ATOMIC ENERGY CENTRAL SCHOOL-KUDANKULAM

Handout –Module-2/5

Subject-Chemistry   **Class-XI**

Lesson No.-Unit-6 (Thermodynamics)

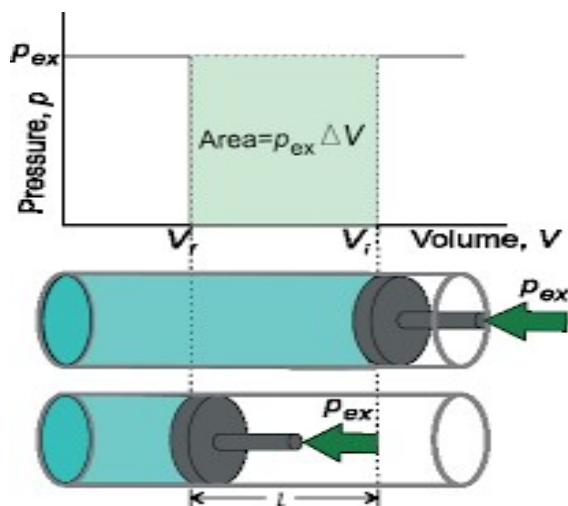**Name of the topic-WORK, HEAT FIRST LAW OF THERMODYNAMICS**

WORK

- Energy that is transmitted from one system to another in such a way that difference of temperature is not directly involved. This definition is consistent with our understanding of work as dw=Fdx. The force F can arise from electrical, magnetic, gravitational and other sources. It is a path function. It is a mechanical way of transfer of energy.

- Various types of work-

- Electrical Work = q x v

- Gravitational work=mgh

- Pressure volume work=f x dx.

- For understanding pressure-volume work, let us consider a cylinder which contains one mole of an ideal gas fitted with a frictionless piston. Total volume of the gas is V_i and pressure of the gas inside is p. *If* external pressure is pex which is greater than *p, piston* is moved inward till the pressure inside becomes equal to *pex*. Let this change be achieved in a single step and the final volume be V_f. During this compression,

Suppose piston moves a distance, *l and is* cross-sectional area of the piston is A

- then, volume change $= l \times A = V = (Vf - Vi)$

- We also know, pressure= Force/area

- Therefore, force on the piston $= pex . A$

- If w is the work done on the system by

- movement of the piston then w = force × distance $= pex . A .l$

  $= pex . (-\triangle V) = - pex\triangle V = - pex (Vf - Vi)$

- The negative sign of this expression is required to obtain conventional sign for W, which will be positive. It indicates that in case of compression work is done on the system. Here $(Vf - Vi)$ will be negative and negative multiplied by negative will be positive. Hence the sign obtained for the work will be positive.

- If the pressure is not constant at every stage of compression, but changes in number of finite steps, work done on the gas will be summed over all the steps and will be equal to $-\Sigma p \; V$

- Litre atmosphere term is unit of energy. It is useful to remember the conversion.

  1 litre atmosphere=101.3joules=24. 206 cal

Isothermal Reversible work

- If the pressure is not constant but changes during the process such that it is always infinitesimally greater than the pressure of the gas, then, at each stage of compression, the volume decreases by an infinitesimal amount, dV. In such a case we can calculate the work done on the gas by the relation.

$$dW = -\text{pex} \int dv$$

$$dw = -(p - dp)dv$$

$$= -pdv + dpdv$$

$$= -pdv \quad ....(\text{due to negligible value of } dp.dv, \text{ the product can be neglected})$$

$$\therefore \ dw = -pdv$$

Integrating the above equation between the **limits of initial volume V_1 and final volume V_2**

$$\int dw = -\int pdv$$

$$= -p \int dv$$

$$= -nRT/V \int dv \ ......PV = nRT \text{ acc. to ideal gas equation}$$

$$= -nRT \int dv /V$$

$$= -nRT \ln$$

$$= -nRT[\ln V_2 - \ln V_1 \ ]$$

$$= -nRT \ln V_2/V_1$$

$$\mathbf{= - 2.303 \ nRT \ log_{10}V_2/V_1}$$

- When Work is done by the system on the surrounding (expansion) the expression is given as......

- **Wmax = - 2.303 nRT $log_{10}V_2/V_1$**

- When work is done by the surrounding on the system (compression) log(V_2 -/V_1) will be negative , the expression becomes……..

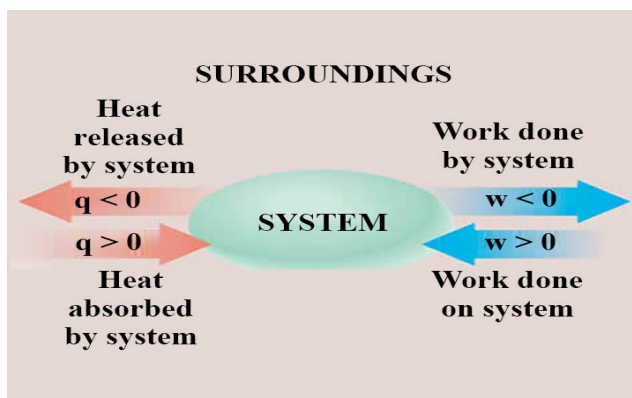   **Wmax = + 2.303 nRT log$_{10}$V$_2$/V$_1$**

- For isothermal reversible work,

- According to Boyel's law $P_1V_1=P_2V_2$

- therforeforeV$_2$/V$_1$= P_1/P_2

- Therefore work maximum in terms of pressure is-

- Expansion work-(Compression work)

- **Wmax = - 2.303 nRT log$_{10}$P$_1$/P$_2$**

- Work done on the system-

    Wmax = + 2.303 nRT log$_{10}$P$_1$/P$_2$

Work done in reversible isothermal process is possible only when the difference between the opposing force and driving force is infinitesimally small

HEAT(q)

- It occurs when there is a difference of temperature between system and surroundings.

- It is a random form of energy and **path dependent**. Its units are joule or calorie.

- According to IUPAC convention heat given by system is expressed with –ve sign and heat given to system is expressed with positive sign

INTERNAL ENERGY(U)

- It is the total energy within the substance. It is the sum of many types of energies like vibrational energy, translational energy. etc.

- It is an extensive property and state function.

- U=Ukinetic + U potential + Unuclear + ……..

- Its absolute value cannot be determined but experimentally change in internal energy (Δ) can be determined by

- $\Delta U = U2 – U1$ or $\Sigma Up – \Sigma UR$

- For exothermic process, ΔU = -ve, whereas for endothermic process

  $\Delta U = +ve$

- U depends on temperature, pressure, volume and quantity of matter.

- It is heat change at constant value since all the heat supplied goes to increase the internal energy of the gas.

- $U=q_v$

- For an ideal gas change in internal energy with change in volume at constant temperature is zero.

First Law of Thermodynamics

- Energy can neither be created nor destroyed although it can be converted from one form to the other.

- Mathematically, $\Delta U = q + W$

- where, ΔU = internal energy change

- q = heat added to system

- W = work added to system

- **Sign convention**

- (i) q is + ve = heat is supplied to the system

- (ii) q is – ve = heat is lost by the system

- (iii) Wis + ve = work done on the system

- (iv) Wis – ve =work done by the system

- If Q heat is absorbed by a sytem which has U1 internal enrgy. Internal energy increases from U1 to U1+Q

- Further if work is done on the system the internal energy further increases and it becomes U1 + Q + W

- U1 + Q + W=U2

- $U_2 - U_1 = Q + W$

- $\therefore \Delta U \quad = Q + W$

- for infinitesimal changes we can write …

- dU = dQ + dW

Zeroth Law of Thermodynamics

- The law states that if the two systems are in thermal equilibrium with a third system then they are also in thermal equilibrium with each other. Temperature is used here to know, the system is in thermal equilibrium or not
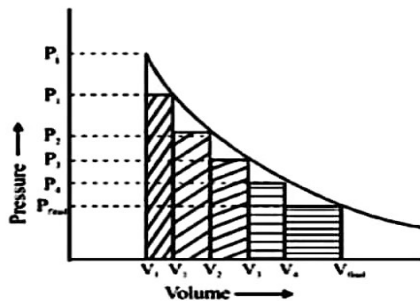
Calculation of work done in various processes

- Isothermal Process-Work done Can be calculated as-

- W= - $\int P dV$

- Since dT=0 so dU=0

- From first law q=-w

- If process is reversible-

- Wmax = - 2.303 nRT $\log_{10} V_2/V_1$

- Irreversible isothermal expansion –If external pressure over the piston is abruptly changed from the equilibrium value, the mechanical equilibrium is disturbed and piston rushes out. This type of p,v work irreversible p,v

work.To calculate irreversible p,v work. Law of conservation of energy is used.$W = -P_{ext} \Delta V$

- P1rreversible isothermal expansion and compression (many steps)

Consider an irreversible expansion of an ideal gas from initial pressure P1 to final Pressure P1 in four steps. The gas is allowed to expand against constant external pressure of P1 P2 P3 P4.Hence system passes through 4 equilibrium states. The work done in the process is shown graphically. The area under the isotherm is the magnitude of reversible work .clearly the magnitude of reversible work is greater than irreversible work. As the number of intermediate steps in irreversible expansion is increased, the magnitude of work increases and as the number of steps tend to infinity Wirr tend to Wrev.

Adiabatic process

As there is no exchange of heat Q = 0

According to first law of thermodynamics..

$\Delta U = Q + W$

$\therefore \Delta U = 0 + W$

$\therefore \Delta U = W$

Isochoric Process

V = 0 as volume remains constant

$\therefore W = P \Delta V = P \times (0) = 0$

According to first law of thermodynamics

$\Delta U = Q + W$

$= Q + 0$

$\therefore \Delta U = Q$

$\therefore$ Change in internal energy of the system = heat transfer at constant volume

Isobaric Process

Reactions carried out at constant pressure ….

 all the chemical reactions are generally carried out <u>at atmospheric pressure</u> which is constant

$\Delta U \quad = Q + W$ … first law of thermodynamics

$\Delta U \quad = Q + (-P \, \Delta V) \qquad \text{... ..} \qquad W = -P \, \Delta V$

Since heat is supplied at constant external pressure (P_{ext}) let $Q = Qp$

$\Delta U \quad = \mathbf{Qp} + (\mathbf{-P_{ext} \, \Delta V})$

$\therefore \mathbf{Qp = \Delta U + P_{ext} \, \Delta V}$

_____