3 Fundamental Notes on Chemical Thermodynamics

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3.1 INTRODUCTION

Thermodynamics is a very useful tool for scientists and engineers such as chemists, geologists, geophysicists, mechanical and chemical engineers, and so on. Especially for chemists and chemical engineers with mathematics they form the cornerstone for their sciences.

It is very useful when we study a handbook comprising chapters from a certain field of chemical engineering to have some handy notes of thermodynamics because this way we are released from the need at any time to seek and open other textbooks for better understanding of what we read.

This is exactly the intention of this chapter. To provide a brief, elementary review of thermodynamics, reminding the reader of the basic laws, glossary, concepts, and relations of this important branch of science so as to make the study of the current volume much easier and pleasant.

This chapter is addressed, as the content of the whole volume, to chemical engineers or chemists, and for this reason after presenting a few clauses of general interest we will next proceed to clauses dealing with chemical thermodynamics that is with mixtures, solutions, phase equilibriums, chemical reactions, and so on.

Simple definitions of the different thermodynamic functions and quantities have been cited, 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 only with reversible processes, so far as an interest is in chemical thermodynamics, and we will not refer to statistical, as nuclear and relativistic phenomena.

3.2 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 have studied the interconversion of heat and work, from N.L.S. Carnot with his famous ideal gas cycle, to Clausius who laid the foundation of the classical thermodynamics with the expression of the first and second law of thermodynamics.

Later, J. Willard Gibbs extended the application of the thermodynamic postulates and relations to chemical reactions and phase equilibriums laying the foundation for the development of the field, which we today call 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 by 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.

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. One very important use of thermodynamics is the possibility to calculate, through its relations, quantities that are measured with difficulty or low accuracy by others measured easily and more accurately. Another advantage is that, very often, through thermodynamic relations we can calculate the values of physical quantities from existing data of other physical quantities and avoiding by this way, from one part long and difficult experiments and from the other part saving time and money.

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

### 3.3 GLOSSARY OF BASIC THERMODYNAMIC TERMS [2–6]

There is 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.

- **Pressure, Volume, Temperature** Pressure and volume are concepts coming 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 where thermal flow does not exist [3].
Temperature scales [4]

- The Celsius scale (°C) is established by assigning the value 0.01°C to the triple point of water and the value 100°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:

\[ T = t (°C) + 273.15 \]

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

\[ T = 273.16 \, K \lim_{P_{273.16} \to 0} \left( \frac{P_T}{P_{273.16}} \right) \]

where \( P_T \) and \( P_{273.16} \) are the pressures of a gas trapped in 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 interpolating instruments and functions, by which we find the temperatures between those points. The fixed points as well as the functions have been determined by constant volume gas thermometers. The IPTS gives the possibility by the above-mentioned instruments and functions to measure the absolute temperature in an easy and accurate way. 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 system for the absolute temperature we use the degree K.

3.3.1 System

By system in thermodynamics we refer to any part of the real world we choose to study. All the remaining parts of the world are the surroundings of the system. 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 stage of the 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 such as temperature, volume, pressure, and so on, 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.”

### 3.3.2 Extensive and Intensive Properties

Considering that we divide a system into 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, mass, internal
energy, and so on.

If a property has the same value in the whole system as well as in its different
parts, then the property is called intensive. Intensive properties are the temperature,
pressure, molar volume, density, and so on.

### 3.3.3 Phase

If for a system, throughout all its parts, all its intensive properties have the same
value, then the system is a homogenous one and is called a phase. One system can
consist of more than one phase. In that case, it is heterogeneous and some of its inten-
sive properties have not the same value as 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.

### 3.3.4 Process

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

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 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 iso-
metric or isochoric, and if the pressure remains constant, the process is called iso-
baric. 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 infini-
tesimal amounts. Otherwise, the process is called irreversible. All natural processes
are irreversible.

### 3.3.5 Molar Quantities

From any extensive quantity $X$ of a phase it is defined as intensity quantity $X_m$ by
the relation:

$$X_m = \frac{X}{\sum_{i} n_i} \tag{3.1}$$
where $\sum n_i$ is the sum of the amounts of the different substances contained in this phase.

### 3.3.6 Mole Fraction

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

$$X_a = \frac{n_a}{\sum n_i}$$  \hspace{1cm} (3.2)

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

It follows immediately from the above definition that

$$\sum_i X_i = 1$$  \hspace{1cm} (3.3)

### 3.3.7 Molality

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

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

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:

$$X_a = \frac{\partial X}{\partial n_a} \Big|_{T,P,n_i \neq a}$$  \hspace{1cm} (3.4)

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

### 3.4 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 the energy 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 $x$, then

$$dW = -P \cdot s \cdot dx \quad \text{or} \quad dW = -P \cdot dV$$  \hspace{1cm} (3.5)

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.

\[ \text{PE} = m \cdot g \cdot h \]  

(3.6)

where \( m \) is the mass of the system, \( g \) the gravity acceleration, and \( h \) the height of the system.

Kinetic energy (KE) is the energy possessed by a system of mass \( m \), because of its velocity (\( \upsilon \)) and is equal to

\[ \text{KE} = \frac{m \upsilon^2}{2} \]  

(3.7)

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 cannot 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 \( Q \),

\[ Q = C \cdot (T_2 - T_1) \]  

(3.8)

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

\[ dS = \frac{dQ}{T} \]  

(3.9)

where \( dS \) is the heat received by it in reversible way at a temperature \( T \). In natural processes \( S \) always increases and

\[ dQ \leq T \cdot dS \]  

(3.10)

The SI unit for \( W, \text{PE}, \text{KE}, \) and \( Q \) is the Joule.

The SI unit for \( S \) is Joule/K.

3.5 THERMODYNAMIC LAWS [2,5–7]

Thermodynamic laws come from experience and there is no exception to them. There are several expressions for these all equivalent with each other. Below are given the most common ones.
3.5.1 FIRST LAW OF THERMODYNAMICS

In any process, the total energy is conserved. In other words, there is no device that 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

\[ dU = dW + dQ \]  \hspace{1cm} (3.11)

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

\( dU \) is an exact differential depending only on the original and final state of the system, but \( dQ \) and \( dW \) are not exact differentials depending on the pathway of the process.

By substituting Equations 3.5 and 3.9 into Equation 3.11 the first law can be expressed as

\[ dU = -P \cdot dV + T \cdot dS \]  \hspace{1cm} (3.12)

3.5.2 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.

3.5.3 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 Planck’s postulate [7]. “At 0 K the entropy of a pure crystalline is zero.”

3.5.4 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].

3.6 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 \( S \) for the last two functions: \( W = -P \cdot dV \) and \( S = dQ/T \).

Furthermore, there are the following very important thermodynamic functions:

\[ \text{Enthalpy} \ H = U + P \cdot V \]  \hspace{1cm} (3.13)
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Helmholtz free energy

$$A = U - T \cdot S$$

(3.14)

and the Gibbs energy or Gibbs function

$$G = H - T \cdot S = A + P \cdot V = U - T \cdot S + P \cdot V$$

(3.15)

All the three 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

$$dH = T \cdot dS + V \cdot dP$$

(3.16)

$$dA = -S \cdot dT + V \cdot dP$$

(3.17)

$$dG = -S \cdot dT + V \cdot dP$$

(3.18)

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

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

(3.19)

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

(3.20)

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

(3.21)

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

(3.22)

and also the following:

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

(3.23)

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

(3.24)

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

(3.25)
\[
\left( \frac{\partial S}{\partial P} \right)_T = - \left( \frac{\partial V}{\partial T} \right)_p \tag{3.26}
\]

\[
\left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial T}{\partial V} \right)_p \left( \frac{\partial V}{\partial P} \right)_T = -1 \tag{3.27}
\]

\[
a = \frac{1}{V} \left( \frac{\partial T}{\partial V} \right)_p \text{ is the coefficient of thermal expansion} \tag{3.28}
\]

\[
K = - \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \text{ is the isothermal compressibility} \tag{3.29}
\]

\[
K_s = - \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_s \text{ is the adiabatic compressibility} \tag{3.30}
\]

\[
C_V = \left( \frac{\partial U}{\partial T} \right)_V \text{ is the heat capacity at constant volume} \tag{3.31}
\]

\[
C_P = \left( \frac{\partial H}{\partial T} \right)_P \text{ is the heat capacity at constant pressure} \tag{3.32}
\]

### 3.7 Fundamental Inequalities

We have already seen (Section 3.4) that although for a reversible process \(dQ = T \cdot dS\) for natural processes \(dQ \leq T \cdot dS\). Similarly, for natural processes from equalities (3.11), (3.16), (3.17), (3.18) we derive:

\[
dU \leq T \cdot dS - P \cdot dV \tag{3.33}
\]

\[
dH \leq T \cdot dS + V \cdot dP \tag{3.34}
\]

\[
da \leq -S \cdot dT - P \cdot dV \tag{3.35}
\]

\[
dG \leq -S \cdot dT + V \cdot dP \tag{3.36}
\]

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]:

\[
\left( \frac{\partial S}{\partial t} \right)_{U,V,n_i} > 0 \tag{3.37}
\]
which means that if anything happens in that system then $S$ is increasing, and if

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

(3.38)

then the system is in equilibrium.

Similarly, from

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

(3.39)

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

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

(3.40)

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

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

(3.41)

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

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

(3.42)

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

Inequality 3.42 is very important for chemists since most chemical reactions take place at constant $T$ and $P$.

3.8 RELATIONS OF THERMODYNAMIC FUNCTIONS IN ONE-PHASE OPEN SYSTEM [2,6,7]

We have already seen from Equation 3.12 $dU = -P \cdot dV + T \cdot dS$, 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:

$$
dU = T \cdot dS - P \cdot dV + \sum_i \mu_i \cdot dn_i
$$

(3.43)
where $dn_i$ is the amount of substance of species $i$ transferred and $\mu_i$ its molar energy.

In a similar way, from Equations 3.16 through 3.18 we derive:

\[ dH = T \cdot dS + V \cdot dP + \sum_i \mu_i \cdot dn_i \]  
\[ (3.44) \]

\[ dA = -S \cdot dT - P \cdot dV + \sum_i \mu_i \cdot dn_i \]  
\[ (3.45) \]

\[ dG = -S \cdot dT + V \cdot dP + \sum_i \mu_i \cdot dn_i \]  
\[ (3.46) \]

Equations 3.43 through 3.46 are called Gibbs equations.

Considering $U$, $H$, $A$, and $G$ as the functions $U(S, V, n_i)$, $H(S, P, n_i)$, $A(T, V, n_i)$, and $G(T, P, n_i)$ we obtain,

\[ \mu_i = \left( \frac{\partial U}{\partial n_i} \right)_{S,V,n_{k \neq i}} = \left( \frac{\partial H}{\partial n_i} \right)_{S,P,n_{k \neq i}} = \left( \frac{\partial A}{\partial n_i} \right)_{T,V,n_{k \neq i}} = \left( \frac{\partial G}{\partial n_i} \right)_{T,P,n_{k \neq i}} \]  
\[ (3.47) \]

where $n_{k \neq i}$ indicates all the other species $n_k$ except $n_i$.

The above-defined quantity $\mu_i$ is called the chemical potential of the substance $i$; it is an intensive thermodynamic function, it has the dimension of energy per amount of substance, and its unit in the SI system is the Joule per mole.

By definition,

\[ \mu_i = R \cdot T \ln \lambda_i \]  
\[ (3.48) \]

where $\lambda_i$ is called the absolute activity of the species $i$ in the multicomponent system.

Integration of Equation 3.43 by keeping $P$, $T$, $n_i$ constant [2] leads to,

\[ U = S \cdot T - P \cdot V + \sum_i n_i \mu_i \]  
\[ (3.49) \]

or

\[ G = \sum_i n_i \mu_i \]  
\[ (3.50) \]

Differentiation of Equation 3.50 gives,

\[ dG = \sum_i n_i \mu_i + \sum_i \mu_i \cdot dn_i \]  
\[ (3.51) \]
Equating the expressions for \( dG \) in Equations 3.46 and 3.47 yields,

\[
S \cdot dT - V \cdot dP + \sum_i n_i d\mu_i = 0
\]

which is known as the Gibbs–Duhem equation.

Using the above-defined activities and fugacities the Gibbs–Duhem equation takes the form,

\[
S \cdot dT - V \cdot dP + \sum_i n_i R T \ln \lambda_i = 0
\]

or

\[
S \cdot dT - V \cdot dP + \sum_i n_i R T \ln f_i = 0
\]

From Equations 3.46 by simple mathematical manipulations we can derive the following useful relations:

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

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

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

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

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

\[
\left( \frac{\partial \mu_i}{\partial n_k} \right)_{T,V,n_{k\neq i}} = -\left( \frac{\partial \mu_k}{\partial n_i} \right)_{T,V,n_{k\neq i}}
\]
3.9 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]:

\[
\mu_i = \mu_i^0 + R T \ln X_i
\]  

(3.61)

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]:

\[
\lambda_i = X_i \lambda_i^0
\]  

(3.62)

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 Equations 3.61 or 3.62 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 behave as in the pure components.

3.9.1 MIXING FUNCTIONS

For a binary mixture of components \(A\) and \(B\) with molar 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

\[
\Delta_{\text{mix}} X_m = X_m (T, P, x) - (1-x) X_m (T, P, 0) - x X_m (T, P, 1)
\]  

(3.63)

or

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

(3.64)

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 Equations 3.63 and 3.64 using Equations 3.50 and 3.62 and for \(X_m = G_m\) we obtain for an ideal mixture

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

(3.65)

From Equations 3.21 and 3.65 at constant \(P, n\) we obtain

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

(3.66)
From Equations 3.65, 3.66, and 3.15:

\[ \Delta_{\text{mix}} H_{\text{id}} = 0 \]  
(3.67)

and from Equations 3.21 and 3.65:

\[ \Delta_{\text{mix}} V_{\text{id}} = 0 \]  
(3.68)

### 3.9.2 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,

\[ X_m^E = \Delta_{\text{mix}} X_m - \Delta_{\text{mix}} V_{\text{id}} \]  
(3.69)

### 3.9.3 Standard and Reference States of Thermodynamic Functions [8,9,12]

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, which 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 function.

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

### 3.9.4 Dilution Thermodynamic Functions

If in one binary or multicomponent one phase homogenous mixture of nonreacting species, one component is in excess related to the others and 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

\[ \Delta X_{\text{m,dil}} = (\Delta X_{\text{m,mix}})_2 - (\Delta X_{\text{m,mix}})_1 \]  
(3.70)
3.10 GASES AND GASEOUS MIXTURES [5,6,8]

The PVT behavior of a pure fluid can be expressed by the equation:

\[ P \cdot V_m = R \cdot T \left(1 + B \cdot P + C_p^2 + \ldots\right) \]  

(3.71)

or

\[ P \cdot V_m = R \cdot T \left(1 + \frac{b}{V_m} + \frac{c}{V_m^2} + \ldots\right) \]  

(3.72)

where \( V_m \) is the molar volume of the gas, \( V_m = V/n \), \( V \) 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 \( \cdot \) mol\(^{-1} \) \cdot K\(^{-1} \).

Equations 3.71 and 3.72 are called virial equations of state of a gas and the coefficients \( b, c, \ldots \) of Equation 3.72 virial coefficients and they depend on the temperature and on the type of chemical species of the gas. The coefficients \( B, C, \ldots \) can be calculated from \( b, c, \ldots \).

When

\[ P \to 0 \quad \text{then} \quad P \cdot V_m = R \cdot T \]  

(3.73)

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 compressibility factor:

\[ z = \frac{PV_m}{RT} \]  

(3.74)

For an ideal gas \( z = 1 \) and \( P \cdot V_m = R \cdot T \).

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

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

(3.75)

which tries to take into account the volume (coefficient \( b \)) of the molecules and the interactions between them.

For an ideal gas we can derive the following relations:

\[ \left( \frac{\partial H}{\partial P} \right)_T = V - T \left( \frac{\partial nRT/\partial P}{T} \right)_P = V - \frac{nRT}{P} = 0 \]  

(3.76)

\[ C_p = C_V + n R \]  

(3.77)
Gibbs–Duhem equation at constant $T$ and for a pure gas becomes

$$ n \, d \mu = V \cdot dP $$

(3.78)

If the gas is ideal, substituting in Equation 3.78 the volume from Equation 3.73 we obtain:

$$ n \, d \mu = \frac{nRT}{P} \, dP $$

(3.79)

or

$$ d\mu = R \, T \, d \ln P $$

(3.80)

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

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

(3.81)

### 3.10.1 Fugacity [7,10]

To express the properties of a real gas in the same way with an ideal gas, Lewis and Randall [9] originated the term *fugacity* ($f$), which has the dimensions of pressure.

So, for a real gas or vapor instead of Equation 3.80 or 3.81 we write [10]:

$$ d\mu = R \, T \, d \ln f $$

(3.82)

or

$$ \mu_2 - \mu_1 = R \, T \, \ln \left( \frac{f_2}{f_1} \right) $$

(3.83)

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

The ratio

$$ \Phi = \frac{f}{P} $$

(3.84)

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

$$ \lim_{P \to 0} \Phi = \lim_{P \to 0} \frac{f}{P} = 1 $$

(3.85)

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:

$$\ln \left( \frac{f}{P} \right) = \left[ \int_{0}^{P} \left( \frac{V_{m}}{RT} - \frac{1}{P} \right) \, dP \right]_{T}$$

(3.86)

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:

$$(d\mu_i)_{T} = R \, T \, d(\ln f_i)_{T}$$

(3.87)

In this case,

$$\lim_{P \to 0} \frac{f_i}{x_i P} = 1$$

(3.88)

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 relation:

$$\ln f_i = \ln(x_i P) + \left[ \int_{0}^{P} \left( \frac{V_{m,i}}{RT} - \frac{1}{P} \right) \, dP \right]_{T}$$

(3.89)

where $(V_{m,i})$ is the partial molar volume of $i$, if we know the equation of state of that gas mixture.

### 3.10.2 The Standard State of a Gas Component [2]

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

$$\left( g, T, P, x_c \right) = \left( g, T \right) + R \, T \, \ln \left( x_B \frac{P}{P_0} \right) + \int_{0}^{P} \left[ \nu \left( g, T, P, x_c \right) - \frac{RT}{P} \right] \, dP$$

(3.90)

where $\mu_B^0 (g, T)$ is the chemical potential of the pure ideal gas, at temperature $T$ and pressure $P_0$. Historically, $P_0 = 1$ atm.

### 3.11 Liquid Mixtures [2,8]

All that was mentioned in Section 3.9 and what it will follow are applicable to liquid and to solid mixtures as well.
For a liquid mixture using Equation 3.48 we obtain:

\[
\mu_i = \mu_i^0 + RT \ln \frac{\lambda_i}{\lambda_i^0}
\]  
(3.91)

or

\[
\mu_i = \mu_i^0 + RT \ln a_i
\]  
(3.92)

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

\[
a_i = \frac{\lambda_i}{\lambda_i^0}
\]  
(3.93)

is what we call relative activity of \(i\) in the mixture. Some authors call \(a_i\) simply activity.

For the absolute activity, the activity coefficient \(f_i\) is defined by the relation:

\[
\lambda_i = f_i x_i
\]  
(3.94)

and for the relative activity the corresponding activity coefficient \(\gamma_i\) is defined by the relation:

\[
a_i = \gamma_i x_i
\]  
(3.95)

When \(a_i = 1\) from Equation 11.2 we obtain \(\mu_i = \mu_i^0\), that is the term \(RT \ln a_i\) 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.

From Equations 3.92 and 3.93 we get

\[
\mu_i = \mu_i^0 + RT \ln x_i + RT \ln \gamma_i
\]  
(3.96)

Since for the case of an ideal mixture \(\mu_i = \mu_i^0 + RT \ln x_i\) (Equation 3.61), then the term \(RT \ln \gamma_i\) 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 particular,

\[
S_i^0 = -\frac{d\mu_i^0}{dT}
\]  
(3.97)

\[
H_i^0 = \mu_i^0 - T \frac{d\mu_i^0}{dT}
\]  
(3.98)

\[
G_i^0 = \mu_i^0
\]  
(3.99)
3.12 EQUILIBRIUM OF PHASES [2,6,8,11,12]

In many industrial processes there is a coexistence of two or more phases. When there is mass transfer from one phase to the other the phases are not at equilibrium. The study of the mass transfer in these processes requires exact knowledge of the phases at equilibrium. In this clause 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, when these properties have the same value in both phases. For example, we have

- Thermal equilibrium when the temperature $T$ is the same in all phases.
- Hydrostatic equilibrium, when the pressure $P$ is the same in all phases.
- 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.

3.12.1 Phase Rule

For a closed, isolated system consisting of several phases $a$, $b$, $c$, … 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 all the phases, since $dP$, $dT$, and $dn_i$ are zero it is derived that, for every component $i$, $\mu_a^i = \mu_b^i = \mu_c^i = \ldots$

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.

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

$$F = C + 2 - P \quad (3.100)$$

For example, in the $P$, $T$ diagram of Figure 3.1 for a pure substance we observe that for the regions of only one phase $P = 1$ and $F = 2$, 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 $T$, that there is no degree of freedom and $P = 3$ and $F = 0$ which means 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 (Figure 3.1) 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 become more and more similar in density and molar volume and the interphasial separation line become less and less distinct. Finally, at the point C the two phases become identical and their interphasial line disappears. Beyond C there is no liquid or vapor phase, but only one single fluid phase.

At the critical point

$$\frac{\partial P}{\partial V} = 0, \frac{\partial^2 P}{\partial V^2} = 0$$

(3.101)

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.

3.12.2 Chemical Potential in Phase Equilibria [7,11]

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

$$\mu_i^a = \mu_i^b$$

(3.102)

or

$$\mu_i^{0,a} + RT \ln n_i^a = \mu_i^{0,b} + RT \ln n_i^b$$

(3.103)
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

$$\mu_{i}^{0,a} = \mu_{i}^{0,b} \quad (3.104)$$

and consequently from Equation 3.103

$$a_{i}^{a} = a_{i}^{b} \quad (3.105)$$

but this does not mean necessarily that the activity coefficients $\gamma_{i}^{a}, \gamma_{i}^{b}$ will be equal since usually $x_{i}^{a} \uparrow x_{i}^{b}$.

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

$$\mu_{i}^{v} = \mu_{i}^{0,v} + R T \ln \frac{f_{i}^{v}}{f_{i}^{0,v}} \quad (3.106)$$

while for the liquid phase

$$\mu_{i}^{l} = \mu_{i}^{0,l} + R T \ln \frac{\lambda_{i}^{l}}{\lambda_{i}^{0,l}} = \mu_{i}^{0,l} R T \ln a_{i}^{l} \quad (3.107)$$

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

$$\frac{f_{i}}{f_{i}^{0}} = \frac{\lambda_{i}}{\lambda_{i}^{0}} = a_{i} \quad (3.108)$$

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

### 3.12.3 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.
Figure 3.2 shows a vapor-pressure-composition ($X = \text{mole fraction}$) diagram for an ideal mixture of two liquids. At any mole fraction between 0 and 1 the vapor pressure of the mixture is

$$P_{\text{mix}} = P_A (1 - X) + P_B X$$  \hspace{1cm} (3.109)

Figure 3.3 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 diagram similar to Figure 3.3 can be drawn relating $T$ with $X$. 

![Figure 3.2](image1.png)

**FIGURE 3.2** Vapor–pressure composition diagram for an ideal mixture of two liquids A and B.

![Figure 3.3](image2.png)

**FIGURE 3.3** Vapor–pressure composition diagram for a real mixture of two liquids.
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 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.

Figure 3.4 shows the P, T diagram of a binary liquid mixture at a constant composition. Since in that 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 Figure 3.4, the region included inside the ABCDE curve is in the place of the vaporization line of Figure 3.1. 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 of 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 a curve ABCDE and one critical point.

Similar behavior is observed for the processes of fusion and sublimation and it is not necessary to be considered.

### 3.12.4 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 $z = P V_m / RT$ defined in Section 3.10 expresses the deviations of the real gases from ideality and it is different for the different gases of the same P and T.
However, it has been observed, by defining as reduced pressure $P_r$, reduced temperature $T_r$, and reduced molar volume $V_{m,r}$ by the relations

$$P_r = \frac{P}{P_C}, \quad T_r = \frac{T}{T_C}, \quad V_{m,r} = \frac{V_m}{V_{m,c}}$$ (3.110)

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

This is known as the Van der Waals principles of corresponding states.

The critical compressibility factor

$$z_C = \frac{P_C V_{m,c}}{R T_C}$$ (3.111)

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

$$z = F(P_r, T_r)$$ (3.112)

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

### 3.12.5 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 relation

$$\Delta M_i^{ab} = M_i^b - M_i^a$$ (3.113)

Thus, for the case of vaporization we have

$$\Delta V_i^{lv} = V_i^v - V_i^l$$ (3.114)

$$\Delta H_i^{lv} = H_i^v - H_i^l$$ (3.115)

$$\Delta S_i^{lv} = S_i^v - S_i^l$$ (3.116)

where by $l$ and $v$ we mean liquid and vapor, respectively.

Knowing that at equilibrium

$$\mu_i^l = \mu_i^v$$
or

\[ G_i^* = G_i \]  \hspace{1cm} (3.117)

For a two phase, one component, system at each phase

\[ G_i = H_i - T S_i \]  \hspace{1cm} (3.118)

and

\[ dG_i = S_i dT - V_i dP \]  \hspace{1cm} (3.119)

From Equations 3.117 through 3.119 it is finally derived

\[ \frac{dP_{i\text{sat}}}{dT} = \frac{\Delta S_{i\text{v}}}{\Delta V_{i\text{v}}} \]  \hspace{1cm} (3.120)

where the \( P_{\text{sat}} \) is the vapor pressure at the equilibrium of the two phases.

\[ \frac{dP_{i\text{sat}}}{dT} = \frac{\Delta H_{i\text{v}}}{\Delta V_{i\text{v}}} \]  \hspace{1cm} (3.121)

From Equations 3.120 and 3.121 we can calculate the entropy and enthalpy change of vaporization.

### 3.13 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 covers the whole range of concentration \textit{solvent}, the component with the limited solubility \textit{solute} and the mixture \textit{solution}. When the solvent is in excess and the solute in low concentration the solution is called dilute solution.

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

\[ \mu_i = \mu_i^0 + R T \ln \gamma_i = \mu_i^0 + R T \ln \gamma_i x_i \]  \hspace{1cm} (3.122)

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 \( x_i \to 1 \) then also \( \gamma_i \to 1 \) and the solvent behaves as an ideal mixture. At these compositions near the pure solvent the partial pressure of fugacity of the solvent is proportional to its mole fraction.
\[ P_i = P_i^0 x_i \quad \text{or} \quad f_i = f_i^0 x_i \] (3.123)

where \( P_i, f_i, x_i \) the partial pressure, fugacity, and mole fraction of the solvent and \( P_i^0, f_i^0 \) are the vapor pressure, 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 (3.123) express what we call as \textit{Raoult's law} (Figure 3.1).

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 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 the 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 \( x_i \)

\[ f_i = K x_i \] (3.124)

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

Relation (3.124) is called \textit{Henry's law} and \( K \) is a constant called Henry’s constant.

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

\[ \mu_i = \mu_i^0 + R T \ln \gamma_i x_i = \mu_i^0 + R T \ln \frac{f_i}{f_i^0} \] (3.125)

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.

In the region of very dilute solutions where relation (3.124) is valid the solute behaves in an, by convention, ideal way which is different from near the pure solvent. Figure 3.5 shows the variation of fugacities of the solute and the solvent in function of the molar fractions for a binary ideal or real system at constant \( P, T \).

The standard chemical potential of a solvent is given by the relation [2]:

\[ \mu_2^0(T, P^0) = \mu_2^* (T, P) + \int_{P^0}^P V_2^*(T, P) dP \] (3.126)

where \( P^0, P \) are the standard pressure and the pressure of the solution, respectively, \( * \) means pure solvent, and \( V_2^* \) volume of pure solvent.
The standard chemical potential of a solute is given by relation [2]:

\[
\mu_1^0(T) = \left[ \mu_1(T, P, m_1) - RT \ln \frac{m_1}{m_1^0} \right] + \int_p^{P^0} V_1^\infty(T, P)dP
\]

(3.127)

where \( \infty \) means conditions at infinite dilution, \( \mu_1(T, P, m_1) \) the chemical potential at \( T, P, m_1 \), \( m_1^0 \) the standard molality, \( P^0 \) the standard pressure, and \( V_1^\infty \) 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.

### 3.14 ELECTROLYTE SOLUTION [1,2,8]

Electrolytes are a special class of solute substance, 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 from which they are constituted. 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 rest of all the 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 ion, respectively, in the molecule of the electrolyte, we can write

\[
\mu_{AB} = V_+ \mu_+ + V_- \mu_-
\]

(3.128)
and using molalities

\[ \mu_+ (T, P, m) = R \, T \, \ln m_+ + R \, T \, \ln \gamma_+ (T, P, m) + \mu_0^+ (T, P) \] (3.129)

\[ \mu_- (T, P, m) = R \, T \, \ln m_- + R \, T \, \ln \gamma_- (T, P, m) + \mu_0^- (T, P) \] (3.130)

Substituting Equations 3.129 and 3.130 into Equation 3.128 we obtain

\[ \mu_{MA} = R \, T \, \ln m_+ \gamma_+ + R \, T \, \ln m_- \gamma_- (T, P, m) + V_+ \mu_+^0 (T, P) + V_- \mu_-^0 (T, P) \] (3.131)

The mean activity coefficient is defined as

\[ \gamma_\pm = \gamma_+ \gamma_- \] (3.132)

and the mean molality

\[ m_\pm = m_+ \gamma_+ m_- \gamma_- \] (3.133)

where \( V = V_+ + V_- \).

From Equations 3.132, 3.133, and 3.131 and by defining

\[ \mu_{MA}^0 (T, P) = V_+ \mu_+^0 (T, P) + V_- \mu_-^0 (T, P) \] (3.134)

\[ \mu_{MA} (P, T) = V \, R \, T \, \ln m_+ + V \, R \, T \, \ln \gamma_+ (T, P, m) + \mu_{MA}^0 (T, P) \] (3.135)

The \( m_\pm \) and \( \gamma_\pm \) and \( \mu_{MA}^0 \) (T, P) have a similar meaning as for the nonelectrolyte solutions when \( \gamma_\pm \rightarrow 0 \) then \( \gamma_\pm \rightarrow 0 \) and \( \mu_{MA}^0 \) (T, P) is equal to \( \mu_{MA}^0 \) (T, P) at the reference state.

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

### 3.14.1 **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 at a formula giving the mean ionic activity coefficient, which for very dilute solutions by approximation takes the form:

\[ \ln \gamma_\pm = C \, I^{1/2} \, z_+ \, z_- \] (3.136)
where \( C = (2 \pi N_0 \rho_s)^{1/2} (e^2/4 \pi \varepsilon K T)^{3/2} \)

\( N_0 \) = Avogadro’s number
\( \rho_s \) = density of the pure solvent
\( e \) = the charge on a proton
\( \varepsilon = \varepsilon_0 \varepsilon_r \), \( \varepsilon_r \) is the dielectric constant of the solvent and \( \varepsilon_0 \) is the dielectric constant of a vacuum
\( T \) = temperature of solution
\( K = R/N_0 \), \( R \) = gas constant

I is called ionic strength and is given for a 1–1 type electrolytes by

\[
I = \frac{1}{2} \left( m_z^+ z_+^2 + m_z^- z_-^2 \right)
\]

(3.137)

\( m_z^+, m_z^- \), the molalities of the ions
\( z_+^2, z_-^2 \), the electrical charges of the ions.

The Debye–Hückel law is very accurate for very dilute solution of strong electrolytes.
For mixed electrolytes the theory is still valid with

\[
I = \frac{1}{2} \sum_i m_i z_i^2
\]

(3.138)

### 3.15 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, various 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, they use catalysts or other means.

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 the appropriate catalyst for this reaction.

#### 3.15.1 ENTHALPY OF FORMATION AND ENTHALPY OF REACTION [4,5]

The heat of formation of any component 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.

\[
\Delta H_F = h_{\text{compound}} - \sum (v_i h_i)_{\text{elements}}
\]

(3.139)

where \( v_i \) is the stoichiometric coefficient.

By conversion, the standard enthalpies of formation \( h_i \) of all elements of their move stable state is considered as zero, therefore

\[
\Delta H_F = h_{\text{compound}}
\]

(3.140)

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

The quantities of heat transferred during the vaporization, or fusion which is for a single compound and constant pressure taking place at constant \( T \) are called heat effects.

These heat effects together with the heat mixing, the heat of solution (heat of mixing for the case of a solution), as well as the heat of reactions are studied by the branch of thermodynamics, called thermochemistry and the instrument of these function are called calorimeters.

### 3.15.2 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

\[
H_P - H_r = (H_P - H_{P0}) + (H_r - H_{r0})
\]

(3.141)

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.

\[
\Delta H_R = H_{P0} - H_{r0} = \sum_{\text{products}} (v h) - \sum_{\text{reactants}} (v h)
\]

(3.142)
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, 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.

\( (H_f - H_{f0}) \) 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.

### 3.15.3 Equilibrium Constant: Affinity of a Reaction [6,7,11]

Let us consider the reaction

\[
\begin{align*}
&v_1c_1 + v_2c_2 + v_3c_3 + v_4c_4 \\
&\text{(3.143)}
\end{align*}
\]

at constant \( T, P \)

where \( c_i \) are the constituents and \( v_i \) the stoichiometric coefficients.

Equation 3.46 at \( P, T \) constant gives

\[
\text{d}G_{T,P} = \mu_1 \text{d}n_1 + \mu_2 \text{d}n_2 + \mu_3 \text{d}n_3 + \mu_4 \text{d}n_4 \quad \text{(3.144)}
\]

and for a reaction

\[
\begin{align*}
-\frac{\text{d}n_1}{v_1} = -\frac{\text{d}n_2}{v_2} = \frac{\text{d}n_3}{v_3} = \frac{\text{d}n_4}{v_4} = \text{d}\xi
\end{align*}
\]

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

Based on Equations 3.144 and 3.145 and Equation 3.42 it follows:

\[
\text{d}G_{T,P} = (\mu_1 \text{d}n_1 + \mu_2 \text{d}n_2 - \mu_3 \text{d}n_3 - \mu_4 \text{d}n_4) \text{d}\xi \leq 0 \quad \text{(3.146)}
\]

the sign of the parentheses determines the sign of the \( \xi \) and consequently the direction of the reaction.

At equilibrium where

\[
\text{d}G_{T,P} = 0 \quad \text{(3.147)}
\]

\[
\mu_1 \text{d}n_1 + \mu_2 \text{d}n_2 = \mu_3 \text{d}n_3 - \mu_4 \text{d}n_4 \quad \text{(3.148)}
\]

The quantity \( \mu_1 \text{d}n_1 + \mu_2 \text{d}n_2 - \mu_3 \text{d}n_3 - \mu_4 \text{d}n_4 \) was introduced by De Dander (16) and was called by him as the affinity \( A_f \).
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From Equation 3.148 using $\mu_i = \mu_i^0 + RT \ln a_i$ (relation (3.91)) it is obtained:

$$A_f = A_f^0 - RT \ln \left( \frac{a_3^{u_i} \cdot a_4^{v_i}}{a_1^{u_i} \cdot a_2^{v_i}} \right)$$ (3.149)

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

The quantity

$$\left( \frac{a_3^{u_i} \cdot a_4^{v_i}}{a_1^{u_i} \cdot a_2^{v_i}} \right) = Q_a$$ (3.150)

is called reaction quotient.

At equilibrium where $A_f^0 = 0$ 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

$$A_f^0 = RT \ln K_a$$ (3.151)

$$A_f = RT \ln \frac{K_a}{Q_a}$$ (3.152)

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.

REFERENCES


