Thermodynamics

(Module -2)

B.Sc. III Year

SAIKRISHNA UGGU

Lecturer in Chemistry

P. R. Govt. College (A)

KAKINADA

CONTENTS...

- Internal energy
- Enthalpy
- Heat capacities
- Relation between Cp and Cv

Internal Energy

Every substance possesses a definite amount of energy which depends upon its chemical nature, temperature, pressure and volume.

This energy associated with every substance is called internal energy or intrinsic energy and is denoted by letter E or U.

Internal Energy

The internal energy of a substance or system is a definite quantity and its exact value cannot be determined because it involves certain quantities like translational, vibrational and rotational kinetic energies which cannot be measured.

$$E = E_{tr} + E_{rot} + E_{vib} + E_{ele} + E_{bon} + \ldots..$$

Internal Energy

Internal energy is state function; therefore its change can be determined instead of its absolute value.

The change in internal energy of a system is,

$$\Delta E = E_2 - E_1$$

Where, E_2 = Internal energy of the system at final stage and

E_1 = Internal energy of the system at initial stage

Internal Energy

- If, $E_1 > E_2$ ($E_R > E_P$), then the extra energy possessed by the system in the initial state would be given out and thus ΔE will be negative.
- If, $E_2 > E_1$ ($E_P > E_R$), energy will be absorbed in the process and ΔE will be positive.

Enthalpy

Heat content of a system at constant pressure is called Enthalpy. It is denoted by H.

The enthalpy of a substance or a system is the total amount of energy stored in that substance.

Enthalpy

Enthalpy of a system is a state function and therefore its change can be determined instead of its absolute value.

The enthalpy of a thermodynamic system is defined as,

$$H = E + PV$$

Where,

H is enthalpy is the internal energy of the system,

P is pressure, V is the volume of the system.

Change in enthalpy

The enthalpy change accompanying a process at constant pressure may be defined as the sum of the increase in internal energy of the system and the pressure – volume work (i.e. the work of expansion)

$$\Delta H = \Delta E + W$$

Change in enthalpy

- The process where, $H_2 > H_1$, in exothermic process ΔH is negative,
- While the process where, $H_2 < H_1$, in endothermic process ΔH is positive.

HEAT CAPACITIES

Heat Capacity: It is defined as the amount of heat required to rise the temperature of a substance by one unit temperature change. Heat capacity of a system means the capacity to absorb and store energy.

We can also write it as $q = C\ \Delta T$, the coefficient, C is called the heat capacity.

HEAT CAPACITIES

Specific heat, also called specific heat capacity is the quantity of heat required to raise the temperature of one unit mass or 1 gram of a substance by one degree Celsius.

HEAT CAPACITIES

The molar heat capacity of a substance is the heat capacity for one mole of the substance and is the quantity of heat required to raise the temperature of one mole of a substance by one degree Celsius.

$$C_m = \left(\frac{C}{n}\right)$$

C_V: Molar heat capacity at constant volume

It is defined as the amount of heat required to rise the temperature of one mole of substance by 1 ^oC at constant volume.

$$C_v = \frac{dE}{dT}$$

C_V: Molar heat capacity at constant volume

Heat capacity of a system at constant volume is defined as the increase in internal energy of the system per degree rise of temperature at constant volume. Or

It is the rate of change of internal energy with temperature at constant volume.

C_p: Molar heat capacity at constant pressure

It is defined as the amount of heat required to rise the temperature of one mole of a substance by 1 ^oC at constant pressure.

$$C_p = \frac{dH}{dT}$$

C_p: Molar heat capacity at constant preure

Heat capacity of a system at constant pressure is defined as the increase in enthalpy of the system per degree rise of temperature at constant pressure.

Or

It is the rate of change of enthalpy with temperature at constant pressure.

The relation between C_p and C_v

The relation between C_P and C_v for an ideal gas is given by,

$$C_P - C_V = R$$

Or

$$C_p = C_v + R$$

Where R is the universal gas constant.

The relation between C_p and C_v

The molar heat capacity of a substance at constant pressure is always greater than the molar heat capacity at constant pressure i.e.

$$C_P > C_V$$

The relation between C_p and C_v

When a substance is heated at constant volume, no work is done by the substance and thus the heat absorbed by the system is used completely to increase the internal energy of the substance.

The relation between C_p and C_v

When a substance is heated at constant pressure, do some external work in addition to increase in the internal energy of the substance.

Hence C_p is always greater then C_v.

$$Cp > Cv$$

Show that $C_p - C_v = R$

The molar heat capacity at constant volume C_V, is given by

$$q_v = C_V \Delta T = \Delta E$$

The molar heat capacity at constant pressure C_P is given by,

$$q_p = C_p \Delta T = \Delta H$$

Show that $C_p - C_v = R$

For one mole of an ideal gas,

$$\Delta H = \Delta E + \Delta (PV) = \Delta E + \Delta (RT) = \Delta E + R \Delta T$$

Thus,

$$\Delta H = \Delta E + R \Delta T$$

Show that $C_p - C_v = R$

We know that,

$$q_p = C_p \Delta T = \Delta H$$

Then,

$$C_p \Delta T = \Delta H$$

$$C_p \Delta T = \Delta E + R \Delta T$$

$$C_p \Delta T = C_V \Delta T + R \Delta T$$

Show that $C_p - C_v = R$

Then,

$$C_p \Delta T = C_V \Delta T + R \Delta T$$

$$C_p = C_V + R$$

Hence,

$$\mathbf{C_p - C_V = R}$$

THANK YOU……