Calculation of w, q, ΔU and ΔH for expansion of ideal gas under isothermal and adiabatic conditions for reversible and irreversible processes:

A. Isothermal expansion of an ideal gas

Calculation of ΔU:

In isothermal expansion, the temperature of the system does not vary. The internal energy U of an ideal gas is the function of temperature, so at constant temperature (isothermal process) the internal energy of the system remains constant.

Therefore, **ΔU=0.**

Calculation of ΔH

Thermodynamically, H= U + PV ………………………………………………………… (1)

Therefore, $\Delta H = \Delta(U + PV) = \Delta U + \Delta PV = \Delta U + \Delta n RT$ (from ideal gas equation) …(2)

But in isothermal process, ΔT=0 and ΔU=0, therefore ΔH=0

Calculation of q and w

From the first law of thermodynamics, we derived that, ΔU= q + w.

Since in isothermal process ΔU = 0, hence w = -q.

This shows that by absorption of heat the work is done by the system in isothermal expansion.

B. Work done in Reversible Isothermal Expansion

Consider a system in which gas is enclosed in a cylinder with frictionless and weightless piston. The temperature of the system remains constant since system is supposed to be in thermal equilibrium with the surroundings. The external pressure P on the piston is equal to the pressure of the gas within the cylinder.

The expansion of the gas occurs and the volume of the gas changes from V to V+dV when the external pressure of the gas is lowered by infinitesimal amount dP to become P-dP. Because of expansion, the pressure of the gas becomes equal to the external pressure. The piston then comes to rest.

Further if the process is repeated and the external pressure is lowered by infinitesimal amount dP then the gas will undergo second infinitesimal expansion dV before the pressure again equals to

new external pressure. Continuing the process, the external pressure will further be lowered which results in increase of volume dV each time.

Since the system is in thermal equilibrium with the surroundings, the infinitesimally small cooling produced as a result of infinitesimally small expansion of the gas at each step, is offset by the heat absorbed from the surroundings and the temperature remains constant throughout the operation. During expansion, pressure decreases and the volume increases.

Thus the work done by the gas for the small volume change in an infinitesimal expansion is given by:

$$dw = -(P - dP)dV = -PdV \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(3)$$

Since the product dPdV is very small quantity therefore ignored.

The total work done w by the gas in expanding from volume V_1 to the volume V_2 will be the sum of the series of the terms PdV in which pressure keeps on decreasing and is given by

$$w = -\int_{V_1}^{V_2} P \, dV \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots..(4)$$

Substituting $P = RT/V$ in the above expression for one mole of an ideal gas thus giving,

$$w = -RT\int_{V_1}^{V_2} \frac{dV}{V} = -RT \ln \frac{V_2}{V_1} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.(5)$$

At constant temperature, $P_1 V_1 = P_2 V_2$ for the case of ideal gas, thus work done can also be written as

$$w = -RT \ln (P_1 / P_2) \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.(6)$$

For n moles of the gas, the work done can be written as:

$$w = -nRT \ln (V_2 / V_1) = -nRT \ln (P_1 / P_2) = -2.303 \, nRT \, log \frac{P_1}{P_2} \quad \dots\dots\dots\dots\dots.(7)$$

As V_2 is greater than V_1 in case of expansion and P_2 is less than P_1 thus in above equation work done will always be negative.

The expansion of a given amount (n mole) of gas results into decrease in the moles per unit volume. Therefore equation (5) can be modified to represent the work done when an ideal solution is diluted from initial concentration c_1 to a final concentration c_2.

Since $c_i = \frac{n_i}{V}$ therefore, $w = -nRT \, ln \frac{c_1}{c_2}$

C. Work done in Reversible Isothermal Compression

Now suppose gas is compressed reversibly from volume V_2 to V_1.

In this case, the external pressure will be greater than pressure inside the cylinder by an infinitesimal amount dP. Thus external pressure will be P+dP.

Let the gas is compressed by an infinitesimal amount, say dV. The two parameters pressure and volume are of opposite signs as during compression the pressure increases and the volume decreases.

Now the expression for the infinitesimal amount of work done on the system by the surroundings is:

$$dw = -(P + dP) \, dV = - PdV \quad\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots..(8)$$

Here the term dPdV is small quantity therefore it is ignored.

Let the gas is compressed from volume V_2 to V_1, then the work done (w') by the surroundings on the gas is given by:

$$w' = -\int_{V_2}^{V_1} P \, dV \quad\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(9)$$

Taking the gas to be ideal, thus substituting P= RT/ V and $P_1 V_1 = P_2 V_2$ in the above expression we get,

$$w' = -RT\int_{V_2}^{V_1} \frac{dV}{V} = -RT \ln (V_1 / V_2) = -RT \ln (P_2 / P_1) \quad\dots\dots\dots\dots\dots. (10)$$

For n moles of the gas, the work done is given by:

$$w' = -nRT \ln (V_1 / V_2) = -nRT \ln (P_2 / P_1) \quad\dots\dots\dots\dots\dots\dots\dots..(11)$$

Since during compression the initial volume $V_2 > V_1$ and $P_2 < P_1$ thus, w' will always be positive.

D. Work done in Irreversible Isothermal Expansion

There are two types of irreversible isothermal expansion: expansion against zero pressure i.e. in vacuum (called free expansion) and expansion against constant external pressure which should be less than the pressure of the gas i.e. $P^{ext} < P$ (called intermediate expansion).

Free expansion:

In free expansion the external pressure is zero, therefore the work done is given by

$$w = -\int dw = -\int P^{ext} \, dV = 0 \qquad \text{............................} \quad (11)$$

Intermediate expansion:

Let the volume expands from V_1 to V_2 against an external pressure P^{ext} then the work done will be:

$$w = -\int_{V_1}^{V_2} P^{ext} \, dV = -P^{ext} (V_2 - V_2) \qquad \text{...................................} (12)$$

The work done during intermediate isothermal expansion is less than the work done during reversible isothermal expansion since P^{ext} is less than P in the case of intermediate isothermal expansion while P^{ext} is almost equal to P in the case of reversible isothermal expansion.

The work done by the gas during expansion is (-w). Therefore,

$$-w = P^{ext}\left(\frac{nRT}{P_2} - \frac{nRT}{P_1}\right)$$

$$-w = nRT\left(1 - \frac{P_2}{P_1}\right) \qquad \text{(if } P_2 \approx P^{ext}\text{)}$$

E. Adiabatic expansion:

In adiabatic expansion no heat is transferred between the system and the surroundings i.e. q=0 Thus equation for first law of thermodynamics becomes

$$\Delta U = 0 + w \text{ or } w = \Delta U \qquad \text{...}(13)$$

Since in expansion, work is done by the system, so 'w' will be negative.

Thus Δ U will also be negative. Due to the decrease in internal energy the temperature of the system also decreases. This states that work is done at the expense of internal energy of the gas.

While in compression w is positive therefore ΔU will be positive which consequently increases the temperature of the system. This states that the work is stored in the system in the form of rise in internal energy.

Calculation of ΔU:

At constant volume the molar heat capacity for an ideal gas is given by:

$$C_V = (\partial U / \partial T)_V$$ …………………………………………………………….…(14)

Accordingly finite change in internal energy will be

$$\Delta U = C_V dT$$ ……………………………..(15)

Calculation of ΔH:

From classical thermodynamics, enthalpy is given by

$$H = U + PV$$

So, change in enthalpy for one mole of the gas is

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + R\Delta T$$ …………………………………………(16)

Substituting the value of ΔH , we get

$$\Delta H = C_V \Delta T + R\Delta T = (C_V + R)\Delta T = C_p \Delta T$$ ………………..…..…(17)

Calculation of w:

In adiabatic process q=0, thus from the first law equation, $\Delta U = q + w$, the work done will be given by:

$$w = \Delta U = C_V \Delta T$$

Thus from the above equations we can say that all the three quantities ΔU, ΔH and w dependent on temperature. Since the variation in temperature depends upon the nature of the process i.e. whether the process is reversible or irreversible, thus the magnitude of thermodynamic properties will also vary with the nature of the process.

F. Final Temperatures in Reversible and Irreversible Adiabatic Expansions:

Reversible Adiabatic Expansion: Relation between Temperature and Volume:

The final temperature in the case of reversible adiabatic expansion is obtained from the expressions which relate the initial and final temperatures to the respective volumes or pressures.

Let the expansion is done against the external pressure Δ P and V be the increase in volume. Then, the external work done by the system is equal to $-\Delta$ PV. Hence, according to the First law equation:

$$\Delta U = -P\Delta V \quad\text{.. (18)}$$

Let the fall in temperature be ΔT and $\Delta U = C_V\Delta T$

Therefore, $C_V\Delta T = -PdV$ .... (19)

For infinitesimally small quantities,

$$C_V dT = -PdV = -RT\, dV/V \text{ (for 1 mole of the gas)}$$

Dividing the above equation by T

$$C_V dT/T = -R\, dV/V$$

Or $\quad C_V d(\ln T) = -R\, d(\ln V)$

Or $\quad \frac{C_v}{R} d(\ln T) = -d(\ln V)$ .... (20)

Integrating the above equation between the limits of temperatures T_1 and T_2 with the corresponding volumes V_1 and V_2 then we get,

$$C_V \ln(T_2/T_1) = -R\ln(V_2/V_1) = R\ln(V_1/V_2) \quad\text{......................... (21)}$$

$$\ln(T_2/T_1) = (R/C_V)\ln(V_1/V_2)$$

Since, $C_p - C_v = R$, and substituting $C_p/C_v = \gamma$, we get

$$T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\frac{nR}{C_v}} = T_1\left(\frac{V_1}{V_2}\right)^{\frac{R}{C_{v,m}}}$$

$$T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1} \quad\text{... (22)}$$

or $\quad T_1/T_2 = (V_2/V_1)^{\gamma-1}$ $\qquad$ (Note that $\gamma > 1$)

Since in the case of expansion $V_2 > V_1$ and $T_2 < T_1$. Hence, a gas cools during reversible adiabatic expansion.

Work done in Irreversible Adiabatic Expansion:

In this section, two cases are considered:

- **Free Expansion:**

In the case of free expansion the external pressure is zero, thus the work done in this expansion is also zero. Therefore, $U\Delta$ which is equal to w, is also zero. In the case of ideal gas, the change in the internal energy is function of temperature thus accordingly if ΔU is zero then ΔT is also zero. The change in enthalpy is given by $\Delta H = \Delta U + nR\,\Delta T$, as ΔU and ΔT are zero therefore ΔH is also zero. Thus, in a free adiabatic expansion, $\Delta T = 0$, w = 0 and $\Delta H = 0$.

- **Intermediate Expansion.**

Let the gas expands from the volume V_1 to V_2 against a constant pressure P^{Ext} of the gas. Then the work done in this case will be:

$$w = -P^{Ext}(V_2 - V_1) \qquad \qquad ...(23)$$

In adiabatic expansion q=0, therefore from first law equation i.e. $\Delta U = q + w$

Thus $w = \Delta U$

Further, $w = \Delta U = C_V(T_2 - T_1)$. $\qquad \qquad ....(24)$

From Equations (23) and (24),

$$P^{Ext}(V_1 - V_2) = -C_V(T_2 - T_1)$$

or $\quad C_V(T_1 - T_2) = P^{Ext}(V_1 - V_2) = P^{Ext}(RT_1/P_1 - RT_2/P_2)$

$$= RP^{Ext}(T_1P_2 - T_2P_1)/P_1P_2$$

Thus, T_2 can be calculated from the values of C_V, T_1, P_1, P_2 and P^{Ext} .

Since the external pressure is constant, work of expansion is given by:

$$-w_{irr} = \int_{V_1}^{V_2} P^{Ext}\,dV = P^{Ext}(V_2 - V_1) = P^{Ext}\left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right)$$