e- learning lectures in the subject Chemistry for B Tech Ist semester Batch 2016

Topic : Thermodynamics **Lecture no : 1**

Teacher Concerned: Dr Kowsar Majid

Pl contact on kowsar@nitsri.net in case of any query.

Dear students:

Welcome to the e-learning in the subject chemistry. Let me inform you about your syllabus in Chemistry. It consists of following six units.

1. **Chemical Thermodynamics**
2. **Chemical kinetics and catalysis**
3. **Electrochemistry**
4. **Corrosion and its prevention**
5. **Fuels**
6. **Modern methods of chemical analysis**

For detailed syllabus please visit

(http://www.nitsri.net/advertise_15/ist_syllabus.pdf)

We shall be discussing Unit I.. Chemical Thermodynamics.

The unit covers following topics:

Unit-I: CHEMICAL THERMODYNAMICS : State Functions, exact and inexact differentials (numerical). Second law: Need of 2nd law. Spontaneous process, concept of entropy, entropy changes as functions of temperature, entropy change during phase transformation (Numerical). Gibbs free Energy: Free energy changes under various conditions, Free energy changes as criteria of reversible and irreversible process. GibbsHelmohltz equation. Clausius – Clapeyron equation, partial molar quantities, Gibbs – Duhem equation, Chemical Potential

Introduction :

Let us start with the a basic question

What do we understand by thermodynamics and why it is important for us to study :

Thermodynamics consists of two words, Thermo means heat and dynamics means motion.

Thermodynamics deals with energy changes and its relationship with work.

It can be taken as mechanical action produced by heat

It deals with energy in its various forms which includes thermal, chemical, electrical and mechanical with the restriction on the transformation of one type of energy into the other type

There are three laws of thermodynamics. First, Second and Third laws of thermodynamics. Zeroth law is also there

Thermodynamics can be studied under:

- **Classical Thermodynamics (Macroscopic properties of Matter)**
- **Statistical Thermodynamics (Quantum Mechanical Behaviour of Matter)**
- **Chemical Thermodynamics (Process in which only chemical energy is involved)**

Importance of studying Thermodynamics:

It occupies an exalted position in chemistry.

- **Usually if there is a conflict between theory and an experiment, the error is ascribed to the theory. But we are so sure of thermodynamics that if a conflict occurs between theory and an experiment, we need to relook on experiment. This shows the importance of studying thermodynamics.**
- **There are three laws. No exception to these laws has been reported.**

- **Generalization of Experimental Results:** **Thermodynamics offers the means by which one can generalize the results of many different experiments.**
- **Direction of Reaction:** **The laws of thermodynamics can be used to predict the direction in which a process would proceed.**
- **Prediction of relationship between directly observable properties:** **With the help of laws of thermodynamics it is possible to predict a relationship between directly observable properties of substances quantitavely.**

Limitations of studying Thermodynamics:

- **Thermodynamics does not give any specific, direct information about the nature or structure of matter**
- **It does not give any indication of how fast a reaction will proceed**
- **No idea about the kinetics of the reaction.**

- **So from above few points, we can understand the importance of studying thermodynamics, however, limitations are also there.**

You have studied thermodynamics at your 12th level. Before we proceed, pl go to your books and refresh your knowledge about basic terms involved . You should know..

What is system and its surroundings. Types of system (Real, Ideal, Isolated, Closed, Open, Homogeneous, Heterogeneous and Macroscopic System.. see with examples), State of a system, Dependent Variables, Independent Variables, Properties of System, Extensive Properties, Intensive properties, Thermodynamic Equilibrium, Thermal Equilibrium, Mechanical Equilibrium, Chemical Equilibrium, Thermodynamic processes (Adiabatic, Isothermal, Isobaric, Isochoric, Cyclic, Reversible, Irreversible Process)

The Laws of Thermodynamics

First Law $dE=dq+dw$

Second Law: $dS = dq_{rev}/T$

Third Law S^0 (0K) = 0

Zeroth Law : A (T_A) $\rightleftharpoons$ C (T_C) $\rightleftharpoons$ B (T_B)

Now let us take the first topic of this unit . It is about

State Functions, exact and inexact differentials (numericals).

Path independent Function: Any function which does not depend on path is called a state function

These are independent of how the change is accomplished. These depend only on initial and final states of the system.

Examples: Let us take two variable height h and work w

Height between the bottom and top of a mountain is fixed but the work required to scale the mountain depends on the path.

In this example h is a state function but w is not a state function.

All thermodynamic functions viz E, H S G A , μ are state functions so are the P, V and T.

Properties of State Functions/Mathematical requirement for a function to behave as a state function:

- ✓ **. It should possess a perfect OR Exact differential**

What is a perfect Differential?

Let us consider a certain quantity z depending upon two other quantities, so that z is a some single valued function of x and y. Mathematically, we can express it as

Z = f (x, y)

Let us consider two mutually perpendicular axes as the axes of coordinate in Figure 1. Then for any particular point A of coordinate x, y the quantity z has a particular and definitive value. That is, when x and y are given, the quantity z is completely determined. Then, the differential dz is called perfect differential.

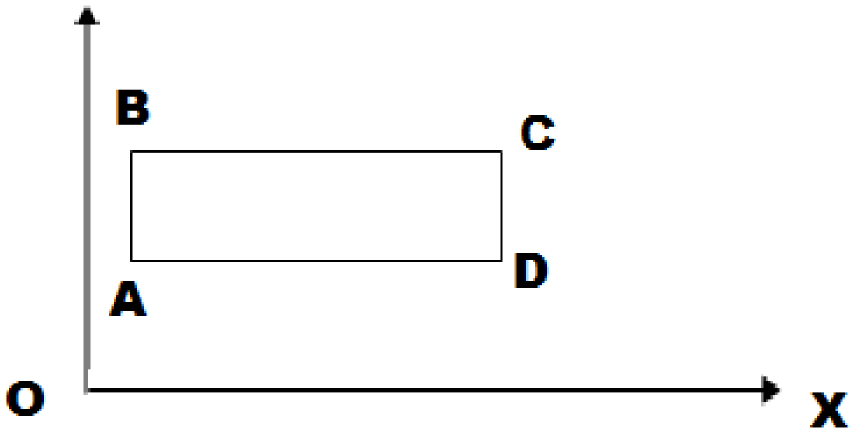

Figure 1

Physical Significance: **By the term perfect differential it means that when we go from a point A to point C, the value of z at C will be independent of the actual path adopted. There are several other paths from A to C but the value of z changes in going from A to C by the same amount whichever path is chosen. From this it follows that if we take the quantity z through a cycle such as ABCD then**

$$\oint dz = 0$$

Clearly the coordinates of D will be (x+dx, y)

The coordinates of B will be (x, y+dy) and the coordinates of C will be (x+dx, y+dy)

Starting from A and reaching at C, we have two paths ABC and ADC

Take Path ABC

Start from A….Go to B and reach C

Value of quantity at A is z

Value at B = $z + \frac{\partial z}{\partial y} dy$

Value at C = $\left(z + \frac{\partial z}{\partial y} dy \right) + \frac{\partial}{\partial x} \left(z + \frac{\partial z}{\partial y} dy \right) dx$

Choose path ADC

Start from A.... go to D and reach C

Value of quantity at A is z

Value at D = $z + \frac{\partial z}{\partial x} dx$

Value at C = $\left(z + \frac{\partial z}{\partial x} dx \right) + \frac{\partial}{\partial y} \left(z + \frac{\partial z}{\partial x} dx \right) dy$

Now id dz is a perfect differential, the value of the z must be the same at C, whichever path is chosen. That is

$$\left(z + \frac{\partial z}{\partial y} dy \right) + \frac{\partial}{\partial x} \left(z + \frac{\partial z}{\partial y} dy \right) dx = \left(z + \frac{\partial z}{\partial x} dx \right) + \frac{\partial}{\partial y} \left(z + \frac{\partial z}{\partial x} dx \right) dy$$

$$z + \frac{\partial z}{\partial y} dy + \frac{\partial z}{\partial x} dx + \frac{\partial^2 z}{\partial x \partial y} dy dx = z + \frac{\partial z}{\partial x} dx + \frac{\partial z}{\partial y} dy + \frac{\partial^2 z}{\partial y \partial x} dx dy$$

$$\frac{\partial^2 z}{\partial x \partial y} dy dx = \frac{\partial^2 z}{\partial y \partial x} dx dy$$

This is the mathematical condition for dz to be a perfect differential.

Thus a state function possess an exact differential and non state function has got an inexact differential

Example 1 : w is not a state function and hence dw is not a exact differential

Solution : To prove let us suppose that w is a state function and dw is an exact differential. If we arrive at absurd conclusion, can prove w is not a state function.

The work done is given as

$$dw = PdV \ldots\ldots\ldots\ldots\ldots(1)$$

Since V is a function of T and P i.e

V = f (T,P)......................(2)

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Putting value of dV in eq 1

$$dw = P\left(\frac{\partial V}{\partial T}\right)_P dT + P\left(\frac{\partial V}{\partial P}\right)_T dP \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

IF T is constant dT = 0 and equation 4 reduces to

$$\left(\frac{\partial w}{\partial P}\right)_T = P\left(\frac{\partial V}{\partial P}\right)_T \ldots\ldots\ldots\ldots\ldots\ldots(5)$$

By differentiation with respect to T at constant P, we get

$$\left(\frac{\partial^2 w}{\partial T \partial P}\right) = P\left(\frac{\partial^2 V}{\partial T \partial P}\right) \ldots\ldots\ldots\ldots\ldots\ldots(6)$$

IF P is constant dP = 0 and equation 4 reduces to

$$\left(\frac{\partial w}{\partial T}\right)_P = P\left(\frac{\partial V}{\partial T}\right)_P \text{.............................(7)}$$

By differentiation with respect to P at constant T, we get

$$\left(\frac{\partial^2 w}{\partial P \partial T}\right) = \left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial^2 V}{\partial P \partial T}\right) \text{....................(8)}$$

For dw to be exact differential, the following relation must be a valid

$$\left(\frac{\partial^2 w}{\partial P \partial T}\right) = \left(\frac{\partial^2 w}{\partial T \partial P}\right) \text{....................(9)}$$

Comparing equation 6 and 8

$$\left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial^2 V}{\partial P \partial T}\right) = P\left(\frac{\partial^2 V}{\partial T \partial P}\right) \text{.................(10)}$$

Since $\left(\frac{\partial^2 V}{\partial P \partial T}\right) = \left(\frac{\partial^2 V}{\partial T \partial P}\right)$

$$\left(\frac{\partial V}{\partial T}\right)_P = 0$$

Which is not true under ordinary conditions and hence dw is not an exact differential so w is a path dependent function or w is not a state function

Worksheet No 1

Please try to solve the following:

Q 1: Show Heat (q) is a path dependent function.

Q 2: If pressure , volume and temperature of one mole of a gas are related as $\left(P+\frac{a}{V^2}\right)V = RT$ **, show that**

(i) P is a state function (ii) dp is an exact differential

Q 3 : If E = f(T,V) and dE is an exact differential then show that $\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$**, relationship can be derived by using the relation dq = dE+ PdV and taking 1/T as an integrating factor.**