# THERMODYNAMICS

## **APPLICATIONS OF THERMODYNAMIC**

## HEAT AND WORK

Heat and work both are mode of energy transfer between system and surrounding.

Heat flows due to temperature gradient while work is done due to imbalance of generalized force.

Sign Convention

Heat absorbed by the system is + ive.

Heat released by the system is – ive

Work is classified into two broad categories as:

(1) **PV Work** – This type of work is done when change in volume occurs under the influence of external pressure.

Consider a cylinder (cross section area A) fitted with a frictionless piston, which enclosed n mole of an ideal gas. Let an external force F pushes the piston inside producing displacement dx in piston.



small change in volume of gas (dV) = A. dx

Small work done dw = F. dx

Also,

$$F = PA$$
$$dW = PA. dx$$

 $P = \frac{F}{A}$ 

$$\Rightarrow$$
 dV = - A. dx

(-ive sign indicates work is done by the system i.e., gas is expanding against P<sub>ext</sub>)

$$\Rightarrow \qquad dW = -P_{ext.} dV$$

 $w = -\int P_{external} dV$ 

$$\Rightarrow$$

Sign Convention

Work done by the system is -ive.

Work done on the system is +ive

- During expansion dV is +ive and hence sign of w is -ive i.e., work is done by the system and hence Expansion Work is always negative.
- During compression, dV is -ive which gives +ive value of w i.e., work is done on the system and hence Compression work is always positive.
- (2) Non-PV Work Following are some examples of non-PV work.

Stretching	Tension ( $\gamma$ ), length (l)	N m = J
Surface expansion	Surface tension ( $\gamma$ mm), area ( $\sigma$ )	$(N m^{-1}) (m^2) = J$
Electrical	Electrical potential ( $\phi$ ),	$w = (q \times V) (V \times C) = J$

Ex. Find the work done, when one mole of ideal gas in 10-liter container at 1 atm.is allowed to enter a vacated bulb of capacity 100 liters.

**Ans.** (a) 
$$W = -P\Delta V$$

But since gas enters the vaccum bulb and pressure in vaccum is zero.

W = 0

- **Ex.** If 1 mole of gas expands from 1 litre to 5 litre against constant atmospheric pressure than calculate thaw work done.
- **Ans.** (b)  $W = -P\Delta V = -1(5-1) = -4$  litre-atm.

## **INTERNAL ENERGY (U OR E)**

Consider a system of mass 'M' is moving in gravitational field with velocity v. The total energy of system (in earth frame of reference) is given as:

E = K + V + U: (K = kinetic energy, V = potential energy, U = internal energy)

A thermodynamic system is studied generally at rest so K = 0. If effect of gravitation field (or other fields are ignored) is also ignored then we left with E = U.

So, "In absence of an external field (no external potential energy), when the system is at rest (no external kinetic energy) the total energy of the system is called its internal energy"

The internal energy of the gas confined in a container is defined relative to a coordinate system fixed on the container. Viewed at a microscopic(atomic) level, the internal energy can take on a number of forms such as.

- > The kinetic energy of the molecules;
- The potential energy of the constituents of the system; for example, a crystal consisting of dipolar molecules will experience a change in its potential energy as an electric field is applied to the system;
- > The internal energy stored in the form of molecular vibrations and rotations;
- The internal energy stored in the form of chemical bonds that can be released through a chemical reaction.

The total of all these forms of energy for the system of interest is given the symbol U and is called the internal energy.

Hence total internal energy of a system can be written as

 $U = U_{translational} + U_{rotational} + U_{vibrational} + U_{intermolecular} + U_{electronic} + U_{vibrational} + U_{$ 

## Urelativistic

out of these **U**<sub>relativistic</sub> and **U**<sub>electronic</sub> is unaffected by ordinary heating. So basically, the kinetic energy terms and **U**<sub>intermolar</sub> accommodate the heat provided to the system. Hence heat capacity of a sample depends upon these four terms.

For an ideal gas, **U**<sub>intermolecular</sub> is equal to zero, because of absence of intermolecular force of attraction in ideal gas. **U**<sub>intermolecular</sub> have large and negative value in solids and liquids.

For an ideal gas U is only function of temperature e.g. U=F(T) +Constant

Due to absence of pressure or volume terms in ideal gas internal energy, U is independent of pressure and volume of ideal gas.

> Internal Energy is an extensive Property and is a state function.

If a system is present in particular thermodynamic state say 'A' it has fixed amount of internal energy  $U_A$ . Suppose by a process the system is taken from state A to state B then



## $\Delta U = U_B - U_A$

Since U is state function. This implies between any two fixed states, there can be infinite



process or path, but  $\Delta U$  in all process will remain the same. (Property of a function of state) Consider a system taken from state A to B by n<sup>th</sup> different paths.

i.e.,  $\Delta U_1 = \Delta U_2 = \Delta U_3$  .....

For a given system, Internal Energy can be represented as a function of volume and temperature U = f(T, V) and the overall change in I.E. can be calculated mathematically as:

#### Chemistry

$$dU = \left(\frac{\partial U}{\partial T}\right)_{V} \cdot dT + \left(\frac{\partial U}{\partial V}\right)_{T} dV$$

> For isochoric process: dV = 0

$$dU = \left(\frac{\partial U}{\partial T}\right)_{v} dT$$

 $dU = C_V \cdot dT$ 

Overall change in I.E.  $\Delta U = \int C_v dT$ 

For an ideal gas

$$\left(\frac{\partial U}{\partial V}\right)_{T} = 0$$
$$dU = C_{V} \cdot dT$$
$$\Delta U = \int C_{V} \cdot dT$$

For a real gas  $\left(\frac{\partial U}{\partial V}\right)_{T}$  is Positive when attractive forces dominate (in both compression

& expansion) and  $\left(\frac{\partial U}{\partial V}\right)_T$  is Negative when repulsive forces dominates

(in both compression & expansion).

Note that heat and work involve in all the process are different but  $\Delta U$  is same. This mean heat and work are indefinite quantities while  $\Delta U$  is a definite quantity.

#### FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics is based on energy conservation principle i.e.

"Total energy of universe remain constant."

Let us consider a system whose internal energy is  $U_1$ . If the system is supplied with heat q,

the internal energy of the system increases to  $U_1 + q$ .

#### Chemistry

If work (w) is now done on the system, the internal energy in the final state of the system,  $U_2$  is given by

$$U_2 = U_1 + q + w$$
  
or 
$$U_2 - U_1 = q + w$$
  
$$\Delta U = q + w,$$

According to IUPAC, heat, added to the system and work done on the system are assigned positive values as both these Modes increase the internal energy of the system.

- **Ex.** A system expands from 5 L to 10 L against a constant external pressure of 2 atom. If it absorbs 800 J of energy in the process. Calculate the change in its internal energy.
- Sol.  $\Delta u = q + w$   $w = -(v_2 - v)$  = -2(10 - 5)  $= -10 \text{ atm } -L \times 101.3 \text{ J} = -1013 \text{ J}$  $\Delta U = -213 \text{ J}$

#### ENTHALPY(H)

Chemical reactions are generally carried out at constant pressure (atmospheric pressure) so it has been found useful to define a new state function Enthalpy (H) as:

H = U + PV $\Delta H = \Delta U + \Delta (PV)$ 

at constant pressure

 $\Delta H = \Delta U + P \Delta V \dots (1)$ 

From First Law  $\Delta U = q + w = q - PdV$ 

$$q = \Delta U + PdV = \Delta H.....(2)$$

combining with first law.  $\Delta H = q_p$ 

Hence transfer of heat at constant volume brings about a change in the internal energy of the system whereas that at constant pressure brings about a change in the enthalpy of the system.

For a given system

## Chemistry

$$H = f(T, P)$$
$$dH = \left(\frac{\partial H}{\partial T}\right)_{P} \cdot dT + \left(\frac{\partial H}{\partial P}\right)_{T} dP$$

For isobaric process: dP = 0

$$dH = \left(\frac{\partial H}{\partial T}\right)_{P} dT$$
$$dH = C_{P} \cdot dT$$

$$\Delta H = \int C_P . dT$$

For an ideal gas

$$\left(\frac{\partial H}{\partial P}\right)_{T} = 0$$
$$dH = C_{P} \cdot dT$$
$$\Delta H = \int C_{P} \cdot dT$$

## RELATIONSHIP BETWEEN $\Delta H \& \Delta U$

The difference between  $\Delta H \& \Delta U$  becomes significant only when gases are involved (insignificant in solids and liquids)

 $\Delta H = \Delta U + \Delta (PV)$ 

If substance is not undergoing chemical reaction or phase change.

 $\Delta H = \Delta U + nR\Delta T$ 

In case of chemical reaction

$$\Delta \mathbf{H} = \Delta \mathbf{U} + (\Delta \mathbf{n}_g) \ \mathbf{RT}$$

#### Chemistry

#### Class-XI

## **Reversible Process**

- > These are very slow processes and do not go for completion or take very long time.
- In a reversible process the driving force is greater than the opposing force by a very small value (infinitesimally small value).
- The reversible process is carried out in such a manner that if at any moment opposing force is increased by a small amount the direction of process can be reversed
- A reversible process is also called "quasi static" process. A quasi-static process is the one in which system remain infinitesimally closer to the state of equilibrium throughout the process.



- During a reversible process, the system and surrounding remain in equilibrium throughout the process.
- The reversible processes are idealized processes which cannot be actually carried out, but nevertheless they are very important because they help in calculation of change in state function in the process. In other words, the reversible processes are hypothetical processes.

## **Irreversible Process**

- > These are very fast processes and are completed in a short interval of time.
- In an irreversible process the driving force is much greater than the opposing force and therefore the process is completed very fast.



All natural processes are example of irreversible process.

S. No.	<b>Reversible Process</b>	Irreversible Process
1	These are slow processes.	These are instantaneous or sudden processes.
2	Driving force is infinitesimally small.	Driving force is large and finite.
3	It is an ideal process.	It is a real process.
4	It takes infinite time for completion of process.	It takes finite time for completion of the process.
5	It is an imaginary process and can not be realised in	It is a natural process and occurs in particular direction under given set of conditions.
6	Throughout the process, the system remain infinitesimally closer to state of equilibrium.	The system is far removed from state of equilibrium and exact path of process can be drawn.