

1st Law of Thermodynamics -

Mathematical expression: -

Let us consider a system whose internal energy is U_1 . If the system is supplied 'q' amount of heat, then the energy of the system becomes $U_1 + q$.

Now if w amount of work is done on the system the energy in the final state is given by -

$$U_2 = U_1 + q + w$$

$$\therefore U_2 - U_1 = q + w$$

$$\boxed{\Delta U = q + w}$$

~~For~~ For isothermal process -

$$\Delta U = 0$$

$$\therefore \boxed{q = -w}$$

thus,

$$q = -w_{\text{rev}} = 2.303 nRT \log \frac{V_2}{V_1}$$

$$q = -w_{\text{rev}} = 2.303 nRT \log \frac{P_1}{P_2}$$



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Free expansion of an ideal gas -

Expansion of gas in vacuum ($P_{\text{ext}} = 0$) is called free expansion. No work is done during free expansion of an ideal gas.

$$\therefore W_{\text{rev}} = P_{\text{ext}} \cdot dV = 0.$$

$$W_{\text{rev}} = - \int 2.303 nRT \log \frac{V_2}{V_1} = 0.$$

$$\Delta V = 0.$$

Q. 0.75 moles of an ideal gas expands isothermally & reversibly at 300 K from a volume 15 L to 25 L. Calculate q and w & ΔU .

$$[R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}].$$

$$W = 955.5 \text{ J}$$

Internal energy -

The total amount of energy associated with a definite amount of a substance under a given set of conditions is termed as internal energy or intrinsic energy, denoted by U or E .

Unit Joule, Kilo Joule, K calories, calories.

$4.184 \text{ J} = 1 \text{ cal.}$

$\Delta E = E_2 - E_1$

State function.

~~Sign Conventions~~

Enthalpy or Heat Content -

The sum of internal energy and pressure-volume work of the system under a particular condition is called Enthalpy of the system.

Mathematically -

$H = E + PV$



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for state-1

$$H_1 = U_1 + PV_1$$

$$H_2 = U_2 + PV_2$$

$$H_2 - H_1 = (U_2 - U_1) + P(V_2 - V_1)$$

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

at
constant P.~~from 1st law~~ ~~$\Delta U = q + w$~~

since,

J mol⁻¹KJ mol⁻¹Unit -~~Joules, KJoules.~~* Relationship between ΔU & q_v .

from 1st law of thermodynamics -

$$\Delta U = q + w.$$

In free expansion at constant volume

$$w = 0.$$

$$\Delta U = q + 0.$$

$$\therefore \Delta U = q_v$$



the Relationship between ΔH & q_p -

We know that Enthalpy -

$$H = U + PV$$

for state -1

$$H_1 = U_1 + PV_1$$

& state-2

$$H_2 = U_2 + PV_2$$

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

To change in internal energy (1st law -

$$\Delta U = q + w$$

at constant P -

$$\Delta U = q_p + w$$

Since, workdone in free expansion -

$$w = -P(V_2 - V_1) = -P\Delta V.$$

$$\therefore \Delta U = q_p - P\Delta V$$

$$U_2 - U_1 = q_p - P\Delta V$$

$$U_2 - U_1 = q_p - P(V_2 - V_1)$$

$$U_2 - U_1 = q_p - PV_2 + PV_1$$



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$$q_p = (U_2 + PV_2) - (U_1 + PV_1)$$

$$q_p = \Delta H$$

* Relationship between q_p & q_v
 ΔH & ΔU

Let us suppose in a gaseous react, the ~~the~~ total volume of the reactant & products are V_A & V_B respectively.

n_A & n_B are the total no. of moles of gaseous reactants and products respectively.

from an ideal gas eqn -

$$PV = nRT$$

At constant T & P .

$$P \cdot V_A = n_A RT$$

$$\& \quad P \cdot V_B = n_B RT$$

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

$$P \Delta V = \Delta n RT \quad \text{--- (1)}$$



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Since, its change in enthalpy at constant P -

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

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

Since, $\Delta H = q_p$

$$\Delta U = q_v$$

$$q_p = q_v + \Delta n RT$$

where, $\Delta n = (\text{no. of moles of gaseous product} - \text{no. of moles of gaseous reactant})$

characteristics -

① If $\Delta n = +ve.$

$$q_p > q_v.$$

② If $\Delta n = -ve.$

$$q_p < q_v$$

③ If $\Delta n = 0.$

$$q_p = q_v.$$