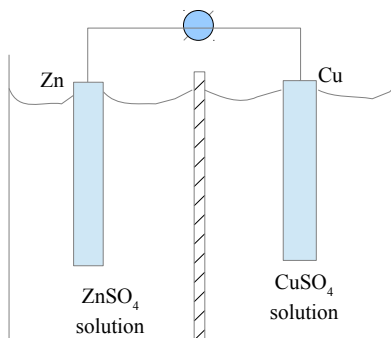
This reduces to :
$$E = \frac{\Delta G}{zF} = E^o - \frac{RT}{zF} \ln \frac{a_{ion}}{a_{metal}}$$

In general for the reaction: $aA + bB = cC + dD$, (which is made up of two half-cell reactions, $aA = cC + ze_a^-$ and $bB + ze_c^- = dD$)

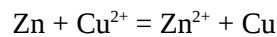
$$\Delta G = c\mu_C + d\mu_D - a\mu_A - b\mu_B \quad \text{from which}$$

$$E = E^o - \frac{RT}{zF} \ln \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b}$$

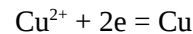
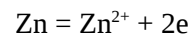
This expression is known as the **Nernst Equation**



Taking a **Daniel Cell** as an example, the cell reaction:



is made of two half-cell reactions:



At equilibrium, $\mu_{\text{Zn}^{2+}}(\text{in solution}) = \mu_{\text{Zn}^{2+}}(\text{in Zn electrode})$

$$\text{and } \mu_{\text{Zn}} = \mu_{\text{Zn}^{2+}} + 2\mu_e^{\text{Zn}}$$

μ_{Zn} is the chemical potential of the atoms in the electrode, $\mu_{\text{Zn}^{2+}}$ is the chemical potential of Zn ions in the ZnSO_4 solution and in the electrode, μ_e^{Zn} is the chemical potential of the electrons in the Zn electrode.

Similarly,

$$\mu_{\text{Cu}^{2+}}(\text{in solution}) = \mu_{\text{Cu}^{2+}}(\text{in Cu electrode}) \quad \text{and}$$

$$\mu_{\text{Cu}^{2+}} + 2\mu_e^{\text{Cu}} = \mu_{\text{Cu}}$$

The equilibrium value of μ_e for both reactions is determined by the activities of the sulphates in solution. In a reversible transfer of electrons, work done is:

$$*w_{\text{max}} = zF(E_2 - E_1) \quad (\text{or } *w_{\text{max}} = zF(E_2 - E_1) dn; \text{ dn is moles of electrons transferred })$$

The work done in the electron transfer at constant T and p involves decrease in free energy, therefore:

$$*w_{\text{max}} = +\Delta G = +(\mu_2 - \mu_1) \quad (\text{where } \mu_2 = \mu_e^{\text{Zn}} \text{ and } \mu_1 = \mu_e^{\text{Cu}})$$

Combining the above equations gives:

$$(\mu_2 - \mu_1) = zF(E_2 - E_1) \quad \text{This expression gives the relationship between the chemical potential difference and the electrical potential difference for electron transfer.}$$

The relationship therefore between the chemical driving force and the electrical driving force therefore is:

$$\Delta G = -zFE$$

If an external opposing electrical potential equal in magnitude to E and equal to the chemical driving force is applied across the electrodes of the cell then equilibrium is achieved. If this external voltage is decreased current flows in the external circuit from the Zn electrode to the Cu electrode and an equivalent ionic current (SO_4^{2-}) flows through the cell at an equal rate. Zn^{2+} ions are added by the corrosion of the Zn electrode to the electrolyte or Cu^{2+} ions are removed by the deposition of Cu on the Cu electrode from the electrolyte. The reaction proceeds (CuSO_4 concentration decreases and ZnSO_4 concentration increases) causing the EMF to decrease until a new equilibrium is reached.

In our earlier discussions we have indicated that some thermodynamic properties are extensive (such as U , S , N , etc), whilst others (such as temperature and pressure) are intensive. Potential difference, just as temperature, is an intrinsic property, which is independent of the quantities of the reacting species. We therefore simply cannot add potentials together when combining electrochemical reactions. Instead, the change in free energy, which is an extensive property and therefore depends on the quantities of the reactants can be calculated from the combination of the ΔG s of the half-cell reaction.

The effect of concentration on EMF

The effect of concentration on the EMF can be seen through the Nernst equation, which is given in general for the cell reaction,

$$aA + bB = cC + dD \quad \text{as} \quad E = E^\circ - \frac{RT}{zF} \ln \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b}$$

American and European Conventions

With American convention:

$$\Delta G^\circ = -zF \mathcal{E}$$

With European convention:

$$\Delta G^\circ = + zF \mathcal{E}^\circ = -zFE$$

This means that $E = - \mathcal{E}$

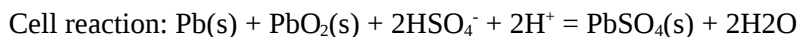
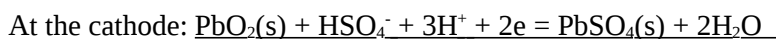
7.3 Electrochemical Cells and Electrode Potentials

7.3.1 Daniel Cell

The Daniel cell has already been discussed above.

7.3.2 Galvanic cell

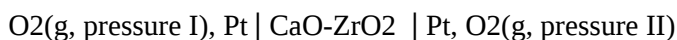
It is a system capable of performing electrical work as a result of the occurrence of chemical reaction, eg galvanic cell or car batteries (Pb plates between PbO₂ sieves, all in sulphuric acid solution).



The overall cell reaction indicates the consumption of acid and the production of water, leading to the change in density.

7.3.3 Concentration cell

It is a cell with identical electrodes inserted into solutions differing in only concentration. An example is the O₂ concentration cell using lime-stabilised zirconia as a solid electrolyte:



for which

$$E = - \frac{RT}{4F} \ln \frac{P_{\text{O}_2(I)}}{P_{\text{O}_2(II)}}$$

The student is referred to discussions in the literature for other types of cells.

7.3.4 Single electrode potentials

When a piece of metal is immersed in an electrolyte, the metal is called an electrode. The dissolution of the metal is represented by the cell reaction:



If the electrons are more “soluble” than the metal ion, then the charge on the electrode surface will be positive, that is the electrode/solution surface will acquire a positive galvanic potential. On the other hand if the metal ion is more soluble the electrode surface will be negatively charged.

Electrodes are termed anodes or cathodes depending on the direction of flow of electrical charge or as to what whether the reaction taking place on the electrode is an oxidation (electron donation) or reduction (electron acceptance) reaction. When negative charge flows from the electrolyte to the electrode, an anodic current is said to be flowing and the electrode is said to be an **anode** (or when oxidation is taking place at the electrode). When electrons leave the electrode and pass into the electrolyte, a cathodic current is said to be flowing and the electrode is said to be a cathode (in other words, where reduction takes place).

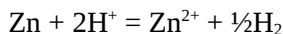
7.3.5 Standard Electrode Potentials

It is impossible to construct a cell with a single electrode and measure its EMF. In order to measure the EMF, we choose a particular single standard electrode and assign to it a zero potential. Such a standard electrode is the standard H₂ electrode (H₂ electrode with gas at 1 bar pressure in contact with an aqueous solution of unit H⁺ activity). The standard potential of the metal in comparison with the hydrogen

electrode, consists of pure metal in contact with an aqueous solution of the metal ion of unit activity. For example to measure the electrode potential of Zn the following cell is used.



for which the cell reaction is,



$$E = E_{\text{anodic cell}} + E_{\text{cathodic cell}} = E_{\text{anodic cell}} = +0.762 \text{ V at } 25^\circ\text{C}$$

(A list of standard potentials can be found in the Table of Electrochemical Series)

7.4 Areas of the application of Electrochemistry.

It is clear from the above that metals can dissolve in solutions or melts after giving out electrons if the electrochemical environment is favourable. The driving force is the EMF/potential difference and the free energy change(ΔG). This knowledge is applied in numerous areas, including corrosion of metals and its prevention, the dissolution of metals or their compounds from minerals (leaching), or the production of metals or their compounds from solutions and melts (electrolysis, electrowinning and electrorefining, electrodeposition), among others.

7.5 Electron activity

The electron activity is defined as:

$$p_e = -\log \{e\} \quad (\text{compare with } \text{pH} = -\log \{a_{\text{H}^+}\})$$

The measure of electron activity gives an indication of whether an electrochemical reaction is taking place under an oxidising or a reducing condition. Usually when the value of the p_e is large and positive then the conditions are strongly oxidizing. However, when the value of p_e is small and negative then strong reducing conditions exist.

For the redox reaction,

$$a\text{A} + b\text{B} + ne = c\text{C} + d\text{D}, \quad \text{the activity quotient, } Q \text{ is given by:} \quad Q = \frac{[a_C]^c \cdot [a_D]^d}{[a_A]^a \cdot [a_B]^b \cdot [e]^n}$$

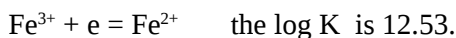
$$\log Q = \log \frac{[a_C]^c \cdot [a_D]^d}{[a_A]^a \cdot [a_B]^b} + n p_e$$

At equilibrium $Q_e = K$ and $\log Q_e = \log K$, therefore:

$$p_e = \frac{1}{n} \log K - \frac{1}{n} \log \frac{[a_C]^c \cdot [a_D]^d}{[a_A]^a \cdot [a_B]^b}$$

$$p_e = p_e^o - \frac{1}{n} \log \frac{[a_C]^c \cdot [a_D]^d}{[a_A]^a \cdot [a_B]^b}$$

Example: Calculate p_e for a solution containing 0.00001 M Fe^{3+} and 0.001 M Fe^{2+} if t for the reaction:



7.6 Electrolysis

7.6.1 Faraday's Laws

The fundamentals of electrolysis have been laid down in **FARADAY'S LAWS**.

1st Law: The amount of chemical decomposition (ie. mass of liberated substance) is proportional to the quantity of electricity passing through the solution (or melt) of electrolyte.

$$m \sim It \quad (m \sim It, \text{ if current varies})$$

where **m** is the mass of substance liberated, g or kg
I is the current, amps (A)
t is time, s

$$m = qIt,$$

where **q** is the electrochemical equivalent, and is characteristic of the element and is defined as the mass in grams of an element liberated by a coulomb of electricity.

In general,

$$q = \frac{A}{F \cdot z}$$

A is the atomic mass
F is Faraday's constant (96520 coulombs)
z is the charge transferred

The electrochemical equivalent of some of the elements are:

H ₂	1.044 x 10 ⁻⁵
Ag	1.118 x 10 ⁻³
Cu	3.29 x 10 ⁻⁴
Au	6.805 x 10 ⁻⁴
Al	9.319 x 10 ⁻⁵

2nd Law: If the same quantity of electricity is passed through a number of different electrolytes, the masses of substances liberated are proportional to their chemical equivalents:

$$\frac{m_A}{m_B} = \frac{z_A}{z_B}$$

We have seen earlier that when a metal is immersed in its salt solution and equilibrium chemical process takes place with the liberation of electrons:



The electrode potential for this reversible process can be thermodynamically derived for small currents. This equilibrium potential can also be measured using the calomel electrode, ie.

$$\phi_e = \phi_m - \phi_{\text{kal}} \quad (E_e = E_m - E_{\text{kal}})$$

When a large current passes across the boundary between the electrode and the solution, there is a shift in

the equilibrium potential and this shift resulting in a potential difference between these values is known as polarization. The difference between the equilibrium potential (E_{eq}) and that of the polarised potential (E_p) gives the overpotential (overvoltage), η :

$$E_p - E_{eq} = \eta$$

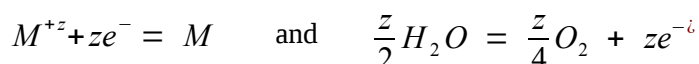
Polarisation is due to the following:

- 1) reaction(s) taking place at the electrodes (**activation polarization**).
- 2) diffusion of ions from the body of electrolyte to areas around the electrode (**concentration polarization**). It can be reduced by agitation and movement of the electrolyte.
- 3) insoluble films formed on the electrode causing ohmic resistance (**resistance polarization**).

7.6.2 Minimum Electrolysing Voltage

If you consider the reaction: $M^{+z} + \frac{z}{2} H_2O = \frac{z}{4} O_2 + zH^{+1} + M$

which can be expressed as the sum of two half-cell reactions:



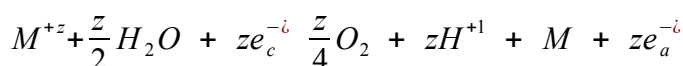
the free energy change can be expressed as: $\Delta G_1 = \frac{z}{4} \mu_{O_2} + z \mu_{H^+} + \mu_M - \mu_{M^{+z}} - \frac{z}{2} \mu_{H_2O}$

The calculated free energy change for these reactions (see Table given), is positive and therefore does not favour spontaneous reaction in the direction of metal deposition.

Metal ion	ΔG_f° (kJ/mol)	Metal ion	ΔG_f° (kJ/mol)
Ag ⁺	41.382	Ni ²⁺	282.15
Au ³⁺	84.436	Pb ²⁺	260.832
Cr ³⁺	151.316	Pd ²⁺	105.754
Cu ²⁺	171.38	Sn ²⁺	263.758
Fe ²⁺	328.966	Zn ²⁺	383.724

The ability to achieve metal deposition via electrolysis is based on the fact that the chemical potentials of the respective electrons associated with the cathodic and anodic reactions can be altered sufficiently to reverse the sign of the free energy change corresponding to the overall reaction. This can be done by applying an external source of electrical energy (eg from a DC supply such as a battery).

By applying an external source for metal deposition to occur, the electrons at the cathode and anode would have acquired different chemical potentials and the overall reaction in this case can be expressed as:



and the free energy change for electrolysis will be:

$$\Delta G_2 = \frac{z}{4}\mu_{O_2} + z\mu_{H^{+1}} + \mu_M - \mu_{M^{+z}} - \frac{z}{2}\mu_{H_2O} + z\mu_{e_a} - z\mu_{e_c}$$

$$\Delta G_2 = \Delta G_1 + z\mu_{e_a} - z\mu_{e_c}$$

In the absence of externally applied voltage, the cathode and anode electrons have the same chemical potential and therefore the free energy change is equal. On the other in the presence of applied potential and at equilibrium, $\Delta G_2 = 0$ and therefore,

$$\Delta G_1 = z (\mu_{e_a} - \mu_{e_c})_{eq}$$

Re-writing this in the form of the relationship between the electrical potential and chemical potential gives:

$$\Delta G_1 = z (\Theta_{e_a} - \Theta_{e_c})_{eq}$$

$$\Delta G_1 = z F E_{min} \quad \text{where } E_{min} \text{ is the minimum electrolyzing potential.}$$

7.7 pH AND Eh Measurements

7.7.1 pH Measurement

Definition:

$$pH = -\log a_{H^+} = -\log [H^+] \quad (\text{involves the activity of a single ion, a quantity that cannot be directly measured}).$$

pH is measured today using an EMF cell, that consists of a glass electrode dipping into the tests solution, together with a reference electrode (usually calomel, Hg/Hg_2Cl_2 , electrode in saturated KCl solution) to complete the circuit.

The glass electrode consists of a bulb of special glass containing an acid solution, and an inner electrode of fixed voltage, usually $Ag/AgCl$, to conduct electrons reversibly into and out of the solution. When the bulb is immersed in a solution, an electric potential is developed between the inner and outer solutions that is proportional to the logarithm of $[H^+]$ in the external solution. Thus the reference electrode has a constant potential, while that of the glass electrode varies with the hydrogen ion activity:

$$\text{Glass electrode, sol. } x \mid KCl(\text{sat}), Hg_2Cl_2(s), Hg(l)$$

The half-cell potential of a hydrogen ion sensitive glass electrode is:

$$E'_x = C_H + \frac{2.303}{F} \frac{RT}{F} \log [H^{+1}]_x \quad ; \quad E'_x = C_H - \frac{2.303}{F} \frac{RT}{F} \log pH$$

C_H is a constant and differs from one electrode to the other, and depends on the specific composition of glass used, the standard solution in the bulb and the particular reference electrode in the circuit.

The overall potential of the cell neglecting the liquid junction potential is:

$$E_x = E'_x - E_{ref} = C_H + \frac{2.303}{F} RT \log [H^{+1}]_x - E_{ref} \quad (*)$$

If solution sol.x is replaced by a standard solution, then:

$$E_s = C_H + \frac{2.303}{F} RT pH_s - E_{ref} \quad (**)$$

Subtracting (**) from (*) and rearranging:

$$pH_x = pH_s - \frac{F(E_x - E_s)}{2.303 RT} \quad \text{This now serves as the basis for the modern definition of pH.}$$

Accuracy of pH measurements depends on the standards used, and also the error due to the liquid junction potential. If standard and test solutions are similar, then pH is more accurate.

The Glass electrode

General purpose glass electrodes are most efficient for pH 0-11. Above this, special "high pH" electrodes are necessary for accurate work. Glass electrodes are calibrated against at least 2, preferably 3 different buffers in order to check the slope of the line relating to the EMF of the glass electrode, which is:

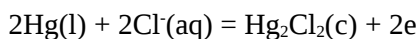
$$\frac{-2.303RT}{F}$$

Therefore at constant T,

$$\frac{dE_s}{d pH} = -\frac{(2.303 RT)}{F} \quad \text{The value of this at 25°C is 0.05916 V/pH}$$

Calomel electrode

This contains mercury in contact with mercurous chloride, which is in turn in contact with a standard solution of KCl. The half-cell reaction and potentials are:



$$E_h = E^o + \frac{RT}{2F} \ln \frac{[\text{Hg}_2\text{Cl}_2]}{[\text{Hg}]^2 [\text{Cl}^-]^2}$$

Mercurous chloride and mercury have unit activity at standard state. Since KCl solution is in equilibrium with solid KCl, chloride activity is constant and therefore,

$$E_h = E^o + \frac{RT}{2F} \ln \frac{1}{k^2}$$

At 25°C, E_h is 0.244 V or more accurately

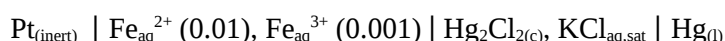
$$E_h = 0.2444 - 0.00066(t-25) \text{ V} \quad (t = \text{temp. } ^\circ\text{C})$$

7.7.2 Eh Measurement

Oxidation potential is measured with an electrode pair consisting of an inert electrode and a reference electrode (eg. calomel). The inert electrode used most is the bright platinum (or Au electrode). The role of the calomel electrode is to supply a known EMF and make electric connection with the system to be measured. The inert electrode acts as an electron acceptor or donor to the ions in the measured solution, that is if the potential of the half-cell containing the dissolved species is greater or less than that of the calomel reference electrode.

Example: Calculate the oxidation potential of a $\text{Fe}^{2+} / \text{Fe}^{3+}$ aqueous solution containing $[\text{Fe}^{2+}] = 0.001$ and $[\text{Fe}^{3+}] = 0.01$.

The cell may be represented by:

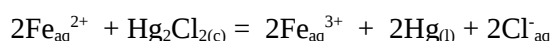


Solution

The half-cell reactions are:



The overall cell reaction is:



and $\text{EMF}_{\text{cell}} = E_{\text{Fe}^{2+}, \text{Fe}^{3+}} - E_{\text{ref}} \quad (E_{\text{ref}} = 0.244 \text{ V at } 25^\circ\text{C})$

$$E_{\text{Fe}^{2+}, \text{Fe}^{3+}} = E_{\text{Fe}^{2+}, \text{Fe}^{3+}}^0 + \frac{0.0592}{2} \log \frac{[\text{Fe}^{+3}]^2}{[\text{Fe}^{+2}]^2}$$

Substituting the appropriate values into the above ($E_{\text{Fe}^{2+}, \text{Fe}^{3+}}^0 = 0.771 \text{ V}$) gives $E_{\text{Fe}^{2+}, \text{Fe}^{3+}} = 0.830 \text{ V}$.
Therefore,

$$\text{EMF}_{\text{cell}} = 0.830 - 0.244 \text{ V} = 0.586 \text{ V} \quad (\text{this would be measured if liquid junction potential is neglected}).$$

In general for an oxidation-reduction system:



$$E_{\text{h}} = E^0 + \frac{RT}{nF} \log \frac{[\text{Ox}]}{[\text{R}]}$$

and $\text{EMF}_{\text{cell}} = E_{\text{Re, Ox}} - E_{\text{ref}}$
($E_{\text{Re, Ox}}$ is calculated from Nernst equation)

Individual ionic activities can also be measured using E_{h} measurement and using their individual electrodes, eg. Ag-AgCl for Cl^- ion, Ag-AgBr for Br^- , Ag-Ag₂S for S^{2-} ion activities, etc:

$$E_{\text{h}} = E^0 - \frac{RT}{nF} \ln a_x ; \quad a_x = \exp \frac{(E^0 - E_{\text{h}}) \cdot nF}{RT}$$

EMF measurement at high T and P: Glass electrodes can be used for EMF measurements up to 150°C and 1000 bars pressure, whilst Ag-AgCl electrode can be used up to 250°C and 40 bars