

Basic Concept of Chemical Thermodynamics



Cyber Tech

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BASIC CONCEPT OF CHEMICAL THERMODYNAMICS

Manish Rathi

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PREFACE

This book "Basic Concept of Chemical Thermodynamics" is based on the latest syllabus for branches of all universities. The Subject matter has been discussed in such a simple way that the students will find no difficulty to understand it. The proofs of various theorems and examples has been given with minute details. This book provides all necessary information. The subject matter has been presented in a simple and systematic manner. To familiarize the student about expected type of questions in the examinations, important summary and review questions have been provided at the end of each chapter. The present edition has many new features. This approach is adopted for some main reasons.

Several sections in all these chapters have been rewritten and enlarged to make the text clear. So, the students written some queries and mistakes in this book. The author shall be gratefully to the readers who point out errors and omissions which inspite of all care might have been there.

The author will feel amply rewarded if the book serve the purpose for which it is meant. Suggestions for the improvement of the book are always welcome.

— Author

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BASIC CONCEPTS OF THERMODYNAMIC

INTRODUCTION

Thermodynamics of a process or partial differentiation and related mathematics without bothering how the process takes place. We shall be mainly discussing in this text what is called as “Equilibrium Thermodynamics” since most of the thermodynamic predictions are valid only for equilibrium phenomena. There is another branch of thermodynamics called “Non-equilibrium thermodynamics” which has developed into an organized discipline in the course of last few decades. Thermodynamic deals with energy changes and its relationship with work. It is based on three laws of thermodynamics which are used as axioms just as Newton’s laws of motion form the basis of classical mechanics. The first two laws based on facts observed in every day life. The predictions based on these laws have been verified in most cases and so far no case has been reported where the laws break down. The laws can be stated in mathematical form.

Hence, thermodynamics is an exact science. The thermodynamic theory can be developed without gaps in the argument using only moderate knowledge of mathematics. The remarkable feature of thermodynamics is that for the development of the theory, it is not necessary to assume the nature of fundamental particles or mechanism of the phenomena or processes as is done in molecular structure and kinetics. Whereas the first law is concerned with the equivalence of different forms of energy, the second law is concerned with the direction of physicochemical change and condition of equilibrium. The two laws deal with changes in thermodynamic variables but the third law attempts to evaluate such variables. Some of the obvious advantages from the first and second laws

of thermodynamics areas follows. Useful relations can be obtained from first law which are valid for both equilibrium and non-equilibrium situations. Further, on the basis of the first and second laws together, one can predict the effect of changes of pressure, temperature and composition on different varieties of physicochemical systems.

THERMODYNAMICS LAWS

The success of thermodynamics in various fields of science is based on the wide application of the laws of thermodynamics which are as well established, as widely accepted and as free from experimental anomalies as any known scientific laws.

First Law $dE = dq + dw$

The change in internal energy (dE) in any system is the sum of the heat entering the system (dq) and the work done on the system (dw). The internal energy of an isolated system is constant and $dq = 0$, $dw = 0$, $dE = 0$.

Second Law $dS \leq dq_{\text{rev}}/T$

The change in entropy (dS) during any change in a system is equal to the heat entering the system (when the change is performed reversibly) divided by the absolute temperature T . In all actual processes the entropy of an isolated system always increases ($dS > 0$).

Third Law

The entropy at absolute zero ($0K$) is zero for any pure crystalline substance *i.e.*, $S^0(0K) = 0$.

Zeroth Law

This law states that if two systems A and B are thermal equilibrium with a third system C then A and B will also be in thermal equilibrium when placed together. This law like other laws is based on human experiences. We can explain this law further as follows. Suppose we have three systems A, B and C placed together. A and C are in contact so that the properties of both change and finally the thermal equilibrium is attained and two come at the same temperature; C is in contact with B also then again thermal equilibrium is attained. If this is so then A and B should also be in thermal equilibrium. That is A, B and C should be at the same temperature.

If $A (T_A) \rightleftharpoons C (T_C) B (T_B)$,

then $A (T_A) \rightleftharpoons B (T_B)$, or if $T_A = T_C = T_B$, then $T_A = T_B$.

Thus the law provides a rational definition of temperature.

In thermodynamic studies the temperature's unit is taken as kelvin (K). The kelvin is strictly defined as the fraction $1/273.16$ of the temperature interval between the absolute zero (-273.16°C) and the triple point of water. In practice the temperature in kelvin is obtained by adding 273.15 to the temperature in degree celcius, e.g.,

$$25^\circ\text{C} = 25 + 273.15 = 298.15 \text{ K.}$$

The use of the symbol $^\circ\text{K}$ is not recommended. The symbol of temperature in kelvin scale is T .

STATE OF EQUILIBRIUM

It denotes a state of rest, of balance, of absence of change on macroscopic level. An object falls over, rolls about for a time and finally comes to rest; we say that it is then in equilibrium. In thermodynamics the equilibrium must satisfy the following two conditions.

- (i) The macroscopic properties such as temperature, pressure, density etc., of the system should not change with time (the submicroscopic properties do change e.g., the Brownian motion is always there even at equilibrium).
- (ii) The system should be at rest without the assistance of any external source. In a system in any of the two conditions are not fulfilled then the system will not be at equilibrium. For example, consider a leaky water tank into which a tap is running to maintain a constant water level. The tank is in a condition which is not observably changing from moment to moment i.e., its water level is constant, but its *state is not one of equilibrium* because the level is maintained by external agency. Thus, though it satisfies the first condition, it does not satisfy the second one. Hence it does not represent the equilibrium state. *It is a steady state or stationary state.*

Both the steady and equilibrium state are dynamic in nature. A steady state is dynamic on the macroscopic as well as microscopic level while an equilibrium state is static on macroscopic level but dynamic on *microscopic* level.

A true state of equilibrium in thermodynamics is characterised by mechanical equilibrium, thermal equilibrium and chemical equilibrium. A system is said to be in a state of mechanical equilibrium when (i) there is no unbalanced force in the interior of a system, and (ii) there is none between the system and its surroundings. When condition (i) is not satisfied the system will undergo a change of state. On the other hand when (ii) is not satisfied, both the system and its surroundings will undergo a change.

Such a change is stopped only when the mechanical equilibrium is attained. The condition of mechanical equilibrium is that each part of the system should be at the same pressure. A system is said to be in thermal equilibrium when its each part is at the same temperature and this temperature is identical with that of the surroundings. When these conditions are not satisfied, either the system alone or both the system and the surroundings will undergo a change of state until thermal equilibrium is reached.

The state of chemical equilibrium is characterised by tendency not to undergo spontaneous change of internal structure *i.e.*, the chemical composition of the system must be uniform, with no *net* chemical reaction taking place. In terms of the thermodynamic function the chemical equilibrium is described by the fact that the chemical potential (μ) of each part of the system must be the same.

Types of Equilibrium

Stable equilibrium. A system is in a state of stable equilibrium if after displacement to a new state and release of the constraint causing the displacement, it always returns to the original state. Fig. 1 (a) depicts an example of stable equilibrium for a ball resting in a hollow. If the ball is displaced in either direction from its initial position it will try to come to its old position. Such equilibrium is quite common in thermodynamics.

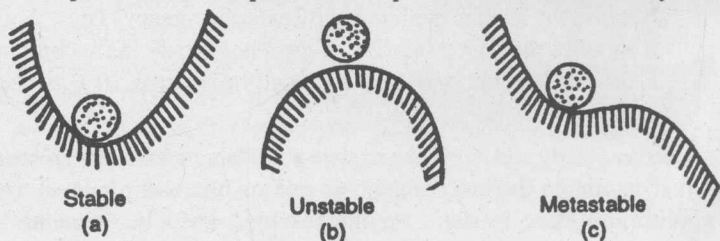


Fig. 1 : Types of mechanical equilibrium.

Unstable equilibrium. A system is said to be in a state of unstable equilibrium if, after displacement to a new state and release of the constraint causing the displacement, it never returns to its original state. An example of such a situation is given in Fig. 1(b) for a ball resting on a hillock. It may be noted that this is not an equilibrium state.

Metastable equilibrium. It is a state between the stable and unstable equilibria. If the displacement is not too large the state is stable but if the displacement is too large then it is unstable equilibrium. Fig. 1(c) depicts an example of metastable equilibrium. A super saturated solution of a super cooled liquid provides an example of the metastable equilibrium.

THERMODYNAMIC FUNCTIONS

The thermodynamic quantities given are quite sufficient to describe the properties of a system. However, new functions of simpler form can be defined, as given in Table 1. These are found to be more useful.

Table 1 : Various Thermodynamic Functions

Definition	Function	Name
$dE = dq + dw$	E	Internal energy
$dS = \frac{dq_{rev}}{T}$	S	Entropy
$H = E + PV$	H	Enthalpy
$G = H - TS$	G	Gibbs free energy
$A = E - TS$	A	Helmholtz free energy (work function)
$\mu_i = (\partial G / \partial n_i)_{T, P, n_j} \quad j \neq i$	μ	Chemical potential
$C_P = (\partial H / \partial T)_P$	C_P	Heat capacity at constant pressure
$C_V = (\partial E / \partial T)_V$	C_V	Heat capacity at constant volume

STATE FUNCTIONS

Thermodynamic functions are state functions. Magnitude of changes in such functions are independent of how the change is accomplished. These depend only upon initial and final states of the system. An analogy of state function can be found in mountain climbing. Suppose that we want to climb a mountain peak 1 km above our lodge. This decision defines our initial (lodge) and final (mountain peak) states. There may

be various paths up the mountain but the vertical distance of the peak from the lodge is all the time 1 km. The height of the mountain peak cannot be altered by choosing the different paths though the actual distance travelled and the amount of work and fatigue will be different depending upon the path followed. Vertical distance in this example corresponds to thermodynamic functions, E, H, S, G, μ, T, P, V . These all are state functions. We cannot alter the energy, enthalpy change etc. of the system by choosing different sequence of processes provided the initial and final states for different paths are not altered.

PROPERTIES OF STATE FUNCTIONS—EXACT DIFFERENTIALS

State functions give exact differentials. These exact differentials can be integrated between limits, without regard for the actual change that occur as the system moves from one limiting condition to the other. The properties of a state function can be understood if we take a concrete example of volume of definite amount of the substance. It depends upon temperature (T) and pressure (P). Mathematically we can speak that volume is a function of temperature and pressure *i.e.*,

$$V = f(T, P) \text{ (for a definite amount)}$$

If T and P are given a particular value of V is thereupon fixed. If T and P are changed the value of V will accordingly be changed. For this reason T and P are called *independent variables* and V is called the *dependent variable*.

The change in V can be estimated provided the derivatives of the function V with respect to T and P are known. The derivative is the rate of change of dependent variable with the independent variable. For the present case the two derivatives are :

$(\partial V / \partial T)_P$ = rate of change of volume with temperature at constant pressure.

$(\partial V / \partial P)_T$ = rate of change of volume with, pressure at constant temperature.

If the derivative is positive the function V increases with the increase of the independent variable; if the derivative is negative the function decreases with the increase of the independent variable. If the derivative is zero the function is independent of the variables, and the value of the function may be maximum or minimum under that condition.

The change of volume due to infinitesimal change of temperature (dT) at constant pressure is equal to the rate of change of volume with temperature $(\partial V/\partial T)_P$ multiplied by dT , and is given by

$$dV = (\partial V/\partial T)_P dT$$

The change in volume due to infinitesimal change of pressure (dP) at constant temperature is given by

$$dV = (\partial V/\partial P)_T dP$$

If both the temperature and pressure are changed simultaneously then the total change in volume (dV) is given by

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

This is called the total differential of the function (V). This equation was obtained by assuming that *whether we first change temperature then pressure or, first change the pressure then temperature, the final total change in volume is the same*. This is true because V is a *state function* and dV is an *exact differential*. In the language of mathematics the condition of exactness is

$$\frac{\partial}{\partial P} \left[\left(\frac{\partial V}{\partial T} \right)_P \right]_T = \frac{\partial}{\partial T} \left[\left(\frac{\partial V}{\partial P} \right)_T \right]_P$$

or $\frac{\partial^2 V}{\partial P \partial T} = \frac{\partial^2 V}{\partial T \partial P}$

This relation is applicable for any state function ϕ .

Let $\phi = f(x, y)$, then total differential $d\phi$ is given by

$$d\phi = \left(\frac{\partial \phi}{\partial x} \right)_y dx + \left(\frac{\partial \phi}{\partial y} \right)_x dy = M(x, y) dx + N(x, y) dy$$

$$\text{where } M(x, y) = \left(\frac{\partial \phi}{\partial x} \right)_y \text{ and } N(x, y) = \left(\frac{\partial \phi}{\partial y} \right)_x \quad \dots(1)$$

If $d\phi$ is an exact differential then

$$\left(\frac{\partial M}{\partial y} \right)_x = \left(\frac{\partial N}{\partial x} \right)_y \quad \dots(2)$$

$$\therefore \frac{\partial^2 \phi}{\partial y \partial x} = \frac{\partial^2 \phi}{\partial x \partial y} \quad \dots(3)$$

Here ϕ can be considered as any thermodynamic function (E, H, G etc). and (x, y) may be thermodynamic T, P, V etc. The relations given by equations (1, 2) and (1.3) are called the Euler's theorem of exactness. Any function and dY is inexact differential.

Some other properties of derivatives :

(i) They can be turned upside down, the subscript remaining the same.

$$1 / \left(\frac{\partial \phi}{\partial x} \right)_y = \left(\frac{\partial x}{\partial \phi} \right)_y$$

However, $1 / \left(\frac{\partial^2 \phi}{\partial x^2} \right) \neq \frac{\partial x^2}{\partial^2 \phi}$

(ii) They can be multiplied together cancelling numerator with denominator provided the subscripts are the same.

$$\left(\frac{\partial \phi}{\partial x} \right)_y \left(\frac{\partial x}{\partial z} \right)_y = \left(\frac{\partial \phi}{\partial z} \right)_y$$

But $\left(\frac{\partial \phi}{\partial x} \right)_y \left(\frac{\partial x}{\partial z} \right)_t \neq \left(\frac{\partial \phi}{\partial z} \right)_t$

COEFFICIENT OF THERMAL EXPANSION (α)

The rate of change of volume with temperature at constant pressure relative to a volume V is thermal expansively α .

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

a has the dimensions of T^{-1} .

Compressibility Coefficient (β)

The rate of change of volume with pressure at constant temperature relative to a volume is defined as the compressibility of a substance.

$$\beta = - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

The dimensions of β are those of P^{-1} . The expression for β bears a minus sign; this stands for the fact that volume decreases with increase of pressure and *vice versa*.

Relation between α and β

$$V = f(T, P)$$

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

$$\text{or } dV = \alpha V dT - \beta V dP \quad \dots(1)$$

For a condition of constant volume, $dV = 0$

$$\therefore \alpha V (\partial T)_V - \beta V - \beta V (\partial P)_V = 0$$

$$\text{or } \left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\beta}$$

At constant pressure $dP = 0$ and equation (1) reduces to

$$\left(\frac{\partial V}{\partial T}\right)_P = \alpha V$$

Differentiating it with respect to P at constant T , we get

$$\begin{aligned} \frac{\partial}{\partial P} \left[\left(\frac{\partial V}{\partial T}\right)_P \right]_T &= \alpha \left(\frac{\partial V}{\partial P}\right)_T + V \left(\frac{\partial \alpha}{\partial P}\right)_T \\ &= -\alpha V \beta + V \left(\frac{\partial \alpha}{\partial P}\right)_T \quad \dots(2) \end{aligned}$$

At constant temperature $dT = 0$ and equation (1) transforms to

$$\left(\frac{\partial V}{\partial P}\right)_T = -\beta V$$

Differentiating with respect to T at constant to T constant P we obtain

$$\begin{aligned} \frac{\partial}{\partial T} \left[\left(\frac{\partial V}{\partial P}\right)_T \right]_P &= -\beta \left(\frac{\partial V}{\partial T}\right)_P - V \left(\frac{\partial \beta}{\partial T}\right)_P \\ &= -\beta V \alpha - V \left(\frac{\partial \beta}{\partial T}\right)_P \quad \dots(10) \end{aligned}$$

Since V is a state function and $\partial^2 V / \partial T \partial P = \partial^2 V / \partial P \partial T$, therefore from equations (2) and (3) we obtain

$$V \left(\frac{\partial \alpha}{\partial P}\right)_T = \left(\frac{\partial \beta}{\partial T}\right)_P$$

$$\text{or } \left(\frac{\partial \alpha}{\partial P} \right)_T + \left(\frac{\partial \beta}{\partial T} \right)_P = 0 \quad \dots(4)$$

THERMODYNAMIC TERMS

System

The thermodynamics system is the part of the physical universe to which we direct our attention for the purpose of experimental or theoretical investigation.

Surroundings

The surroundings are the remainder of the universe which can exchange matter of energy with the system. Usually, the surroundings are restricted to a region in the immediate vicinity of the system under investigation.

Boundary

The region or interface separating the system from the surroundings is called the boundary.

Let us consider a gas (or liquid) contained in a cylinder and let the cylinder be placed in a constant temperature bath maintained at 25°C, as shown in Fig. 2.

In this case the substance (liquid or gas) constitutes the system, the walls of the cylinder are the boundaries and the constant temperature bath is the surrounding.

Since we shall encounter various types of systems as well as walls or boundaries, it will be helpful at this point to define some of the more important type of walls.

- (i) *A rigid wall.* A wall whose shape and position are fixed.
- (ii) *An impermeable wall.* A wall that prevents passage of matter.
- (iii) *A permeable wall.* A wall that allows that passage of matter and consequently, also of energy.
- (iv) *An adiabatic wall.* It is wall which, when held rigid will prevent the passage of matter or energy provided no external force field are present (e. g. thermos bottle).