THE CONCEPTS OF EQUILIBRIUM CHEMICAL THERMODYNAMICS

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Abstract

The thermodynamic criteria for equilibrium between phases are expressed in terms of special properties; thermodynamics also provides the equations which relate these properties to phase compositions, temperature, and pressure. Thus, the connection between equilibrium criteria and physical reality is established primarily through the fugacity coefficient 0j for vapour phases and the activity coefficient 71 for liquid phases. Equations are presented and illustrated for the special case for which the liquid phase is an ideal solution and the vapour phase is an ideal gas. The various relationships among thermodynamic properties developed in this paper apply to systems in equilibrium. Equilibrium, thus, implies a situation in which there is no macroscopic change with respect to time. Actually, a true state of equilibrium is probably never reached, owing to continual variations in the surroundings and to retarding resistances.

Introduction

The word 'thermodynamics' means heat power, or power developed from heat. In its broader sense, thermodynamics is the science, which deals with transformation of energy of all kinds from one form to another. The general restrictions within which all such transformations are observed to occur are known as the first and second laws of thermodynamics. These laws cannot be proved in the mathematical sense. Rather, their validity rests upon experience (Smith et al., 1996).

Thermodynamics deals with systems in equilibrium. It may be used to predict the amount of energy required to change a system from one equilibrium state to another; it may not be used to predict how fast a change will take since the system is not in equilibrium during the process. Heat transfer supplements the first and second principles of thermodynamics by providing additional experimental rules, which may be used to establish energy-transfer rates (Holman, 1983). Thermodynamics may be used to predict the final equilibrium temperature of a hot steel bar-water combination, it will not tell us how long it takes to reach this equilibrium condition or what the temperature of the bar will be after a certain length of time before the equilibrium condition' is attained. This limitation is solved by the application of heat transfer (Treybal, 1980).

Thermodynamics Relation

The basic relation connecting the Gibbs energy to the temperature and pressure in any closed system is expressed as:

$$D(nG) = (nV)dP - (nS)dT \qquad , \qquad \dots\dots\dots\dots\dots \qquad (1)$$

If the different amount of liquid is caused to evaporate at constant temperature and pressure, the equation reduces to $d(nG) = 0$ for the process. This is because the number of moles, n, is constant and this requires the molar Gibbs energy of the vapour to be identical with that of the liquid. Thus, we have that for two phases A and B of a pure species coexisting at equilibrium,

$$G^A = G^B \qquad \dots\dots\dots\dots\dots\dots \qquad (2)$$

where G^A and G^B are the molar Gibbs energies of the individual phases. If the two phases continue to coexist and the temperature is changed, then the pressure must also change in accordance with relation between vapour pressure and temperature. Thus, we have that.

$$dG^A = dG^B \qquad \dots\dots\dots\dots \qquad (3)$$

Substituting for dG^A and dG^B from the equation

$$dG = VdP - SdT \qquad \text{...............} \qquad (4)$$

we have that

$$V^A dP^{sat} - S^A dT = V^B dP^{sat} - S^B dT \qquad \text{.........} \qquad (5)$$

On rearranging, we have

$$\frac{dP^{sat}}{dT} = \frac{S^B - S^A}{V^B - V^A} = \frac{\Delta S^{AB}}{\Delta V^{AB}} \qquad \text{...........} \qquad (6)$$

The changes ΔS^{AB} and ΔV^{AB} **are the** changes, which **occur when a unit amount of a pure chemical** specie **is transferred from** phase A to phase B **at constant temperature and pressure. Integration** of the relation,

$$dH = TdS + VdP \qquad \text{.................} \qquad (7)$$

gives the latent heat of phase transition:

$$\Delta H^{AB} = T \Delta S^{AB} \qquad \text{.............................} \qquad (8)$$

Substituting for ΔS^{AB} from equation (8) into equation (6) gives

$$\frac{dP^{sat}}{dT} = \frac{\Delta H^{AB}}{T \Delta V^{AB}} \qquad \text{.............................} \qquad (9)$$

Equation (9), the Clapeyron equation, is an exact thermodynamic relation that provides a vital connection between the properties of different phases. On application to the calculation of latent heats of vaporization, its use presupposes knowledge of a suitable vapour pressure vs temperature relation (Smith et al., 1996). Empirical in nature, the relation *is* approximated by the equation

$$\ln P^{sat} = A - B \qquad \text{...........} \qquad (10) \ '$$
$$\overline{} \ T$$

where A and B are constants for a given species. Equation (10) gives a rough approximation of the vapour pressure relation for its entire temperature range, from the triple point to the critical point. Moreover, it is an excellent basis for interpolation between values that are reasonably spaced (Perry, 1998). Satisfactory for more general use, the Antoine equation has the form

$$\ln P^{sat} = A - \frac{B}{T+C} \qquad \text{.............} \qquad (11)$$

A principal advantage of this equation is that valuer of the constant A, B and C readily available for a large number of species.

In this work, the Clapeyron equation is preferred to the Antoine equation because the values for the Antoine constants are available for only a specific temperature range unlike the Clapeyron equation, which approximates the entire temperature range.

The objective of this work is to elucidate, extol and rekindle the basic phenomenal principles of equilibrium chemical thermodynamics in the minds of chemical engineers and the allied professionals so as to make the application continuously fresh and worthwhile.

Theory
Solution Thermodynamics
The Ideal Gas and Ideal Solution

An ideal gas is a model gas comprising imaginary molecules of zero volume that do not interact. For ideal gases, a mixture property depends only on the properties of the pure ideal gases which comprise the mixture. No information about the mixture other than its composition is required. This circumstance is not limited to ideal gases, but extends more generally to any solution wherein all the molecules are of the same size and all the forces between molecules are equal. Equations based on these characteristics provide a model of behaviour known as the ideal solution (Smith et al, 1996; Smith, 1963).

The ideal gas, thus, fulfils the conditions of solution ideality as a special case. Each chemical species in an ideal gas mixture, therefore, has its own private properties uninfluenced by the presence of other species. The partial pressure of species / in a gas mixture is given by

$$PI = x_jP \qquad (j = 1, 2, \ldots, N) \qquad \ldots\ldots\ldots(12)$$

where X_j is the mole fraction of species j. The sum of partial pressures clearly equals the total pressure; Dalton's law of partial pressure.

Gibbs theorem for a mixture of ideal gases states that, a total thermodynamic property of an ideal gas mixture is the sum of the total properties of the individual species, each evaluated at the mixture temperature but at its own partial pressure.

This is expressed mathematically for general property M by the equation,

$$M^{ig}(T, P) = \Sigma y_i M_i^{ig}(T, PI) \qquad \ldots\ldots\ldots\ldots \qquad (13)$$

where the superscript "ig" denotes an ideal gas property.

Since he enthalpy of an ideal gas is independent of pressure, we have that

$$H_i^{ig}(T, Pi) = H_i^{ig}(T, P) \qquad \ldots\ldots\ldots\ldots \qquad (14)$$

Hence, equation (13) becomes

$$H_j^{ig} = \Sigma y_j H_j^* \qquad \ldots\ldots\ldots\ldots \qquad (15)$$

Analogous equations apply for U^{ie} and Cp^{is} which are properties that are independent of pressure. The entropy of an ideal gas depends on pressure. Thus,

$$dS_i^{ig} = - Rd \ln P \text{ at constant } T \qquad \ldots\ldots\ldots \qquad (16)$$

Integrating from Pi to P, we have

$$S_i^{ig}(T, P) - S_j^{ig}(T, PO = - R \quad \ln P \qquad Pi = ViER \ln_{yi} P - \ln P = - R \ln V_j \qquad . \qquad (17)$$

hence, $S_i^{ig}(T, Pi) S_i^{is}(T, P) - R \ln y_i \qquad P \qquad \ldots\ldots\ldots\ldots \qquad (18)$

Substituting into equation (12) and rearranging gives

$$S^{ig} = \Sigma y_i S_i^{ie} - R \Sigma y_i \ln y_i \qquad \ldots\ldots\ldots\ldots (19)$$

For the Gibbs energy of an ideal gas mixture,

$$G^{ig} = H^{ig} - TS^{ig} \qquad \ldots\ldots\ldots\ldots\ldots(20)$$

Substituting for H^{ig} and S^{ig} from equation (15) and (19),

$$G^{is} - \Sigma y_i G_i^{ie} + RT \Sigma y_i \ln y_i \qquad \ldots 7\ldots (21)$$

or $\qquad n^{ig} = G_i^{ig} \qquad RT \ln y_j \qquad \ldots\ldots\ldots\ldots\ldots(22)$

When ideal gases are mixed, there is no volume change of mixing because the molar volume of the mixture, V^s and the molar volumes of the pure species V_j^{ig} are all equal to $/P$. Thus for ideal gases, the equation $\qquad V^{ig} - \Sigma y_i V^{ig} \qquad \ldots\ldots\ldots \qquad (23)$

is a simple identity. However, an analogous equation written for the ideal solution model provides an essential relation,

$$V^{id} = \Sigma x_i V_i \qquad \ldots\ldots\ldots\ldots \qquad (24)$$

where V^{id} is the molar volume of the ideal solution formed from pure species with actual molar volumes V_i at the temperature and pressure of the mixture. We can also write,

$$H^{id} = \Sigma x_j H_j \qquad \ldots\ldots\ldots\ldots\ldots\ldots \qquad (25)$$
$$S^{id} = \Sigma x_j S_i - R \Sigma x_i \ln x_i \qquad \ldots\ldots\ldots\ldots\ldots\ldots \qquad (26)$$
$$G^{id} = \Sigma x_i G_i + RT \Sigma x_j \ln x_i \qquad \ldots\ldots\ldots\ldots\ldots\ldots \qquad (27)$$
$$\mu_j^{id} = G_j + RTS \ln X_i \qquad \ldots\ldots\ldots\ldots\ldots\ldots \qquad (28)$$

for the enthalpy, entropy, Gibbs energy and chemical potential of species respectively.

Ideal solution behaviur is often approximated by solutions comprised of molecules not too different in size and of the same chemical nature. Thus, a mixture of isomers such as ortho-, meta-, and para-xylene, conforms very closely to ideal solution behaviour. So do mixtures of adjacent members of a homologous series such as benzene and toluene (King, 1992).

Fugacity and Fugacity Coefficient

The chemical potential, μ_i, plays a vital role in both phase and chemical reaction equilibrium. However, the chemical potential exhibits certain unfortunate characteristics which discourages its use in the solution of practical problems. The Gibbs energy, and hence μ_i, is defined in relation to the internal energy and entropy, both positive quantities, for which absolute values are unknown. Moreover, μ_i approaches negative infinity when either P or x_j approaches zero. While these characteristics do not preclude the use of chemical potential, the application of equilibrium criteria is facilitated by introduction of the fugacity, a quantity that takes the place of μ but which does not exhibit its less desirable characteristics (Perry, 1008; Smith, 1963). The origin of the fugacity concept resides in the equation

$$G^{ig} = Fi(T) + RT \ln P \qquad \ldots\ldots\ldots(29)$$

where r,(T) is a function of temperature only and is the integration constant for a given temperature. For a real fluid, an analogous equation is

$$Gi^\wedge \quad F,(T) + RTIn/j \qquad\qquad (30)$$

Here, a new property $f\backslash$ replaces the pressure P. This serves as a partial definition of the fugacity, $f\backslash$. Subtracting equation (29) from equation (30) at the same temperature and pressure, we have

$$Gj - Gi^{ig} = RTIn'Vp \qquad .... \qquad (31)$$

$Gj - Gi^{is}$ is the residual Gibbs energy, Gj^R. The dimensionless ratio $^{fl}/_P$ gives another new property called the fugacity coefficient, Φ_i. This,

$$G_i^R \quad RT \ In \ \Phi_i \qquad .... \qquad (32)$$

The definition of fugacity is completed by setting the ideal-gas-state fugacity of pure species *i* equal to its pressure,

$$f_i^{ig} \quad P \qquad .... \qquad (33)$$

Thus, for an ideal gas, $Gj^R = O, \quad Oj = 1.$

Thus, for an ideal gas, $GI^R = \quad O, O_; = 1.$

The definition of the fugacity of a species in solution is parallel to the definition of the pure species fugacity.

An equation analogous to the ideal gas expression is written for species I in a fluid mixture.

$$Hi \quad = r^*i(T) + RTIn/j \qquad .... \qquad (34)$$

where the partial pressure x_iP is replaced by $f\backslash$, the fugacity of species *i* in solution. (Since it is not a partial molar property, it is identified by a circumflex rather than an over bar).

Subtracting from equation (34), we have at the same pressure, temperature and composition that,

$$u.i - Uj^{ig} = RTIn'Vxtp \qquad .... \qquad (35)$$

Analogous to the defining equation for the residual Gibbs energy of a mixture, $G^R \quad G - G^{i8}$, is the definition of a partial molar residual Gibbs energy.

$$G^R = Gi-Gi^{ig} = m-Hi^{i8} \qquad ....(36)$$

Therefore, $G_(^R = RT \ In \ \Phi_i \qquad ....7 .... (37)$

where by definition, $\Phi i = {}^{fl}/_{x-iP} \qquad .... \qquad (38)$

The dimensionless ratio <t>j is called the fugacity coefficient of species *i* in solution.

For an ideal gas, Q^R is necessarily 0; therefore $\Phi_i lg = 1$ and $f_j^{lg} = X_iP$

Thus, the fugacity of species I in an ideal gas mixture is equal to its partial pressure (Smith et al, 1996; Underwood, 1932).

Equilibrium

For a PVT system, its intensive state is established when its temperature, pressure and the compositions of all phases are fixed. However, for equilibrium states, these variables are not all independent and fixing a limited number of them automatically establishes the others. This number of independent variables is given by the phase rule, and is called the number of degrees of freedom of a system. It is the number of variables which may be arbitrary and which must be so specified in order to fix the intensive state of a system at equilibrium. This number is the difference between the number of variables needed to characterize the system and the number of equations that may be written connecting these variables.

Discussion
Vapour - Liquid Equilibrium (VLE)

Vapour - liquid equilibrium relationships are needed for the solution of many engineering problems. The required data can be, and often are, directly measured by experiment. However, such measurements become rapidly more difficult as the number of constituents increases. This is the incentive for application of thermodynamics to the calculation of phase equilibrium relationships (McCabe et al, 1976). The general VLE problem involves a multi-component system of N constituent species for which the independent variables are T, P, N-l liquid phase mole fraction's and N-l vapour phase mole fractions. Thus, there are 2N independent variables, and application of the phase rule shows that exactly N of these variables must be fixed to establish the intensive state of the system. This means that once N variables have been specified, the remaining N variables can be determined by simultaneous solution of the N equilibrium relations.

$$/,' = /i^v \ (i=1,2,\ldots, N) \qquad\qquad (39)$$

where superscripts i and v denote the liquid and vapour phase respectively.

In practice, either T or P and either the liquid phase or vapour phase composition are specified, thus fixing $1 + (N-l) = N$ independent variables. The remaining N variables are subject to calculation, provided that sufficient information is available to allow determination of all necessary thermodynamics properties (Billet, 1979).

Gamma I Phi Approach

For many systems, the Pressure is low enough that a relatively simple equation of state, such as the two-term viral equation is satisfactory for the vapour phase. Liquid phase behaviour, on the other hand, may be conveniently described by an equation for the excess Gibbs energy, from which activity coefficients are derived. The fugacity of species ; in the liquid phase is then given by

$$f_\backslash = Y_iX_i/i \qquad \text{.........................} \qquad (40)$$

while the vapour phase fugacity is given by

$$f_i \quad = \quad O_{iyi}P \qquad \text{.........................} \qquad (41)$$

Thus, from equation (39)

$$Y_iX_i/i = 4>,y,P(/ \quad 1,2,....N) \qquad \text{...............} \qquad (42)$$

Application of the above equation represents what is called the gamma/phi approach to VLB calculations.

The fugacity, $f_\backslash$ of pure compressed liquid / must be evaluated at the temperature and pressure of the equilibrium mixture. Two steps are involved:

First, the fugacity coefficient of saturated vapour $O_j^v = Q_j^{sal}$ is calculated by an integrated form of

$$InO> = I \qquad (z-1)dP$$
$$* \qquad P \qquad \text{............} \qquad (43)$$

Written for pure species / and evaluated at temperature T and the corresponding vapour pressure $P - P_j^{sal}$ for pure species, equation (39) becomes

$$\_ f_i^v = f_f = /r \qquad \text{.....................} \qquad (44)$$

where $/j^{"at}$ indicates the value both for saturated liquid and for saturated vapour. The corresponding fugacity coefficient is given as

$$\frac{fh.sat \quad \_ \quad r\,sat}{P_i^U} \qquad \text{.................................} \qquad (45)$$

This applies equally to saturated vapour and to saturated liquid at a given temperature T. Thus, we can write

$$4>_i^v = CIV \qquad \text{.........................} \qquad (46)$$

The second step is the evaluation of the change in fugacity of the liquid with a change in pressure to a value above or below P_j^{sat}. For this isothermal change of state from saturated liquid at P_i^{sat} to liquid at pressure P, equation (43) is integrated to give

$$Gi-Gj^{;631} = \quad I \quad sat \qquad \text{............} \qquad (47)$$
$$PI$$

where

$$G_f - Gi^{sal} - RTIn/\_V_jdP \qquad \text{..............} \qquad (48)$$
$$\underset{Ji}{/\bullet sat}$$

so that

$$In/L^\wedge \quad 1\_| \qquad sat \quad {}^{V_i\,dp} \qquad \text{.......................} \qquad (49)$$
$$y T^{at} \quad RT$$

Since V_j, the liquid phase molar volume, is a very weak function of P at temperatures well below T_c, an excellent approximation is often obtained when evaluation of the integral is based on the assumption that V_j is constant at the value for saturated liquid, V_j^l. Thus,

$$\frac{InJL - V_i'(P\sim P_i^{Sat})}{J?* \qquad RT} \qquad \text{...................} \qquad (50)$$

Substituting for fisat from equation (45) and solving for fj gives

$$f_i - \Phi^{sat}P_i^{sat}exp V_i'(P-p_i^{sat}) \underline{\quad\quad} \qquad \text{..................} \qquad (51)$$
$$RT$$

The exponential is known as the Poynting factor.

Equation (42) can now be written as

$$y_i P \phi_i = X_i Y_i P_i^{sat} \quad (l = 1, 2, \ldots N) \quad \ldots\ldots\ldots\ldots \quad (52)$$

where $\quad \dfrac{\Phi_i}{\Phi_i^{\,sat}} = \Phi_i \exp\dfrac{-V_i^l(P - P_j^{sat})}{RT} \qquad \ldots\ldots\ldots\ldots \quad (53)$

Application of equation (52) to VL'E for which the vapour phase is an ideal gas and the liquid phase an ideal solution reduces it to a very simple expression. For ideal gases, fugacity coefficients are unity and for ideal solutions, the activity coefficients are also unity (Daza et al, 2003; Savarit, 1922). Thus equation (52) reduces to

$$Y_i P = X_i P_j^{*''} \qquad \ldots\ldots\ldots\ldots \quad (54)$$

This is an expression for Raoult's law. If the vapour pressure - temperature functions of the components are at hand, Raoult's law is used to calculate the entire boiling point - mole fraction relations of both vapour and liquid phases for a constant pressure system (McCabe et al., ,1976).

Equilibrium Ratio

The equilibrium ratio, also known as K-value, is a measure of how a given chemical species distributes itself between liquid and vapour phases $K_{\hat{v}_1} = y_i / x_i \cdot$

Although it adds nothing to thermodynamic knowledge of VLE, its use may make for computational convenience, allowing the formal elimination of one set of mole fractions $y\backslash$ or $X\{$, in favour of the other. Moreover, it characterizes lightness of a constituent species. For a light species, tending to concentrate in the vapour phase, $K > 1$, and for a heavy species, tending to concentrate in the liquid phase, $K < 1$ (Perry, 1998; Henley et al., 1981). Empirical correlations for K-values found in older literature have little relation to thermodynamics Their proper evaluation comes directly from equation (42) Thus,

$$K_i - \dfrac{YJ = Yi/i}{xi \quad \&P} \qquad \ldots\ldots\ldots\ldots \quad (56)$$

When Raoult's law applies, this becomes $\qquad\qquad\qquad$ i

$$K_l = P_i^{Sal}/P \qquad \ldots\ldots\ldots\ldots \quad (57)$$

In general, K-values are functions f T, P, liquid composition and vapor composition, making their direct and accurate correlation impossible. Equation (57) is an equivalent statement of Raoult's law.

Where applicable, it gives a simple method of calculation vapour - liquid equilibria. The equation applies at a specific temperature ad requires only values of P_i^{sat} the vapour pressures of the components at that temperature.

An Idea Binary Solution

For an idea solution, the equilibrium partial pressure Pi of a constituent at a fixed temperature equals the product of its vapour pressure when pure at this temperature and it's me fraction in the liquid (Iglesias, 2003) This is Raoult's law.

$$P_A = P_A^{SH'}X \qquad \ldots\ldots\ldots\ldots \quad (58)$$

and $\qquad P_B = P_B^{sat}(1->0) \qquad \ldots\ldots\ldots\ldots \quad (59)$

If the vapour phase is also ideal,

$$P-P_A + P_B = P_A^{sat}x + P_B^{sat}(1-x) \qquad \ldots\ldots\ldots\ldots \quad (60)$$

and the total, as well as the partial pressures, are linear in x at a fixed temperature. The equilibrium vapour composition can then be computed at this temperature. *

$$y \sim\sim f_i A_{-i} {}^\wedge A\_JL— \dfrac{p}{P} \quad \dfrac{p\ sac.}{P} \qquad \ldots\ldots\ldots\ldots \quad (61)$$

and $\quad 1 - y^* = \dfrac{PE\_}{P} = \dfrac{P_B^{Si''}(1-x)}{P} \qquad \ldots\ldots\ldots\ldots \quad (62)$

The greater the distance between the equilibrium curve and the diagonal, the greater the difference in liquid and vapour compositions and the easier the separation by distillation CQaza et al., 2003). One numerical measure of this is called the separation factor, or, particularly, in the case of

distillation, the relative volatility, a . This is the ratio of the concentration ratio of A and B in one phase to that in the other and is a measure of separability.

$$a = \frac{y^*/(1-y^*)}{x/(1-x)} = \frac{y^*(1-x)}{x(1-y^*)} \qquad \text{...............} \qquad (63a)$$

Equation (63) can also be written as shown below b substitution of equations (61) and (62). Thus, we have

$$\alpha = \frac{P_A^{sat}}{P_B^{SAT}} \qquad \text{.......................} \qquad (63b)$$

Relative volatility can also be expressed as the ratio of the K-values. The value of a will ordinarily change as x varies from 0 to 1. If $y^* = 1$ (except at $x = 0$ or 1), $a = 1$ and no separation is possible. The larger the value of a above unity, the greater the degree of separability (Trebal, 1980).

$$a - K_1/K_2 \qquad \text{.............................} \qquad (64)$$

Substituting and/or rearranging equation (63a) gives

$$y^* = \frac{ax}{1 + (a-1)x} \qquad \text{....................} \qquad (65)$$

Equation (65) provides an expression which for main purposes is a satisfactory empirical relation between y* and x for an ideal binary system at a given temperature and pressure (Henley et al., 1981).

Conclusion

The value of thermodynamics lies in he fact that its laws and certain accompanying definitions have been given mathematical expression. This has led to he development of a consistent network of equations from which a wide range of practical results and conclusions may be deduced. The universal applicability of this science is shown by the fact that it is employed alike by Physicists, chemists, and engineers. In each case the basic principles are the same, but the applications differ. The chemical engineer must be able to cope with a particularly wide variety of problems. Among the most important of these problems are the determination of heat and work requirements for man physical and chemical processes, and the determination of equilibrium conditions for chemical reactions and for the transfer of chemical species between phases (Smith et al, 1996, Billet, 1979).

Main practical applications of thermodynamics are to processes that involve multi-component mixtures, either gases or liquids. Since the composition of such a system frequently changes as the result of mass transfer or chemical reaction, a thermodynamics description of the system must take into account the influence of composition on its properties. The principal special case in solution thermodynamics, the ideal solution, does not adequately represent the behaviour of many systems of practical interest to chemical engineers. Nevertheless, the ideal solution is important, not only as a special case of approximate validity for certain systems, but also as a reference to which real solutions may be compared.

In engineering, the important thermodynamic systems are a gas, such as air; a vapour, such as stream; a mixture, such as gasoline vapour and air, and a vapour in contact with its liquid, such as liquid vaporized ammonia. Chemical thermodynamics deals with these systems and, in addition, with solids, surface films, and electric cells (Zemansky et al, 1984).

However, there are limitations. Thermodynamic considerations by themselves are not sufficient to allow calculations of the rates of chemical or physical processes. Rates depend on both driving force and resistance. Although driving forces are thermodynamics variables, resistances are not. Moreover, thermodynamics offers no clue to the mechanisms of either physical or chemical processes. The numerical results of a thermodynamics analysis are accurate only to the extent that the required data are accurate. The chemical engineer must work with a large number of chemical substances, frequently in mixtures, and adequate data are known for only a relatively few. Thus, he must learn to estimate results when only meager data are available (Smith et al, 1996; Zemansky et al., 1984; Underwood, 1932).

In spite of these limitations, the science of thermodynamics is remarkable in the number and variety of

conclusions that are based on two fundamental laws. All the rest is either definition or deduction. Thus, in order to apply the thermodynamic method, one must develop the ability to proceed logically from one deduction to the next, always making use of precisely defined terms.

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- The foundation of the concept of equilibrium relies on THERMODYNAMICS. - How fast will it achieve equilibrium? This question requires a KINETCS study. $2Fe + O_2 + 2H_2O$. Most chemical processes in living organisms take place at constant pressure. It is therefore convenient to have a specific definition of heat transfer under these conditions. The thermal content of a constant pressure substance is called enthalpy H. In a chemical transformation the variation of enthalpy is: $\Delta h = h_{final} - h_{initial}$. The concept of entropy is born from the idea that a spontaneous transformation leads to a dispersion of energy. Often in this process a dispersion of matter is also involved and this can contribute to the dispersal of energy in some systems.