B: Physical Chemistry

Paper IV - Physical and organic Chemistry

B.Sc. Part II

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Thermodynamics

Work

For a container of uniform area, A and length, l, with one mole of ideal gas fitted with frictionless piston, by doing work, with external pressure (P_{ext}). initial volume (V_i) is changed to final volume (V_f).

$$w = force, f \times distance, l$$

$$w = (P_{ex} \times A) \times l = P_{ex} \times (A \times l) = P_{ex} \times (-\Delta V) = P_{ex} \times \left(V_f - V_i\right)$$

Or $w = -P_{ex}\Delta V$

Equilibrium change

For a change in volume in series of infinitesimal steps in equilibrium with each other

$$w = \int_{V_i}^{V_f} dw = \int_{V_i}^{V_f} -P_{ex}dV = -\int_{V_i}^{V_f} P_{ex}dV$$

Thermodynamics

Reversible change

During equilibrium change if internal pressure, P_{in} is only infinitesimally different from P_{ex}

$$or, P_{ex} = (P_{in} \pm dp)$$

$$w = -\int_{V_i}^{V_f}(P_{in} \pm dp)dV = -\int_{V_i}^{V_f}(P_{in}dV \pm dpdV) \approx$$

$$-\int_{V_i}^{V_f} P_{in}dV = -\int_{V_i}^{V_f} PdV = -\int_{V_i}^{V_f} nRT\,\frac{dV}{V}$$

$$w = -nRT\int_{V_i}^{V_f}\frac{dV}{V} = -nRT\,ln\frac{V_f}{V_i} = -2.303nRT\,log\frac{V_f}{V_i}$$

Thermodynamics

Irreversible change

$$w = P_{ex}(V_f - V_i)$$

This means

There exists a function u(x,y)

$$du = \frac{\partial u}{\partial x}dx + \frac{\partial u}{\partial y}dy$$

$$du = Pdx + Qdy$$

During a process

System changes from one state to other
heat can be taken or given and
work can be done by the system or to the system.

There has to be some relation between path functions with the state functions.

Thermodynamics

First law of thermodynamics

For a closed system, the increment in the internal energy is equal to the difference between the heat accumulated by the system and the work done by it.

$$Change\ in\ internal\ energy, \Delta U = Q - W$$

where

Q denotes the net quantity of heat supplied to the system by its surroundings and

W denotes the net work done by the system.

the internal energy, a state function, can be stored in the system,

heat and work, a path function, cannot be stored or conserved independently since they depend on the process.

Thermodynamics

Sign convention

Claussius

$$Change\ in\ internal\ energy, \Delta U = Q - W$$

It originated with the study of heat engines that produce useful work by consumption of heat.

Used in science

Max Planck or the IUPAC convention

$$Change\ in\ internal\ energy, \Delta U = Q + W$$

considers all net energy transfers to the system as positive irrespective of any use for the system as an engine or other device.

Used in engineering

Thermodynamics

Application

when $W = 0$ and $Q = 0$

$dU = 0$

This gives **law of conservation of energy**

Energy of isolated system is constant

or

Energy cannot be created nor be destroyed.

Thermodynamics

Free Expansion

When P_{ext}= 0, w = 0, $\Delta U = q$

Isothermal free expansion

When q = 0, $\Delta U = 0$

At constant volume

$\Delta V = 0$, w = 0, $\Delta U = q_v$

Thermodynamics

Isothermal change

$\Delta U=0$, $q=-w$

Irreversible change

$$q = P_{ex}(V_f - V_i)$$

Reversible change

$$q = 2.303nRT\ log\frac{V_f}{V_i}$$

Internal energy

one and only *cardinal* thermodynamic potential. All other thermodynamic potentials are formulated from the internal energy.

The *U* term can be interpreted as the energy required to create the system.

In basic physics, to study the internal properties of the system, the internal energy is used.

Thermodynamics

Enthalpy

At constant pressure as in case of chemical reaction under atmospheric pressure

$$\Delta U = q_P - P\Delta V$$

$$(U_f - U_i) = q_v - P(V_f - V_i) = q_v - PV_f + PV_i$$

$$q_P = (U_f - U_i) + PV_f - PV_i = (U_f + PV_f) - (U_i + PV_i) = H_f - H_i = \Delta H$$

Heat content or Enthalpy, H = U+PV

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

SI Unit= joule.

British thermal unit (BTU): calorie.

Enthalpy is a state function identified by the system's internal energy, pressure, and volume.

It is an extensive quantity.

Thermodynamics

Significance

Enthalpy at constant pressure is the heat absorbed by the system.

when ΔP=0

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

In a closed system, for processes at constant pressure, the heat absorbed or released equals the change in enthalpy.

Exothermic reaction has +ve ΔH

Endothermic reactions have –ve ΔH

Thermodynamics

At constant volume when $\Delta V = 0$ in cases of solids and liquids

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

In case of gaseous reactants and products $\Delta V \neq 0$

For a reaction $nA(g) \rightarrow nB(g)$

$$PV_A = n_A RT \ \ and\ PV_B = n_B RT$$

$$PV_A - PV_B = n_A RT - n_B RT$$

$$P(V_A - V_B) = (n_A - n_B)RT$$

$$P\Delta V = \Delta n_g RT$$

$$\Delta H = \Delta U + \Delta n_g RT$$

Molar enthalpy, H_m or simply H is enthalpy of one mole of substance