



EDO UNIVERSITY IYAMHO  
**Department of Industrial Chemistry**  
**CHM 314: Advanced Physical Chemistry**

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Lectures: Mon. 9.00am – 10.00 am, Wed. 10.00am – 12.00pm LT6, phone: (+234) 8036237514

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**General overview of lecture:**

This course takes the learners through a review of Gibbs Function and then introduces the concepts of Chemical and statistical thermodynamics. The concepts of Ideal and Non-Ideal solutions are also discussed accordingly. Fundamental properties of electrolytes and Colligative properties are also treated. The practical applications of Gibbs function and thermodynamic principles, theories and derivations in real life situations will also be considered.

**Prerequisite:**

Advanced Physical Chemistry is a course for students in the Department of Chemistry and Biochemistry. The intended learners for this course are expected to have passed their course in Basic Physical Chemistry which is a prerequisite to this. The course shall include lectures and embedded practical exercises.

**Learning outcomes:**

At the end of this course the students should be able to:

- i. Calculate Gibb's free energy, enthalpy and entropy for various thermodynamic systems.
- ii. Outline the colligative properties of solutions.
- iii. Explain the functioning of heat engines Carnot engine and other related systems.
- iv. Determine molecular weights of unknown compounds using the idea of colligative properties.
- v. Classify thermodynamic systems based on their properties: isochoric, adiabatic isobaric etc.
- vi. Solve given problems based on the laws of thermodynamics.

- vii. Apply the laws of thermodynamic to real life situation.

### **Assignments:**

Assessment for this course shall include three (3) assignments together with the mi-term test and final examination. Students will also be expected to make term paper presentation towards the end of the semester. Individual and group projects will also be assessed.

### **Grading:**

Continuous assessment (CA) shall be assigned 30 % while the final examination takes 70%. Distribution of marks for the CA shall be as follows: 10% for home works; 10% for projects and 10% for midterm test. The Final exam is comprehensive.

**Textbook:** The recommended textbooks for this course are as follows:

Title: *Physical Chemistry*

Authors: Atkins, P. and De Paula, J.

Publisher: Freeman Publisher,

Edition: 8th ed

Year: 2006

Title: *Chemistry Precision and Design*

Author(s): Biddle, V. and Parker, G.

Publisher: Pensacola: Pensacola Christian College.

ISBN: 0-321-32221-5.

Year: 2000

Title: *Kinetics and Mechanism*

Author: Moore J.W. and Pearson, R.G.

Publisher: John Wiley,

Edition: 3rd ed

Year: 2000

### **Courseware: CHM 314 – Advanced Physical Chemistry**

The courseware for CHM 314 – Advanced Physical Chemistry is outline below. The recommended textbooks will be very relevant in covering this content.

### **Introduction of the concept of thermodynamics**

Thermodynamics is the study of the flow of heat or any other form of energy into or out of a system as it undergoes a physical or chemical transformation. It is associated with the study of heat, mechanical work and internal energy.

In studying and evaluating the flow of energy into or out of a system, it will be useful to consider changes in certain properties of the system. These properties include

- i. Temperature
- ii. Pressure
- iii. volume and
- iv. concentration of the system.

### **Scope of Thermodynamics**

(1) Most of the important laws of Physical Chemistry, including the Van't Hoff law of lowering of vapor pressure, Phase Rule and the Distribution Law, can be derived from the laws of thermodynamics.

(2) It tells whether a particular physical or chemical change can occur under a given set of conditions of temperature, pressure and concentration.

(3) It also helps in predicting how far a physical or chemical change can proceed, until the equilibrium conditions are established.

### **Limitations of Thermodynamics**

(1) Thermodynamics is applicable to macroscopic systems consisting of matter in bulk and not to microscopic systems of individual atoms or molecules. It ignores the internal structure of atoms and molecules.

(2) Thermodynamics does not bother about the time factor. That is, it does not tell anything regarding the rate of a physical change or a chemical reaction. It is concerned only with the initial and the final states of the system.

## **THERMODYNAMIC TERMS AND BASIC CONCEPTS**

An important part of the study of thermodynamics is a few terms and definitions which must be understood clearly.

### **System and Surroundings**

A system is whatever is of thermodynamic interest, in other words the part of the universe which is under study. The surroundings are part of the universe with which the system can exchange energy or matter. It is the rest of the universe outside system.

### **Boundary**

The real or imaginary surface separating the system from the surroundings is called the boundary.

For instance a given mass of sodium hydroxide solution in a conical flask is an example of a thermodynamic system. The beaker and the air in contact are the surroundings.

A molecule of nitrogen in a confined vessel with a piston attached is typical of a thermodynamic system. The cylinder and the piston and all other objects outside the cylinder, form the surroundings.

### **Homogeneous and Heterogeneous Systems**

When a system is uniform throughout, it is called a Homogeneous System. Examples are: a pure single solid, liquid or gas, mixtures of gases, and true solution of a solid in a liquid. A homogeneous system is made of one phase only.

A heterogeneous system is one which consists of two or more phases. In other words it is not uniform throughout. Examples of heterogeneous systems are: ice in contact with water, ice in contact with vapor etc. Here ice, water and vapor constitute separate phases.

### **TYPES OF THERMODYNAMIC SYSTEMS**

There are three types of thermodynamic systems depending on the nature of the boundary. If the boundary is closed or sealed, no *matter* can pass through it. If the boundary is insulated, no *energy* (say heat) can pass through it.

#### **Isolated System**

A system is isolated if the boundary both sealed and insulated, thus there is no interaction with the surroundings. Therefore, an isolated system is one that can transfer neither matter nor energy to and from its surroundings.

In this system no energy or matter can flow into or out hence for such a system,  $q = 0$  and  $w = 0$

Hence  $\Delta U = 0$ , since there is no change in internal energy.

Typical example is 100 ml of water in contact with its vapor in a closed and insulated vessel. Since the vessel is sealed, no water vapor (matter) can escape from it. Also, because the vessel is insulated, no heat (energy) can be exchanged with the surroundings. A substance, say boiling water, contained in a *thermos flask*, is another example of an isolated system.

#### **Closed System**

A close system is capable of exchanging mass, but cannot exchange energy. Matter cannot enter or leave the system. However, heat can flow in and out. The boundary is sealed.

A specific quantity of hot water contained in a sealed tube, is an example of a closed system. While no water vapour can escape from this system, it can transfer heat through the walls of the tube to the surroundings.

#### **Open System**

In such a system the boundary is open and un-insulated. Therefore, an open system is one which can transfer both energy and matter to and from its surroundings. Hot water contained in a beaker placed on laboratory table is an open system.

### **Adiabatic Systems**

Those systems, in which no thermal energy passes into or out of the system, are said to be adiabatic systems.

### **Intensive and Extensive Properties**

The macroscopic or bulk properties of a system (volume, pressure, mass, etc.) can be divided into two classes:

(a) Intensive properties

(b) Extensive properties

### **Intensive Properties**

A property which does not depend on the quantity of matter present in the system is known as intensive Property. Some examples of intensive properties are *pressure, temperature, density, and concentration*.

If the overall temperature of a glass of water (our system) is 20°C, then any drop of water in that glass has a temperature of 20°C. Similarly if the concentration of salt, NaCl, in the glass of water is 0.1 M, then any drop of water from the glass also has a salt concentration of 0.1 M.

### **Extensive Properties**

A property that does depend on the quantity of matter present in the system is called an extensive property. Some examples of extensive properties are *volume, number of moles, enthalpy, entropy, and Gibbs' free energy*. By definition, the extensive properties are additive while intensive properties are not.

## **A review of Thermodynamic potentials and Functions**

### **Internal energy**

Internal energy (U) is a function of entropy (S) and volume (V). Hence written as U(S, V). A change in entropy and volume can affect the internal energy of a system.

$$dU = dQ - dw \text{ (from first law of thermodynamics)}$$

$$\text{hence } dQ = dU + dw \text{ .....(i)}$$

$$\text{but } dS = \frac{dQ}{T}$$

$$TdS = dQ \dots\dots\dots(ii)$$

$$TdS = dU + dw$$

$$TdS = dU + PdV$$

$$dU = TdS - PdV$$

There are two conditions for dU, at constant entropy and at constant volume.

When S is constant

$$dS = 0$$

dU = TdS - PdV becomes

$$dU = T(0) - PdV$$

$$dU = -PdV$$

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

This shows pressure as the rate of change of internal energy with volume at constant entropy.

When V is constant

$$dV = 0$$

dU = TdS - PdV becomes

$$dU = TdS - P(0)$$

$$dU = TdS$$

$$T = \left( \frac{dU}{dS} \right)_V$$

This expression shows that temperature is the rate of change of internal energy with entropy at constant volume.

### **Enthalpy**

The expression  $H(S,P)$  simply means that enthalpy is a function of entropy and pressure. A change in entropy ( $S$ ) and pressure ( $P$ ) also affect enthalpy.

$$H = U + PV$$

$$dH = dU + PdV + VdP$$

$$dH = TdS - PdV + PdV + VdP$$

$$dH = TdS + VdP$$

The expression  $dH = TdS + VdP$  shows that enthalpy is brought about by a change in  $S$  and  $P$ . Since  $T$  and  $V$  remain constant.

There are two conditions of enthalpy at constant  $S$  and at constant  $P$

When  $S$  is constant

$$d(S) = 0$$

hence

$$dH = T (0) + VdP$$

$$dH = VdP$$

$$V = \left(\frac{dH}{dP}\right)_s$$

This shows volume as the rate of change of enthalpy with pressure at constant entropy.

When P is constant

$$d(P) = 0$$

$$dH = TdS + V (0)$$

$$dH = TdS$$

$$T = \left(\frac{dH}{dS}\right)_P$$

### **Helmholtz function**

This is a very important thermodynamic potential. It refers to the energy available for work in a system interacting with the surrounding under a constant temperature and volume. Helmholtz free energy it is represented as F. This function depends on change in volume and temperature since P and S are constant. This statement is represented as F (V, T) i.e F is a function of volume and temperature.

$$F = U - TS$$

Where F is Helmholtz free energy, U is internal energy and S is entropy while T is temperature in Kelvin.

$$F = U - TS$$

$$dF = dU - TdS - SdT$$

$$\text{but } dU = TdS - PdV$$

hence

$$dF = TdS - PdV - TdS - SdT$$

$$dF = -PdV - SdT$$

There are two conditions for this expression, that is, at constant volume and at constant temperature:

At constant volume:

$$dV = 0$$

$$dF = -PdV - SdT$$

$$dF = -P(0) - SdT$$

$$dF = -SdT$$

$$S = - \left( \frac{dF}{dT} \right)_V$$

At constant temperature:

$$dF = -PdV - SdT$$

$$dT = 0$$

$$dF = -PdV - S (0)$$

$$dF = -PdV$$

$$P = -\left(\frac{dF}{dV}\right)_T$$

### **Gibb's Function**

Gibbs free energy is represented at G. This is the energy available for doing work in a system under constant temperature and pressure.

$$G = H - TS$$

Where G is Gibb's free energy, H is enthalpy; T is absolute temperature while S is entropy.

The spontaneity of a reaction is determined by G. this parameter incorporates entropy, enthalpy and temperature.

$$G = H - TS$$

Differentiating the equation above

$$dG = dH - TdS - SdT$$

$$\text{but } dH = TdS + VdP$$

$$dG = TdS + VdP - TdS - SdT$$

$$dG = VdP - SdT$$

There are two conditions for this expression, at constant pressure and at constant temperature

At constant P

$$d(P) = 0$$

$$dG = V (0) - SdT$$

$$dG = - SdT$$

$$S = - \left( \frac{dG}{dT} \right)_P$$

At constant temperature,  $dT = 0$

$$dG = VdP - S (0)$$

$$dG = VdP$$

$$V = \left( \frac{dG}{dP} \right)_T$$