A: Physical Chemistry

Paper III - Physical and organic Chemistry

B.Sc. Part II

By

Sonu Ram Shankar

Assistant Professor

Department of Chemistry

Marwari College, Darbhanga

A constituent Unit of

Lalit Narayan Mithila University, Kameshwar Nagar, Darbhanga

Thermodynamics

In an adiabatic system enthalpy can be measured by heat generated.
This will be shown as increase in temperature.

Relation between the heat and the increase in temperature of a substance.
Heat capacity: It is change in temperature with heat

$$q \propto change\ in\ temperature, \Delta T\ or\ q = heat\ capacity, C \times \Delta T$$

At constant volume i.e. when ΔV = 0 in cases of solids and liquids

$$\Delta H = \Delta U = q_V$$

$$du = C_v dT$$

$$C_v = \left(\frac{dU}{dT}\right)_v$$

Thermodynamics

Heat capacity is the heat required to raise the temperature by 1°C

Molar heat capacity, C_m = C/n, where n is 1 mole,

$$C_{v,m} = \frac{C_V}{number\ of\ moles, n}$$

Molar heat capacity of gas is 25 $kJK^{-1}mol^{-1}$

Specific heat capacity,

Specific heat capacity, c, heat required to raise the temperature of 1 kg of substance by 1°C.

$$C_{v,s} = \frac{C_V}{mass, m}$$

Specific heat capacity For H_2O 4 KJ $K^{-1}g^{-1}$

Thermodynamics

C_p and C_v

Heat capacity at constant volume,

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

Heat capacity at constant pressure,

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

Relationship between C_p and C_v

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

$$\Delta H = \Delta U + \Delta(RT) = \Delta U + R\Delta T$$

$$C_P\Delta T = C_V\Delta T + R\Delta T = (C_V + R)\Delta T$$

$$C_P = C_V + R$$

$$C_P - C_V = R$$

Thermodynamics

Relationship between P, V and T in adiabatic process

Adiabatic process:

change occurring within a system as a result of transfer of energy to or from the system in the form of work only; i.e., no heat is transferred.

A rapid expansion or contraction of a gas is very nearly adiabatic.

Any process that occurs within a container that is a good thermal insulator is also adiabatic.

adiabatic compression

causes a rise in temperature of the gas.

Example:

a piston compressing a gas contained within a cylinder and raising the temperature where heat conduction through walls can be slow compared with the compression time. in diesel engines during the compression stroke elevate the fuel vapor temperature sufficiently to ignite it.

Adiabatic heating occurs in the Earth's atmosphere when an air mass descends, for example, wind flowing downhill over a mountain range.

Thermodynamics

Adiabatic expansion

causes a drop in temperature.

Example:

Adiabatic cooling occurs in the Earth's atmosphere this can form lenticular clouds.

Rising magma also undergoes adiabatic cooling before eruption, particularly significant in the case of magmas that rise quickly from great depths such as kimberlites.

adiabatic demagnetisation, where the change in magnetic field on a magnetic material is used to provide adiabatic cooling.

the contents of an expanding universe can be described as an adiabatically cooling fluid.

The adiabatic process provided a way of nearly directly relating quantities of heat and work

Thermodynamics

T-V Relation

Adiabatic expansion

$$dU = q + w$$

For adiabatic process q=0

$$dU = w = -PdV = C_v dT$$

Thermodynamics

As per ideal gas equation

$$PV = RT \ or \ p = \frac{RT}{V}$$

Substituting in the equation

$$-\frac{RT}{V}dV = C_v dT$$

$$-R\frac{dV}{V} = C_v\frac{dT}{T}$$

Integrating both side

$$-Rln\frac{V_2}{V_1} = C_v ln\frac{T_2}{T_1}$$

Thermodynamics

$$R = C_P - C_V$$

Substituting the equation

$$-(C_P - C_V) ln \frac{V_2}{V_1} = C_v ln \frac{T_2}{T_1}$$

$$-\frac{(C_P - C_V)}{C_v} ln \frac{V_2}{V_1} = ln \frac{T_2}{T_1}$$

$$-\left(\frac{C_P}{C_v} - 1\right) ln \frac{V_2}{V_1} = ln \frac{T_2}{T_1}$$

Thermodynamics

If

$$\frac{C_P}{C_v} = \gamma, \text{adiabatic index}$$

$$-(\gamma - 1) ln \frac{V_2}{V_1} = ln \frac{T_2}{T_1}$$

$$-\left(\frac{V_2}{V_1}\right)^{(\gamma-1)} = \frac{T_2}{T_1}$$

$$\left(\frac{V_1}{V_2}\right)^{(\gamma-1)} = \frac{T_2}{T_1}$$

$$T_1 V_1^{(\gamma-1)} = T_2 V_2^{(\gamma-1)}$$

$$TV^{(\gamma-1)} = constant$$

Thermodynamics

P-V Relation

It is known

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{P_1V_1}{P_2V_2} = \frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{(\gamma-1)}$$

$$\frac{P_1}{P_2} = \left(\frac{V_2}{V_1}\right)^{\gamma}$$

$$P_1{V_1}^{\gamma} = P_2{V_2}^{\gamma}$$

$$PV^{\gamma} = constant$$