

# Thermodynamics

## TOPICS COVERED

- Internal energy (U)
- First law of Thermodynamics
- Some Special Forms of First Law of Thermodynamics

## INTERNAL ENERGY ( $\Delta U$ or $\Delta E$ )

- Any system have 100 kinds of energies but those energies are counted in internal energy of system, which can change the temperature of the system.
- Internal energy is the function of Temperature (T) i.e. U depends upon the temperature.
- $\Delta U$  (or  $\Delta E$ ) is the **difference in energy between reactants and products** in a chemical reaction.
- $\Delta U$  (or  $\Delta E$ ) is the **sum of all of the kinetic and potential energies of all particles in the system.**
- Internal energy of a system is a state function.
- It is a extensive property.

## UNITS OF INTERNAL ENERGY

The SI unit for internal energy of a system is the joule (J). Another unit of energy which is not an SI unit is the calorie,  $1 \text{ cal} = 4.184 \text{ J}$ .

$\Delta E \propto \Delta T$  (by definition)

- In solids / liquids:-

$\Delta E \propto \text{mass}$

$\Delta E \propto m \Delta T$

$\Delta E = m S \Delta T$

## INTERNAL ENERGY ( $\Delta U$ or $\Delta E$ )

- For Gas:-

- $\Delta E \propto n$  (n - no. of moles)

$$\Delta E \propto n \Delta T$$

$\Delta E = n C_v \Delta T$ , where  $C_v$  = Molar heat capacity at const. V

If  $q_v = n C_v \Delta T$  [ heat give to any system at const. volume]

So,  $\Delta E = q_v$  - Heat given to any system at const. volume is called in internal energy.

## FIRST LAW OF THERMODYNAMICS

- **Energy neither be created nor be destroyed but it can transfer from one form to another.**
  - **$U = q + w$  i.e** internal energy of any system is equal to heat supplied to the system and work done on the system.

## FIRST LAW OF THERMODYNAMICS

**The total energy of an isolated system remains constant though it may change from one form to another.**

When a system is changed from state  $A$  to state  $B$ , it undergoes a change in the internal energy from  $E_A$  to  $E_B$ . Thus, we can write

$$\Delta E = E_B - E_A$$

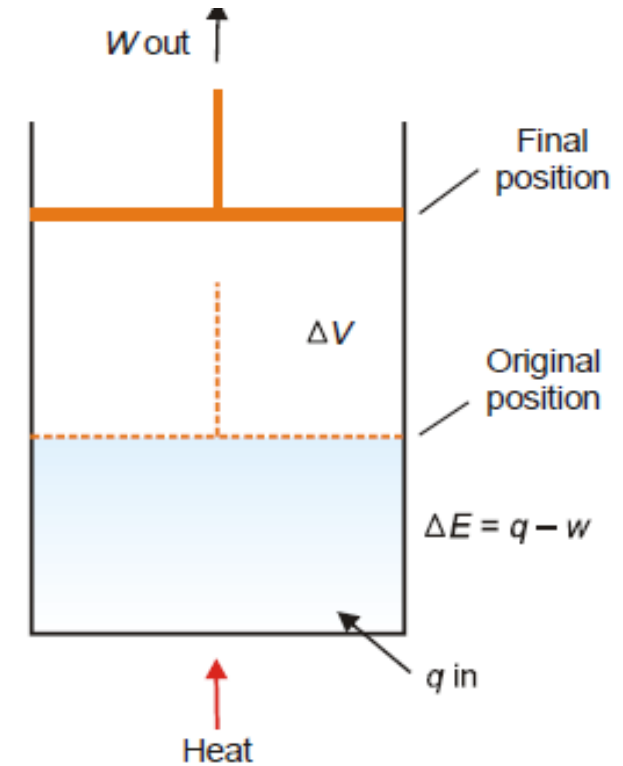
This energy change is brought about by the evolution or absorption of heat and/or by work being done by the system. Because the total energy of the system must remain constant, we can write the **mathematical statement of the First Law** as :

$$\Delta E = q - w \quad \dots(1)$$

where  $q$  = the amount of heat supplied to the system

$w$  = work done by the system

Thus First Law may also be stated as : **the net energy change of a closed system is equal to the heat transferred to the system minus the work done by the system.**



## FIRST LAW OF THERMODYNAMICS

- If we supply any heat to the system it will convert into two form of energy.

1. It can change in internal energy of the system  $\Delta U$

2. It can do work

$$q = \Delta U + \text{work done}$$

$$q = \Delta U + (-w)$$

$$w = -\int P dV \quad \text{put the value of } w$$

$$q = \Delta U + \int P dV$$

- Heat can be supplied to the system by two ways

1. Heat at const. volume

2. Heat at const. pressure

➤ Heat at const. volume

$$w=0$$

$$q_v = \Delta U = n C_v \Delta T$$



## Heat at const. Pressure

$$W = -\int_{v_1}^{v_2} P dV = -P\Delta V$$

$$\Delta V = V_2 - V_1$$

$$Q_p = \Delta U + P\Delta V = \Delta H$$

So, at const pressure the change in heat is equal to enthalpy

$$\Delta H = nC_p\Delta T$$

$$q_p = \Delta H = \Delta U + P\Delta V = nC_p\Delta T$$

## Some Special Forms of First Law of Thermodynamics

Mathematical statement of the First law of Thermodynamics is

$$\Delta E = q - w$$

**Case 1 : For a cyclic process involving isothermal expansion of an ideal gas**

$$\Delta E = 0$$

$$\therefore q = w$$

**Case 2 : For an isochoric process (no change in volume) there is no work of expansion i.e.**

$$w = 0.$$

*Hence* 
$$\Delta E = q_v$$

**Case 3 : For an adiabatic process there is no change in heat gained or lost i.e.  $q = 0$ . Hence**

$$\Delta E = -w$$

In other words, the decrease in internal energy is exactly equal to the work done on the system by surroundings.

**Case 4 : For an isobaric process there is no change in pressure, i.e.  $P$  remains constant. Hence**

$$\Delta E = q - w$$

or 
$$\Delta E = q - P\Delta V$$

✓ Find  $\Delta E$ ,  $q$  and  $w$  if 2 moles of hydrogen at 3 atm pressure expand isothermally at 50°C and reversibly to a pressure of 1 atm.

## SOLUTION

Since the operation is isothermal and the gas is ideal

$$\Delta E = 0$$

From the First Law  $\Delta E = q - w$

$$\therefore q - w = 0$$

when  $\Delta E = 0$

or  $q = w$

For a reversible process

$$w = -nRT \ln (P1/P2)$$

$$\begin{aligned} w &= -2 \times 1.987 \times 323 \times 2.303 \times \log 3 \\ &= -1410 \text{ cal} \end{aligned}$$

Since  $q = w$

$$q = -1410 \text{ cal}$$

- ✓ A gas contained in a cylinder fitted with a frictionless piston expands against a constant external pressure of 1 atm from a volume of 5 litres to a volume of 10 litres. In doing so it absorbs 400 J thermal energy from its surroundings. Determine  $\Delta E$  for the process.

## SOLUTION

$$\Delta E = q - w \dots(1)$$

Here  $q = 400 \text{ J}$

$$\begin{aligned} w &= -P(V_2 - V_1) \\ &= -(1)(10 - 5) \\ &= -5 \text{ l atm} [1 \text{ l atm} = 101.2 \text{ J}] \\ &= -506 \text{ J} \end{aligned}$$

Substituting values in (1)

$$\begin{aligned} \Delta E &= 400 \text{ J} - (-506 \text{ J}) \\ &= 400 \text{ J} + 506 \text{ J} \\ &= \mathbf{906 \text{ J}} \end{aligned}$$

- ✓ 1g of water at 373 K is converted into steam at the same temperature. The volume of water becomes 1671 ml on boiling. Calculate the change in the internal energy of the system if the heat of vaporisation is 540 cal/g.

## SOLUTION

As the vaporisation takes place against a constant pressure of 1 atmosphere, work done for an irreversible process,  $w$ , is

$$\begin{aligned}w &= P (V_2 - V_1) \\ &= nRT \\ &= (1/18) \times 1.987 \times 373 \\ &= 41 \text{ cal/g}\end{aligned}$$

$$\text{Now } q = 540 \text{ cal/g}$$

$$\begin{aligned}\text{Since } \Delta E &= q - w \text{ (First Law)} \\ &= 540 - 41\end{aligned}$$

$$\therefore \Delta E = 499 \text{ cal/g}$$

## References

### Text Books

1. Atkins, P. W. & Paula, J. de *Atkin's Physical Chemistry* 10th Ed., Oxford University Press (2014).

### Reference Books

1. Castellan, G. W. *Physical Chemistry* 4th Ed. Narosa (2004).
2. Engel, T. & Reid, P. *Physical Chemistry* 3rd Ed. Pearson (2013).
3. Levine, I .N. *Physical Chemistry* 6th Ed., Tata Mc Graw Hill (2010)
4. Puri Sharma Pathania Physical Chemistry Book.

THANK YOU

