

# 1

## Introduction

### Fundamental Notes on Chemical Thermodynamics

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## I. INTRODUCTION

Thermodynamics is a very useful tool for many scientists and engineers, including geologists, geophysicists, and mechanical engineers, and is considered the scientific cornerstone for chemical engineers.

When we study a handbook containing papers from a certain field of chemical engineering, it is very useful to have some notes on thermodynamics on hand to help us understand what we're reading. This is the purpose of this chapter; to give a brief, elementary review of thermodynamics, reminding to the reader the basic laws, glossary, concepts, and relations of this important branch of science so as to make the study of the present volume much easier and pleasant.

This chapter is intended for chemical engineers and chemists, and for this reason we devote most of this chapter to dealing with chemical thermodynamics, covering mixtures, solutions, phase equilibria, chemical reactions, etc.

We are going to cite simple definitions of the different thermodynamic functions and quantities, and we will not enter to any analytical description or philosophical discussion about them; similarly we will not prove the mentioned thermodynamic relations, as these are beyond the scope of this chapter.

We will deal mainly with reversible processes, so far as an interest is in chemical thermodynamics, and we will not refer to statistical or nuclear and relativistic phenomena.

## II. SCOPE

Thermodynamics is a branch of physical sciences concerned with the study of the transformation of heat, work, and other kinds of energy (electrical, light energy, etc.) from one form to another, in the different physicochemical phenomena and determines the laws and relations governing and describing these energy transformations.

Historically (1), many scientists studied the interconversion of heat and work, from N.L.S. Carnot with his famous ideal gas cycle, to Clausius, who laid the foundations of the classical thermodynamics with the expression of the first and second laws of thermodynamics.

Later, J. Willard Gibbs extended the application of the thermodynamic postulates and relations to chemical reaction and phase equilibria putting the foundations for the development of the field, which we call today chemical thermodynamics.

Thermodynamics consists of a collection of equalities and inequalities which interrelate physical and chemical properties of substances as well as some physical or chemical phenomena. These relations are deduced in a mathematical way from some laws, the thermodynamic laws, which are derived directly from experience. The physical quantities used are taken either from physics, or they are introduced in thermodynamics. Using these relations, we can predict the possible direction of chemical reactions or the final result of a physical process, as well as the quantities of the different kinds of energy involved in these transformations.

Thermodynamics is an experimental science (2). All the physical or chemical quantities used in its relations are independently measurable, but some of them are easier to be measured than others. Another feature of thermodynamics that makes it very important and useful is the capability of calculation, through its relations, quantities measured with difficulty or low accuracy by others measured easier and more accurately.

Another advantage is that very often from existed data of some physical quantities we can calculate through thermodynamic relations the values of the physical quantities we are interested in, in this way avoiding long and difficult experiments and also saving time and money.

Therefore, it becomes obvious that thermodynamics can be a very useful tool to a chemist or a chemical engineer.

## III. GLOSSARY OF BASIC THERMODYNAMIC TERMS (2–6)

There are a variety of thermodynamic terms, the most common of which are defined below, together with their SI units (3).

The amount of substance (2)  $n_b$  of an entity  $b$  is a physical quantity proportional to the number  $n_b$  of entities  $b$  in the system. The SI unit of the amount of substance is the *mol*.

## A. Pressure, Volume, Temperature

Pressure and volume are concepts taken from physics.

*Pressure* is defined as the ratio of a perpendicular force to a surface by the area of this surface. The SI unit of pressure is the Pa.

*Volume* ( $m^3$ ) is the three-dimensional space occupied by a substance. *Specific volume* ( $m^3/kg$ ) is the volume per unit mass. *Molar volume* is the volume divided by the amount of substance. *Density* is the reciprocal of the specific volume.

*Temperature* is a fundamental concept used in thermodynamics, and its definition is a very difficult matter. However we could simply describe it as the degree of hotness of a substance or as the property of matter which has equal magnitude in systems, connected by diathermic walls and where thermal flow does not exist (3).

## B. Temperature Scales (4)

The *Celsius scale* ( $^{\circ}C$ ) is established by assigning the value  $0.01^{\circ}C$  to the triple point of water and the value  $100^{\circ}C$  to the boiling point of water at an atmospheric pressure of 1 standard atm (760 torr).

The *absolute temperature scale* ( $T$ ) is a scale which is related to the Celsius scale by the relation:

$$T = t (^{\circ}C) + 273.15$$

$T$  is given in degrees Kelvin. In this scale it is enough to define just one point and this is the triple of water equal to 273.16 K. The freezing point of water at 1 atm is 273.15 K.

The *ideal gas temperature scale* defined as:

$$T = 273.16K \lim_{P_{273.16} \rightarrow 0} \left( \frac{P_T}{P_{273.16}} \right)$$

where  $P_T$  and  $P_{273.16}$  are the pressures of a gas trapped in a gas thermometer at the temperatures  $T$  and 273.16 K. The ideal gas temperature scale is the same with the absolute scale. Constant volume gas thermometers are used to determine the thermodynamic absolute temperatures.

The *International Practical Temperature Scale (IPTS-68)*. This scale gives the temperatures at some reproducible fixed points together with some interpo-

lating instruments and functions, by which we find the temperatures between these points. The fixed points as well as the functions have been determined by constant volume gas thermometers. The IPTS-68 gives the possibility by the above mentioned instruments and functions to measure in an easy and accurate way the absolute temperature. In the literature (4), we can find temperatures at different fixed points as well as the instruments used to measure the absolute temperature between these points. In the SI system for the absolute temperature we use the degree K.

### C. System

In thermodynamics, we call any part of the real world we are choosing to study a *system*. All the rest of the parts of the world are the *surroundings* of the system. Practically by surroundings we consider the part of the world around the system which can interact with it.

A system is *closed* if no matter enters or leaves it during any process we study. Otherwise it is *open*. A system is called *isolated* if neither matter nor energy enters or leaves it.

The *state* of a system is defined by the values of its properties. *Properties* are physical quantities like temperature, volume, pressure, etc., which are related with a system and they have fixed values at any given state of the system. In order to define the state of a system, it is not necessary to know the values of all its properties, but only a certain number of them, which are called independent and all the rest (dependent) can be calculated by the values of the independent ones. Since a property is fixed by the state of a system it is also called a *state function*. A mathematical relationship between thermodynamic state functions is called an “equation of state.”

### D. Extensive and Intensive Properties

Considering that we divide a system in different parts, if for one property its value for the whole system is equal to the sum of its values for the different parts, then this property is called *extensive*. Extensive properties are the volume, the mass, the internal energy, etc.

If the value of a property for the whole system is equal to the values for its different parts, then the property is called *intensive*. Intensive properties are the temperature, the pressure, the molar volume, the density, etc.

### E. Phase

If for a system, throughout all its parts, all its intensive properties have the same value, then the system is a homogeneous one and is called a *phase*. One system

can consist of more than one phases. In that case it is heterogeneous and some of its intensive properties have not the same value at all its parts.

One phase can be *open* when it exchanges matter either with its surroundings or with another phase within the system. In the opposite case it is called *closed*.

## F. Process

*Process* is the pathway through which one system passes from one state to another.

If during a process the temperature of the system remains constant, the process is called *isothermic*, if the volume of the system remains constant, the process is called *isometric* or *isochoric*, and if the pressure remains constant, the process is called *isobaric*. If no heat enters or leaves a system undergoing one process the system and the process are called *adiabatic*.

A process is called *reversible* if it takes place slowly and in such a way that at any stage of the process the properties of the system differ from equilibrium by infinitesimal amounts. Otherwise the process is called *irreversible*. All natural processes are irreversible.

## G. Molar Quantities

From any extensive quantity  $X$  of a phase, it is defined an intensive quantity  $X_m$  by the relation:

$$X_m = \frac{X}{\sum_i n_i} \quad (1)$$

where  $\sum_i n_i$  is the sum of the amounts of the different substances contained in this phase.

## H. Mole Fraction

The mole fraction  $X_a$  of a substance  $a$  in a phase is defined by the ratio:

$$X_a = \frac{n_a}{\sum_i n_i} \quad (2)$$

where  $n_a$  the amount of substance of  $a$  and  $\sum_i n_i$  the sum of the amounts of all substances in this phase.

It follows immediately from the above definition that

$$\sum_i X_i = 1 \quad (3)$$

## I. Molality

Molality  $m$  is the number of moles of a substance in 1 kg of solvent.

## J. Molarity

Molarity  $c$  is the number of moles of a substance in 1 L of solvent.

## K. Partial Molar Quantities

From any extensive quantity  $X$  of a phase we define an intensive quantity called the partial molar quantity  $X_a$  of the substance  $a$  in the phase by the relation:

$$X_a = \left( \frac{\partial X}{\partial n_a} \right)_{T,P,n_i \neq n_a} \quad (4)$$

where  $n_i \neq n_a$  means all  $n$ 's except  $n_a$  in this phase.

## IV. THE CONCEPTS OF W, PE, KE, U, Q AND S (6–8)

W (work), PE (potential energy), and KE (kinetic energy) are concepts borrowed from physics.

*Work* ( $W$ ) is produced by a force ( $F$ ) acting on a system and replacing it by a distance ( $ds$ ) in the direction of the force and equals to:

$$dW = F \cdot ds$$

In the case of a uniform pressure  $P$  acting on a system's wall of surface  $S$  and replacing it by a distance  $x$

$$dW = -P \cdot s \cdot dx \quad \text{or} \quad dW = -P \cdot dV \quad (5)$$

By energy we mean the ability of a system to produce work.

*Potential energy* ( $PE$ ) is the energy possessed by a system because of its position.

$$PE = m \cdot g \cdot h \quad (6)$$

where  $m$  is the mass of the system,  $g$  the gravity acceleration and  $h$  the height of the system from zero level.

*Kinetic energy* ( $KE$ ) is the energy possessed by a system of mass  $m$ , because of its velocity ( $v$ ) and is equal to:

$$KE = \frac{mE^2}{2} \quad (7)$$

*Internal energy (U)* is the total energy, except potential and kinetic, contained within a system at a certain state. It is a magnitude determined by the state of a system. We can't measure the absolute value of U, but only differences  $\Delta U = U_2 - U_1$  between two states (1) and (2).  $\Delta U$  depends only on the states (1) and (2) and not on the path followed to pass from one to the other.

*Heat (Q)* is the amount of energy, transferred from one system to another because of the difference in the temperature of the two systems. The amount of heat depends on the followed path and not on the original and final states of a procedure.

For a system receiving heat Q,

$$Q = C \cdot (T_2 - T_1) \quad (8)$$

where C is the heat capacity of the system and  $T_2$ ,  $T_1$  its final and original temperatures.

*The entropy (S)* (6) is an extensive property, depending on the state of a system. It can be defined as:

$$dS = \frac{dQ}{T} \quad (9)$$

where dS is the heat received by it in a reversible way at a temperature T.

In natural processes S always increases and

$$dQ \leq T \cdot dS \quad (10)$$

The SI unit for W, PE, KE, and Q is the Joule.

The SI unit for S is  $\frac{\text{Joule}}{\text{K}}$ .

## V. THERMODYNAMIC LAWS (2, 5, 6, 7)

Thermodynamic laws are laws formed from experience, and there is no exception to them. There are several expressions for them all equivalent with each other. Below are given the most common ones.

### A. First Law of Thermodynamics

In any process the total energy is conserved. In other words, there is no device which can create or eliminate energy. Considering the transformation of heat to work or vice-versa in a system, the first law can be expressed as:

$$dU = dW + dQ \quad (11)$$

where  $dU$  is the variation of the internal energy of the system,  $dW$  is the work produced, and  $dQ$  is the heat transferred.

$dU$  is an exact differential depending only upon the original and final state of the system, but  $dQ$  and  $dW$  are not exact differentials and depend upon the pathway of the process. By substituting Eqs. (5) and (9) to (11), the first law can be expressed as:

$$dU = -P \cdot dV + T \cdot dS \quad (12)$$

## B. Second Law of Thermodynamics

It is not possible to transfer heat from a lower temperature to a higher temperature without the expenditure of work. In other words, in any process the total entropy of an isolated system increases.

## C. Third Law of Thermodynamics

The expression of the third law is not possible without reference to statistical mechanics (2). As expression for the third law we could give Plank's postulate (7): "At 0K the entropy of a pure crystalline is zero."

## D. Law of Thermal Equilibrium

If two systems are in thermal equilibrium with a third one, then they are also in thermal equilibrium between them.

This law is not an independent one but it is derived from the first and second thermodynamic laws (2).

## VI. THERMODYNAMIC FUNCTIONS AND SOME RELATIONS FOR ONE-PHASE CLOSED SYSTEM (6, 7)

We have already met the properties  $P$ ,  $V$ ,  $T$  and the thermodynamic functions  $U$ ,  $Q$ ,  $W$ , and  $S$  and for the last two functions:

$$W = -P \cdot dV \text{ and } dS = \frac{dQ}{T}$$

Furthermore, there are the following very important thermodynamic functions:

$$\text{the } \textit{enthalpy} \ H = U + P \cdot V \quad (13)$$

$$\text{the } \textit{Helmholtz free energy} \ A = U - T \cdot S \quad (14)$$



and the *Gibbs energy* or *Gibbs function*

$$G = H - T \cdot S = A + P \cdot V = U - T \cdot S + P \cdot V \quad (15)$$

All the three above functions are state functions and they have the dimensions of energy.

Since they are state functions their differentials are exact differentials and for reversible processes we have:

$$dH = T \cdot dS + V \cdot dP \quad (16)$$

$$dA = -S \cdot dT - P \cdot dV \quad (17)$$

$$dG = -S \cdot dT + V \cdot dP \quad (18)$$

By applying the properties of exact differentials we can obtain the following very useful relations:

$$\left(\frac{\partial U}{\partial V}\right)_S = -P, \quad \left(\frac{\partial U}{\partial S}\right)_V = T \quad (19)$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S, \quad \left(\frac{\partial A}{\partial V}\right)_T = -P \quad (20)$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V, \quad \left(\frac{\partial G}{\partial T}\right)_P = -S \quad (21)$$

$$\left(\frac{\partial H}{\partial S}\right)_P = T, \quad \left(\frac{\partial H}{\partial P}\right)_S = V \quad (22)$$

and also the following:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad (23)$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad (24)$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad (25)$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad (26)$$

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1 \quad (27)$$

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \text{ is the coefficient of thermal expansion} \quad (28)$$

$$K = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \text{ is the isothermal compressibility} \quad (29)$$

$$K_s = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_S \text{ is the adiabatic compressibility} \quad (30)$$

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V \text{ is the heat capacity at constant volume} \quad (31)$$

$$C_P = \left( \frac{\partial H}{\partial T} \right)_P \text{ is the heat capacity at constant pressure} \quad (32)$$

## VII. FUNDAMENTAL INEQUALITIES

We have already seen (Sec. IV.) that although for a reversible process  $dQ = T \cdot dS$  and for natural processes  $dQ \leq T \cdot dS$ . Similarly for natural processes from Eqs. (12), (16), (17), and (18) we derive:

$$dU \leq T \cdot dS - P \cdot dV \quad (33)$$

$$dH \leq T \cdot dS + V \cdot dP \quad (34)$$

$$dA \geq -S \cdot dT - P \cdot dV \quad (35)$$

$$dG \geq -S \cdot dT + V \cdot dP \quad (36)$$

This means that for a natural process at equilibrium the above functions get the lowest value, except the entropy which gets the maximum.

In other words for any closed isolated system (2):

$$\left( \frac{\partial S}{\partial t} \right)_{U,V,n_i} > 0 \quad (37)$$

which means, that if anything happens in that system then  $S$  is increasing, and if

$$\left( \frac{\partial S}{\partial t} \right)_{U,V,n_i} = 0 \quad (38)$$

then the system is in equilibrium.

Similarly, from:

$$\left(\frac{\partial U}{\partial t}\right)_{S,V,n_i} < 0 \quad (39)$$

that if anything happens in a system at constant  $V$ ,  $S$  and content then  $U$  is decreasing, from:

$$\left(\frac{\partial H}{\partial t}\right)_{S,P,n_i} < 0 \quad (40)$$

that if anything happens in a system at constant  $S$ ,  $P$  and content then  $H$  is decreasing, from:

$$\left(\frac{\partial A}{\partial t}\right)_{T,V,n_i} < 0 \quad (41)$$

that is anything happens in a system at constant  $T$ ,  $V$ , and content then  $A$  is decreasing, and from:

$$\left(\frac{\partial G}{\partial t}\right)_{T,P,n_i} < 0 \quad (42)$$

that if anything happens in a system at constant  $T$ ,  $P$ , and content then  $G$  is decreasing.

The above (42) inequality is very important for chemists since most chemical reactions take place at constant  $T$  and  $P$ .

If in the place of the above inequalities we consider the respective equalities, this will mean that the system to which they are referred is in equilibrium.

## VIII. RELATIONS OF THERMODYNAMIC FUNCTIONS IN ONE-PHASE OPEN SYSTEM (2, 6, 7)

We have already seen the Eq. (12)  $dU = -P \cdot dV + T \cdot dS$ , which is the expression of the first law of thermodynamics for a change involving only the transformation of energy. If we suppose that in the system under consideration there is also addition or removal of matter, then the above equation should be written under the following form:

$$dU = T \cdot dS - P \cdot dV + \sum_i \mu_i dn_i \quad (43)$$

where  $dn_i$  is the amount of substance of species  $i$  transferred and  $\mu_i$  its molar energy.

In a similar way, from Eqs. (16), (17), and (18) we derive:

$$dH = T \cdot dS + V \cdot dP + \sum_i \mu_i dn_i \quad (44)$$

$$dA = -S \cdot dT - P \cdot dV + \sum_i \mu_i dn_i \quad (45)$$

$$dG = -S \cdot dT + V \cdot dP + \sum_i \mu_i dn_i \quad (46)$$

Eqs. (43) through (46) are called *Gibbs equations*.

Considering U, H, A and G as the functions U(S, V, n<sub>i</sub>), H(S, P, n<sub>i</sub>), A(T, V, n<sub>i</sub>) and G(T, P, n<sub>i</sub>) we can prove in a very easy way that the μ<sub>i</sub>'s in the previous four relations are equal and that:

$$\mu_i = \left( \frac{\partial U}{\partial n_i} \right)_{S, V, n_{k \neq i}} = \left( \frac{\partial H}{\partial n_i} \right)_{S, P, n_{k \neq i}} = \left( \frac{\partial A}{\partial n_i} \right)_{T, V, n_{k \neq i}} = \left( \frac{\partial G}{\partial n_i} \right)_{T, P, n_{k \neq i}} \quad (47)$$

where n<sub>k ≠ i</sub> indicates all the other species n<sub>k</sub> except n<sub>i</sub>.

The above defined quantity μ<sub>i</sub> is called the *chemical potential* of the substance i; it is an intensive thermodynamic function, it has the dimensions of energy per amount of substance and its unit in the SI system is the Joule per mole.

By definition:

$$\mu_i = R T \ln \lambda_i \quad (48)$$

where λ<sub>i</sub> is called the absolute *activity* of the species i in the multicomponent system.

Integration of the Eq. (43) by keeping P, T, and n<sub>i</sub> constant (2) leads to:

$$U = S \cdot T - P \cdot V + \sum_i n_i \mu_i \quad (49)$$

or

$$G = \sum_i n_i \mu_i \quad (50)$$

Differentiation of (50) gives:

$$dG = \sum_i n_i d\mu_i + \sum_i \mu_i dn_i \quad (51)$$

Equating the expressions for dG in Eqs. (46) and (51) yields:

$$S \cdot dT - V \cdot dP + \sum_i n_i d\mu_i = 0 \quad (52)$$

which is known as the Gibbs-Duhem equation.

Replacing in (52) μ<sub>i</sub> by its form in function of activity (48) the Gibbs-Duhem equation takes the form:

$$S \cdot dT - V \cdot dP + \sum_i n_i RT d \ln \lambda_i = 0 \quad (53)$$

From Eqs. (46) by simple mathematical manipulations we can derive the following useful relations:

$$\left( \frac{\partial \mu_i}{\partial T} \right)_{P, n_i} = - \left( \frac{\partial S}{\partial n_i} \right)_{T, P, n_{k \neq i}} \quad (54)$$

$$\left( \frac{\partial \mu_i}{\partial P} \right)_{T, n_i} = \left( \frac{\partial V}{\partial n_i} \right)_{T, P, n_{k \neq i}} \quad (55)$$

$$\left( \frac{\partial \mu_i}{\partial n_k} \right)_{T, P, n_{k \neq i}} = \left( \frac{\partial \mu_k}{\partial n_i} \right)_{T, P, n_{k \neq i}} \quad (56)$$

$$\left( \frac{\partial \mu_i}{\partial T} \right)_{V, n_i} = - \left( \frac{\partial S}{\partial n_i} \right)_{T, V, n_{k \neq i}} \quad (57)$$

$$\left( \frac{\partial \mu_i}{\partial V} \right)_{T, n_i} = - \left( \frac{\partial P}{\partial n_i} \right)_{T, V, n_{k \neq i}} \quad (58)$$

$$\left( \frac{\partial \mu_i}{\partial n_k} \right)_{T, V, n_{j \neq i}} = - \left( \frac{\partial \mu_k}{\partial n_i} \right)_{T, V, n_{j \neq i}} \quad (59)$$

## IX. MIXTURES (2, 6, 7)

A system consisting of more than one substance is called mixture. A mixture may exist in gaseous, liquid, or solid phase. We shall confine ourselves to binary mixtures, from which the extension to multicomponent ones is straightforward.

By definition a mixture is said to be *ideal* if for any component  $i$  (6):

$$\mu_i = \mu_i^0 + R T \ln X_i \quad (60)$$

where  $\mu_i$ ,  $\mu_i^0$  are the chemical potentials of component  $i$  with a mole fraction  $X_i$  in the mixture and of pure  $i$  respectively, both at the same  $P$  and  $T$ .

In other words if for any component  $i$  in the mixture (2):

$$\lambda_i = X_i \lambda_i^0 \quad (61)$$

where  $\lambda_i$ ,  $\lambda_i^0$  are the absolute activities of the component  $i$  with a mole fraction  $X_i$  in the mixture and of pure  $i$  respectively, again at the same  $P$  and  $T$ .

A mixture for which (60) or (61) are not valid is called a *real* mixture.

In an ideal mixture the interactions between like and unlike species are the same and the components in the mixture they behave as in the pure components.

## A. Mixing Functions

For a binary mixture of components A and B with mole fractions  $(1-x)$  and  $x$  respectively and for any extensive thermodynamic quantity  $X$ , such as  $G$ ,  $A$ ,  $H$ ,  $S$ , or  $V$  the mixing function is defined as:

$$\Delta_{\text{mix}} X_m = X_m(T, P, x) - (1-x) X_m(T, P, 0) - x X_m(T, P, 1) \quad (62)$$

or

$$\Delta_{\text{mix}} X_m = (1-x) [X_A(T, P, 1-x) - X_m(T, P, 0)] + x [X_B(T, P, x) - X_m(T, P, 1)] \quad (63)$$

where  $X_m(T, P, x)$  is the molar function of the mixture at  $(T, P, x)$ ,  $X_A(T, P, 1-x)$ ,  $X_B(T, P, x)$  the molar functions of A and B in this mixture at mole fractions  $1-x$  and  $x$  and  $X_m(T, P, 0)$ ,  $X_m(T, P, 1)$  the molar functions of the pure components A and B respectively.

From (62) and (63) using Eqs. (50) and (61) and for  $X_m = G_m$  we obtain for an ideal mixture:

$$\Delta_{\text{mix}} G_m^{\text{id}} = R T [(1-x) \ln(1-x) + x \ln x] > 0 \quad (64)$$

From (21) and (64) at constant  $P$ ,  $n$  we obtain:

$$\Delta_{\text{mix}} S_m^{\text{id}} = -R [(1-x) \ln(1-x) + x \ln x] < 0 \quad (65)$$

From (64), (65), and (15):

$$\Delta_{\text{mix}} H_m^{\text{id}} = 0 \quad (66)$$

and from (21) and (64):

$$\Delta_{\text{mix}} V_m^{\text{id}} = 0 \quad (67)$$

## B. Excess Functions

By definition Excess function  $X_m^E$  is the difference between the real  $\Delta_{\text{mix}} X_m$  and the ideal one. That is:

$$X_m^E = \Delta_{\text{mix}} X_m - \Delta_{\text{mix}} X_m^{\text{id}} \quad (68)$$

## C. Thermodynamic Functions of Dilution

If in one binary or multicomponent one-phase homogeneous mixture of nonreacting species, one component is in excess related to the others, and more of this is added to the mixture, this process is called *dilution*.

The thermodynamic functions of the dilution process are given as the difference of thermodynamic functions of mixing between the final diluted state and the original one, that is

$$\Delta X_{m,dil} = (\Delta X_{m,mix})_2 - (\Delta X_{m,mix})_1 \quad (69)$$

## D. Standard and Reference States of Thermodynamic Functions (8, 9)

We define as *standard thermodynamic function* of a component *i* in a system at any temperature and at a fixed pressure the thermodynamic function of *i* at a given composition. The state thus defined is called *standard state*.

Historically the standard states are defined at the fixed pressure of 1 atm (= 101.325 Pa) and in that case the standard Thermodynamic functions depend only on the temperature.

Usually, for gases as standard state is accepted the pure ideal gas at 1 atm and for liquids and solids the pure liquids or solids at certain *P*, *T* where *P* can be defined as 1 bar.

As *reference state* is called one state that is used as reference for the calculation of the different thermodynamic functions.

Any thermodynamic function can be expressed in function of its standard or reference state.

## X. GASES AND GASEOUS MIXTURES (5, 6, 8)

The PVT behavior of a pure fluid, e.g., a gas, can be expressed by the equation:

$$P \cdot V_m = R \cdot T (1 + B \cdot P + C \cdot P^2 + \dots) \quad (70)$$

or

$$P \cdot V_m = R \cdot T \left(1 + \frac{b}{V_m} + \frac{c}{V_m^2} + \dots\right) \quad (71)$$

where  $V_m$  is the molar volume of the gas,  $V_m = \frac{V}{n}$ , *V* the volume and *n* the mol of the gas, and *R* is the gas constant, which in SI units is equal to 8.3144 J · mol<sup>-1</sup> · K<sup>-1</sup>.

Eqs. (70) and (71) are called virial equations of state of a gas and the coefficients *b*, *c*, ... of (71) virial coefficients and they depend on the temperature and on the type of chemical species of the gas. The coefficients *B*, *C*, ... can be calculated from *b*, *c*, ...

$$\text{when } P \rightarrow 0 \text{ then } P \cdot V_m = R \cdot T \quad (72)$$

This is the equation of state of an ideal gas. The virial coefficients show the deviation of a real gas from ideality.

The PVT behavior of the gases is also expressed by the aid of the compressibility factor:

$$z = \frac{PV_m}{RT} \quad (73)$$

For an ideal gas  $z = 1$  and  $P \cdot V_m = R \cdot T$

One other attempt to express the PVT behavior of the real gases is the van der Waals equation:

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = R \cdot T \quad (74)$$

which tries to take in account the volume (coefficient  $b$ ) of the molecules and the interactions between them (coefficient  $a$ ).

For an ideal gas we can derive the following relations:

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T \left(\frac{\partial \left(\frac{nRT}{P}\right)}{\partial T}\right)_P = V - \frac{nRT}{P} = 0 \quad (75)$$

$$C_P = C_V + n R \quad (76)$$

The Gibbs-Duhem equation at constant  $T$  and for a pure gas becomes:

$$n d\mu = V \cdot dP \quad (77)$$

If the gas is ideal, substituting in (77) the volume from (72) we obtain:

$$n d\mu = \frac{nRTdP}{P} \quad (78)$$

or

$$d\mu = R T d \ln P \quad (79)$$

and for a change at constant  $T$  from  $P_1$  to  $P_2$

$$\mu_2 - \mu_1 = R T \ln \left(\frac{P_2}{P_1}\right) \quad (80)$$

## A. Fugacity (7, 10, 11)

To express the properties of a real gas in the same way with an ideal gas, Lewis and Randall (10) originated the term *fugacity* ( $f$ ), which has the dimensions of pressure.



So, for a real gas or vapor instead of (79) or (80) we write (10):

$$d\mu = R T d\ln f \quad (81)$$

or

$$\mu_2 - \mu_1 = R T \ln \frac{f_2}{f_1} \quad (82)$$

where  $f$  is the fugacity of the gas or vapor.

$$\text{The ratio } \Phi = \frac{f}{P} \quad (83)$$

is called *fugacity coefficient*. Since ideal gas behavior is approached as  $P \rightarrow 0$  then

$$\lim_{P \rightarrow 0} \Phi = \lim_{P \rightarrow 0} \frac{f}{P} = 1 \quad (84)$$

As we will see in the phase equilibrium the fugacity of a liquid or a solid which is in equilibrium with its vapor is equal to the fugacity of its vapor.

The fugacity of a real pure gas at a given  $P$ ,  $T$  can be evaluated (7) through the relation:

$$\left( \ln \frac{f}{P} \right) = \left[ \int_0^P \left( \frac{V_m}{RT} - \frac{1}{P} \right) dP \right]_T \quad (85)$$

if we know the equation of state of that gas.

For multicomponent real gases, the partial fugacity  $f_i$  of a component  $i$  is defined in terms of the chemical potential  $\mu_i$  as follows:

$$d\mu_i = R T d(\ln f_i) \quad (86)$$

In this case:

$$\lim_{P \rightarrow 0} \frac{f_i}{x_i P} = 1 \quad (87)$$

where  $x_i$  is the mole fraction of component  $i$  and  $P$  is the total pressure (not the partial pressure  $P_i$ ).

For multicomponent gases, the fugacity  $f_i$  can be also evaluated (7) through the following relation, if we know the equation of state of that gas mixture:

$$\ln f_i = \ln(x_i P) + \left[ \int_0^P \left( \frac{(V_m)_i}{RT} - \frac{1}{P} \right) dP \right] \quad (88)$$

where  $(V_m)_i$  is the partial molar volume of species  $i$ .

## B. The Standard State of a Gas Component (2)

The standard state of a gas component in a mixture of gases is given by:

$$\mu_B(g, T, P, x_c) = \mu_B^0(g, T) + R T \ln \left( x_B \frac{P}{P_0} \right) + \int_0^P \left[ V_B(g, T, P, x_c) - \frac{RT}{P} \right] dP \quad (89)$$

where  $T, P, x_c$  are the temperature, pressure and composition of the gas mixture,  $x_B$  the mole fraction of  $B$  in the mixture and  $\mu_B^0(g, T)$  is the chemical potential of the pure ideal gas, at temperature  $T$  and pressure  $P_0$ . Historically  $P_0 = 1$  atm.

## XI. LIQUID MIXTURES (2, 8)

All that was mentioned in Sec. IX and what it will follow are applicable to liquid and to solid mixtures as well.

For a liquid mixture using Eq. (48) we obtain:

$$\mu_i = \mu_i^0 + R T \ln \frac{\lambda_i}{\lambda_i^0} \quad (90)$$

or

$$\mu_i = \mu_i^0 + R T \ln a_i \quad (91)$$

where  $\mu_i, \mu_i^0$  are the chemical potentials of component  $i$  with mole fraction  $x_i$  and of the pure liquid  $i$  at certain  $P, T, \lambda_i, \lambda_i^0$  the absolute activities of  $\mu_i$  and  $\mu_i^0$  respectively and

$$a_i = \frac{\lambda_i}{\lambda_i^0} \quad (92)$$

is what we call *relative activity* of component  $i$  in the mixture. Some authors call  $a_i$  simply *activity*.

For the absolute activity, the *activity coefficient*  $f_i$  is defined by the relation:

$$\lambda_i = f_i x_i \quad (93)$$

and for the relative activity the corresponding *activity coefficient*  $\gamma_i$  is defined by the relation:

$$a_i = \gamma_i x_i \quad (94)$$

When  $a_i = 1$  from (91) we obtain  $\mu_i = \mu_i^0$ , that is the term  $R T \ln a_i$  gives the difference between  $\mu_i$  and its reference state  $\mu_i^0$  at certain P, T and if  $P = 1$  bar then the difference of  $\mu_i$  from its standard state.

$$\text{From (91) and (94) we get } \mu_i = \mu_i^0 + R T \ln x_i + R T \ln \gamma_i \quad (95)$$

Since for the case of an ideal mixture  $\mu_i = \mu_i^0 + R T \ln x_i$  (Eq. [60]), the term  $R T \ln \gamma_i$  expresses the deviation of  $\mu_i$  from ideality.

After defining the standard state for  $\mu_i$  the standard states for the other thermodynamic functions can be derived in an easy way. In particular

$$S_i^0 = - \frac{d\mu_i^0}{dT} \quad (96)$$

$$H_i^0 = \mu_i^0 - T \frac{d\mu_i^0}{dT} \quad (97)$$

$$G_i^0 = \mu_i^0 \quad (98)$$

where  $S_i^0$ ,  $H_i^0$ , and  $G_i^0$  are the standard molar functions of S, H, and G respectively.

## XII. EQUILIBRIUM OF PHASES (2, 6, 8, 11, 12)

In many industrial processes there is coexistence of two or more phases. When there is mass transfer from one phase to the other the phases are not in equilibrium. The study of the mass transfer in these processes requires exact knowledge of the phases at equilibrium. In this section, we will treat liquid-vapor equilibrium states. Similar results can be derived from the treatment of liquid-solid and solid-vapor equilibrium.

We say that two or more phases are in equilibrium regarding several intensive properties if these properties have the same value in both phases. For example we have:

Thermal equilibrium, when the temperatures T of the different phases are equal

Hydrostatic equilibrium, when the pressures P of the different phases are equal

Chemical equilibrium, when there is no reaction between the constituents of all the phases

Osmotic equilibrium, when P, T, and several  $\mu_i$  are the same

Diffusive equilibrium, when P, T, and all  $\mu_i$  are the same

We will deal here with equilibrium states between phases where  $P$ ,  $T$ ,  $\mu_i$  are equal in all phases.

### A. The Phase Rule (4, 6, 8, 11)

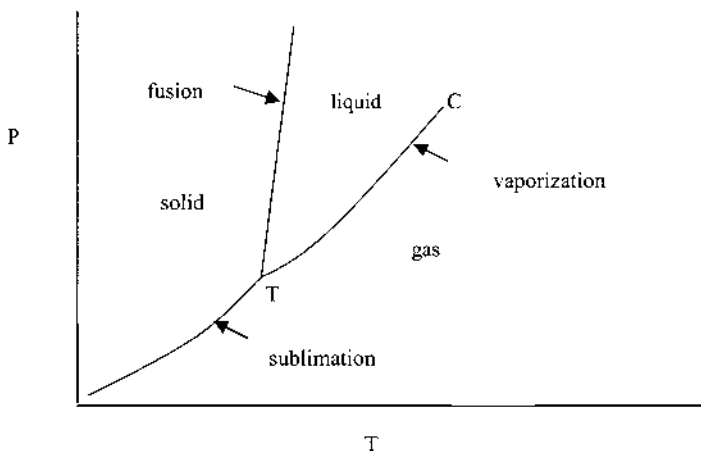
For a closed, isolated system consisting of several phases  $a, b, c, \dots$  in thermal, hydrostatic and chemical equilibrium (fixed composition) and where there is no transfer of mass, at macroscopic observation, from one phase to the other, writing the Gibbs-Duhem equations for each phase, since  $dP$ ,  $dT$  and  $dn_i$  are zero it is derived that, for every component  $i$ ,  $\mu_i^a = \mu_i^b = \mu_i^c = \dots$

The minimum number of intensive properties (pressure, temperature, mole fractions, etc.) needed so that the state of a closed, isolated nonreacting system is completely defined is called the *degrees of freedom*  $F$ .

Gibbs derived a very important rule involving phase equilibria which connects the degrees of freedom  $F$  with the number of phases  $P$  and the number of different substances  $C$  in the system. This rule is given by the following relation:

$$F = C + 2 - P \quad (99)$$

For example in the  $P, T$  diagram of Fig. 1 for a pure substance we observe that for the regions of only one phase ( $P = 1$ ), the relation (99) yields  $F = 2$ , which means that both  $P, T$  are needed for the definition of the state. For points on the curves we have two phases  $P = 2$  and  $F = 1$  which means that only one of  $P, T$  is needed for the definition of the state and finally at the triple point  $T$ ,



**Figure 1**  $P$ - $T$  diagram for a pure substance.

$P = 3$  and  $F = 0$ , which means that there is no degree of freedom and only one pair of  $P$ ,  $T$  corresponds to the state of coexistence of three phases.

If a reaction is taking place in the system or we want to take in account a peculiarity of the equilibrium phases, for instance an azeotrope, then the phase rule must be modified.

For a single-component two phase system, following the vaporization curve (Fig. 1) up to the end point C, we observe that by increasing gradually the temperature of the system we pass to vapor and liquid phases which they become more and more similar in density and molar volume and the meniscus separating the two phases becomes more indistinct. Finally at the point C the two phases become identical and the meniscus between the two phases disappears. Beyond C there is no liquid or vapor phase, but only one single-fluid phase.

At the critical point

$$\left(\frac{\partial P}{\partial V}\right)_{T_C} = 0, \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_C} = 0 \quad (100)$$

Point C is called the *critical point* and the corresponding  $P$ ,  $T$  the *critical Pressure*  $P_C$  and the *critical Temperature*  $T_C$  of the studying substance.

## B. The Chemical Potential in Phase Equilibria (7, 11)

In the previous section we saw that between two phases a, b in equilibrium for every substance i

$$\mu_i^a = \mu_i^b \quad (101)$$

or

$$\mu_i^{0,a} + R T \ln a_i^a = \mu_i^{0,b} + R T \ln a_i^b \quad (102)$$

Since the  $\mu_i^{0,a}$  and  $\mu_i^{0,b}$  are the chemical potentials of the pure i at the same  $P$ ,  $T$  then

$$\mu_i^{0,a} = \mu_i^{0,b} \quad (103)$$

and consequently from (103)

$$a_i^a = a_i^b \quad (104)$$

but this does not mean that necessarily the activity coefficients  $\gamma_i^a$ ,  $\gamma_i^b$  will be equal since usually  $x_i^a \neq x_i^b$

For the case of liquid–vapor equilibrium we have seen for the vapor phase that

$$\mu_i^v = \mu_i^{0,v} + R T \ln \frac{f_i^v}{f_i^{0,v}} \quad (105)$$

while for the liquid phase

$$\mu_i^l = \mu_i^{0,l} + R T \ln \frac{\lambda_i^l}{\lambda_i^{0,l}} = \mu_i^{0,l} + R T \ln a_i \quad (106)$$

From the previous relations it is obtained the following relation, connecting the absolute activity, the relative activity and the fugacity of a component  $i$  in a system at equilibrium

$$\frac{f_i}{f_i^0} = \frac{\lambda_i}{\lambda_i^0} = a_i \quad (107)$$

The equations relating the thermodynamic functions of phases at equilibrium are very important since from data of one phase we can calculate the properties of the other phase.

### C. Binary Vapor-Liquid Systems (7, 9, 11)

There are important differences between the behavior of a single component vapor-liquid system and a multicomponent one. For instance, in a single component the vapor and liquid phases have the same composition, but not in a multicomponent system.

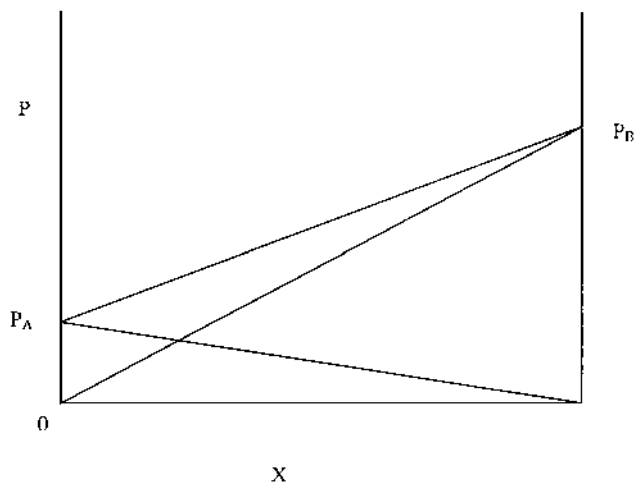
During the evaporation at constant pressure for a single-component system the temperature remains constant, but in a multicomponent system at constant  $P$  the temperature changes during the evaporation. It is obvious that the behavior of a multicomponent system is more complicated than that of a single component. As an example of multicomponent system we study here a two-phase binary system.

Fig. 2 shows a vapor-pressure, composition ( $X$  = mole fraction) diagram for an ideal mixture of two liquids. At any mole fraction  $X$  between 0 and 1 the vapor pressure  $P_{\text{mix}}$  of the mixture is

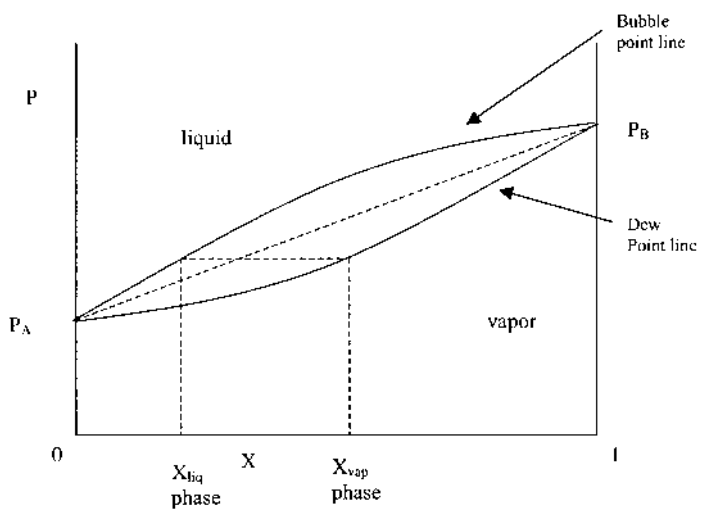
$$P_{\text{mix}} = P_A (1 - X) + P_B X \quad (108)$$

where  $P_A$ ,  $P_B$  the vapor pressures of the pure components A, B.

Fig. 3 shows the  $P$ ,  $X$  diagram of a real mixture of two component liquids A and B, completely miscible through the whole range of  $X$ . At any pressure a composition of the liquid phase  $X_{\text{liq}}$  corresponds to a different composition  $X_{\text{vap}}$  of the vapor phase, which is in equilibrium with the liquid. The compositions of the liquid phase form a curve called *bubble point line* and the corresponding compositions of the vapor phase form another curve called *dew point line*. A similar to Fig. 3 diagram can be drawn relating  $T$  with  $X$ .



**Figure 2** Vapor-pressure composition diagram for an ideal mixture of two liquids, A and B.



**Figure 3** Vapor-pressure composition diagram for a real mixture of two liquids.

Each liquid component, when its mole fraction tends to 1, behaves like in an ideal solution.

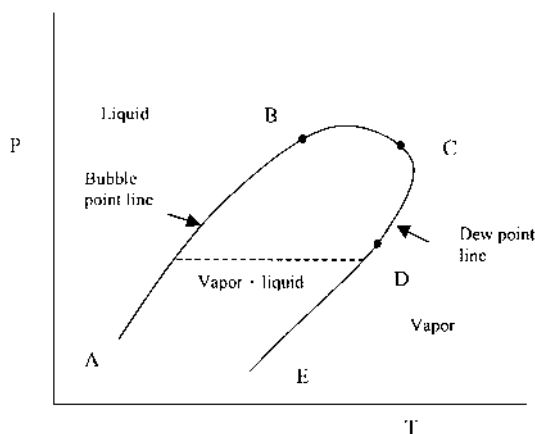
Some binary liquid mixtures, at a fixed composition, have identical composition in both the liquid and vapor phase. This composition is called *azeotropic* and the mixture *azeotrope*. In these cases, although the compositions of the two phases are equal, it does not mean that the mixture is an ideal one.

There are positive azeotropes with azeotropic pressure  $P_{az}$  higher than the vapor pressure of the two pure components and negative azeotropes with  $P_{az}$  lower than the vapor pressure of the two pure components of the mixture.

Fig. 4 shows the P, T diagram of a binary liquid mixture at a constant composition. Since in this case there is one more degree of freedom from the single component system, in order to define the state of the system for the vapor + liquid region we need both P, T (for the single component system it is needed either only P or only T).

In Fig. 4, the region included inside the ABCDE curve is in the place of the vaporization line of Fig. 1. To pass from the pure liquid to the vapor under constant pressure the temperature is changing. This passage becomes shorter as we approach the critical point C. The end temperatures, at the start and the end of this process, are called *bubble point* and *dew point temperatures* respectively at the pressure of vaporization. At each composition there is one curve ABCDE and one critical point.

Similar behavior is observed for the processes of fusion and sublimation and it is not necessary to study them separately.



**Figure 4** P-T diagram at constant composition for a mixture of two liquids.



## D. Principle of Corresponding States (7, 12)

For different real gases at the same pressure and temperature the molar volumes  $V_m$  are different. The compressibility factor  $z = \frac{PV_m}{RT}$  defined in Sect. X expresses the deviations of the real gases from ideality and it is different for the different gases at the same  $P$  and  $T$ .

However, it has been observed, by defining the reduced pressure  $P_r$ , the reduced temperature  $T_r$  and the reduced molar volume  $V_{m,r}$  by the relations:

$$P_r = \frac{P}{P_C}, \quad T_r = \frac{T}{T_C}, \quad V_{m,r} = \frac{V_m}{V_{m,C}} \quad (109)$$

where  $P_C$ ,  $T_C$ ,  $V_{m,C}$  are the critical  $P$ ,  $T$  and  $V_m$  that for equal  $P_r$ ,  $T_r$  the  $V_{m,r}$  of all gases are approximately equal.

This is known as the van der Waals *principle of corresponding states*.

The critical compressibility factor

$$z_C = \frac{P_C V_{m,C}}{RT_C} \quad (110)$$

is also found experimentally to be in the narrow range 0.2–0.3 and it can be considered as a universal constant.

So we finally have

$$z = F(P_r, T_r) \quad (111)$$

where  $F$  is the same function for all the gases.

## E. Enthalpy and Entropy Change in a Two-Phase Transition (2, 7, 12)

When there is transition from one phase to another we define a property called *change of transition of state* by the relation

$$\Delta M_i^{ab} = M_i^b - M_i^a \quad (112)$$

Thus for the case of vaporization we have:

$$\Delta V_i^{lv} = V_i^v - V_i^\ell \quad (113)$$

$$\Delta H_i^{lv} = H_i^v - H_i^\ell \quad (114)$$

$$\Delta S_i^{lv} = S_i^v - S_i^\ell \quad (115)$$

where by  $\ell$  and  $v$  we mean liquid and vapor respectively.

Knowing that at equilibrium

$$\mu_i^\ell = \mu_i^v \quad \text{or} \quad G_i^\ell = G_i^v \quad (116)$$

for a two-phase one-component system at each phase:

$$G_i = H_i - T S_i \quad (117)$$

$$\text{and } dG_i = S_i dT - V_i dP \quad (118)$$

From (117) and (118), it is finally derived

$$\frac{dP_i^{\text{sat}}}{dT} = \frac{\Delta S_i^{\text{lv}}}{\Delta V_i^{\text{lv}}} \quad (119)$$

$$\frac{dP_i^{\text{sat}}}{dT} = \frac{\Delta H_i^{\text{lv}}}{T \Delta V_i^{\text{lv}}} \quad (120)$$

where  $P_i^{\text{sat}}$  is the vapor pressure at the equilibrium of the two phases.

From Eqs. (119) and (120) we can calculate the entropy and enthalpy change of vaporization.

### XIII. SOLUTIONS (2, 5, 11, 13)

For several mixtures it is convenient to distinguish some components from the others, for instance when one solid, liquid, or gas has a limited solubility in a liquid and its mole fraction in the mixture does not cover the whole range from 0 to 1.

In this case, by convention we call the liquid which has the higher mole fraction the *solvent*, the component with the limited solubility *solute*, and the mixture the *solution*. When the solvent is in excess and the solute in low concentration, the solution is called a *dilute solution*.

For a binary solution the chemical potential of the solvent is given as in mixtures of liquids by the relation:

$$\mu_i = \mu_i^0 + R T \ln a_i = \mu_i^0 + R T \ln \gamma_i x_i \quad (121)$$

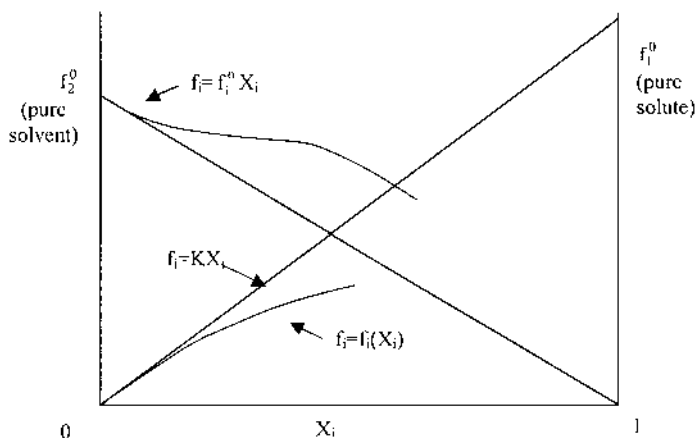
where  $\mu_i^0$  is the reference chemical potential of pure solvent at certain P, T.  $a_i, \gamma_i$  are, respectively, its relative activity and activity coefficient.

When  $x_i \rightarrow 1$  then also  $\gamma_i \rightarrow 1$ , and the solvent behaves as in an ideal mixture. At these compositions near the pure solvent the partial pressure and the fugacity of the solvent are proportional to its mole fraction.

$$P_i = P_i^0 x_i \quad \text{or} \quad f_i = f_i^0 x_i \quad (122)$$

where  $P_i, f_i, x_i$  are the partial pressure, fugacity, and mole fraction of the solvent and  $P_i^0, f_i^0$  are the vapor pressure and the fugacity of the pure solvent respectively at the temperature of the solution.

In this region, the solvent behaves in an ideal way and the relations, Eq. (122), express what we call as *Raoult's law* (Fig. 5).



**Figure 5** Fugacity of a solvent and a solute as function of their mole fraction.

The standard chemical potential of the solvent is that of the pure liquid at 1 atm and the temperature of the solution. For the solute, however, it is not possible to define a similar standard state since there cannot be solutions after a certain composition, with higher solute concentrations. In this case, it is adopted as standard state for the solute the hypothetical, ideal unit concentration of solute solution, at certain pressure and temperature (reference state) or at the fixed pressure of 1 atm (standard state).

This solute standard state is derived by the extrapolation of the fugacity of the solute at conditions of infinite dilution (the mole fraction of all the solutes in the solution tend to zero), where the fugacity of the solute  $f_i$  is proportional to its mole fraction  $x_i$ ,

$$f_i = K x_i \quad (123)$$

to the hypothetical state of solution with solute mole fraction 1.

The relation (123) is called *Henry's law* and  $K$  is a constant called Henry's constant.

In the region of very dilute solutions where the relation (123) is valid the solute behaves in an, by convention, ideal way which is different from the ideal conditions near the pure solvent.

From the above mentioned the chemical potential of the solute in a solution is given by:

$$\mu_i = \mu_i^0 + R T \ln \gamma_i x_i = \mu_i^0 + R T \ln \frac{f_i}{f_i^0} \quad (124)$$

where  $\gamma_i$ ,  $f_i$  are the activity coefficient and the fugacity of  $i$  at a mole fraction  $x_i$  and  $f_i^0$ ,  $\mu_i^0$  are the fugacity and the chemical potential of pure  $i$  at the reference state of infinite dilution conditions and at the temperature and pressure of the solution.

The standard chemical potential of a solvent is given by the relation (2):

$$\mu_2^0(T, P^0) = \mu_2^*(T, P) + \int_P^{P^0} V_2^* (T, P) dP \quad (125)$$

where  $P^0$ ,  $P$  are the standard pressure and the pressure of the solution respectively,  $*$  means is pure solvent, and  $V_2^*$  the volume of pure solvent.

The standard chemical potential of a solute is given by the relation (2):

$$\mu_i^0(T) = \left[ \mu_i(T, P, m_1) - RT \ln \frac{m_1}{m_1^0} \right]_{m_1^0}^{\infty} + \int_P^{P^0} V_i^{\infty} (T, P) dP \quad (126)$$

where  $\infty$  means conditions at infinite dilution,  $\mu_i(T, P, m_1)$  the chemical potential at  $T$ ,  $P$ ,  $m_1$ ,  $m_1^0$  the standard molality,  $P^0$  the standard pressure and  $V_i^{\infty}$  the volume of solute at conditions of infinite dilution.

All the other thermodynamic functions and relations for the solution can be derived in a straight mathematical way from the above relations.

#### XIV. ELECTROLYTE SOLUTION (2, 8, 14)

Electrolytes are a special class of solute substances, which involve several complications in their thermodynamic study, not found in solutions of nonelectrolytes.

The difficulties arise from the fact that the electrolytes in solution are found under complete or partial dissociation in the ions of which they are consisted. Because of the restriction of electrical neutrality in an electrolyte solution it is not possible to define thermodynamic functions of one ion, for example its chemical potential, since this would imply the change of the amount of substance of this ion by keeping constant the amount of substance of all the rest ions, which has no physical meaning.

To overcome this difficulty, we consider all the thermodynamic functions with both the anions and the cations of one electrolyte.

For example, for the case of a strong, completely dissociated electrolyte of the type  $M_{v+}A_{v-}$ , where  $v_+$  and  $v_-$  are the number of positive and negative ions, respectively, in the molecule of the electrolyte, we can write:

$$\mu_{MA} = v_+ \mu_+ + v_- \mu_- \quad (127)$$

and using molalities

$$\mu_+(T, P, m) = R T \ln m_+ + R T \ln \gamma_+(T, P, m) + \mu_+^0(T, P) \quad (128)$$

$$\mu_-(T, P, m) = R T \ln m_- + R T \ln \gamma_-(T, P, m) + \mu_-^0(T, P) \quad (129)$$

Substituting (128) and (129) to (127) we obtain:

$$\begin{aligned} \mu_{MA} &= R T \ln m_+^{\nu_+} m_-^{\nu_-} + R T \ln \gamma_+^{\nu_+} \gamma_-^{\nu_-}(T, P, m) + \\ &+ \nu_+ \mu_+^0(T, P) + \nu_- \mu_-^0(T, P) \end{aligned} \quad (130)$$

The mean activity coefficient is defined as:

$$\gamma_{\pm}^{\nu} = \gamma_+^{\nu_+} \gamma_-^{\nu_-} \quad (131)$$

and the mean molality:

$$m_{\pm}^{\nu} = m_+^{\nu_+} m_-^{\nu_-} \quad (132)$$

where  $\nu = \nu_+ + \nu_-$

From (131), (132) and (130) and by defining:

$$\mu_{MA}^0(T, P) = \nu_+ \mu_+^0(T, P) + \nu_- \mu_-^0(T, P) \quad (133)$$

$$\mu_{MA}(T, P) = \nu R T \ln m_{\pm} + \nu R T \ln \gamma_{\pm}(T, P, m) + \mu_{MA}^0(T, P) \quad (134)$$

The  $m_{\pm}$ ,  $\gamma_{\pm}$  and  $\mu_{MA}^0(T, P)$  have a similar meaning as for the nonelectrolyte solutions when  $m_{\pm} \rightarrow 0$  then  $\gamma_{\pm} \rightarrow 1$  and  $\mu_{MA}(T, P)$  is equal to  $\mu_{MA}^0(T, P)$  at the reference state. To obtain the standard state for an electrolyte solute it is followed a similar procedure to that of a nonelectrolyte solute providing that the appropriate quantities are plotted (13, 14).

For the case of weak electrolytes the method to obtain expressions for the chemical potentials are the same as for strong electrolytes.

## A. The Debye–Hückel Limiting Law (2, 6)

In 1923 Debye and Hückel developed a theory about the behavior of strong electrolytes in dilute solutions. This theory was a mathematical treatment of some ideas previously assumed by Arrhenius regarding the dissociation of electrolytes in solution.

By this theory after a series of mathematical calculations we arrive to a formula giving the mean ionic activity coefficient, which for very dilute solutions by approximation takes the form:

$$\ln \gamma_{\pm} = C I^{1/2} z_+ z_- \quad (135)$$

where  $C = (2 \pi N_0 \rho_s)^{1/2} (e^2 / 4 \pi \epsilon K T)^{3/2}$

$N_0$  = Avogadro's number

$\rho_s$  = density of the pure solvent

$e$  = the charge on a proton

$\epsilon = \epsilon_0 \epsilon_r$ , where  $\epsilon_r$  is the dielectric constant of the solvent and  $\epsilon_0$  is the dielectric constant of a vacuum

$T$  = temperature of the solution

$K = \frac{R}{N_0}$ ,  $R$  = gas constant

$I$  is called ionic strength and is given for a 1-1 type electrolyte by:

$$I = \frac{1}{2} (m_+ z_+^2 + m_- z_-^2) \quad (136)$$

$m_+$ ,  $m_-$ , the molalities of the ions

$z_+$ ,  $z_-$ , the electrical charges of the ions.

The Debye-Hückel law is very accurate for very dilute solutions of strong electrolytes.

For mixed electrolytes the theory is still valid with

$$I = \frac{1}{2} \sum_i m_i z_i^2 \quad (137)$$

## **XV. THERMOCHEMISTRY—CHEMICAL REACTION EQUILIBRIUM (11, 15)**

The application of thermodynamics to chemically reacting systems is very important. Together with mass balance the first thermodynamic law under certain conditions gives exactly the energy absorbed (endothermic) or released (exothermic) by a chemical reaction. For instance we can calculate the energy needed to produce from some substances other useful substances or the energy released from the combustion of a fuel.

The second thermodynamic law can predict if one chemical reaction will proceed to one direction or to the opposite and at which extent it will stop (equilibrium state).

However, in several cases, although from the second thermodynamic law it results that one reaction should proceed to one direction, this reaction does not start and to overcome this hindrance, catalysts or other means are used.

But still, in these cases thermodynamics is useful, since through the prediction by the second thermodynamic law of the possibility of realization of a reaction, it can allow us or release us from the trouble, to seek finding the appropriate catalyst for this reaction.

## A. Enthalpy of Formation and Enthalpy of Reaction (4, 5)

The *heat of formation* of any compound is the heat required to form that compound from its elements at a certain temperature and pressure. When this formation is considered under constant pressure then the heat of formation is equal to the enthalpy of formation.

The standard enthalpy of formation,  $\Delta H_F$ , of a compound is defined as the heat required to form the compound in its standard state of 1 atm pressure and 25°C from its elements at the same standard conditions.

$$\Delta H_F = h_{\text{compound}} - \sum_i (v_i h_i)_{\text{elements}} \quad (138)$$

$v_i$  is the stoichiometric coefficient  $h_{\text{compound}}$ ,  $h_i$  the standard molar enthalpies of formation of the compound and of its elements respectively.

By convention the standard enthalpies of formation  $h_i$  of all elements at their more stable state are considered as zero, therefore

$$\Delta H_F = h_{\text{compound}} \quad (139)$$

Tables with standard enthalpies of formation of many compounds are given in books on thermodynamics.

The *heat of reaction* is the heat absorbed or rejected by the reaction. If the reaction takes place at constant P, the heat of reaction is equal to the enthalpy of reaction.

The *standard enthalpy of reaction* is defined as the change in enthalpy from a reaction taking place at a constant pressure of 1 atm and constant temperature of 25°C.

The *heat of combustion* of any compound is defined as the heat of reaction resulting from the oxidation of this compound with oxygen.

Quantities of heat transferred at constant T, like heat of vaporization, or fusion for a single compound at constant pressure are called *heat effects*.

These heat effects together with the heat of mixing, the heat of solution (heat of mixing for the case of a solution), as well as the heat of reaction are studied by the branch of thermodynamics, called thermochemistry, and the instruments used for the experimental determination of these functions are called calorimeters.

## B. Determination of the Enthalpy of Reaction (4, 5, 7)

For a reaction under constant P, where variations in potential and kinetic energy are negligible and no work is produced the change in enthalpy is given by

$$H_P - H_R = (H_P - H_{P0}) + \Delta H_R - (H_R - H_{R0}) \quad (140)$$

where  $H_p$ ,  $H_r$  enthalpies of products and reactants at a pressure  $P$  respectively and  $H_{p0}$ ,  $H_{r0}$  enthalpies of products and reactants at a pressure of 1 atm and temperature of 25°C and

$$\Delta H_R = H_{p0} - H_{r0} = \sum_{\text{products}} (v_h) - \sum_{\text{reactants}} (v_h) \quad (141)$$

where the  $v$ 's are the stoichiometric coefficients and the  $h$ 's are the standard molar enthalpies of formation of the compounds in the reaction.  $\Delta H_R$  is the standard enthalpy of reaction and can be calculated from the standard enthalpies of formation of the products and reactants using existed relative tables.

$(H_p - H_{p0})$  and  $(H_r - H_{r0})$  can be calculated either from known data, experimentally or by simplification considering, for instance, that the reactants and products behave as ideal gases. In several cases we can determine the enthalpy of a certain reaction by simply adding or subtracting other reactions of which we know the enthalpies of reaction.

### C. Equilibrium Constant-Affinity of a Reaction (6, 7, 11)

Let us consider the reaction



at constant  $T$ ,  $P$ , where  $c_i$  are the constituents and  $v_i$  the stoichiometric coefficients.

Eq. (46) at  $P$ ,  $T$  constant gives

$$dG_{T,P} = \mu_1 dn_1 + \mu_2 dn_2 - \mu_3 dn_3 - \mu_4 dn_4 \quad (143)$$

and for a reaction

$$-\frac{dn_1}{v_1} = -\frac{dn_2}{v_2} = \frac{dn_3}{v_3} = \frac{dn_4}{v_4} = d\xi \quad (144)$$

where  $\xi$  is the extent of the reaction (16).

Based on (143), (144), and (42) it follows

$$dG_{T,P} = (\mu_1 dn_1 + \mu_2 dn_2 - \mu_3 dn_3 - \mu_4 dn_4) d\xi \leq 0 \quad (145)$$

the sign of the parenthesis determines the sign of the  $\xi$  and consequently the direction of the reaction.

$$\text{At equilibrium where } dG_{T,P} = 0 \quad (146)$$

$$\mu_1 dn_1 + \mu_2 dn_2 = \mu_3 dn_3 + \mu_4 dn_4 \quad (147)$$

The quantity  $\mu_1 dn_1 + \mu_2 dn_2 - \mu_3 dn_3 - \mu_4 dn_4$  was introduced by De Donder (16) and called by him the *affinity*  $A_f$ .



From (147) using  $\mu_i = \mu_i^0 + RT \ln a_i$ , [Eq. (90)] it is obtained:

$$A_f = A_f^0 - RT \ln \left( \frac{a_3^{v_3} \cdot a_4^{v_4}}{a_1^{v_1} \cdot a_2^{v_2}} \right) \quad (148)$$

where  $A_f^0$  is the affinity for the  $\mu_i^0$ 's.

$$\text{The quantity } \left( \frac{a_3^{v_3} \cdot a_4^{v_4}}{a_1^{v_1} \cdot a_2^{v_2}} \right) = Q_a \quad (149)$$

is called *reaction quotient*.

At equilibrium where  $A_f = 0$ , the  $Q_a$  depends only on the temperature and on  $A_f^0$  and not on the activities and is called the *equilibrium constant*  $K_a$ .

Thus we have

$$A_f^0 = R T \ln K_a \quad (150)$$

$$A_f = RT \ln \frac{K_a}{Q_a} \quad (151)$$

Since one reaction proceeds only when  $A_f > 0$  this means that:

when  $K_a > Q_a$  the reaction proceeds to the right

when  $K_a < Q_a$  the reaction proceeds to the left

and

when  $K_a = Q_a$  there is equilibrium.

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