Thermodynamics - I

Thermodynamics means flow of heat and it deals with energy changes accompanying all types of physical and chemical processes.

The primary objectives of thermodynamics are —

(1) To establish criteria for predicting the feasibility or chemical transformation under given sets of conditions.

(2) To determine the extent to which a process including a chemical reaction would proceed under some given conditions after its feasibility is established.

(3) To deduce some direction generalization of physical chemistry such as Vant Hoff law of dilute solution, Raoult's law of vapour pressure lowering and law of chemical equilibrium.

Limitations of Thermodynamics:

(1) The laws of thermodynamics apply only to matter in bulk and not to individual atoms or molecules.

(2) It can only predict the possibility of a process but not its success.

(3) It does not tell anything about the rate of reaction.

(4) Thermodynamics does not explain the mechanism of the process.

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Some basic terms used in thermodynamics:

System: The part of the universe selected for thermodynamic study is called a system.

Surrounding: The remaining part of the universe around the system which is not under study is called surrounding.

Types of system:

① **Open system:** A system which can exchange both matter as well as energy with the surrounding is called an open system.

② **Closed system:** The system which may exchange energy but not matter with surroundings is called closed system.

③ **Isolated system:** A system which can neither exchange matter nor energy with the surroundings is called isolated system.

Macroscopic system:

A system is said to be macroscopic when it consists of a very large no. of molecules, atoms or ions.

Homogeneous and Heterogeneous systems:

A system is said to be homogeneous, when it is completely uniform throughout. It consists of only one phase.

A system is said to be heterogeneous, when it is not uniform throughout. It consists of two or more phases.

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State of a system:

The condition of existence of a system when its macroscopic properties have a definite value is called a state of a system.

When a process occurs, the state of the system changes. The first and the last state of the system are called initial system state and final state respectively.

State variables:

Those macroscopic properties which when change cause change in the state of the system are called state variables. The most common of macroscopic properties are — composition, pressure, temperature and volume.

The two variables generally specified are pressure and temperature. These are called independent variables. The variables such as volume, whose value depends upon the value of pressure and temperature are called dependent variables.

Equation of State:

The relationship between pressure, temperature and volume is called eqn of state. e.g. The eqn of state of an ideal gas is, $PV = RT$ (for 1 mole of the gas).

Thermodynamic Equilibrium:

A system in which the macroscopic properties do not undergo any change with time is called thermodynamic equilibrium. Three kinds of equilibria exist —

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① Isothermal process: A system is said to be in thermal equilibrium if there is no flow of heat from one part of the system to another.

② Mechanical equilibrium: A system is said to be in mechanical equilibrium, if no mechanical work is done by one part of the system on another part of the system.

③ Chemical equilibrium: A system is said to be in chemical equilibrium if the composition of the various phase in the system remains the same throughout.

Extensive and Intensive properties:

A system which depends upon the amount of the substance or substances present in the system is called extensive property e.g. Mass, volume and energy.

A system which ~~depends~~ does not depend on the amount of the substance present in the system is called intensive property. eg. Temperature, pressure, density, viscosity, surface tension, etc.

Thermodynamic processes:

A process is defined as an operation by which system changes from one state to another. The various types of processes are—

② Isothermal process: It is defined as the one in which temp^{r} of the system remains constant during each stage of the process.

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(b) Adiabatic process: It is defined as the one in which no heat enters or leaves the system during any step of the process.

(c) Isobaric process: It is defined as the one in which the pressure of the system remains constant during each stage of the process.

(d) Isochoric process: It is defined as the one in which the volume of the system remains constant during each stage of the process.

(e) Cyclic process: A process is said to be cyclic if a system after completing a series of changes returns to its original state.

Reversible & Irreversible process:

A process is said to be reversible process if it is carried out infinitesimally slowly so that the driving force is only infinitesimally greater than the ~~other~~ opposing force, is called a reversible process.

A process is said to be irreversible, if it is not carried out infinitesimally slowly so that the system does not get a chance to attain equilibrium.

An irreversible process can't be reversed without the help of an external energy.

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Nature of work (w) and heat (q):

In molecular terms, heat is the transfer of energy that makes use of chaotic molecular motion. The chaotic motion of the molecule is called thermal motion.

S.I. unit of heat energy is Joule and C.G.S. unit is erg. q is +ve if heat is absorbed by the system and q is -ve if heat is released by the system.

Work is a transfer of energy that makes use of organised motion. When a system does work, it stimulates orderly motion in the surrounding. Work done,

$$w = \text{Force} \times \text{displacement}$$
$$= \text{mass} \times \text{acceleration} \times \text{displacement}.$$

$$\therefore \text{S.I. unit of } w = kg \times ms^{-2} \times m.$$
$$= kg\, m^2 s^{-2}.$$
$$= \text{Newton} \times m.$$
$$= J.$$

In C.G.S, $1\ J = 10^7$ erg.

$4.184\ J = 1$ cal.

If work is done on the system, then w is +ve.
If work is done by the system, then w is -ve.

1st Law of Thermodynamics: This law was first started by Mayer and Helmholtz in 1842. The law may be stated in any one of the following ways —

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① Energy can neither be created nor destroyed. It can be converted from one form to another. Thus, 1st law of thermodynamics is also called law of conservation of energy.

② The total energy of universe is constant.

③ The total energy and mass of an isolated system remains constant.

④ It is impossible to construct a perpetual motion machine, ie. a machine which can produce work without the consumption of energy.

Internal energy (U):

Every substance is associated with a definite amount of energy which depends upon its chemical nature as well as upon its temp^{r}, pressure and volume. This energy is known as internal energy.

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* **Internal energy and the first law:**

Suppose, a system is subjected to change of pressure and volume. Let, the initial state be represented by A and the final state by B and. let, U_A and U_B represent energies associated with the system in the states A and B, respectively.

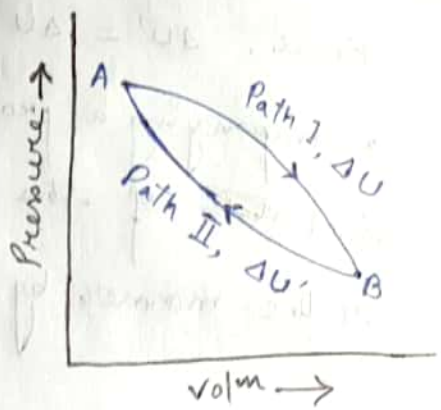

Fig: Change of internal energy.

$\therefore$ change in internal energy, $\Delta U = U_B - U_A$.

$\because U_A$ and U_B are definite quantities, hence ΔU must also be a definite quantity, irrespective of the path or the manner in which the change is brought about. If it were not so, it could be possible to construct a perpetual motion machine.

Let, the system changes from state A to state B by following path I with change in energy ΔU. Again, let the system changes from state B to state A by following path II with change in energy $\Delta U'$. Suppose $\Delta U > \Delta U'$.

$\therefore$ i.e. $A \longrightarrow B$ (Path I)

$B \longrightarrow A$ (Path II).

When the system returns to its initial state, a surplus of energy $(\Delta U - \Delta U')$ would become available. By repeating the same cycle, over and over again, energy would be generated continuously and a perpetual motion machine would

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be possible. But, this is contrary to the first law.
Hence, $\Delta U' = \Delta U$. i.e. The change in internal energy accompanying a process is a function only of the initial and final states of the system and is independent of the path or the manner by which the change is brought about.

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Mathematical form of 1st law of Thermodynamics :

Let, U_A be the internal energy of a system in its state A and U_B be the energy in its state B. Let, q be the heat absorbed from the surroundings and w be the work done when the system undergoes change from state A to state B. Hence, change of internal energy,

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$$\Delta U = U_B - U_A = q - w .$$

Again, if the quantity of heat transferred from the surroundings to the system is q and work done is w,

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

Note :

① If work is done by the surroundings, w is taken as positive. Hence, $\Delta U = q + w$.

② If work is done on the surroundings, w is taken as negative. Hence, $\Delta U = q - w$.

State function, path function, exact and inexact differential

A function is a state function when changes in its value from the initial state to final state doesn't depend on the path of the process. e.g. Pressure, temp^{r}, volume and energy are state functions. A differential of such a property is called exact differential. $\int_{U_1}^{U_2} dU = U_2 - U_1$

The property of the system whose change in value depends upon the path followed for the process is called path function. e.g. work is a path function because it depends upon the manner in which it is brought about. A differential of path functions like ~~work~~. dq, dw are called inexact differentials. $\int_{q_1}^{q_2} dq \neq q_2 - q_1$, $\int_{w_1}^{w_2} dw \neq w_2 -$

∵ In first law eqn, $\Delta U = q + w$., w is not a state function, q is also not a state function, because ΔU is a definite quantity.

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Work of expansion or P-V work:

Let us consider a gas enclosed in a cylinder fitted with a piston.

Let, initial volume of the gas $= V_1$

area of cross-section of the cylinder or piston $= a\ cm^2$

Let, external pressure against which gas has to expand $= P_{ext}$

$= P.$

Suppose, during expansion of the gas, the piston move through a small distance dl so that final volume of the gas becomes $= V_2$.

Let, the force acting across the cross-section of the piston $= f$

$\therefore$ Pressure $= \frac{\text{Force}}{\text{Area}}$

$\Rightarrow P = \frac{f}{a}$

$\Rightarrow f = P.a.$

$\therefore$ work done during expansion = force $\times$ distance

$\Rightarrow dw = f.dl$

$\Rightarrow dw = P.a.dl.$

$\Rightarrow dw = P.dV.$

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If the expansion takes place from V_1 to V_2, total work done

$$\int \delta\omega = \int_{V_2}^{V_1} P \cdot dV \quad [\because P \text{ is constant}].$$

$$\Rightarrow \int \delta\omega = P \int_{V_2}^{V_1} dV.$$

$$\Rightarrow \omega = P.(V_2 - V_1).$$

$$\Rightarrow \boxed{\omega = P.\Delta V}$$

$$\Rightarrow \boxed{\omega = P_{ext}.\Delta V}$$

Enthalpy or Heat content of a system:

Let, the volume of a system ~~change~~ increases from V_A to V_B at constant pressure P.

$\therefore$ Work done, $\omega = -P.(V_B - V_A)$. $\longrightarrow$ (I)

We know,

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

$$\Rightarrow \Delta U = q - P(V_B - V_A). \quad [\text{From eqn (I)}].$$

$$\Rightarrow U_B - U_A = q - PV_B + PV_A.$$

$$\Rightarrow q = (U_B + PV_B) - (U_A + PV_A). \longrightarrow (II).$$

The quantity $(U + PV)$ is called enthalpy of the system and is denoted by H. It is the total energy stored in the system.

$$\therefore H = U + PV. \longrightarrow (III).$$

where U is the internal energy, P is pressure and V is the volume of the system.

eqn (II) & (III) $\Rightarrow \Delta H = q$. $\longrightarrow$ (IV) $\quad [\Delta H = H_B - H_A]$.

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again from eqⁿ (II),

$$q = (U_B - U_A) + P(V_B - V_A)$$

$$\Rightarrow \boxed{\Delta H = \Delta U + P\Delta V} \quad [\text{From eqⁿ (IV)}].$$

Hence, the enthalpy change accompanying a process may be defined as the sum of the increase in internal energy of the system and the pressure volume work done by the system.

Enthalpy of Vapourisation:

Enthalpy of vapourisation or Heat of vapourization (ΔH_v) of a substance may be defined as the amount of heat absorbed to convert 1 mole of the substance from liquid stat into vapours at 298 K (25°C).

Enthalpy of Fusion:

Enthalpy of fusion of a substance may be described as the amount of enthalpy (heat) required to change 1 mole of its solid into liquid at its melting point.

Heat capacity:

Heat capacity of a system, between any two temperatures is defined as the quantity of heat (q) required to raise the temperature of the system from the lower to the higher temperature divided by the temperature difference.

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If the mass of the system is one gram, the heat capacity is called specific heat of the system.

If the mass of the system is one mole, the heat capacity is called molar heat capacity of the system (C).

$$C = \frac{q}{T_2 - T_1} = \frac{q}{\Delta T} \quad \ldots (1)$$

If small amount of heat δq is absorbed by the system and the change in temperature is dT, then

$$C = \frac{\delta q}{dT}$$

$\because$ q is not a state function.

$\therefore$ C is also not a state function.

Types of Heat Capacities:

(1) Heat capacity at constant volume (C_v):

Heat capacity at constant volume at a given temp^r of gas may be defined as the heat required to raise the temp^r of one mole of the gas through one degree when volume of the gas is kept constant.

$$\text{i.e. } C = \frac{q}{\Delta T} \longrightarrow (I)$$

where, q is the amount of heat absorbed by one mole of the gas when temp^r changes by ΔT degrees.

$$\text{Also, } C = \frac{\delta q}{dT} \longrightarrow (II)$$

where δq is the small amount of heat absorbed

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and dT is small increase in temp^{e}.

From first law of thermodynamics,

$$\delta q = dU + P\,dV.$$

$$\therefore \text{Eq}^{n}\ (II) \Rightarrow C = \frac{dU + P\,dV}{dT} \longrightarrow (III)$$

When volume is constant, $dV = 0$.

$$\therefore \boxed{C_V = \left(\frac{\partial U}{\partial T}\right)_V} \longrightarrow (IV)$$

$\because$ For an ideal gas, the internal energy is independent of volume.

$\therefore$ For an ideal gas, eq^{n} (IV) can be written as,

$$C_V = \frac{dU}{dT}$$

Thus, C_V is the rate of change of internal energy with temperature when the volume is kept constant.

Heat capacity at constant pressure, C_P:

We have,

$$C = \frac{dU + P\,dV}{dT} \longrightarrow (I)$$

When pressure is constant, the volume of the gas increases on heating the gas. Then, the expansion is carried out reversibly such that,

$$P_{ext} = P_{gas} = P.$$

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$\therefore$ Eq^n ① $\Rightarrow C_p = \left(\frac{dU + pdV}{dT}\right)_p$

$\Rightarrow C_p = \left(\frac{\partial U}{\partial T}\right)_p + p\cdot\left(\frac{\partial V}{\partial T}\right)_p \longrightarrow$ ⑪

We know,

$$H = U + PV.$$

Differentiating both sides w.r.t. temperature at constant P,

$$\left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + p\cdot\left(\frac{\partial V}{\partial T}\right)_p \longrightarrow$$ ⑫

From eq^n ⑪ & ⑫, we have,

$$\boxed{C_p = \left(\frac{\partial H}{\partial T}\right)_p}$$

For an ideal gas, $C_p = \frac{dH}{dT}$.

Thus, C_p is the rate of change of molar enthalpy with temperature at constant pressure.

Relation between C_p and C_v :

We know,

$$C_p = \frac{dH}{dT} \quad \text{and} \quad C_v = \frac{dU}{dT}.$$

$\because C_p > C_v$

$\therefore (C_p - C_v)$ will give work done by one mole of the gas in expansion when heated through 1°C at constant pressure.

$\therefore C_p - C_v = \frac{dH}{dT} - \frac{dU}{dT}. \longrightarrow$ ①.

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But, $H = U + PV$

and $PV = RT$ (for 1 mole of an ideal gas).

$\therefore H = U + RT$.

Differentiating this eqⁿ w.r.t. T, we get.

$$\frac{dH}{dT} = \frac{dU}{dT} + R.$$

$$\Rightarrow \frac{dH}{dT} - \frac{dU}{dT} = R$$

$$\Rightarrow \boxed{C_p - C_v = R} \longrightarrow (11) \quad [\text{From eqⁿ } (1)].$$

i.e. C_p is greater than C_v by the gas constant R whose value is 1.987 calories or 8.314 Joules.

Eqⁿ (11) can also be written as,

$$\boxed{C_p - C_v = nR}$$ (for n mole of an ideal gas)

Calculation of ΔU, ΔH, q and w for isothermal expansion of an ideal gas:

(a) Calculation of ΔU:

Since in an isothermal process, the temp^{r} of the system remains constant throughout the process of expansion, $\boxed{\Delta U = 0}$. It is because, for an ideal gas, internal energy U depends only on temperature.

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(b) Calculation of ΔH:

Enthalpy, $H = U + PV$.

$\Rightarrow \Delta H = \Delta U + \Delta PV$.

$\Rightarrow \Delta H = \Delta U + \Delta nRT$.

$\because$ For an isothermal process, T is constant.

$\therefore \Delta T = 0$ and $\Delta U = 0$.

$\therefore$ $\boxed{\Delta H = 0}$.

(c) Calculation of q and w:

From first law of thermodynamics,

$$\Delta U = q + w$$

$\because$ For an isothermal process, $\Delta U = 0$.

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

Work done in Reversible Isothermal Expansion:

Since, during expansion, pressure decreases and volume increases, work done by the gas is given by,

$$\delta w = -P_{ext} \cdot dV$$

$$= -(P - dP)dV$$

$$= -PdV + dPdV.$$

{ where $(P - dP)$ is the fall in pressure, when the gas expands by an infinitesimal volume dV }.

$\because$ $dP.dV$ is very very small, hence it can be neglected.

$\therefore$ $\delta w = -PdV$.

$\therefore$ ~~Wor~~ Total work done by the ~~exp~~ gas in expansion from original volume V_1 to final volume V_2,

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$$W = -\int_{V_1}^{V_2} P\,dV \quad \longrightarrow (1).$$

$\because PV = RT$ for 1 mole of an ideal gas.

$\Rightarrow P = \frac{RT}{V}$.

$\therefore$ eqn (1) $\Rightarrow W = -\int_{V_1}^{V_2} \frac{RT}{V}\,dV$.

$\Rightarrow W = -RT \int_{V_1}^{V_2} \frac{dV}{V}$.

$\Rightarrow W = -RT \left[\ln V\right]_{V_1}^{V_2}$.

$\Rightarrow W = -RT\left(\ln V_2 - \ln V_1\right)$.

$\Rightarrow \boxed{W = -RT \ln \frac{V_2}{V_1}}$. $\longrightarrow (11)$.

$\because$ For an ideal gas, at constant temperature,

$P_1 V_1 = P_2 V_2$.

$\Rightarrow \frac{P_1}{P_2} = \frac{V_2}{V_1}$.

$\therefore$ eqn (11) $\Rightarrow \boxed{W = -RT \ln \frac{P_1}{P_2}}$

For n moles of an ideal gas,

$$\boxed{W = -nRT \ln \frac{V_2}{V_1}}$$

$$\boxed{W = -nRT \ln \frac{P_1}{P_2}}$$

where, $V_2 > V_1$ and $P_1 > P_2$.

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Work done in Irreversible Isothermal Expansion:

(a) Expansion against zero pressure (free expansion):

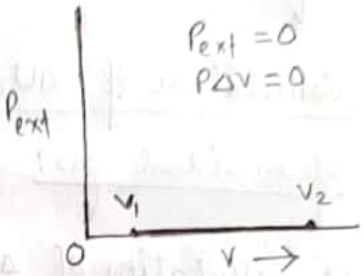
We have, work done during expansion,

$$w = -\int_{V_1}^{V_2} P_{ext}\, dV$$

When $P_{ext} = 0$, i.e. when the gas is expanding against no pressure (vacuum),

$$w = -0 \cdot \int_{V_1}^{V_2} dV$$

$$\Rightarrow \boxed{w = 0}$$



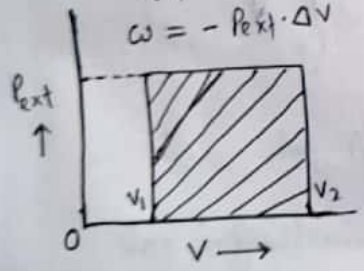
(b) Work against constant external pressure:

Here, $P_{ext} < P_{gas}$.

$\therefore$ Work done, $w = -\int_{V_1}^{V_2} P_{ext}\, dV$.

P_{ext} = constant

$w = -P_{ext} \cdot \Delta V$



$$= -P_{ext} \int_{V_1}^{V_2} dV.$$

$$= -P_{ext}(V_2 - V_1)$$

$$= -P_{ext} \cdot \Delta V.$$

(c) Variable external pressure:

Area under PV curve is the work done.

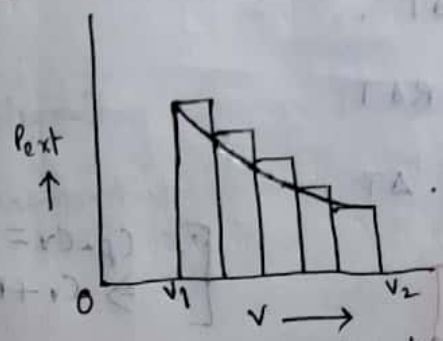


Fig: P_{ext} is varying systematically

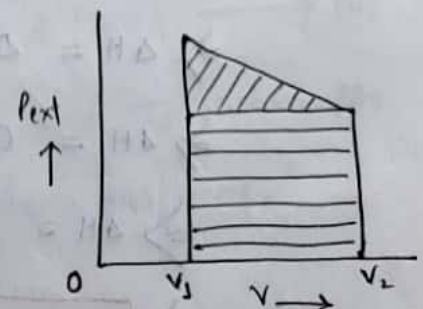


Fig: P_{ext} is varying linearly

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Maximum Work:

Work done by the system will be maximum if the expansion takes place reversibly, i.e. when the external pressure differs from the pressure of the gas only by an infinitesimal amount.

Calculation of ΔU, ΔH, q and w for adiabatic expansion of an ideal gas:

(a) Calculation of ΔU:

We know, molar heat capacity at constant volume of an ideal gas.

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

$$\Rightarrow dU = C_v \cdot dT .$$

For finite change in temperature, keeping C_v constant,

$$\boxed{\Delta U = C_v \cdot \Delta T} .$$

(b) Calculation of ΔH:

$\because H = U + PV$.

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

$\Rightarrow \Delta H = \Delta U + \Delta(RT)$.

$\Rightarrow \Delta H = \Delta U + R \cdot \Delta T$.

$\Rightarrow \Delta H = C_v \cdot \Delta T + R\Delta T$.

$\Rightarrow \Delta H = (C_v + R) \cdot \Delta T$.

$\Rightarrow \boxed{\Delta H = C_p \cdot \Delta T}$

$\left[\because C_p - C_v = R \Rightarrow C_v + R = C_p\right]$

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© Calculation of ω and q:

$\because$ In adiabatic process, $q = 0$.

$\therefore$ From 1st law eqⁿ,

$$\Delta U = \omega.$$

$$\Rightarrow \boxed{\omega = C_v . \Delta T}.$$

Reversible Adiabatic Expansion:

(a) Relation between Temperature T and volume V:

Let, P be the external pressure against which expansion is taking place and ΔV be the increase in volume. Then, the external work done by the system is equal to $-P.\Delta V$.

For adiabatic expansion, $q = 0$.

$\therefore$ From first law eqⁿ, $\Delta U = q + \omega$.

$$\Rightarrow \Delta U = 0 + \omega$$

$$\Rightarrow \Delta U = -P\Delta V.$$

If ΔT is the fall in temp^{r}, then,

$$\because \Delta U = C_v . \Delta T.$$

$$\Rightarrow C_v . \Delta T = -P . \Delta V. \longrightarrow (1)$$

For infinitesimally small quantities,

$$C_v dT = -PdV = -RT.\frac{dV}{V} \quad \left[\because P = \frac{RT}{V}\right].$$

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

$$\Rightarrow C_v . d(\ln T) = -R . d(\ln V). \longrightarrow (4).$$

Integrating between temperatures T_1 and T_2 when the corresponding volumes are V_1 and V_2, we have,

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$$C_v \int_{T_1}^{T_2} d\ln T = -R \int_{V_1}^{V_2} d\ln V$$

$$\Rightarrow C_v \left[\ln T\right]_{T_1}^{T_2} = -R \left[\ln V\right]_{V_1}^{V_2}$$

$$\Rightarrow C_v \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1} \longrightarrow (III)$$

$$\Rightarrow C_v \ln \frac{T_2}{T_1} = R \ln \frac{V_1}{V_2}$$

$$\Rightarrow \ln \frac{T_2}{T_1} = \left(\frac{R}{C_v}\right) \ln \frac{V_1}{V_2}$$

$$\Rightarrow \ln \frac{T_2}{T_1} = \ln \left(\frac{V_1}{V_2}\right)^{R/C_v}$$

$$\Rightarrow \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{R/C_v} \longrightarrow (IV)$$ [Taking anti Log on both sides]

$$\Rightarrow V_1^{R/C_v} \cdot T_1 = V_2^{R/C_v} \cdot T_2 \longrightarrow (V).$$

$\because C_p - C_v = R.$

$\therefore$ Eqn (IV) $\Rightarrow \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\frac{C_p - C_v}{C_v}}$

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

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

where, $\frac{C_p}{C_v} = \gamma$ is the ratio of two heat capacities.

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

$$\Rightarrow \boxed{T V^{\gamma-1} = \text{constant}}$$

This is the relationship between T and V in adiabatic process.

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(b) Relation between Pressure P and Volume V:

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

$$\Rightarrow \frac{P_2V_2}{P_1V_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \qquad \left[\because \frac{T_2}{T_1} = \frac{P_2V_2}{P_1V_1} \text{ for ideal gases}\right].$$

$$\Rightarrow P_2V_2 \cdot V_2^{\gamma-1} = P_1V_1 \cdot V_1^{\gamma-1}$$

$$\Rightarrow P_2 \cdot V_2^{\gamma} = P_1V_1^{\gamma}.$$

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

$$\Rightarrow \boxed{PV^{\gamma} = \text{constant}}.$$

This is the relationship between P and V in adiabatic process.

(c) Relationship between Temp T and pressure P:

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

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

For an ideal gas, $\frac{P_2V_2}{T_2} = \frac{P_1V_1}{T_1}$

$$\Rightarrow \frac{V_2}{V_1} = \frac{P_1T_2}{P_2T_1}.$$

$$\therefore \text{Eqn } (1) \Rightarrow \frac{T_1}{T_2} = \left(\frac{P_1T_2}{P_2T_1}\right)^{\gamma-1}.$$

$$\Rightarrow \left(\frac{T_1}{T_2}\right)\left(\frac{T_1}{T_2}\right)^{\gamma-1} = \left(\frac{P_1}{P_2}\right)^{\gamma-1}.$$

$$\Rightarrow \left(\frac{T_1}{T_2}\right)^{\gamma} = \left(\frac{P_2}{P_1}\right)^{1-\gamma}.$$

$$\Rightarrow \frac{T_1}{T_2} = \left(\frac{P_2}{P_1}\right)^{\frac{1-\gamma}{\gamma}}.$$

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$$\Rightarrow T_1 P_1^{\left(\frac{1-\gamma}{\gamma}\right)} = T_2 P_2^{\left(\frac{1-\gamma}{\gamma}\right)}$$

$$\Rightarrow \boxed{T P^{\left(\frac{1-\gamma}{\gamma}\right)} = \text{constant}}.$$

Irreversible Adiabatic expansion:

(a) For free expansion:

$\because$ In a free expansion, $P_{ext} = 0$.

$\therefore w = -P_{ext} \cdot dV = 0$.

$\because$ In an ideal gas, the ~~energy~~ internal energy depends on temperature only.

$\therefore$ If $\Delta U = 0$, then $\Delta T = 0$

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

$= \Delta U + \Delta(RT)$

$= \Delta U + R \cdot \Delta T$.

$= 0 + 0$

$= 0$.

Thus, in a free adiabatic expansion,

$\Delta T = 0$, $\Delta H = 0$ and $w = 0$.

(b) For Intermediate Expansion:

Let, the volume of the gas increases from V_1 to V_2 against a constant external pressure P_{ext} of the gas.

$\therefore$ Work done, $w = -P_{ext}(V_2 - V_1)$. $\longrightarrow$ (i)

From first law eqn, $\Delta U = q + w$. $\longrightarrow$ (ii).

$\because$ for an adiabatic expansion, $q = 0$

$\therefore$ eqn (ii) $\Rightarrow \Delta U = w$.

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Again, we know,

$$\Delta U = C_v \cdot \Delta T.$$

$$\Rightarrow w = C_v \cdot (T_2 - T_1).$$

$$\Rightarrow -P_{ext}(V_2 - V_1) = C_v (T_2 - T_1) \quad \{\text{from eqn (I)}\}.$$

$$\Rightarrow C_v (T_2 - T_1) = P_{ext}(V_1 - V_2). \quad \{\because PV = RT \Rightarrow V = \frac{RT}{P}\}.$$

$$\Rightarrow C_v (T_2 - T_1) = P_{ext}\left(\frac{RT_1}{P_1} - \frac{RT_2}{P_2}\right).$$

$$\Rightarrow C_v (T_2 - T_1) = R \cdot P_{ext}\left(\frac{T_1 P_2 - T_2 P_1}{P_1 P_2}\right).$$

Thus knowing the values of C_v, T_1, P_1, P_2 and P_{ext}, the value of final temp^r i.e. T_2 can be calculated.

Comparision of Isothermal and Adiabatic Expansions:

Let us consider isothermal and adiabatic expansions of an ideal gas from initial volume V_i and pressure P_i to a final volume V_f.

If P_{iso} and P_{adia} are the final pressures, then.

$$P_i V_i = P_{iso} \cdot V_f \quad \text{for isothermal expansion} \rightarrow (I)$$

$$P_i V_i^{\gamma} = P_{adia} (V_f)^{\gamma} \quad \text{for adiabatic expansion} \rightarrow (II).$$

$\therefore$ eqn (I) $\Rightarrow \frac{V_f}{V_i} = \frac{P_i}{P_{iso}}$

eqn (II) $\Rightarrow \left(\frac{V_f}{V_i}\right)^{\gamma} = \frac{P_i}{P_{adia}}$.

$\because$ During expansion, $V_f > V_i$ and for all gases, $\gamma > 1$,

$$\therefore \left(\frac{V_f}{V_i}\right)^{\gamma} > \frac{V_f}{V_i}.$$

$$\Rightarrow \frac{P_i}{P_{adia}} > \frac{P_i}{P_{iso}}$$

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$\Rightarrow P_{adia} < P_{iso}$.

i.e. Since, in adiabatic expansion, there is a fall of temp^{r}, hence, according to Charle's law ($P \propto T$ at const. V), there is a corresponding fall of pressure.

$\therefore P_{adia} < P_{iso}$

Again, let us consider the expansions in which the final ~~expansion~~ pressure P_f is the same in both cases. If V_{iso} and V_{adia} are the final volumes in isothermal and adiabatic expansions, respectively, then.

$$P_f V_f = P_f V_{iso} \quad \text{for isothermal expansion} \longrightarrow (iii)$$

$$P_i V_i^{\gamma} = P_f (V_{adia})^{\gamma} \quad \text{for adiabatic expansion.} \longrightarrow (iv)$$

$\therefore$ eq^{n} (iii) $\Rightarrow \dfrac{P_i}{P_f} = \dfrac{V_{iso}}{V_i}$. $\longrightarrow (v)$

eq^{n} (iv) $\Rightarrow \dfrac{P_i}{P_f} = \left(\dfrac{V_{adia}}{V_i}\right)^{\gamma}$ $\longrightarrow (vi)$

From eq^{n}s (v) and (vi), we get,

$$\frac{V_{iso}}{V_i} = \left(\frac{V_{adia}}{V_i}\right)^{\gamma}.$$

$$\Rightarrow \ln\left(\frac{V_{iso}}{V_i}\right) = \gamma \ln\left(\frac{V_{adia}}{V_i}\right)$$

$\because$ for all gases, $\gamma > 1$.

$$\therefore \frac{V_{adia}}{V_i} < \frac{V_{iso}}{V_i}$$

$$\Rightarrow V_{adia} < V_{iso}$$

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i.e. Since in an adiabatic expansion, there is a fall of temp^{r}. hence according to Charles law ($V \propto T$ at const. P), there is a corresponding decrease in volume so that $V_{adia} < V_{iso}$.

Reversible Isothermal Expansion of a Real gas (Vander Waals gas)

(a) Work of expansion:

We know, work done in the expansion of a gas,

$$dw = -PdV.$$

$$\therefore \quad -w = \int_{V_1}^{V_2} PdV \quad \longrightarrow (1)$$

For the Vander Waals gas,

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

$$\Rightarrow P = \frac{nRT}{V-nb} - \frac{an^2}{V^2}.$$

$\therefore$ Eq^{n} (1) $\Rightarrow$

$$-w = \int_{V_1}^{V_2} \left(\frac{nRT}{V-nb} - \frac{an^2}{V^2}\right) dV.$$

$$\Rightarrow -w = \int_{V_1}^{V_2} \frac{nRT}{V-nb}\, dV - \int_{V_1}^{V_2} \frac{an^2}{V^2}\, dV.$$

$$\Rightarrow -w = nRT\left[\ln(V-nb)\right]_{V_1}^{V_2} - an^2\left[-\frac{1}{V}\right]_{V_1}^{V_2}$$

$$\Rightarrow -w = nRT \ln \frac{V_2 - nb}{V_1 - nb} - an^2\left[-\frac{1}{V_2} + \frac{1}{V_1}\right].$$

$$\boxed{\Rightarrow -w = nRT \ln \frac{V_2 - nb}{V_1 - nb} + an^2\left[\frac{1}{V_1} - \frac{1}{V_2}\right]}$$

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(b) **Internal energy change:**

For a Vander Waals gas, internal pressure of the gas $= \frac{an^2}{V^2}$

Also, internal pressure of the gas $= \left(\frac{\partial U}{\partial V}\right)_T$.

$$\therefore \left(\frac{\partial U}{\partial V}\right)_T = \frac{an^2}{V^2}.$$

$$\Rightarrow dU = \frac{an^2\, dV}{V^2} \quad \text{at constant } T.$$

Integrating between limits,

$$\int_{U_1}^{U_2} dU = \int_{V_1}^{V_2} an^2 \frac{dV}{V^2}.$$

$$\Rightarrow U_2 - U_1 = -an^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

$$\Rightarrow \boxed{\Delta U = an^2\left(\frac{1}{V_1} - \frac{1}{V_2}\right)}.$$

(c) **Enthalpy change:**

$\because H = U + PV$.

Let, at initial state, $H_1 = U_1 + P_1V_1$ ⟶ (i)

At final state, $H_2 = U_2 + P_2V_2$. ⟶ (ii)

$\therefore$ Enthalpy change,

$$\Delta H = H_2 - H_1$$

$$= (U_2 + P_2V_2) - (U_1 + P_1V_1)$$

$$= (U_2 - U_1) + (P_2V_2 - P_1V_1)$$

$$= \Delta U + (P_2V_2 - P_1V_1) \quad \longrightarrow \text{(iii)}$$

For real gas, $P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$.

$$\Rightarrow PV = \frac{nRTV}{V - nb} - \frac{an^2}{V} \quad \longrightarrow \text{(iv)}.$$

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Substituting the expressions for P_2V_2 and P_1V_1 in equ (iv),

$$\Delta H = \Delta U + nRT\left[\frac{V_2}{V_2-nb} - \frac{V_1}{V_1-nb}\right] + an^2\left[\frac{1}{V_1} - \frac{1}{V_2}\right] \longrightarrow (v)$$

Now,

$$\frac{V_2}{V_2-nb} - \frac{V_1}{V_1-nb} = \frac{V_2(V_1-nb) - V_1(V_2-nb)}{(V_2-nb)(V_1-nb)}$$

$$= \frac{V_2V_1 - V_2 \cdot nb - V_1V_2 + V_1nb}{(V_2-nb)(V_1-nb)}$$

$$= \frac{nb(V_1-V_2)}{(V_2-nb)(V_1-nb)}$$

$$= \frac{nb}{V_2-nb} - \frac{nb}{V_1-nb} \longrightarrow (vi)$$

Substituting (vi) in equ (v),

$$\Delta H = \Delta U + nRT\left[\frac{nb}{V_2-nb} - \frac{nb}{V_1-nb}\right] + an^2\left[\frac{1}{V_1} - \frac{1}{V_2}\right]$$

$$\Rightarrow \Delta H = an^2\left[\frac{1}{V_1} - \frac{1}{V_2}\right] + nRT\left[\frac{nb}{V_2-nb} - \frac{nb}{V_1-nb}\right] + an^2\left[\frac{1}{V_1} - \frac{1}{V_2}\right]$$

$$\Rightarrow \Delta H = n^2RTb\left[\frac{1}{V_2-nb} - \frac{1}{V_1-nb}\right] + 2an^2\left[\frac{1}{V_1} - \frac{1}{V_2}\right]$$

(d) Heat change, q:

From first law equ,

$$\Delta U = q + \omega$$

$$\Rightarrow q = \Delta U - \omega$$

$$\Rightarrow q = an^2\left[\frac{1}{V_1} - \frac{1}{V_2}\right] + nRT\ln\left[\frac{V_2-nb}{V_1-nb}\right] - an^2\left[\frac{1}{V_1} - \frac{1}{V_2}\right]$$

$$\Rightarrow q = nRT\ln\left[\frac{V_2-nb}{V_1-nb}\right]$$

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Comparison of Work of Expansion of an Ideal Gas and a Vander Waals Gas:

For an ideal gas,

$$-w_{ideal} = nRT \ln\left(\frac{V_2}{V_1}\right). \longrightarrow (1)$$

For a Vander Waals gas,

$$-w_{vdw} = nRT \ln\left(\frac{V_2 - nb}{V_1 - nb}\right) + an^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right). \longrightarrow (11)$$

If $V >> nb$, then eqn (11) becomes,

$$-w_{vdw} = nRT \ln\left(\frac{V_2}{V_1}\right) + an^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right).$$

$$\therefore (-w_{ideal}) - (-w_{vdw}) = nRT \ln\left(\frac{V_2}{V_1}\right) - nRT \ln\left(\frac{V_2}{V_1}\right) - an^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right).$$

$$\Rightarrow (-w_{ideal}) - (-w_{vdw}) = an^2\left(\frac{V_2 - V_1}{V_1 V_2}\right). \longrightarrow (111).$$

∵ during expansion, $V_2 > V_1$, from eqn (111) it is clear that work done in the reversible isothermal expansion of an ideal gas is greater than that for a vander Waals gas.

Irreversible Isothermal Expansion of a Real Gas (Vander Waals Gas):

(a) Work of expansion:

$$dw = -P_{ext} \cdot dV.$$

$$\Rightarrow \boxed{dw = -P_{ext} \cdot (V_2 - V_1).}$$

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(b) Internal Energy Change:

$$\Delta U = an^2\left(\frac{1}{V_1} - \frac{1}{V_2}\right).$$

(c) Heat change:

From the first law eqn,

$$\Delta U = q + \omega$$

$$\Rightarrow q = \Delta U - \omega.$$

$$\Rightarrow q = an^2\left(\frac{1}{V_1} - \frac{1}{V_2}\right) - (-P_{ext}).(V_2 - V_1).$$

$$\Rightarrow q = an^2\left(\frac{1}{V_1} - \frac{1}{V_2}\right) + P_{ext}.(V_2 - V_1)$$

(c) Free expansion:

For an isothermal free expansion,

$$d\omega = 0$$

$$\therefore \Delta U = an^2\left(\frac{1}{V_1} - \frac{1}{V_2}\right).$$

$$\therefore \Delta U = \omega + q$$

$$\Rightarrow q = \Delta U - \omega$$

$$\Rightarrow q = an^2\left(\frac{1}{V_1} - \frac{1}{V_2}\right) - 0$$

$$\Rightarrow q = an^2\left(\frac{1}{V_1} - \frac{1}{V_2}\right).$$

Reversible Adiabatic Expansion of a Real gas (Vander Waals gas):

(a) Heat change:

For adiabatic process, $q = 0$

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⑥ Work of expansion:

From first law eqⁿ,

$$\Delta U = q + \omega$$

$$\Rightarrow \omega = \Delta U \qquad [\because q = 0].$$

⑦ Internal energy change:

Taking U as the function of T and V, we get,

$$dU = \left(\frac{\partial U}{\partial T}\right)_V . dT + \left(\frac{\partial U}{\partial V}\right)_T . dV.$$

$$\Rightarrow dU = nC_V . dT + \frac{an^2}{V^2} . dV \longrightarrow (i) \quad [\text{For } n \text{ moles}].$$

Integrating within limits,

$$\Delta U = \int_{T_1}^{T_2} nC_V . dT + \int_{V_1}^{V_2} \frac{an^2}{V^2} . dV$$

$$\Rightarrow \boxed{\Delta U = nC_V (T_2 - T_1) - an^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right)} \longrightarrow (ii)$$

[C_V is considered to be independent of T]

Hence, eqⁿ (ii) can be used to calculate the value of ΔU if T_1, T_2, V_1 and V_2 are known.

But, if T_2 is not given, then it is first calculated as follows —

$$dU = d\omega = -PdV. \longrightarrow (iii)$$

∵ For real gas, $\boxed{P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}}$.

and $\boxed{dU = nC_V . dT + \frac{an^2}{V^2} . dV}$.

∴ Eqⁿ (iii) $\Rightarrow nC_V . dT + \frac{an^2}{V^2} . dV = -\frac{nRT}{V - nb} . dV + \frac{an^2}{V^2} . dV$

$$\Rightarrow C_V . dT = -\frac{RT}{V - nb} . dV.$$

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$$\Rightarrow C_V \cdot \frac{dT}{T} = -R \cdot \frac{dV}{V-nb}$$

Integrating between limits,

$$\int_{T_1}^{T_2} C_V \cdot \frac{dT}{T} = -R \int_{V_1}^{V_2} \frac{dV}{V-nb}$$

$$\Rightarrow C_V \cdot [\ln T]_{T_1}^{T_2} = -R \left[\ln (V-nb)\right]_{V_1}^{V_2}$$

$$\Rightarrow C_V \cdot \ln \frac{T_2}{T_1} = -R \ln \frac{V_2-nb}{V_1-nb}$$

$$\Rightarrow \ln \left(\frac{T_2}{T_1}\right)^{C_V} = \ln \left(\frac{V_1-nb}{V_2-nb}\right)^{R}$$

$$\Rightarrow \left(\frac{T_2}{T_1}\right)^{C_V} = \left(\frac{V_1-nb}{V_2-nb}\right)^{R}$$ [Taking antilogs on both sides]

$$\Rightarrow \frac{T_2}{T_1} = \left(\frac{V_1-nb}{V_2-nb}\right)^{\frac{R}{C_V}}$$

$$\Rightarrow \boxed{T_2 = T_1 \left(\frac{V_1-nb}{V_2-nb}\right)^{R/C_V}}$$

Thus T_2 can be calculated if T_1, V_1 and V_2 are known.

(d) Enthalpy change:

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

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

$$= \Delta U + \Delta\left[\left(\frac{nRT}{V-nb} - \frac{an^2}{V^2}\right)V\right]$$

$$= \Delta U + nR\left(\frac{V_2T_2}{V_2-nb} - \frac{V_1T_1}{V_1-nb}\right) - an^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right).$$

$$= nC_V(T_2-T_1) - an^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right) + nR\left(\frac{V_2T_2}{V_2-nb} - \frac{V_1T_1}{V_1-nb}\right)$$

$$- an^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right).$$

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$$\Rightarrow \Delta H = nC_v(T_2 - T_1) - 2an^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right) + nR\left(\frac{V_2T_2}{V_2 - nb} - \frac{V_1T_1}{V_1 - nb}\right)$$

Comparison of work of expansion of an ideal gas and a real gas (vander Waals gas):

For an ideal gas, $-W_{ideal} = nRT\ln\left(\frac{V_2}{V_1}\right)$. ⟶ (1)

For a vander Waals gas,

$$-W_{vdw} = nRT\ln\left(\frac{V_2 - nb}{V_1 - nb}\right) + an^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right). \longrightarrow (11)$$

If $V >> nb$, then eqn (11) becomes,

$$-W_{vdw} = nRT\ln\left(\frac{V_2}{V_1}\right) + an^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

$$\therefore W_{ideal} - W_{vdw} = -nRT\ln\left(\frac{V_2}{V_1}\right) - \left\{-nRT\ln\left(\frac{V_2}{V_1}\right) + an^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right)\right\}$$

$$= -an^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right).$$

$$= an^2\left(\frac{V_2 - V_1}{V_1V_2}\right), \quad [\text{where } V_2 > V_1].$$

i.e. Work done in the reversible expansion of an ideal gas is greater than that for a Vander Waals gas.

or $W_{ideal} > W_{vdw}$ *

Irreversible Adiabatic expansion of a Real gas (Vander Waals gas):

(1) For Intermediate expansion:

(a) Heat change and work done:

For adiabatic process, $q = 0$.

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$\therefore dw = -P_{ext} \cdot dV$

$\Rightarrow dw = -P_{ext} \cdot (V_2 - V_1)$.

(b) Internal energy change :

From 1st law eqn,

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

$$\Rightarrow dU = dw \quad [\because q = 0].$$

Taking U as the function of T and V,

$$dU = \left(\frac{\partial U}{\partial T}\right)_V . dT + \left(\frac{\partial U}{\partial V}\right)_T . dV$$

$$\Rightarrow dw = \left(\frac{\partial U}{\partial T}\right)_V . dT + \left(\frac{\partial U}{\partial V}\right)_T dV.$$

We know, for real gas,

$$dU = nC_V . dT + \frac{an^2}{V^2} . dV.$$

$$\Rightarrow dw = nC_V dT + \frac{an^2}{V^2} . dV.$$

~~$\Rightarrow -P_{ext}(V_2 - V_1) = nC_V . dT + \frac{an^2}{V^2} . dV.$~~

$$\Rightarrow -P_{ext} \cdot \Delta V = nC_V . dT + \frac{an^2}{V^2} . dV.$$

$$\Rightarrow -P_{ext} (V_2 - V_1) = nC_V . (T_2 - T_1) - an^2 \left(\frac{1}{V_2} - \frac{1}{V_1}\right).$$

$$\Rightarrow nC_V . (T_2 - T_1) = an^2 \left(\frac{1}{V_2} - \frac{1}{V_1}\right) - P_{ext} (V_2 - V_1)$$

$$\Rightarrow T_2 = \frac{1}{nC_V} \left[an^2 \left(\frac{1}{V_2} - \frac{1}{V_1}\right) - P_{ext} (V_2 - V_1)\right] + T_1.$$

$\because V_2 > V_1$ during expansion.

$\therefore T_2 < T_1$.

If T_2 is known, then ΔH can be determined as follows —

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

$$\Rightarrow \Delta H = \Delta U + \Delta\left[\left\{\frac{nRT}{V-nb} - \frac{an^2}{V^2}\right\}V\right].$$

$$\Rightarrow \Delta H = \Delta U + nR\left(\frac{V_2T_2}{V_2-nb} - \frac{V_1T_1}{V_1-nb}\right) - an^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right).$$

© Free expansion:

For free expansion,

$$q = 0, \quad w = 0.$$

∴ From 1st law eqⁿ,

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

$$\Rightarrow \Delta U = 0.$$

The temp^{re} of the gas after expansion is

$$T_2 = T_1 + \frac{1}{nC_v}\left[an^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right) - P_{ext}(V_2 - V_1)\right]. \quad \longrightarrow (1)$$

∵ For free expansion, $w = 0$.

$$\Rightarrow -P_{ext}(V_2 - V_1) = 0.$$

∴ eqⁿ (1) $\Rightarrow$ $$\boxed{T_2 = T_1 + \frac{1}{nC_v}\left[an^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right)\right]}.$$

Zeroth Law of Thermodynamics:

The law states that,

"If two bodies say A and B are in thermal equilibrium with ~~each other~~ another body C separately, then A and B are also in thermal equilibrium with each other."

i.e. If $A \leftrightarrow C$ & $B \leftrightarrow C$, then $A \leftrightarrow B$.

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