CHB-201: Section (B) – Physical Chemistry-I

(Thermodynamics)

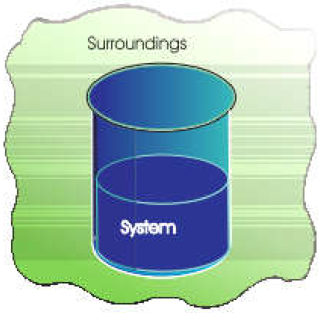
The word '**thermodynamics**' implies flow of heat. It deals with energy changes accompanying all types of physical and chemical processes.

Limitation of thermodynamics: 1. Laws of thermodynamics are not applicable to small particles like individual atoms or molecule, but laws can be applied to macroscopic system or very large system.
2. Thermodynamics does not give information about rate at which a given chemical reaction/process may proceed and also time for this change.

Basic terms used in thermodynamics

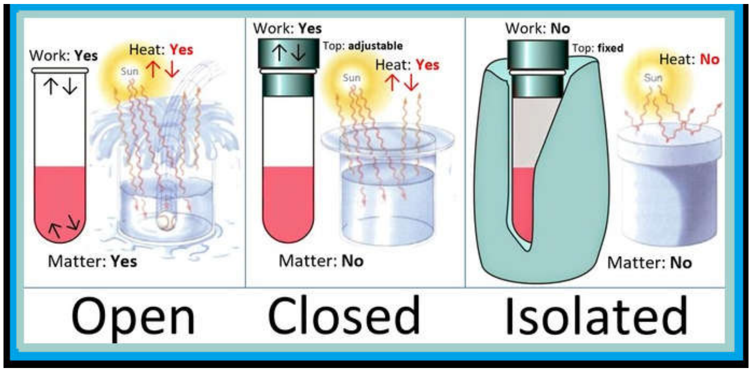
System: Any specified portion of the universe or matter, real or imaginary, separated from the rest of the universe, which is selected for the thermodynamic treatment is called a system.

Surroundings: Leaving the system the rest of the universe, which may exchange matter or energy or both with the system, is called surroundings.



Types of system

Open system:-A system which can exchange energy as well as matter with its surroundings. Ex: water in an open beaker.



Closed system: When a system can exchange only energy and not matter with its surroundings. Ex: a chemical reaction taking place in a closed vessel can exchange only heat with surrounding

Isolated system: A system which can neither exchange matter nor energy with its surrounding. Ex: The presence of reactants in a thermos flask or any other closed insulated vessel is an example of an isolated system.

Macroscopic system: A system which consist of a large number of atoms, particles, molecules, radicals.

Macroscopic properties: Properties of macroscopic system is known as macroscopic properties. Ex: pressure, temperature, volume, composition, density, viscosity, surface tension, etc. Change of any macroscopic property changes the state of the system or vice-versa.

State of a system: It is defined by the macroscopic properties. When the macroscopic properties of a system have specific or definite value it is said that the system is in definite state.

Thermodynamic Equilibrium: If macroscopic properties like temperature, pressure, volume composition etc. do not change with time.

Types of thermodynamic equilibrium

1. Thermal equilibrium: A system whose temperature do not change along with the temperature of the surroundings.
2. Mechanical equilibrium: A system which do not perform any mechanical work.
3. Chemical equilibrium: A system whose chemical composition does not change with time (remains same throughout).

Physical properties of the system

Physical properties of the system are of two types-

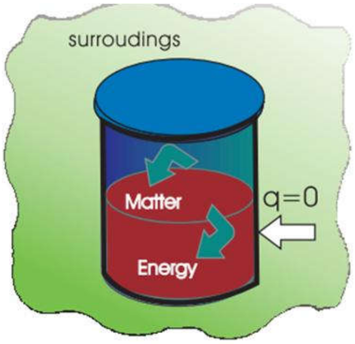
1. **Extensive property:** This property depends on quantity or amount of matter present in the system. Ex: Mass, volume, energy, no. of moles, enthalpy, entropy etc.
2. **Intensive property:** This property do not depends on quantity or amount of matter present in the system. Ex: temperature, pressure, density, viscosity, surface tension and specific heat.

State function: It is the property of the thermodynamic system whose value is definite for a particular state of the system. When a change is brought about in this particular state of system, change in state function also occurs. ***It depends only on initial and final state of the system***. Ex: pressure, temperature, volume, energy are state function.

Path function: When a system passes from one state A to another state B depends on the nature of the path followed, not on initial and final state. Ex: work done is path function.

Thermodynamic process: If a thermodynamic system changes from one state to another state the operation is known as thermodynamic process.

Types of process: 1. Isothermal process: in this process temperature of the system remains constant throughout the process i.e. ***dT=0***



(Adiabatic system)

2. Adiabatic process: in this process no heat enters or leaves the system during any stage of the process i.e. ***dq=0***

3. Isobaric process: in this process pressure of the system remains constant throughout the process i.e. ***dP=0***

4. Isochoric process: in this process volume of the system remains constant throughout the process i.e. ***dV=0***

Cyclic process or cycles: When a system return to its initial state after completing the process in various stages, that is system has completed one cycle and process is known as cyclic process. **Reversible process:** If a thermodynamic process is carried out infinitesimally slowly so that at every stage of it, the system in temperature and pressure remains in equilibrium with surrounding, This type of process is called reversible process.

Irreversible process: If a thermodynamic process is not carried out infinitesimally slowly so that at every stage of it, the system do not remains in equilibrium with surrounding, this type of process is called irreversible process.

"A reversible process cannot be realized in practice because it would require infinite time for its completion. Hence, almost all processes occurring in nature or laboratory are irreversible."

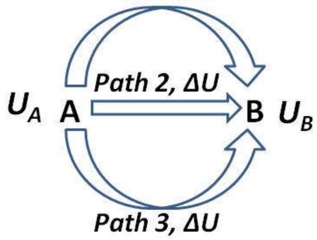
Signs for heat (*q*) and work (*w*):

- *q* is positive, when heat is transferred from the surroundings to the system.
- *q* is negative when heat is transferred from system to the surroundings.
- *w* is positive when work is done on the system.
- *w* is negative when work is done by the system.

First law of Thermodynamics

First law of thermodynamics states that "*Energy can neither be created nor destroyed but can only be transformed from one form to another*." This law is also known as law of conservation of energy.

Internal Energy (*U*): It is sum of all possible types of energy present in the system. It is impossible to calculate the internal energy (U) of a system. Instead, the change in the U of a system, ΔU, must be measured.



Let U_A be the energy of a system in state A and U_B in state B. The system changes from state A to state B by following path 1, path 2 and path 3. Since, U is the state function, so ***ΔU depends only on initial and final state of the system i.e.***

$\Delta U = U_B - U_A$

The change in ΔU of a system is affected by two distinct variables. These two variables are designated at heat (q), and work (w). Suppose the system while undergoing change absorbs heat ***q*** from the surroundings and also perform some work equal to ***w***. Hence the change of internal energy ΔU in the above process will given by

$\Delta U = q + w$ -----------------------(1)

Equation (1) is the mathematical statement of the **first law of thermodynamics**.

For isothermal process $\Delta U = 0$***, since internal energy (U) of an ideal gas only depends on temperature.***

Case 1: if work is done on the system by the surroundings (as during the compression of gas) w is taken as positive so that

$\Delta U = q + w$

Case 2: if work is done by the system on surroundings (as during the expansion of gas) w is taken as negative so that

$\Delta U = q - w$

For infinitesimal change equation (1) can be written as

$dU = dq + dw$ --------------------(2)

Enthalpy (*H*): Suppose the change of state of a system is brought at constant pressure. In that case, there will be change of volume. Let the volume increase from V_A to V_B, at constant pressure *P*. Then, the work done (*w*) by the system will be given by

$w = -P\ (V_B - V_A)$

Substituting in equation (1)

$\Delta U = q - P\ (V_B - V_A)$ or $U_B - U_A = q - PV_B + PV_A$ or $(U_B + PV_B) - (U_A + PV_A) = q$ ------(3)

The quantity U+PV is known as enthalpy. It is equal to the internal energy of the system plus the product of pressure and volume.

$H = U + PV$

The equation (3) can be written as

$H_B - H_A = \Delta H = q$

Enthalpy is equivalent to the total heat content of a system.

Enthalpy is a state function which depends entirely on the state functions *T*, *P* and *U*. Enthalpy is usually expressed as the change in enthalpy (ΔH) for a process between initial and final states:

$\Delta H = \Delta U + P\Delta V$ (Where ΔV is the increase in volume undergone by the system)
For infinitesimal change the above expression can be written as:
$dH = dU + PdV$

Variation of heat of reaction with temperature (Kirchhoff's equation)

Heat Capacity: *Heat capacity* is defined as the amount of *heat* (q) required to a given mass to raise the temperature of the system from the lower to higher temperature divide by the temperature difference.

If the mass of the system is one gram, the heat capacity is called "specific heat". If the mass of the system is one mole then the heat capacity is called "molar heat capacity". It is denoted by ***C***. Thus the molar heat capacity of a system between temperature T_1 and T_2 will be given by expression

$C = q/(T_2 - T_1)$

Since the heat capacity varies with T, hence the C is defined by differential equation

$C = dq/dT$ ……………………….(1)

The molar heat capacity of a gaseous system is determined at constant volume and constant pressure.

Molar Heat capacity at constant volume (*Cv*): From 1st law of thermodynamics

$dU = dq + dw$ *or* $dU = dq + PdV$ *at constant volume* $dV = 0$

$\therefore dU = dq$

From the equation $C = dq/dT$

$\therefore C_v = (\partial U/\partial T)_v$

Molar Heat capacity at constant pressure (*Cp*): At constant pressure, there is a change of volume and some work is done. Suppose the volume increased is dV and some work is done by the system is dw.

From 1st law of thermodynamics

$dU = dq - dw$ ($\because$ *work is done by the system so dw is negative*)

or $dU = dq - PdV$

$\therefore dq = dU + PdV$

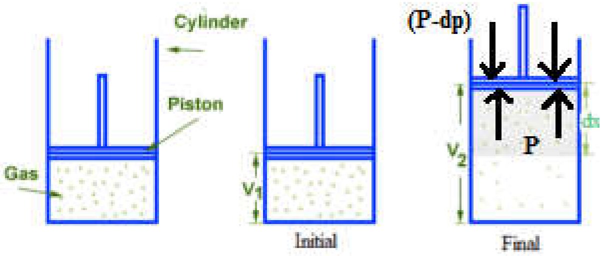
or $dq = dH$ ($\because dH = dU + PdV$)

From the equation $C = dq/dT$

$C_p = (\partial H/\partial T)_p$

Work done in Reversible Iothermal Expansion of an Ideal gas (Maximum work)

Consider one mole of an ideal gas is enclosed in a cylinder fitted with a weightless, frictionless, movable piston. Let the pressure of the gas be P which is equal to external atmospheric pressure P. Let the external pressure be reduced by an infinitesimally small amount dP and the corresponding small increase in volume be dV. So the small work done in the expansion process:



$dw = -P_{ext}.dV$

$\therefore dw = -(P-dP).dV$

$\therefore dw = -(P.dV - dP.dV)$

Since both dP and dV both are small so their product dP.dV is very small and can be neglected in comparison to P.dV. Then the above equation becomes

$dw = -P.dV$

When the expansion of gas is carried out reversibly then there will be series of such P.dV terms. The total maximum work can be obtained by integrating above equation between the limits V_1 (initial volume) to V_2 (final volume).

$w = \int dw = -\int_{V_1}^{V_2} PdV$

$\because PV = RT, \quad \therefore P = RT/V$

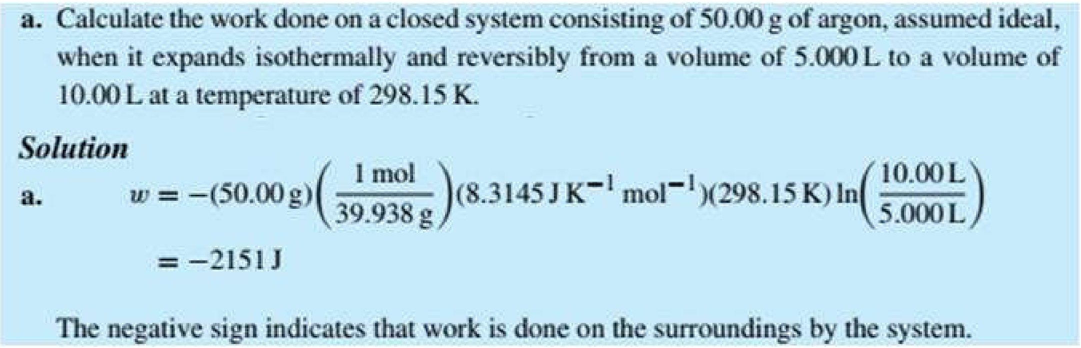
$w = -RT\int_{V1}^{V2} \frac{1}{V} dV = -RT \ln\frac{V_2}{V_1} = -2.303RT \log\frac{V_2}{V_1}$

for n mole of gas: $\mathbf{w = -2.303nRT\log\frac{V_2}{V_1}}$

for an isothermal expansion, Boyle's law is applicable, Hence $P_1V_1=P_2V_2$ or $V_2/V_1 = P_1/P_2$

$\mathbf{w = -2.303nRT \log\frac{P_1}{P_2}}$ (where P_1 and P_2 are initial and final pressure, respectively)

- In a reversible isothermal expansion maximum work is obtained because $\mathbf{P_{ext} \approx P}$
- If, $\mathbf{P_{ext} \neq P}$, process is not reversible.
- In vacuum, $\mathbf{P_{ext} = 0}$, hence the work done will be zero during expansion.



a. Calculate the work done on a closed system consisting of 50.00 g of argon, assumed ideal, when it expands isothermally and reversibly from a volume of 5.000 L to a volume of 10.00 L at a temperature of 298.15 K.

Solution

a.
$$w = -(50.00\,\mathrm{g})\left(\frac{1\,\mathrm{mol}}{39.938\,\mathrm{g}}\right)(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298.15\,\mathrm{K})\ln\left(\frac{10.00\,\mathrm{L}}{5.000\,\mathrm{L}}\right)$$
$$= -2151\,\mathrm{J}$$

The negative sign indicates that work is done on the surroundings by the system.

Reversible Adiabatic Expansion of an Ideal gas

From first law of thermodynamics,

$dU = dq + dw$

For adiabatic process $dq = 0$, *and for expansion i.e. work done by the system is -ve*

$\therefore dU = -dw = -PdV$

For ideal gas: $dU = CvdT$ *(Cv is molar heat capacity at constant volume)*

$CvdT = -PdV = -(RT/V)dV$ *(From gas law* $PV=RT \therefore P=(RT/V)$*)*

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

Integrating above equation between temperatures T_1 and T_2 when the corresponding volumes are V_1 and V_2.

$C_v \int_{T_1}^{T_2} \frac{dT}{T} = -R \int_{V_1}^{V_2} \frac{dV}{V}$ or $\ln(T_2/T_1) = -(R/Cv)\ln(V_2/V_1)$

or $(T_2/T_1) = (V_1/V_2)^{(R/Cv)}$

$\because C_p - C_v = R$, $\therefore (T_2/T_1) = (V_1/V_2)^{(Cp-Cv/Cv)}$

$\mathbf{(T_2/T_1) = (V_1/V_2)^{(\gamma-1)}}$ $(\gamma = C_p/Cv)$ *and* $\gamma > 1$

or, $\mathbf{(T_1/T_2) = (V_2/V_1)^{(\gamma-1)}}$ ……..(1)

Thus, $\because V_2 > V_1$ *and* $\gamma > 1$

$\therefore \mathbf{T_2 < T_1}$. **Hence a gas cools during reversible adiabatic expansion.**

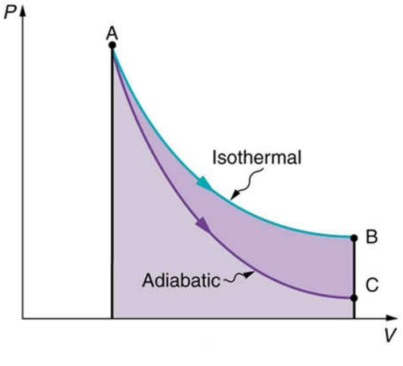
For ideal gas $(P_1V_1)/T_1 = (P_2V_2)/T_2$ or $T_1/T_2 = P_1V_1/P_2V_2$ ---------(2)

From equation (1) and (2) $\mathbf{P_1/P_2 = (V_2/V_1)^{\gamma}}$ or $\mathbf{P_1V_1^{\gamma} = P_2V_2^{\gamma}}$

or $\mathbf{PV^{\gamma} = constant}$ **(This is ideal gas equation for Reversible Adiabatic Expansion)**

For isothermal expansion *PV = constant*

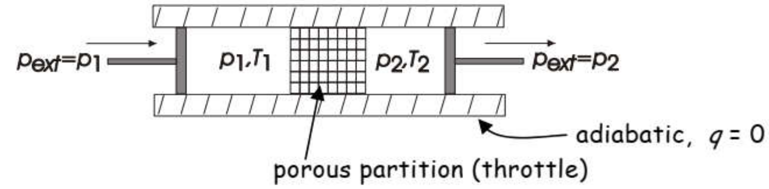
The two expansions are shown in P-V diagram. The work done is given by the area under the PV curve. ***The work done in isothermal expansion is greater than the work done in adiabatic expansion.***



Joule-Thomson effect

If the system of a gas at high pressure is allowed to expand by passing thorough a porous plug into vacuum or region of low pressure under adiabatic conditions the gas cooled. This effect called **Joule-Thomson effect.** Only hydrogen and helium gases are exceptions as they get warmed up under expansion (compressibility factor Z>1).

- $\left(\frac{\partial H}{\partial p}\right)_T \quad \Rightarrow$ Joule-Thomson expansion



gas (p, T_1) = gas (p, T_2)

$$w = p_1V_1 - p_2V_2 \quad \Rightarrow \quad \Delta U = q + w = p_1V_1 - p_2V_2 = -\Delta(pV)$$

$$\therefore \quad \Delta U + \Delta(pV) = 0 \quad \Rightarrow \Delta(U + pV) = 0$$

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

Joule-Thomson is a constant Enthalpy process.

$$dH = C_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp \quad \Rightarrow \quad C_p dT = -\left(\frac{\partial H}{\partial p}\right)_T dp_H$$

$$\Rightarrow \quad \left(\frac{\partial H}{\partial p}\right)_T = -C_p\left(\frac{\partial T}{\partial p}\right)_H \quad \leftarrow \text{ can measure this } \left(\frac{\Delta T}{\Delta p}\right)_H$$

$$\text{Define} \quad \lim_{\Delta p \to 0}\left(\frac{\Delta T}{\Delta p}\right)_H = \left(\frac{\partial T}{\partial p}\right)_H \equiv \mu_{JT} \quad \leftarrow \text{ Joule-Thomson Coefficient}$$

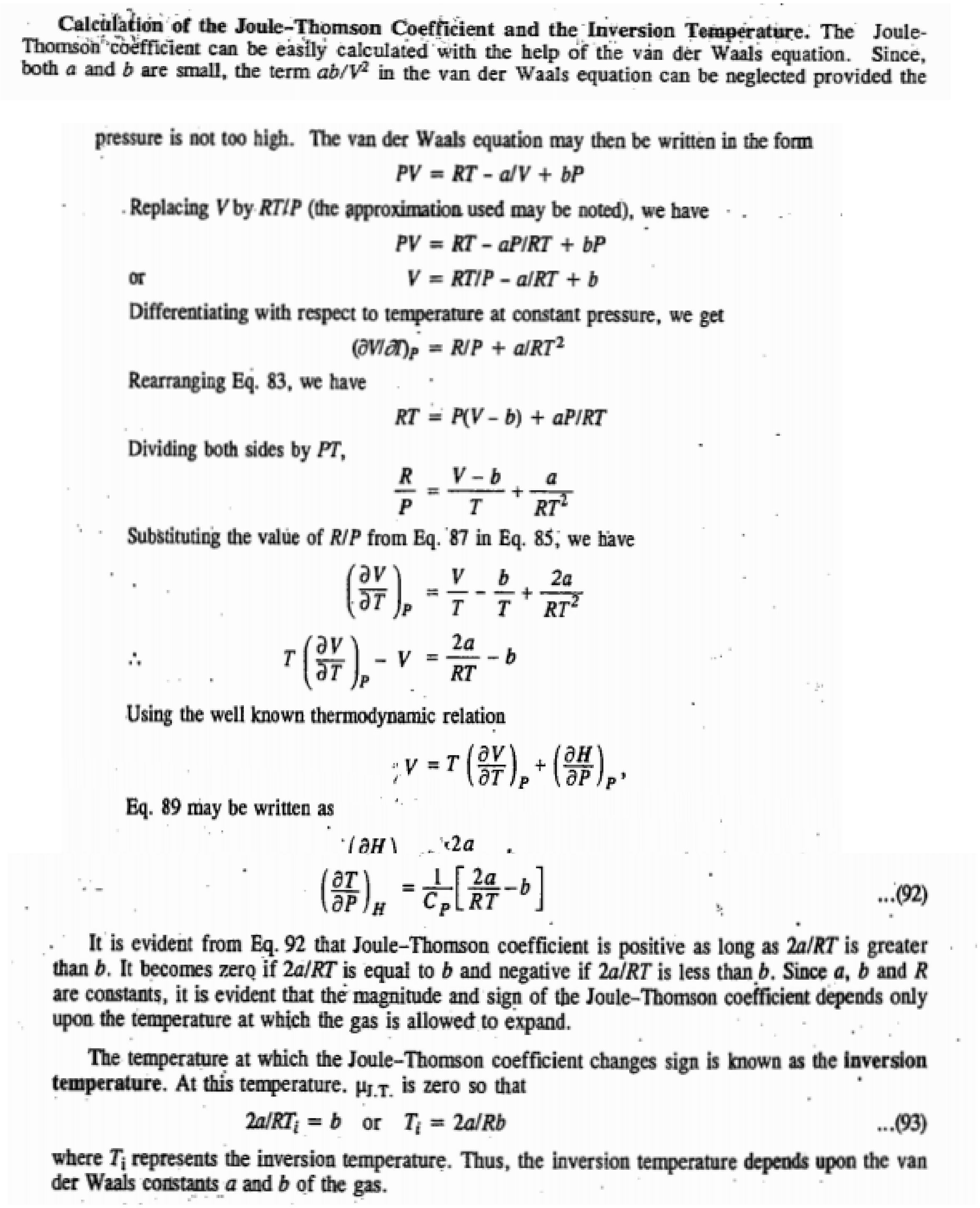
$$\therefore \quad \boxed{\left(\frac{\partial H}{\partial p}\right)_T = -C_p\mu_{JT}} \quad \text{and} \quad \boxed{dH = C_p dT - C_p\mu_{JT}dp}$$

For an ideal gas: $U(T)$, $pV=nRT$

$$H \equiv U(T) + pV = \underbrace{U(T) + nRT}_{\text{only depends on } T, \text{ no } p \text{ dependence}}$$

$$H(T) \quad \Rightarrow \quad \left(\frac{\partial H}{\partial p}\right)_T = \mu_{JT} = 0 \quad \text{for an ideal gas}$$

Joule-Thomson Coefficient for Real gases (Vander Walls gases):



Calculation of the Joule-Thomson Coefficient and the Inversion Temperature. The Joule-Thomson coefficient can be easily calculated with the help of the van der Waals equation. Since, both a and b are small, the term ab/V^2 in the van der Waals equation can be neglected provided the pressure is not too high. The van der Waals equation may then be written in the form

$$PV = RT - a/V + bP$$

Replacing V by RT/P (the approximation used may be noted), we have

$$PV = RT - aP/RT + bP$$

or

$$V = RT/P - a/RT + b$$

Differentiating with respect to temperature at constant pressure, we get

$$(\partial V/\partial T)_P = R/P + a/RT^2$$

Rearranging Eq. 83, we have

$$RT = P(V - b) + aP/RT$$

Dividing both sides by PT,

$$\frac{R}{P} = \frac{V-b}{T} + \frac{a}{RT^2}$$

Substituting the value of R/P from Eq. 87 in Eq. 85, we have

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{V}{T} - \frac{b}{T} + \frac{2a}{RT^2}$$

$$\therefore \quad T\left(\frac{\partial V}{\partial T}\right)_P - V = \frac{2a}{RT} - b$$

Using the well known thermodynamic relation

$$V = T\left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial H}{\partial P}\right)_T,$$

Eq. 89 may be written as

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[\frac{2a}{RT} - b\right] \qquad ...(92)$$

It is evident from Eq. 92 that Joule-Thomson coefficient is positive as long as $2a/RT$ is greater than b. It becomes zero if $2a/RT$ is equal to b and negative if $2a/RT$ is less than b. Since a, b and R are constants, it is evident that the magnitude and sign of the Joule-Thomson coefficient depends only upon the temperature at which the gas is allowed to expand.

The temperature at which the Joule-Thomson coefficient changes sign is known as the **inversion temperature**. At this temperature, $\mu_{J.T.}$ is zero so that

$$2a/RT_i = b \quad \text{or} \quad T_i = 2a/Rb \qquad ...(93)$$

where T_i represents the inversion temperature. Thus, the inversion temperature depends upon the van der Waals constants a and b of the gas.

From the equation (92),

Case 1: if $\frac{2a}{RT} > b \quad \rightarrow \quad T < \frac{2a}{Rb} = T_i$ if T is below inversion temperature, $\mu_{J.T.}$ is positive. Gas cools upon expansion.

Case 2: if $\frac{2a}{RT} < b \quad \rightarrow \quad T > \frac{2a}{Rb} = T_i$ if T is above inversion temperature, $\mu_{J.T.}$ is negative. Gas heats upon expansion.

Case 3: if $\frac{2a}{RT} = b \quad \rightarrow \quad T = \frac{2a}{Rb} = T_i$ if T is equal to inversion temperature, $\mu_{J.T.}$ is zero. Gas neither cools nor heats upon expansion (ideal gas).

Conclusions: First, since μ_{JT} is positive at low temperatures and negative at high temperatures, it must have an inversion temperature. Second, the effect seems to depend (as we expected) on the attractive and repulsive forces acting between molecules. At low temperatures the *attractive* forces predominate. At high temperatures the *repulsive* forces predominate. So the Joule-Thomson effect can be explained this way: At low temperatures the intermolecular attraction is the most important interaction. When the gas is expanded, the average distance between molecules is increased. This means that the molecules are pulled apart. Since they attract each other this *takes* energy and since the process is adiabatic, the only source of energy is the internal energy of the gas itself. So, with the internal energy reduced, the gas *cools*.

On the other hand, at high enough temperatures the predominant interaction is *repulsion*. The gas wants to separate. It wants to expand. When it does expand energy is obtained as the molecules separate. This *increases* the internal energy of the gas and the gas *heats*.

“**The limitation of the first law of thermodynamics** is that it does not say anything about the direction of flow of heat. It does not say anything whether the process is a spontaneous process or not. The reverse process is not possible. In actual practice, the heat doesn't convert completely into work.” There is thus need for another law, *viz.,* the Second law of thermodynamics.

Carnot Cycle

Carnot employed a reversible cycle to demonstrate the maximum convertibility of heat into work. The system consists of one mole of an ideal gas which is subjected to series of four operations, commonly termed as four strokes.

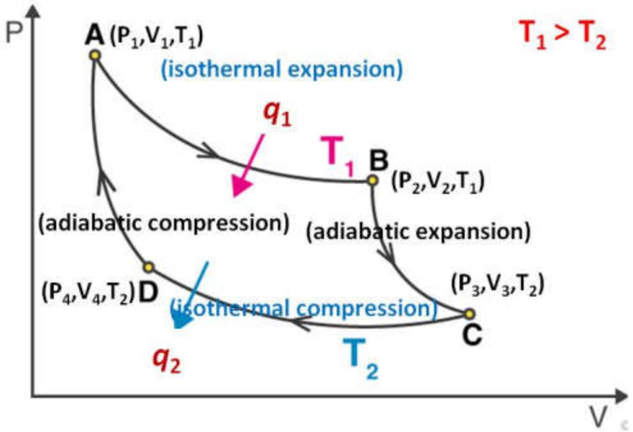
The Carnot cycle consists of the following four processes:

1. Reversible isothermal expansion at thermodynamic temperature T_1 with heat q_1 taken in (curve AB).

2. Reversible adiabatic expansion with a fall of temperature to T_2 (curve BC).

3. Reversible isothermal compression at temperature T_2 with heat q_2 given out (curve CD).

4. Reversible adiabatic compression at temperature back to T_1 (curve DA).



1. Reversible isothermal expansion:

The gas is taken from A (P_1,V_1,T_1) to B (P_2,V_2,T_1). Heat q_1 is absorbed from the reservoir at temperature T_1. Since the expansion is isothermal, the total change in internal energy is zero (***$\Delta U=0$***) and the heat absorbed by the gas is equal to the work done (w_1) by the gas on the surroundings, which is given as:

From 1st law of thermodynamics

$\Delta U = q_1 + w_1 \quad (\because \Delta U=0)$

$\therefore q_1 = -w_1 = RT_1 \ln\frac{V_2}{V_1}$

2. Reversible adiabatic expansion:

The gas expand adiabatically from B (P_2,V_2,T_1) to C (P_3,V_3,T_2). Since the expansion is **adiabatic**, the heat absorbed by the gas is equal to zero **($q=0$).** The work done (w_2) by the gas on the surroundings, which is given as:

From 1st law of thermodynamics

$\Delta U = q + w_2 \quad (\because q=0)$

$\Delta U = w_2$

$\Delta U = -w_2$ (by convention, w is negative because work is done by the system on the surroundings during expansion)

The internal energy (ΔU) of *one* mole of an ideal gas at temperature T is $Cv\Delta T$. This is the kinetic energy of the molecules, and does not depend on the volume occupied by the gas. Therefore, the change in internal energy in adiabatic expansion is

$$\Delta U = Cv\Delta T = Cv(T_2-T_1) = -w_2$$

$$\therefore -w_2 = Cv(T_2-T_1)$$

3. Reversible isothermal compression: The gas is compressed isothermally from the state C (P_3,V_3,T_2) to D (P_4,V_4,T_2). Here, the work done (w_3) on the gas by the surroundings is given by:

$\Delta U = q_2 + w_3$ ($\because \Delta U=0$ *and* by convention, w is positive because work is done on the gas by surroundings during compression, q_2 is heat given to the surroundings)

$$\therefore -q_2 = w_3 = RT_2\ln\frac{V_4}{V_3}$$

4. Reversible adiabatic compression: The gas is compressed adiabatically from the state D (P_4, V_4, T_2) to A (P_1, V_1, T_1). The heat absorbed by the gas is equal to zero **($q=0$).** The work done (w_4) on the gas by surroundings, which is given as:

From 1st law of thermodynamics

$\Delta U = q + w_4$ ($\because q=0$ and by convention, w is positive because work is done on the gas by surroundings during compression)

$$\Delta U = w_4$$

$$\Delta U = Cv\Delta T = Cv(T_1-T_2) = w_4$$

$$\therefore w_4 = Cv(T_1-T_2)$$

The net heat absorbed (q) by the ideal gas in the whole cycle is given by:

$$q = q_1 + (-q_2) = RT_1\ln\frac{V_2}{V_1} + RT_2\ln\frac{V_4}{V_3} = RT_1\ln\frac{V_2}{V_1} - RT_2\ln\frac{V_3}{V_4} \qquad \text{…………(1)}$$

Net work done (w) in the whole cycle = $(-w_1) + (-w_2) + w_3 + w_4$

$$= RT_1\ln\frac{V_2}{V_1} + Cv(T_2-T_1) + RT_2\ln\frac{V_4}{V_3} + Cv(T_1-T_2)$$

$$= RT_1\ln\frac{V_2}{V_1} + RT_2\ln\frac{V_4}{V_3} = RT_1\ln\frac{V_2}{V_1} - RT_2\ln\frac{V_3}{V_4} \qquad \text{…….(2)}$$

From the equation (1) and (2), $q = w$. Thus the essential condition for cyclic process that the net work done is equal to the net heat absorbed is fully satisfied.

A (P_1,V_1) and B (P_2,V_2) lies on same isothermal $\therefore P_1V_1=P_2V_2$ …………….(3)

B (P_2,V_2) and C (P_3,V_3) lies on same adiabatic $\therefore P_2V_2^{\gamma}= P_3V_3^{\gamma}$ …………….(4)

Again C (P_3,V_3) and D (P_4,V_4) lies on same isothermal ∴ $P_3V_3=P_4V_4$ ……….(5)

Finally D (P_4, V_4) and A (P_1, V_1) lies on same adiabatic ∴ $P_4V_4^{\gamma}= P_1V_1^{\gamma}$ ……(6)

Multiplying equation (1), (2), (3) and (4)

$P_1V_1 * P_2V_2^{\gamma} * P_3V_3 * P_4V_4^{\gamma} = P_2V_2 * P_3V_3^{\gamma} * P_4V_4 * P_1V_1^{\gamma}$

or, $V_2^{\gamma-1} * V_4^{\gamma-1} = V_3^{\gamma-1} * V_1^{\gamma-1} \rightarrow V_2V_4=V_3V_1 \rightarrow \frac{V_2}{V_1} = \frac{V_3}{V_4}$

Now the equation (1) and (2) can be written as:

$q = RT_1\ln\frac{V_2}{V_1} - RT_2\ln\frac{V_2}{V_1} = R(T_1-T_2)\ln\frac{V_2}{V_1}$ …..(7)

$w = RT_1\ln\frac{V_2}{V_1} - RT_2\ln\frac{V_3}{V_4} = R(T_1-T_2)\ln\frac{V_2}{V_1}$ ……..(8)

Efficiency of a Heat Engine (η): The Efficiency (η) of an engine is the net work done (*w*) on the surroundings divided by heat absorbed (q_1).

$\eta = \frac{w}{q_1} = (q_1 - q_2)/ q_1 = (T_1 - T_2)/ T_1$……….(9)

$\eta = 1-\frac{q_2}{q_1} = 1-\frac{T_2}{T_1}$ ……….(10)

$\because T_2<T_1$

$\therefore \eta<1$

It means heat cannot be completely converted in to work.

Question: calculate the maximum efficiency of an engine operating between 110°C and 25°C.

Solution: $\eta = 1-\frac{T_2}{T_1} = 1-\frac{298K}{383K} = 0.222 = 22.2\%$

Question: Heat supplied to a Carnot engine is 1897.8 kJ. How much useful work can be done by the engine works between 0°C and 100°C.

Solution: $\eta = \frac{w}{q_1} = (T_1- T_2)/ T_1 \quad \therefore w = q_1(T_1- T_2)/ T_1$

Work done by the engine (w) = 1897.8kJ(373K-273K)/373K = 508.7kJ

Entropy

From Carnot cycle: $\mathbf{1-\frac{q_2}{q_1} = 1-\frac{T_2}{T_1}}$

or $\frac{q_1}{T_1} = \frac{q_2}{T_2}$ **……(1)** **or** $\frac{q_{rev}}{T} = constant$

q_{rev} is the heat exchanged in a process carried out reversibly at a temperature T.

$\frac{q_{rev}}{T}$**,** represents a definite quantity or state function called **"Entropy".** It is shown by 'S'.

Thus, $\frac{q_{rev}}{T} = S$ **=Entropy**

Concept of Entropy: In equation (1) giving +ve sign to heat absorbed (q_1) and giving –ve sign to heat giving out to surroundings. Thus the equation (1) can be written as

$$\frac{q_1}{T_1} = -\frac{q_2}{T_2}$$

or $\frac{q_1}{T_1} + \frac{q_2}{T_2} = \mathbf{0}$

In a cyclic process carried out reversibly the summation of $\frac{q}{T}$ terms is equal to **zero.**

Thus in a cyclic process the entropy of system is zero.

Any cyclic process, if carried out reversibly, can be shown to consist of a series of Carnot cycles. Consider a cyclic process in which the change from state A to state B and back to state A (see Fig.) is carried out reversibly. The path ABA may consider a series of small Carnot cycles. The lines slanting horizontally stand for an isothermal and slanting vertically stand for adiabatic processes.

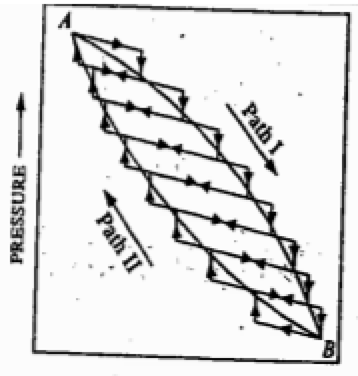


Fig. 2. Entropy change in a reversible cyclic process.

In this cyclic process,

$$\frac{q_1}{T_1} + \frac{q_2}{T_2} + \frac{q_3}{T_3} + \frac{q_4}{T_4} + \ldots\ldots\ldots\ldots\ldots\ldots = 0$$

$\therefore \sum\frac{q}{T} = 0$

When the change are infinitesimal $\sum\frac{dq}{T} = 0$

Since the cycle is performed in two steps A→B and B→A

Then $\sum\frac{dq}{T} = \int_A^B\frac{dq}{T} + \int_B^A\frac{dq}{T} = 0$

$\therefore \int_A^B\frac{dq}{T} = -\int_B^A\frac{dq}{T}$

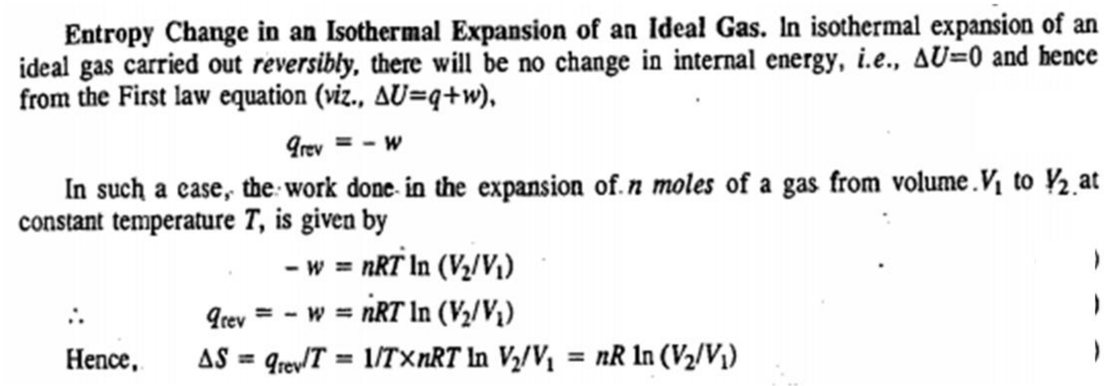
The quantity $\int_A^B \frac{dq}{T}$ is called entropy and denoted by S. If S_A is the entropy in initial stae A and S_B is the entropy in final state B, then change in entropy is given by

$\Delta S = S_B - S_A = \int_A^B \frac{dq}{T}$

For infinitesimal small change: $dS = \frac{dq}{T}$

At constant temperature for finite change: $\Delta S = \frac{q}{T}$

Entropy is an extensive property and its unit is J/K.



Entropy Change in an Isothermal Expansion of an Ideal Gas. In isothermal expansion of an ideal gas carried out *reversibly*, there will be no change in internal energy, *i.e.*, $\Delta U = 0$ and hence from the First law equation (*viz.*, $\Delta U = q + w$),

$$q_{rev} = -w$$

In such a case, the work done in the expansion of *n moles* of a gas from volume V_1 to V_2 at constant temperature *T*, is given by

$$-w = nRT \ln (V_2/V_1) \qquad)$$

$$\therefore \quad q_{rev} = -w = nRT \ln (V_2/V_1) \qquad)$$

Hence, $\Delta S = q_{rev}/T = 1/T \times nRT \ln V_2/V_1 = nR \ln (V_2/V_1)$)

Calculation of Entropy Change of an Ideal Gas with Change in P, V and T. Since entropy of a system varies with the state of the system, its value for a pure gaseous substance will depend upon any two of the three variables T, P and V. Since T is taken generally as one of the variables, the second variable to be considered may be V or P. Thus, the two variables to be considered are either T and V or T and P.

When T and V are the two variables. The increase in entropy of the gas for an infinitesimally small change is given by the expression

$$dS = dq_{rev}/T$$

where dq_{rev} is the small amount of heat *absorbed* by the gas (system) *reversibly* from the surroundings at temperature T.

According to the equation of the First law of thermodynamics, *viz.*, $\Delta U = q+w$, we have

$$dq_{rev} = dU - dw$$

If the work involved is due to *expansion of the gas*, then, for an infinitesimal increase in volume dV against a pressure P,

$$-dw = PdV$$

Substituting the value of dU from $C_V = (\partial U/\partial T)_v$ and $-dw$ from Eq. 38, we have

$$dq_{rev} = C_V\,dT + PdV$$

For one mole of an ideal gas,

$$dq_{rev} = C_V\,dT + RT\,dV/V$$

$$\therefore \quad dq_{rev}/T = dS = C_V\,dT/T + R\,dV/V$$

For a finite change of state of a system, the entropy change (ΔS) is obtained by integrating the above equation between the limits of the initial state 1 and the final state 2. Assuming C_V to be constant within the temperature range T_1 and T_2, for one mole of the gas we have

$$\Delta S = S_2 - S_1 = C_V \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{V_1}^{V_2} \frac{dV}{V}$$

Thus,

$$\Delta S = C_V \ln T_2/T_1 + R \ln V_2/V_1 \qquad \ldots(42)$$

For n moles of the ideal gas, the above equation may be written as

$$\Delta S = nC_V \ln (T_2/T_1) + nR \ln (V_2/V_1)$$

It is evident that the entropy change for the change of state of an ideal gas depends upon the initial and final volumes as well as on the initial and final temperatures.

At constant Volume $V_1=V_2$, $\therefore \Delta S = nC_v\ln(T_2/T_1)$

When T and P are the two variables. If P_1 is the pressure of the ideal gas in the initial state and P_2 in the final state, then

$$P_1V_1 = RT_1 \text{ for one mole of the gas in the initial state}$$

$$P_2V_2 = RT_2 \text{ for one mole of the gas in the final state.}$$

$$\therefore \quad V_2/V_1 = P_1T_2/(P_2T_1)$$

Substituting in Eq. 42, for one mole of the gas, we have

$$\Delta S = C_V \ln T_2/T_1 + R \ln T_2/T_1 - R \ln P_2/P_1$$

Remembering that $C_P - C_V = R$

$$\Delta S = C_P \ln T_2/T_1 - R \ln P_2/P_1$$

For n moles of the ideal gas,

$$\Delta S = nC_P \ln (T_2/T_1) - nR \ln (P_2/P_1)$$

It is evident from the above equations that the entropy change for the change of state of an ideal gas depends on the initial and final pressure as well as on the initial and final temperature.

At constant pressure $P_1=P_2$, $\therefore \Delta S = nC_p\ln(T_2/T_1)$

“**The Second Law of Thermodynamics states** that the state of entropy of the entire universe will always increase over time. The second law also states that the changes in the entropy in the universe can never be negative.”

$\Delta Suniv = \Delta Ssys + \Delta Ssurr \geq 0$

Entropy change in spontaneous processes:

$\Delta Suniv > 0$ for spontaneous process

$\Delta Suniv < 0$ for non-spontaneous process (spontaneous in opposite direction which is impossible)

$\Delta Suniv = 0$ for reversible process (system is at equilibrium)

Physical significance of entropy: (1) Entropy is measure of disorder of system. Higher the disorder of system higher is the entropy. Melting of a solid or evaporation of a liquid always increases the entropy.

(2) Entropy is measure of probability. Therefore there is a relationship between entropy (S) and thermodynamic probability (W).

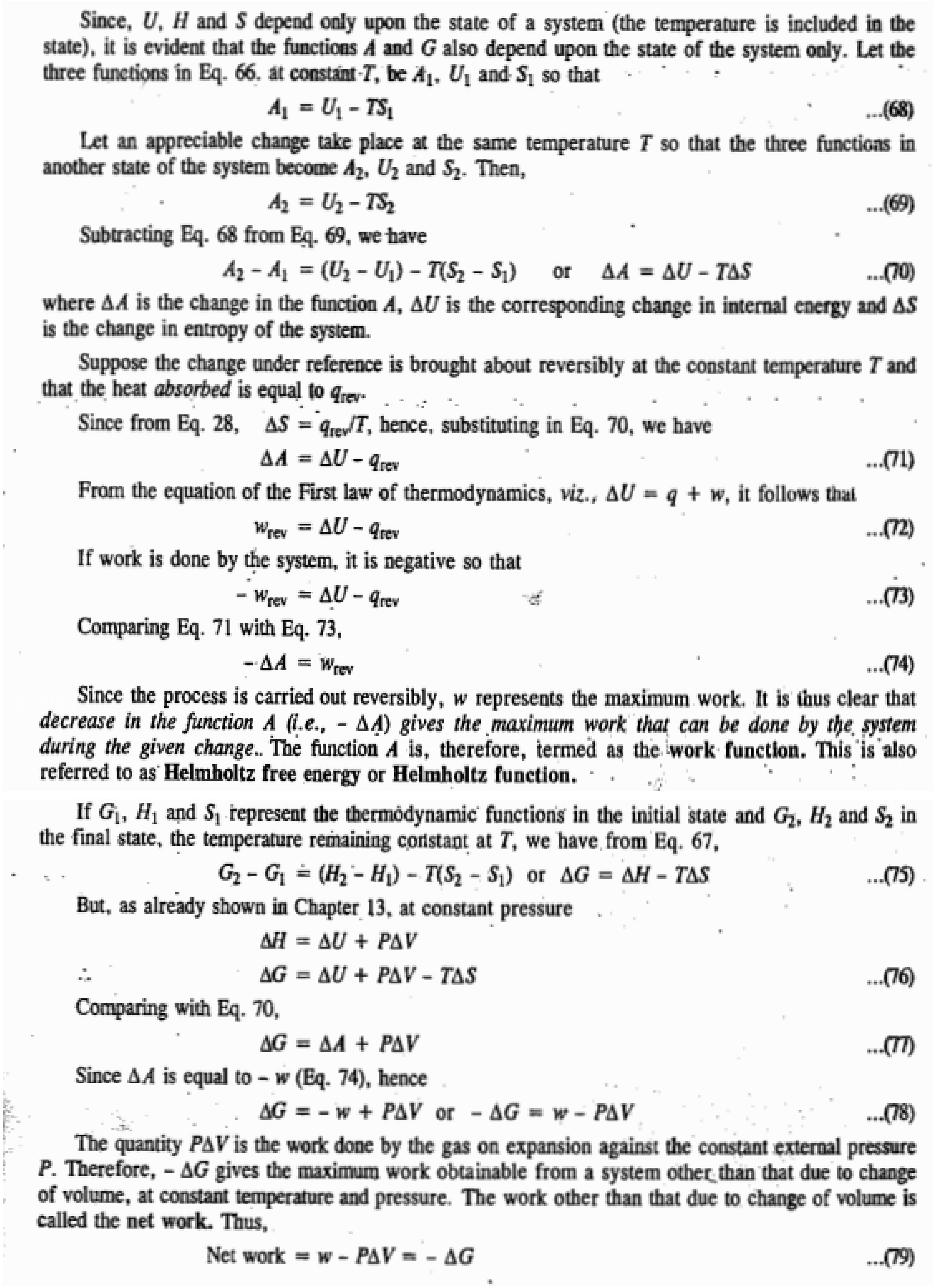
$S = k * \ln W$

A solid at absolute zero considered to be in a most ordered state. In this case W=1 i.e. S =0. The entropy of crystalline solid at absolute zero (0 K) is zero. **This is third law of thermodynamics.**

Free energy and maximum work functions

Work function (A) and the free energy function (G) are given by equatio:

A =U –TS …….(66) and G = H-TS ……………(67)



Since, U, H and S depend only upon the state of a system (the temperature is included in the state), it is evident that the functions A and G also depend upon the state of the system only. Let the three functions in Eq. 66. at constant T, be A_1, U_1 and S_1 so that

$$A_1 = U_1 - TS_1 \qquad ...(68)$$

Let an appreciable change take place at the same temperature T so that the three functions in another state of the system become A_2, U_2 and S_2. Then,

$$A_2 = U_2 - TS_2 \qquad ...(69)$$

Subtracting Eq. 68 from Eq. 69, we have

$$A_2 - A_1 = (U_2 - U_1) - T(S_2 - S_1) \quad \text{or} \quad \Delta A = \Delta U - T\Delta S \qquad ...(70)$$

where ΔA is the change in the function A, ΔU is the corresponding change in internal energy and ΔS is the change in entropy of the system.

Suppose the change under reference is brought about reversibly at the constant temperature T and that the heat *absorbed* is equal to q_{rev}.

Since from Eq. 28, $\Delta S = q_{rev}/T$, hence, substituting in Eq. 70, we have

$$\Delta A = \Delta U - q_{rev} \qquad ...(71)$$

From the equation of the First law of thermodynamics, *viz.*, $\Delta U = q + w$, it follows that

$$w_{rev} = \Delta U - q_{rev} \qquad ...(72)$$

If work is done by the system, it is negative so that

$$-w_{rev} = \Delta U - q_{rev} \qquad ...(73)$$

Comparing Eq. 71 with Eq. 73,

$$-\Delta A = w_{rev} \qquad ...(74)$$

Since the process is carried out reversibly, w represents the maximum work. It is thus clear that *decrease in the function A (i.e., – ΔA) gives the maximum work that can be done by the system during the given change.*. The function A is, therefore, termed as the **work function.** This is also referred to as **Helmholtz free energy** or **Helmholtz function.**

If G_1, H_1 and S_1 represent the thermodynamic functions in the initial state and G_2, H_2 and S_2 in the final state, the temperature remaining constant at T, we have from Eq. 67,

$$G_2 - G_1 = (H_2 - H_1) - T(S_2 - S_1) \quad \text{or} \quad \Delta G = \Delta H - T\Delta S \qquad ...(75)$$

But, as already shown in Chapter 13, at constant pressure

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

$$\therefore \quad \Delta G = \Delta U + P\Delta V - T\Delta S \qquad ...(76)$$

Comparing with Eq. 70,

$$\Delta G = \Delta A + P\Delta V \qquad ...(77)$$

Since ΔA is equal to $-w$ (Eq. 74), hence

$$\Delta G = -w + P\Delta V \quad \text{or} \quad -\Delta G = w - P\Delta V \qquad ...(78)$$

The quantity $P\Delta V$ is the work done by the gas on expansion against the constant external pressure P. Therefore, $-\Delta G$ gives the maximum work obtainable from a system other than that due to change of volume, at constant temperature and pressure. The work other than that due to change of volume is called the **net work.** Thus,

$$\text{Net work} = w - P\Delta V = -\Delta G \qquad ...(79)$$

Hence, $-\Delta G$ is a measure of the net work that can be obtained from a system at constant temperature and pressure. The quantity G is called the **Gibbs function** or **Gibbs free energy** or merely **free energy**. Thus, $-\Delta G$ is a measure of the decrease in free energy. The net work that it measures may be electrical work or chemical work. This quantity is of great importance in physical chemistry ; it is named in honour of the great American physicist, J.W. Gibbs (1839-1903).

Variation of Free Energy Change with Temperature and Pressure. The variation of free energy change with variation of temperature and pressure may now be considered. According to Eq. 67,

$$G = H - TS$$

Since $H = U + PV$, hence $G = U + PV - TS$ ...(80)

Upon differentiation, $dG = dU + PdV + VdP - TdS - SdT$ ... (81)

The First law equation for an infinitesimal change may be written as

$$dq = dU - dw \quad ...(82)$$

If the work done is only due to expansion, then, $-dw = PdV$

$$\therefore \quad dq = dU + PdV \quad ...(83)$$

For a reversible process,

$$dS = dq/T \quad \text{or} \quad TdS = dq = dU + PdV \quad ...(84)$$

Combining Eqs. 81 and 84, we have

$$dG = VdP - SdT \quad ...(85)$$

This equation gives change of free energy when a system undergoes, reversibly, a change of pressure as well as change of temperature.

If pressure remains constant, *i.e.*, $dP=0$, then, from Eq. 85

$$dG = -SdT \quad \text{or} \quad (\partial G/\partial T)_P = -S \quad ...(86)$$

On the other hand, if temperature remains constant, *i.e.*, $dT=0$, then, from Eq. 85,

$$dG = VdP \quad \text{or} \quad (\partial G/\partial P)_T = V \quad ...(87)$$

Let the free energy of a system be G_1 in the initial state and G_2 in the final state when an appreciable change in pressure has taken place, at constant temperature. Then, integrating Eq. 87, the free energy change, ΔG, is given by

$$\Delta G = G_2 - G_1 = \int_{P_1}^{P_2} VdP \quad ...(88)$$

where P_1 and P_2 are the initial and final pressures, respectively.

If one mole of an ideal gas is under consideration, then $PV = RT$.

$$\therefore \quad \Delta G = RT\int_{P_1}^{P_2} \frac{dP}{P} = RT \ln \frac{P_2}{P_1} = RT \ln \frac{V_1}{V_2} \quad ...(89)$$

where V_1 and V_2 are the initial and final volumes, respectively.

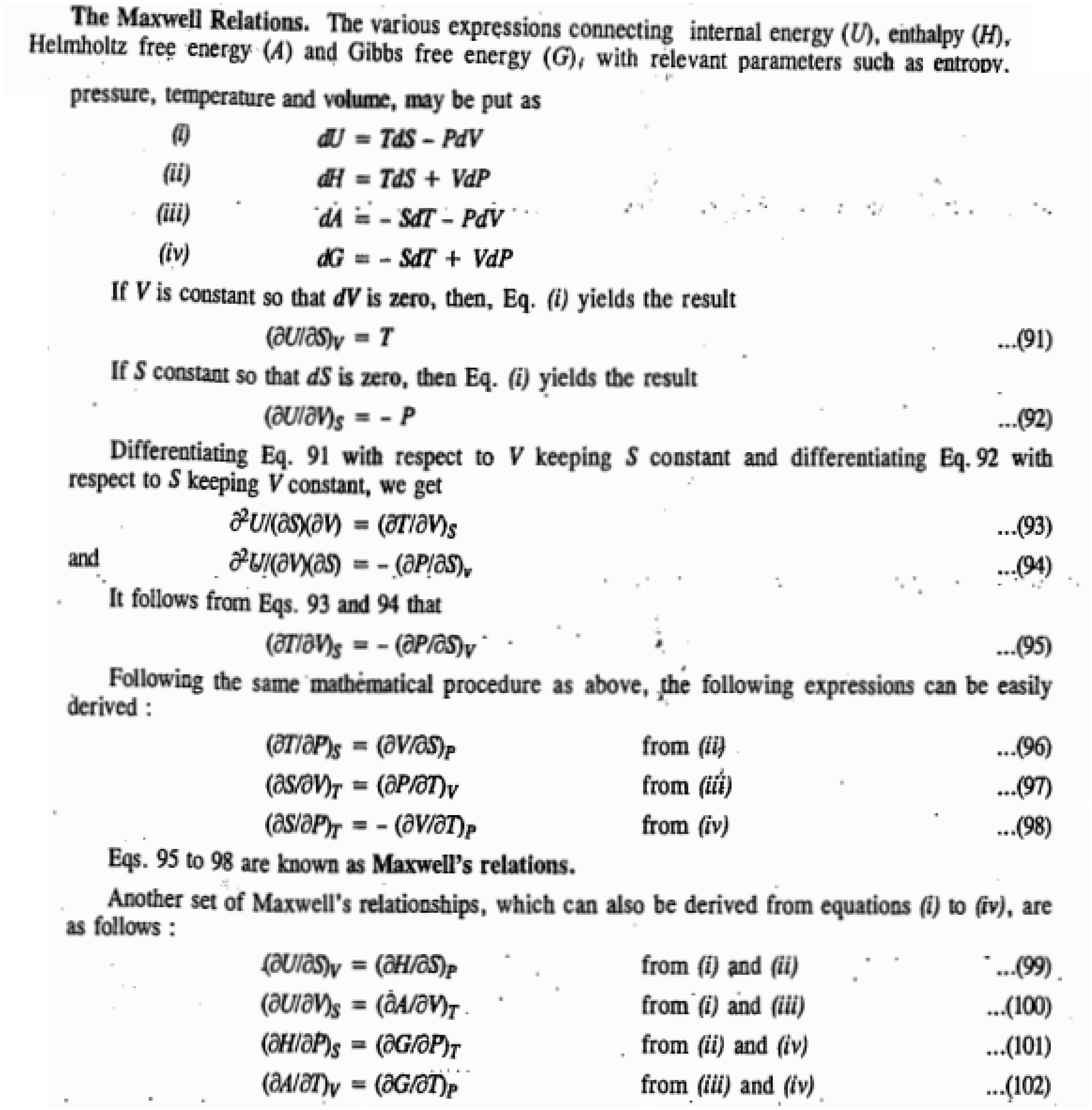
For n moles of the gas,

$$\Delta G = nRT \ln (P_2/P_1) = nRT \ln (V_1/V_2) \quad ...(90)$$

Example 17. Calculate the free energy change (ΔG) which occurs when 1 mole of an ideal gas expands reversibly and isothermally at 37°C from an initial volume of 55 dm^3 to 1000 dm^3.

Solution : Substituting the given data in Eq. 90, we have

$$\Delta G = (8{\cdot}314 \text{ J K}^{-1} \text{ mol}^{-1}) (310 \text{ K}) \ln (55 \text{ dm}^3/1000 \text{ dm}^3) = -7476{\cdot}8 \text{ J mol}^{-1}$$



The Maxwell Relations. The various expressions connecting internal energy (U), enthalpy (H), Helmholtz free energy (A) and Gibbs free energy (G), with relevant parameters such as entropy, pressure, temperature and volume, may be put as

(i) $dU = TdS - PdV$

(ii) $dH = TdS + VdP$

(iii) $dA = -SdT - PdV$

(iv) $dG = -SdT + VdP$

If V is constant so that dV is zero, then, Eq. (i) yields the result

$$(\partial U/\partial S)_V = T \qquad ...(91)$$

If S constant so that dS is zero, then Eq. (i) yields the result

$$(\partial U/\partial V)_S = -P \qquad ...(92)$$

Differentiating Eq. 91 with respect to V keeping S constant and differentiating Eq. 92 with respect to S keeping V constant, we get

$$\partial^2 U/(\partial S)(\partial V) = (\partial T/\partial V)_S \qquad ...(93)$$

and

$$\partial^2 U/(\partial V)(\partial S) = -(\partial P/\partial S)_V \qquad ...(94)$$

It follows from Eqs. 93 and 94 that

$$(\partial T/\partial V)_S = -(\partial P/\partial S)_V \qquad ...(95)$$

Following the same mathematical procedure as above, the following expressions can be easily derived :

$(\partial T/\partial P)_S = (\partial V/\partial S)_P$ from (ii) ...(96)

$(\partial S/\partial V)_T = (\partial P/\partial T)_V$ from (iii) ...(97)

$(\partial S/\partial P)_T = -(\partial V/\partial T)_P$ from (iv) ...(98)

Eqs. 95 to 98 are known as **Maxwell's relations.**

Another set of Maxwell's relationships, which can also be derived from equations (i) to (iv), are as follows :

$(\partial U/\partial S)_V = (\partial H/\partial S)_P$ from (i) and (ii) ...(99)

$(\partial U/\partial V)_S = (\partial A/\partial V)_T$ from (i) and (iii) ...(100)

$(\partial H/\partial P)_S = (\partial G/\partial P)_T$ from (ii) and (iv) ...(101)

$(\partial A/\partial T)_V = (\partial G/\partial T)_P$ from (iii) and (iv) ...(102)

The Gibbs-Helmholtz equation

From Maxwell's relation: $dG = -SdT + VdP$ ….1

At constant pressure $dP = 0$: $\therefore (\partial G/\partial T)_P = -S$ …………..2

Also $\Delta G = \Delta H - T\Delta S$

or $-\Delta S = (\Delta G - \Delta H)/T$ ………………3

From equation 2 and 3

$(\partial G/\partial T)_P = (\Delta G - \Delta H)/T$ $\therefore$ $\Delta G = \Delta H + T(\partial G/\partial T)_P$ ……..4 The equation (4) known as Gibbs -Helmholtz equation. The **Gibbs-Helmholtz Equation** is very **important** because it relates the change in **Gibbs** energy to its temperature dependence, and the position of equilibrium to change in enthalpy.

Van't-Hoff equation

The Van't Hoff equation relates the change in the equilibrium constant, K_p, of a chemical reaction to the change in temperature, T, given the standard enthalpy change, ΔH^0, for the process. From Gibbs -Helmholtz equation,

$$\Delta G^0 = \Delta H^0 + \left[\frac{\partial\left(\Delta G^0\right)}{\partial T}\right]_P$$

Zero superscripts are indicating standard values

$$or, -\frac{\Delta H^0}{T^2} = -\frac{\Delta G^0}{T^2} + \left[\frac{\partial\left(\Delta G^0\right)}{\partial T}\right]_P$$

$$or, -\frac{\Delta H^0}{T^2} = \left[\frac{\partial}{\partial T}\left(\frac{\Delta G^0}{T}\right)\right]_P$$

Van't Hoff isotherm

$$-\text{RT}\ \ln K_P = \Delta G^\circ$$

$$\text{or, } -\text{R}\ \ln K_P = \Delta G^\circ/T$$

Differentiating with respect to temperature at constant pressure

$$-R\left(\frac{\partial lnK_P}{\partial T}\right)_P = \left[\frac{\partial}{\partial T}\left(\frac{\Delta G^0}{T}\right)\right]_P$$

Comparing the above two-equation

$$\frac{\partial lnK_P}{\partial T} = \frac{\Delta H^0}{RT^2}$$

This is the differential form of the van 't Hoff equation; it's not the most useful thing to us though because it only tells you the slope of a plot of ln*Kp* against *T* at one given point. We usually separate the variables and integrate with respect to both sides:

$$\int_{\ln Kp_1}^{\ln Kp_2} \mathrm{d}(\ln K) = \int_{T_1}^{T_2} \frac{\Delta H^\circ}{RT^2}\,\mathrm{d}T$$

$$\ln Kp_2 - \ln Kp_1 = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

So, if you know the equilibrium constant Kp_1 at a certain temperature T_1 and you want to find the equilibrium constant Kp_2 at a different temperature T_2, you can just plug in your values into the equation and solve for Kp_2.

Note that this equation supports what you know of Le Chatelier's principle; if the reaction is exothermic, $\Delta H^\circ<0$, and if you increase the temperature from T_1 to $T_2>T_1$ then $(1/T_1-1/T_2)>0$. The RHS of the equation is therefore negative, and that means that $\ln Kp_2<\ln Kp_1 \Rightarrow Kp_2< Kp_1$ which implies that the equilibrium position has shifted to the left.

Van't Hoff equation: The above equation can be written at temperature (T)

$$\mathbf{lnKp} = -\frac{\Delta H^0}{RT} + c$$

where c is integrated constant

<u>For an exothermic reaction</u>, heat is released, making the net enthalpy change negative. Thus, according to the definition of the slope: slope $=-\frac{\Delta H^0}{R}$

For an <u>exothermic</u> reaction, $\Delta H^0 < 0$ (and the <u>gas constant</u> $R > 0$), so slope $= -\frac{\Delta H^0}{R} > 0$

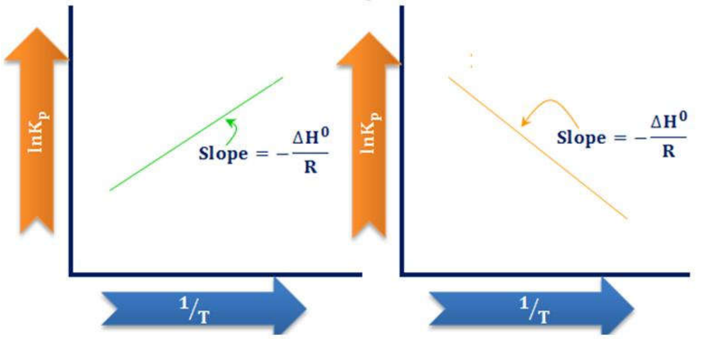
Thus, for an exothermic reaction, the van 't Hoff plot should always have a positive slope.

<u>For an endothermic reaction</u>, heat is absorbed, making the net enthalpy change positive. Thus, according to the definition of the slope: slope $=-\frac{\Delta H^0}{R}$

For an <u>endothermic</u> reaction, $\Delta H^0 > 0$

(and the <u>gas constant</u> $R > 0$), so
slope $= -\frac{\Delta H^0}{R} < 0$

Thus, for an endothermic reaction, the van 't Hoff plot should always have a negative slope.



Exothermic Reaction Endothermic Reaction