

Syllabus: Unit II - Thermodynamic potentials : Internal Energy; Enthalpy; Helmholtz free energy; Gibbs free energy and their significance; Maxwell's thermodynamic relations (using thermodynamic potentials) and their significance; TdS relations; Energy equations and Heat Capacity equations; Third law of thermodynamics (Nernst Heat theorem)

Thermodynamics deals with the conversion of heat energy to other forms of energy or vice versa in general.

A **thermodynamic system** is the quantity of matter under study which is in general macroscopic in nature. Examples: Gas, vapour, vapour in contact with liquid etc..

Thermodynamic state or condition of a system is one which is described by the macroscopic physical quantities like pressure (P), volume (V), temperature (T) and entropy (S).

The physical quantities like P, V, T and S are called **thermodynamic variables**. Any two of these variables are independent variables and the rest are dependent variables. A general relation between the thermodynamic variables is called **equation of state**. The relation between the variables that describe a thermodynamic system are given by first and second law of thermodynamics.

According to **first law of thermodynamics**, when a substance absorbs an amount of heat dQ at constant pressure P , its internal energy increases by dU and the substance does work dW by increase in its volume by dV .

Mathematically it is represented by $dQ = dU + dW = dU + P dV \dots (1)$

If a substance absorbs an amount of heat dQ at a temperature T and if all changes that take place are perfectly reversible, then the change in entropy from the **second law of thermodynamics** is $dS = \frac{dQ}{T}$ or $dQ = T dS \dots (2)$

From equations (1) and (2), $T dS = dU + P dV$

This is the basic equation that connects the first and second laws of thermodynamics. The functions of the state variables, P, V, T and S, together with the two laws of thermodynamics that gives the complete knowledge of the state of a system are called **thermodynamic functions or thermodynamic potentials**.

Thermodynamic potentials are extensive state variables of dimensions of energy. Their purpose is to allow for simple treatment of equilibrium for systems interacting with the environment. These functions are the energy functions formed by combining the basic thermodynamic variables.

The four fundamental thermodynamic potentials are 1. Internal energy (U), 2. Enthalpy or total heat function (H), 3. Helmholtz function (F) and 4. Gibbs function (G).

Internal Energy (U) :Internal energy of a system is the energy possessed due to kinetic energy and potential energy of the constituents of the system. Kinetic energy refers to energy possessed by the molecules by virtue of its motion and potential energy is due to intermolecular forces.

1. From the first and second laws of thermodynamics $T dS = dU + P dV$

or $dU = T dS - P dV$(1) This equation gives the change in internal energy of a system in terms of variables P, V, T and S.

2. From first law, $dQ = dU + P dV$,

Dividing both the sides of the above equation by dT , we get $\frac{dQ}{dT} = \frac{dU}{dT} + P \frac{dV}{dT}$

At constant volume, (as $dV = 0$) the above equation would be $\left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V = C_V$

where C_V is the specific heat at constant Volume.

Also, for an adiabatic process (no exchange of heat) $dQ = 0$.

Thus $0 = dU + PdV$ or $dU = -PdV$

For a isochoric process (Constant volume, i.e. $dV = 0$), from the above relation, $dU = 0$.

Thus internal energy of a system is a constant in a isochoric - adiabatic process.

This potential is also called **Isochoric - Isentropic potential** where thermodynamic potential is the internal energy U and the independent variables are Entropy S and volume V.

Enthalpy (H) :

Consider two states 1 and 2 of a thermodynamic system. If U_1 and U_2 are the internal energies, then if dQ is the heat absorbed by the system, from first law

$dQ = (U_2 - U_1) + dW$. If work is done at constant pressure due to change in volume, then $dW = P(V_2 - V_1)$. Thus $(U_2 - U_1) = dQ - P(V_2 - V_1)$ or $(U_2 + PV_2) - (U_1 + PV_1) = dQ$

Thus $H_2 - H_1 = dQ$ where in general $H = U + PV$

Enthalpy of a system is the total heat energy of a system given by $H = U + PV$(1)

1. When a system undergoes an infinitesimal process from an initial equilibrium state to a final equilibrium state, $dH = dU + P dV + V dP$(2) (by differentiating (1))

From first law. $dQ = dU + PdV$(3) Thus eqn. (2) is $dH = dQ + V dP$

Dividing both the sides of the above equation by dT , we get $\frac{dH}{dT} = \frac{dQ}{dT} + V \frac{dP}{dT}$

At constant pressure, (as $dP = 0$) the above equation would be $\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial Q}{\partial T}\right)_P = C_P$

where C_P is the specific heat at constant pressure. Also $dH = T dS + V dP$ and $Q = TdS$

2. Since $dH = dQ + V dP$, the change in enthalpy during isobaric process (constant pressure $dP = 0$) is the heat transferred (ie $dH = dQ$). Thus the latent heat measured

during phase transition (e.g. melting, boiling, sublimation) is simply the change in enthalpy. i.e. $H_f - H_i = Q$ or $H_f - H_i = \int C_p dT$. (since $dQ = C_p dT$). This indicates isobaric process.

3. For an adiabatic process, $dQ = 0$. Thus for adiabatic and isobaric process, $dH = 0$. Thus H is a constant.

The potential is also called **isentropic - isobaric potential** where independent variables are entropy S and pressure P.

Note : In a throttling process, enthalpy remains constant as explained below.

A process in which a gas at high pressure passes through a porous material into a low pressure region is the throttling process. During this process $U + PV$ remains constant. Applying first law to the throttling process, $Q = U_f - U_i + (-W)$ (W is negative as work is done on the system). Here $Q = 0$, and $W = -(P_f V_f - P_i V_i)$ Thus $0 = U_f - U_i + P_f V_f - P_i V_i$ or $U_i + P_i V_i = U_f + P_f V_f$

or $H_i = H_f$. Thus initial enthalpy of a system is equal to the final enthalpy of the system in a throttling process.

Comparison of properties of U and H for a hydrostatic system

Internal energy (U)	Enthalpy (H)
Free expansion (irreversible) $U_i = U_f$	Throttling process (irreversible) $H_i = H_f$
In general $dU = dQ - PdV$ and $\left(\frac{\partial U}{\partial T}\right)_V = C_V$	In general $dH = dQ + VdP$ and $\left(\frac{\partial H}{\partial T}\right)_P = C_P$
Isochoric process $U_f - U_i = Q_V$	Isobaric process $H_f - H_i = Q_P$
For an ideal gas $U_f - U_i = - \int_i^f C_V dT$	For an ideal gas $H_f - H_i = - \int_i^f C_P dT$
For a adiabatic process $U_f - U_i = - \int_i^f PdV$	For a adiabatic process $H_f - H_i = - \int_i^f VdP$
Nearly equilibrium state $dU = T dS - P dV$ $\left(\frac{\partial U}{\partial S}\right)_V = T$ and $\left(\frac{\partial U}{\partial V}\right)_S = -P$	Nearly equilibrium state $dH = T dS + V dP$ $\left(\frac{\partial H}{\partial S}\right)_P = T$ and $\left(\frac{\partial H}{\partial P}\right)_S = V$

Helmholtz Function : From the first and second law of thermodynamics

$TdS = dU + dW$ If heat is exchanged between the system and surroundings at constant temperature $TdS = d(TS)$. Thus $dU = d(TS) - dW$ or $d(U - TS) = -dW$ where $(U - TS) = F$ called Helmholtz free energy or work function

The Helmholtz function (called Helmholtz free energy) is defined as $F = U - TS$

For an infinitesimal reversible process,

$$dF = dU - TdS - SdT \quad (\text{by differentiating above equation})$$

From laws of thermodynamics $TdS = dU + PdV$

$$\text{Hence } dF = dU - (dU + PdV) - SdT \quad \text{or} \quad dF = -PdV - SdT$$

Thus for a reversible isothermal process (for a isothermal process, temperature remains constant i.e. $dT = 0$) $dF = -PdV$

$$\text{Thus } F_f - F_i = - \int_i^f PdV$$

Hence the change of Helmholtz function during a reversible isothermal process equals the work done on the system.

For a reversible isothermal and isochoric process $dF = -PdV = 0$ or $F = \text{constant}$. (In a isochoric process, Volume is constant. Thus $dV = 0$) Also, from $dF = -PdV - SdT$ $\left(\frac{\partial F}{\partial V}\right)_T = -P$ and $\left(\frac{\partial F}{\partial T}\right)_V = -S$

The potential is also called **isothermal - isochoric function** where independent variables are temperature T and volume V.

Gibbs Function (G) :

For enthalpy $H = U + PV$. For a infinitesimal change $dH = TdS + VdP$

If the system is isothermal and pressure is remaining constant, from above equation $dH = d(TS)$ or $d(H - TS) = 0$. Thus $H - TS = \text{constant}$ where $H - TS = G$ is called Gibbs free energy.

The Gibbs function (Gibbs free energy) is defined as $G = H - TS$ or $G = U + PV - TS$

For an infinitesimal reversible process,

$$dG = dH - TdS - SdT \quad \text{Also } dH = TdS + VdP$$

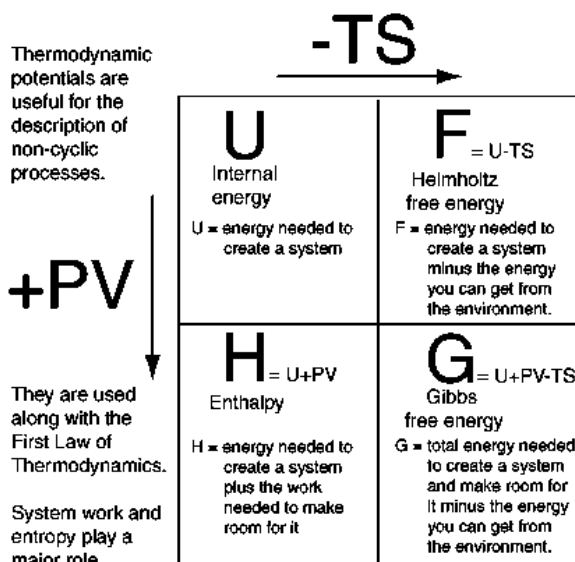
$$\text{Hence } dG = (TdS + VdP) - TdS - SdT \quad \text{or}$$

$$dG = VdP - SdT$$

$$\text{Also } \left(\frac{\partial G}{\partial P}\right)_T = V \quad \text{and} \quad \left(\frac{\partial G}{\partial T}\right)_P = -S$$

For a reversible isothermal and isobaric process $dG = 0$ or $G = \text{constant}$. (In a isobaric process, pressure is constant. Thus $dP = 0$).

The potential is also called the **isothermal - isobaric potential** where the independent variables are temperature and pressure P.



Significance of thermodynamic potentials

A mechanical system is said to be in stable equilibrium if the potential energy of the system is minimum. For example heat flows from higher to lower temperature region till equilibrium is achieved. Also water flows from higher to lower level to achieve minimum potential energy.

As U, H, F and G are all energy functions in thermodynamics, they behave similar to potential energy in mechanics.

1. In an isochoric – adiabatic process, the internal energy tends to a minimum.
2. In an isobaric – adiabatic process, the enthalpy tends to a minimum.
3. In an isochoric – isothermal process, the Helmholtz free energy tends to a minimum.
4. In an isobaric – isothermal process, the Gibbs free energy tends to a minimum.

Maxwell's thermodynamic relations

Maxwell's equations refer to relations between the thermodynamic variables that hold at any equilibrium state of a hydrostatic system. They provide relationships between measurable quantities and those which either cannot be measured or difficult to measure.

If a relation exists between the variables x, y and z, then z can be expressed in terms of x and y as $dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$

Let $\left(\frac{\partial z}{\partial x}\right)_y = M$ and $\left(\frac{\partial z}{\partial y}\right)_x = N$, then $dz = M dx + N dy \dots(1)$

Partially differentiating M with respect to y and N with respect to x, we get

$$\left(\frac{\partial M}{\partial y}\right)_x = \frac{\partial^2 z}{\partial x \partial y} \quad \text{and} \quad \left(\frac{\partial N}{\partial x}\right)_y = \frac{\partial^2 z}{\partial x \partial y}.$$

The right hand side of the above equation is same. Thus $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \dots(2)$

This is the condition for exact differential and is applicable to all thermodynamic potentials. This result is applied to the four exact differentials, dU, dF, dH and dG, to get the Maxwell equations.

1. **First Maxwell equation -Internal energy** :From the first law of thermodynamics $dQ = dU + dW = dU + P dV$ and from the second law $dQ = TdS$

Combining the above two relations, $TdS = dU + P dV \dots\dots(3)$

Or $dU = TdS - PdV \dots\dots(4)$

Comparing eqn. (1) with (4), $M = T$, $N = -P$, $x = S$ and $y = V$

Substituting these variables in eqn. (2) $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \dots(5)$

2. **Second Maxwell equation - Helmholtz Function** :The Helmholtz function (is defines as $F = U - TS$

For an infinitesimal reversible process, $dF = dU - TdS - SdT$

From laws of thermodynamics $TdS = dU + PdV$

Hence $dF = dU - (dU + PdV) - SdT$ or $dF = -PdV - SdT$(6)

Comparing eqn. (1) with (6), $M = -P$, $N = -S$, $x = V$ and $y = T$

Substituting these variables in eqn. (2) $\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$ or $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ (7)

3. **Third Maxwell equation - Enthalpy (H)** : Enthalpy of a system is the total heat energy of a system given by $H = U + PV$

When a system undergoes an infinitesimal process, $dH = dU + P dV + V dP$

From laws of thermodynamics $TdS = dU + PdV$

Thus $dH = TdS + V dP$ (8)

Comparing eqn. (1) with (8), $M = T$, $N = V$, $x = S$ and $y = P$

Substituting these variables in eqn. (2) $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$ (9)

4. **Fourth Maxwell equation - Gibbs Function (G)** : The Gibbs function is defined as $G = H - TS$ or For an infinitesimal reversible process, $dG = dH - TdS - SdT$

Also $dH = TdS + VdP$, Hence $dG = VdP - SdT$(10)

Comparing eqn. (1) with (10), $M = V$, $N = -S$, $x = P$ and $y = T$

Substituting these variables in eqn. (2) $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$ or $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ (11)

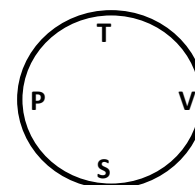
Note :To remember the Maxwell's relations – remember the sentence **T VS** special Programme, taken clockwise along a circle as shown

First relation – Start from T and read anticlockwise (negative) T - P - S - V

Second relation – Start from S and read clockwise (positive) S - P - T - V

Third relation – Start from T and read clockwise (positive) T - V - S - P

Fourth relation – Start from S and read anticlockwise (negative) S - V - T - P



The TdS equations

1. **First TdS equation** : The entropy of a pure substance can be imagined as a function of T and V. This can be written as $dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$

Multiplying the above equation throughout by T, $TdS = T \left(\frac{\partial S}{\partial T}\right)_V dT + T \left(\frac{\partial S}{\partial V}\right)_T dV$ (1)

For a reversible process $TdS = dQ$. Thus $T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial Q}{\partial T}\right)_V = C_V$, ... (2) where C_V is the specific heat at constant volume.

Also from Maxwell's second relation, $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ (3)

Substituting (2) and (3) in (1) we get $TdS = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$

This is the first TdS equation.

Application – Consider one mole of a van der Waals gas undergoes isothermal expansion from volume V_i to V_f , then to find the amount of heat transferred,

From the first TdS equation $TdS = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$ (1)

From van der Waals equation, $(P + \frac{a}{V^2})(V - b) = RT$

or $P = \frac{RT}{V-b} - \frac{a}{V^2}$, thus $\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}$ (2)

For an isothermal change $dT = 0$. The TdS equation becomes

$TdS = 0 + T\frac{R}{V-b} dV$ (by inserting (2) in (1) along with $dT = 0$)

Hence heat transferred is $Q = \int TdS = RT \int_{V_i}^{V_f} \frac{dV}{V-b}$. Thus $Q = RT \ln \frac{V_f - b}{V_i - b}$.

2. Second TdS equation

If entropy of a pure substance is regarded as a function of T and P , then

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

Multiplying the above equation throughout by T , $TdS = T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP$ (1)

As $T\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial Q}{\partial T}\right)_P = C_P$... (2) where C_P is the specific heat at constant pressure.

From Maxwell's fourth equation $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ (3)

Putting (2) and (3) in (1), we get $TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$. This is the second TdS equation.

Application : 1. To find the amount of heat transferred during an isothermal change of pressure. As temperature is a constant, the second TdS can be written as

$TdS = -T\left(\frac{\partial V}{\partial T}\right)_P dP$ (putting $dT = 0$ in TdS equation)

The heat $Q = \int TdS = -T \int \left(\frac{\partial V}{\partial T}\right)_P dP$

As the volume expansivity is $\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$, We obtain $Q = -T \int V\beta dP$

In most of the solids and liquids, β behave similarly. Thus V and β can be taken out of integration sign by taking their averages. We obtain,

$Q = -T\bar{V}\bar{\beta} \int_i^f dP = -T\bar{V}\bar{\beta}(P_f - P_i)$.

It is seen from this result that, as the pressure is increased isothermally, heat will flow out if β is positive. In case of water as β is negative (between 0° and 4°C), an isothermal increase of pressure causes an absorption of heat.

Application 2. : Reversible adiabatic change of pressure. Since entropy remains constant ($dS = 0$). The TdS equation is

$$TdS = 0 = C_p dT - T \left(\frac{\partial V}{\partial T} \right)_P dP \quad \text{or} \quad C_p dT = T \left(\frac{\partial V}{\partial T} \right)_P dP$$

$$\text{or} \quad dT = \frac{T}{C_p} \left(\frac{\partial V}{\partial T} \right)_P dP = \frac{TV\beta}{C_p} dP$$

In a solid or a liquid, increase of pressure produces only a small change of temperature. Also C_p does not vary. Hence above equation is $\Delta T = \frac{TV\beta}{C_p} (P_f - P_i)$.

It is clear from the above discussion that an adiabatic increase of pressure will produce an increase of temperature in any substance with a positive expansivity and a decrease in temperature in a substance with a negative expansivity.

Energy equations

1. First energy equation : If a pure substance undergoes infinitesimal reversible process between two equilibrium states, the change in internal energy is (from the two laws of thermodynamics) $dU = TdS - PdV$

$$\text{Dividing by } dV \text{ we get} \quad \frac{dU}{dV} = T \frac{dS}{dV} - P$$

U , S and P are regarded as functions of T and V . If T is held constant, the derivatives become partial derivatives. i.e. $\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial S}{\partial V} \right)_T - P$,

Using Maxwell's second relation $\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$ in the above equation, we get

$$\boxed{\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P.} \quad \text{This is the first energy equation.}$$

An example of the usefulness of this equation is as follows

(a) Ideal gas

$$\text{For an ideal gas } P = \frac{nRT}{V} \text{ Differentiating } \left(\frac{\partial P}{\partial T} \right)_V = \frac{nR}{V} \quad \dots(1)$$

$$\text{From the energy equation } \left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P \quad \dots(2)$$

$$\text{Equation (1) in (2) gives } \left(\frac{\partial U}{\partial V} \right)_T = T \frac{nR}{V} - P = P - P = 0$$

Therefore U does not depend on V but is a function of T only.

(b) Van der Waals gas (1 mol) :

$$\text{From the van der waals equation for one mole of a gas } P = \frac{RT}{V-b} - \frac{a}{V^2} \quad \dots(1)$$

$$\text{Differentiating } \left(\frac{\partial P}{\partial T} \right)_V = \frac{R}{V-b} \quad \dots(2)$$

From the energy equation $\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P \dots\dots\dots(3)$

Putting (1) and (2) in (3) $\left(\frac{\partial U}{\partial V}\right)_T = T \frac{R}{V-b} - \frac{RT}{V-b} + \frac{a}{V^2} = \frac{a}{V^2}$ or $T \left(\frac{\partial P}{\partial T}\right)_V - P = \frac{a}{V^2}$

As $dU = TdS - PdV$ and substituting for TdS from the relation $TdS = C_V dT + T \left(\frac{\partial P}{\partial T}\right)_V dV$

We get $dU = C_V dT + T \left(\frac{\partial P}{\partial T}\right)_V dV - PdV = C_V dT + \left[T \left(\frac{\partial P}{\partial T}\right)_V - P\right] dV$

Thus $dU = C_V dT + \frac{a}{V^2} dV$ and $U = \int C_V dT - \frac{a}{V} + const.$

It follows, therefore, that the internal energy of a van der Waals gas increases as the volume increases, with the temperature remaining constant.

2. Second energy equation :The change of internal energy is (from the two laws of thermodynamics) $dU = TdS - PdV$

Dividing this equation by dP , we get $\frac{dU}{dP} = T \frac{dS}{dP} - P \frac{dV}{dP}$

Where U , S and V are imagined to be functions of T and P . If T is held constant, the derivatives become partial derivatives, and

$$\left(\frac{\partial U}{\partial P}\right)_T = T \left(\frac{\partial S}{\partial P}\right)_T - P \left(\frac{\partial V}{\partial P}\right)_T$$

Using Maxwell's fourth relation $\left(\frac{\partial S}{\partial P}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_P$, the above equation becomes,

$\left(\frac{\partial U}{\partial P}\right)_T = - T \left(\frac{\partial V}{\partial T}\right)_P - P \left(\frac{\partial V}{\partial P}\right)_T$

 This is the second energy equation.

Heat capacity equations - Expression for difference in molar specific heat capacities :The first and the second TdS equations are given by

$$TdS = C_V dT + T \left(\frac{\partial P}{\partial T}\right)_V dV \dots(1) \quad \text{and} \quad TdS = C_P dT - T \left(\frac{\partial V}{\partial T}\right)_P dP \dots\dots\dots(2)$$

Equating the above equations, we get,

$$C_P dT - T \left(\frac{\partial V}{\partial T}\right)_P dP = C_V dT + T \left(\frac{\partial P}{\partial T}\right)_V dV$$

Solving for dT we get, $C_P dT - C_V dT = T \left(\frac{\partial V}{\partial T}\right)_P dP + T \left(\frac{\partial P}{\partial T}\right)_V dV$

or $(C_P - C_V) dT = T \left(\frac{\partial V}{\partial T}\right)_P dP + T \left(\frac{\partial P}{\partial T}\right)_V dV$

$$\text{or } dT = \frac{T \left(\frac{\partial P}{\partial T}\right)_V}{(C_P - C_V)} dV + \frac{T \left(\frac{\partial V}{\partial T}\right)_P}{(C_P - C_V)} dP \dots\dots\dots(3)$$

As dT is a perfect differential, $dT = \left(\frac{\partial T}{\partial V}\right)_P dV + \left(\frac{\partial T}{\partial P}\right)_V dP \dots\dots(4)$

Equating coefficients of dP and dV of equations (3) and (4)

$$\left(\frac{\partial T}{\partial V}\right)_P = \frac{T \left(\frac{\partial P}{\partial T}\right)_V}{(C_P - C_V)} \dots\dots\dots(5)$$

$$\text{and} \quad \left(\frac{\partial T}{\partial P}\right)_V = \frac{T \left(\frac{\partial V}{\partial T}\right)_P}{(C_P - C_V)} \dots\dots\dots(6)$$

Both the above equations yields the same relation after rearranging, ie.,

$$C_p - C_v = \frac{T \left(\frac{\partial P}{\partial T} \right)_V}{\left(\frac{\partial V}{\partial T} \right)_P} = T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P \dots\dots\dots(7)$$

Consider P as a function of T and V, since dP is a perfect differential,

$$dP = \left(\frac{\partial P}{\partial V} \right)_T dV + \left(\frac{\partial P}{\partial T} \right)_V dT$$

If the changes take place at constant pressure, dP = 0. Then,

$$0 = \left(\frac{\partial P}{\partial V} \right)_T dV + \left(\frac{\partial P}{\partial T} \right)_V dT \quad \text{or} \quad \left(\frac{\partial P}{\partial T} \right)_V dT = - \left(\frac{\partial P}{\partial V} \right)_T dV$$

$$\text{or} \left(\frac{\partial P}{\partial T} \right)_V = - \left(\frac{\partial P}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P \dots\dots\dots(8)$$

Substituting (8) in (7) we get, $C_p - C_v = -T \left(\frac{\partial V}{\partial T} \right)_P^2 \left(\frac{\partial P}{\partial V} \right)_T$

The above equation shows that

1. Since $\left(\frac{\partial P}{\partial V} \right)_T$ is always negative for all known substances and $\left(\frac{\partial V}{\partial T} \right)_P^2$ must be positive, then $C_p - C_v$ can never be negative or C_p can never be less than C_v .
2. As $T \rightarrow 0$, $C_p \rightarrow C_v$, or at absolute zero the two heat capacities are equal.
3. $C_p = C_v$ when $\left(\frac{\partial V}{\partial T} \right)_P = 0$. For example, at 4°C, at which density of water is a maximum, $C_p = C_v$
4. For a **perfect gas** of 1 mole, $PV = RT$, $\left(\frac{\partial P}{\partial T} \right)_V = \frac{R}{V}$ and $\left(\frac{\partial V}{\partial T} \right)_P = \frac{R}{P}$

From equation (7) $C_p - C_v = T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P$. Putting the above conditions in (7) we get, $C_p - C_v = T \times \frac{R}{V} \times \frac{R}{P} = \frac{TR^2}{PV} = \frac{TR^2}{RT} = R$ Thus $C_p - C_v = R$ called Mayer's equation.

To find the ratio of specific heat capacities :The two TdS equations are

$$TdS = C_v dT + T \left(\frac{\partial P}{\partial T} \right)_V dV \dots\dots(1) \quad \text{and} \quad TdS = C_p dT - T \left(\frac{\partial V}{\partial T} \right)_P dP \dots\dots\dots(2)$$

At constant entropy, the equations become

$$C_v dT = -T \left(\frac{\partial P}{\partial T} \right)_V dV \dots\dots(3) \quad \text{and} \quad C_p dT = T \left(\frac{\partial V}{\partial T} \right)_P dP \dots\dots(4)$$

Dividing (4)/(3) we get, $\frac{C_p}{C_v} = - \left[\frac{\left(\frac{\partial V}{\partial T} \right)_P}{\left(\frac{\partial P}{\partial T} \right)_V} \right] \left(\frac{\partial P}{\partial V} \right)_S$

But the quantity in the square bracket is equal to $-\left(\frac{\partial P}{\partial V} \right)_T$. Therefore $\frac{C_p}{C_v} = \frac{\left(\frac{\partial P}{\partial V} \right)_S}{\left(\frac{\partial P}{\partial V} \right)_T}$

The adiabatic compressibility is defined as $\chi_s = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S$

Also $\chi = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$ We therefore have $\frac{C_p}{C_v} = \frac{\chi_s}{\chi} = \gamma$

Third law of thermodynamics – Nernst heat theorem

Statements : By no finite series of processes is the absolute zero attainable.

The entropy change associated with any isothermal reversible process of a condensed system approaches zero as the temperature approaches zero. This is the Nernst statement of third law of thermodynamics.

Explanation :Experiments show that the fundamental feature of all cooling processes is that the lower the temperature achieved, the more it is to go lower. For example the colder the liquid is , the lower is the vapour pressure, and the harder it is to produce further cooling by pumping away the vapour. The third law is known as principle of unattainability of absolute zero. Just as the second law of thermodynamics , the third law has the alternative statement. The Nernst statement is the result of experiments leading to calculation of the way the entropy change of a condensed system during a reversible, isothermal process ΔS_T behaves as T approaches zero.

From the third law, it is observed that, heat capacities of a system vanish at absolute zero. Also the coefficient of volume expansion of any substance vanishes at absolute zero. These facts shows the unattainability of absolute zero.

Descriptive questions

1. (a) What are thermodynamic potentials? Explain.
(b) Distinguish between internal energy and enthalpy of a system consisting of a system consisting of a pure substance.
2. (a) What is Helmholtz function? Show that it represents the free energy of the system in a reversible isothermal process or the energy available for work.
(b) What is Gibbs function? Show that it represents the free energy of the system in a reversible isothermal-isobaric process.
(c) Give the significance of thermodynamic potentials.
3. Derive Maxwell's thermodynamic relations from thermodynamic potentials.
4. (a) Obtain the first TdS equation from the Maxwell's thermodynamic relations.
(b) Explain an application of first TdS equations.
5. (a) Obtain second TdS equation from the Maxwell's thermodynamic relations.
(b) Explain an application of second TdS equations.
6. Obtain the first energy equation and second energy equation from the TdS equation.
7. (a) Arrive at the expression for the difference in molar specific heats using TdS equation.
(b) Give the significance of the expression of the difference in molar specific heats.
8. (a) Arrive at the expression for ratio of specific heats using TdS equation.
(b) State and explain third law of thermodynamics.

Syllabus :Phase transitions of the first order : Melting, vaporization and sublimation; Condition of equilibrium of phases in terms of Gibbs potential; Clausius-Clapeyron equation - elevation of boiling point, depression of freezing point; Equilibrium between phases - triple point

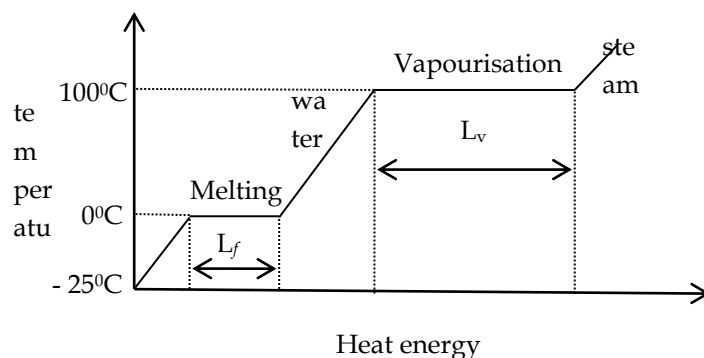
Phase transition is a process of change of state of matter. For example from solid to liquid state or liquid to vapour state or vapour state to solid state i.e. Melting, vapourisation and sublimation. Other known phase transition is change of system of one crystalline modification to another.

A **first order phase transition** is one in which a system absorbs heat or releases heat without any change in pressure or temperature but the entropy and volume of the system changes.

Example : Change of state on heating - The constant temperature at which change of state from solid to liquid occurs is **Melting point**. Similarly from liquid to vapour state is the **Boiling point** and from solid to vapour state is **Sublimation**.

The heat energy cannot produce both a change of state and a change in temperature simultaneously.

The **specific latent heat of fusion** is the heat energy required to change unit mass of a substance from the solid to the liquid state at its melting point. In case of water $L_f = 3.35 \times 10^5 \text{ J kg}^{-1}$. The **specific latent heat of vapourisation** is the quantity of heat



required to change unit mass of a substance from the liquid to the vapour state without a change in temperature i.e at the boiling point. $L_v = 2.26 \times 10^6 \text{ J kg}^{-1}$. The variation of temperature of ice with heat energy when heated is as shown above.

Characteristics of first order phase transition

1. During the phase transition, pressure and temperature remains constant and both entropy and volume undergoes change.
2. In this phase transition, the Gibbs energy remains constant in both the phases but the first derivative of Gibbs energy with respect to pressure and temperature is discontinuous at the transition point.

The Gibbs function is defined as $G = H - TS \dots\dots(1)$ or $G = F + PV$

For an infinitesimal reversible process, $dG = dH - TdS - SdT$ Also $dH = TdS + VdP$

Hence $dG = (TdS + VdP) - TdS - SdT$ or $dG = VdP - SdT$

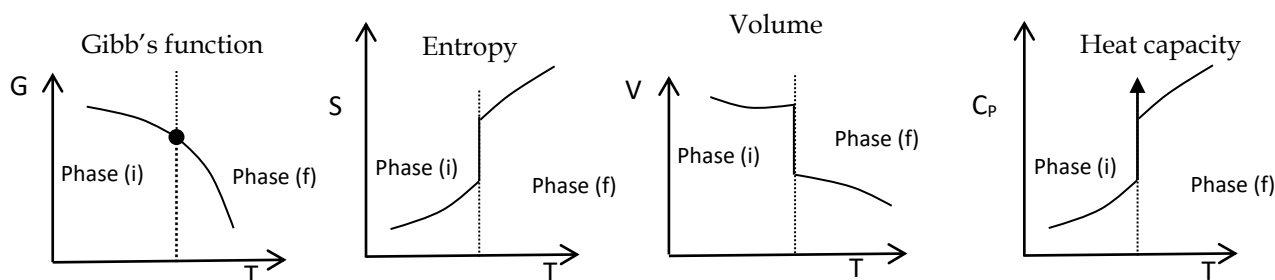
At constant temperature $dT = 0$. Thus $\left(\frac{\partial G}{\partial P}\right)_T = V$ (2)

And at constant pressure $dP = 0$. Thus $\left(\frac{\partial G}{\partial T}\right)_P = -S$(3)

3. From the T dS equation, $TdS = C_p dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$

As $dP = 0$, the above equation is $TdS = C_p dT$ or $C_p = T\left(\frac{\partial S}{\partial T}\right)_P$ (4)

For the first order phase transitions the variations of G, V, S and C_p with temperature are as shown in the graphs.



To show that Gibbs function is a constant during first order phase transition

Consider a system of liquid and vapour in equilibrium state. The temperature and pressure of the system are constants in both the phases. Thus the product of specific value of functions U, S, V and G and their masses are equal to the thermodynamic coordinates U, S, V and G.

If g_1 and g_2 are the Gibbs function of the two phases ie. Liquid and vapour with m_1 and m_2 as their masses, then $G = m_1 g_1 + m_2 g_2$ (1) where G is the Gibbs potential of the whole system. If a small quantity of liquid changes to vapour, then differentiating the above equation, $dG = \delta m_1 g_1 + \delta m_2 g_2$

As this process take place at constant temperature and pressure, ie under isothermal and isobaric condition, Gibbs potential does not change ie. $dG = 0$.

The above equation becomes $0 = \delta m_1 g_1 + \delta m_2 g_2$

Or $\delta m_1 g_1 = -\delta m_2 g_2$

In a closed system, the gain in mass of vapour δm_2 is equal to loss in mass of liquid δm_1 . Thus $\delta m_1 = -\delta m_2$. Thus $g_1 = g_2$.

Thus the value of Gibbs function in the two phases are equal.

Clausius - Clapeyron equation

Consider an enclosed system of liquid with its saturated vapour in equilibrium. As the system is undergoing isothermal and isobaric change, Gibbs potential is a constant during the phase change. ie. $g_1 = g_2$(1)

Let temperature change from T to T + dT and pressure from P to P + dP. Then for equilibrium condition $g_1 + dg_1 = g_2 + dg_2$ (2)

Using the condition (1) in (2) we get $dg_1 = dg_2$

If the condition of saturation is satisfied, then $\left(\frac{dg_1}{dT}\right)_{sat} = \left(\frac{dg_2}{dT}\right)_{sat} \dots(3)$

As the pressure is also changing from P to P + dP, we have

$$dg = \left(\frac{\partial g}{\partial T}\right)_P dT + \left(\frac{\partial g}{\partial P}\right)_T dP$$

Dividing throughout by T, we get $\left(\frac{\partial g}{\partial T}\right) = \left(\frac{\partial g}{\partial T}\right)_P + \left(\frac{\partial g}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right) \dots\dots\dots(4)$

As change in Gibb's function is given by $dg = VdP - SdT$

We have $\left(\frac{\partial g}{\partial P}\right)_T = V$ and $\left(\frac{\partial g}{\partial T}\right)_P = -S$.

Putting these values in equation (4) $\left(\frac{\partial g}{\partial T}\right)_{sat} = -S + V\left(\frac{\partial P}{\partial T}\right)$

The above equation for the two phases can be written as $\left(\frac{\partial g_1}{\partial T}\right)_{sat} = -S_1 + V_1\left(\frac{\partial P}{\partial T}\right)$

And $\left(\frac{\partial g_2}{\partial T}\right)_{sat} = -S_2 + V_2\left(\frac{\partial P}{\partial T}\right)$

Now, by substituting above equations in (3) we get $-S_1 + V_1\left(\frac{\partial P}{\partial T}\right) = -S_2 + V_2\left(\frac{\partial P}{\partial T}\right)$

$$\left(\frac{\partial P}{\partial T}\right) = \frac{S_2 - S_1}{V_2 - V_1} \dots\dots(5)$$

The amount of heat absorbed $dQ = T dS = T (S_2 - S_1)$ or $S_2 - S_1 = \frac{dQ}{T}$

As phase change occurs at constant temp. if L is the latent heat and m is the mass of the system, then $dQ = mL$. Thus $S_2 - S_1 = \frac{mL}{T}$. If $m = 1$, then $S_2 - S_1 = \frac{L}{T} \dots\dots(6)$

By substituting for change of entropy from (6) in (5), we get $\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$

This equation is called Clausius - Clapeyron equation.

Applications of Clausius - Clapeyron equation

1. Effect of pressure on the boiling point of liquids :

When a liquid changes its state to vapour state, its volume increases. That is V_2 is greater than V_1 . This means, $V_2 - V_1$ is a positive quantity. From the Clausius-clapeyron equation, $\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$, if $V_2 - V_1$ is positive, then $\left(\frac{dP}{dT}\right)$ is also positive. Thus, as the pressure is increased, the boiling point also increases. In case of water, it boils at a temperature greater than 100°C if the pressure is increased beyond 1 atmosphere.

2. Effect of pressure on the melting point of solids:

When a solid changes its state to liquid state, its volume increases. That is V_2 is greater than V_1 . This means, $V_2 - V_1$ is a positive quantity. From the clausiusclapeyron equation, $\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$, if $V_2 - V_1$ is positive, then $\left(\frac{dP}{dT}\right)$ is also positive. Thus as the pressure is increased, the melting point also increases. Eg. Wax and sulphur.

In case of ice, gallium and bismuth V_2 is less than V_1 . That is $V_2 - V_1$ is a negative quantity. Thus $\left(\frac{dP}{dT}\right)$ is a negative quantity. This means, as pressure is increased, the

melting point decreases. In case of ice whose melting point is 0°C , at 1 atmosphere, it will be less than this value at higher pressures.

Triple point of water

The triple point of a substance is the temperature and pressure at which three phases (gas, liquid, and solid) of that substance may coexist in thermodynamic equilibrium. For example, the triple point temperature of mercury is at -38.8344°C , at a pressure of 0.2 mPa.

The triple point of water is used to define the kelvin, the SI base unit of thermodynamic temperature.

The number given for the temperature of the triple point of water is an exact definition rather than a measured quantity.

The single combination of pressure and temperature at which pure water, pure ice, and pure water vapour can coexist in a stable equilibrium occurs at exactly 273.16 kelvins (0.01°C) and a pressure of 611.73 pascals (0.006037 atm). At that point, it is possible to change all of the substance to ice, water, or vapor by making infinitesimally small changes in pressure and temperature.

Triple point is the intersection on a phase diagram where three phases coexist in equilibrium. The most important application of triple point is water, where the three-phase equilibrium point consists of ice, liquid, and vapour.

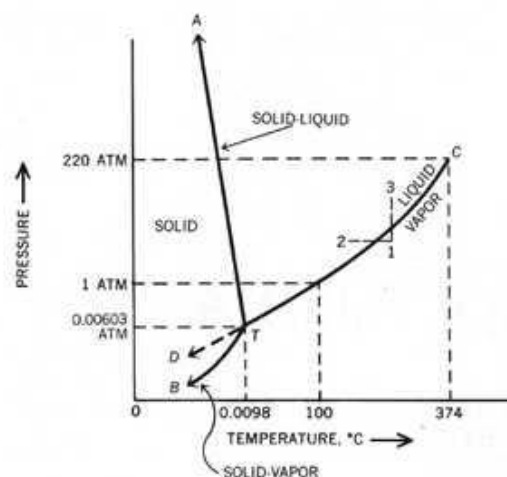
The line TC gives the vapor pressure of liquid water up to the critical point C. Along this line, liquid and vapor coexist in equilibrium. At temperatures higher than that of point C, condensation does not occur at any pressure.

The line TB is the vapour pressure of solid ice,

which is a plot of the temperatures and pressures at which the solid and vapour are in equilibrium. Finally, line TA gives the melting point of ice and liquid water. The plot shows the temperatures and pressures at which ice and liquid water are in equilibrium.

(Note: At the dashed line TD, liquid water can be cooled below the freezing point to give supercooled water.)

This explanation show that two phases are in equilibrium along the three solid lines. But when these lines intersect at one point C, three phases coexist in equilibrium. This intersection is the triple point, where a substance may simultaneously melt, evaporate, and sublime.



1. Mention the characteristics of a first order phase transitions?
2. Obtain the condition of equilibrium of phases in terms of Gibbs potentials.
3. Derive the first order phase transition or Clausius-Clapeyron equation.

4. Explain the applications of Clausius-Clapeyron equation.
5. Write a note on triple point of water.

1 Calculate change in boiling point of water by taking the normal boiling point as 100°C with the latent heat of vapourization as $2.26 \times 10^6 \text{ Jkg}^{-1}$, specific volume of water 1 m^3 and that of steam is 2.676 m^3 and change in pressure is 1 atmosphere (1 atmosphere $1.015 \times 10^5 \text{ Nm}^{-2}$).

$$\left[\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)} \quad \text{or} \quad dT = \frac{T(V_2 - V_1)}{L} dP = 27.97^\circ\text{C} \quad (\text{here } T = 373 \text{ K}) \quad (\text{Here the transition is from water to steam } V_1 = 1 \text{ m}^3 \text{ and } V_2 = 2.676 \text{ m}^3) \right]$$

2 Calculate the depression in melting point of water assuming normal melting point of ice as 0°C, latent heat of ice as $3.35 \times 10^5 \text{ Jkg}^{-1}$ Specific volume of water is $1 \times 10^{-3} \text{ m}^3$ and that of ice is $1.091 \times 10^{-3} \text{ m}^3$ and change in pressure is 1 atmosphere.

$$\left[\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)} \quad \text{or} \quad dT = \frac{T(V_2 - V_1)}{L} dP = -0.0074^\circ\text{C} \quad (\text{here } T = 273 \text{ K. The depression in freezing point means decrease in freezing point. Thus } V_1 = 1 \times 10^{-3} \text{ m}^3 \text{ and } V_2 = 1.091 \times 10^{-3} \text{ m}^3) \text{ Negative sign is taken due to decrease in melting point of ice with increase in pressure } \right]$$

3 Mercury melts at -40°C at 1 atmosphere pressure. Its density is 13590 kgm^{-3} . The density of solid mercury is 14190 kgm^{-3} and the latent heat of fusion is 9786 Jkg^{-1} . What would be the melting point of mercury at 800 atmosphere.

$$\left[T = -40^\circ\text{C} = 273 - 40 = 233\text{K}, \quad dP = P_2 - P_1 = 800 - 1 = 799 \text{ atm.} = 838 \times 10^5 \text{ Nm}^{-2}.$$

$$\text{Specific Volume } V_1 = 1/13590 \text{ m}^3, \quad V_2 = 1/14190 \text{ m}^3 \quad dT = \frac{T(V_2 - V_1)}{L} dP = 5.916 \text{ K}$$

Melting point = $-40 + 5.916 = -34.08^\circ\text{C}$ (Here pressure is increasing and melting point also increases as it is Mercury. The value of V_1 is at 1atm and V_2 at 800atm.) Thus positive sign is taken for dT]

4 Calculate the pressure required to lower the melting point of ice by 1°C, $L=3.35 \times 10^5 \text{ Jkg}^{-1}$, specific volume of water at 0°C = 1000 m^3 , specific volume of ice at 0°C = 1091 m^3 .

$$\left[\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)} \quad \text{or} \quad dP = \frac{L}{T(V_2 - V_1)} dT = -13.46 \text{ atm.}, \quad \text{pressure required to lower the melting point is } P = 1 + 13.46 = 14.46 \text{ atm.} \quad (\text{Here melting point is lowered from } 0^\circ\text{C} \text{ starting from water to ice. Thus } V_1 = 1000 \text{ m}^3 \text{ and } V_2 = 1091 \text{ m}^3) \text{ With increase in pressure melting point decreases in case of water. Thus negative sign is taken } \right]$$

5 Calculate the change in boiling point of water when the pressure is increased by one atmosphere. Boiling point of water at the atmospheric pressure is 373 K Specific volume of water is 1 m^3 and Specific heat of steam is 1.671 m^3 and the specific latent heat of steam is $2.268 \times 10^6 \text{ Jkg}^{-1}$.

$$\left[dT = \frac{T(V_2 - V_1)}{L} dP = 11.04 \text{ K} \right]$$

6 Calculate the pressure required to lower the melting point of ice by 1°C . Given Latent heat of fusion of ice is $3.35 \times 10^5 \text{ Jkg}^{-1}$, specific volume of water at 0°C is 1000 m^3 , specific volume of ice at 0°C is 1091 m^3 .

$$\left[dP = \frac{L}{T(V_2 - V_1)} dT = 14.4 \text{ atm. Here even though } dT \text{ is negative pressure difference is taken as positive } \right]$$

7 Calculate the depression in melting point of ice for an increase in the external pressure of 2 atmosphere. Latent heat of ice as $3.35 \times 10^5 \text{ Jkg}^{-1}$ Specific volume of water is $1 \times 10^{-3} \text{ m}^3$ and that of ice is $1.01 \times 10^{-3} \text{ m}^3$ at 0°C . and 1 atmospheric pressure = 10^5 Nm^{-2} .

$$\left[\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}, \quad dT = \frac{T(V_2 - V_1)}{L} dP = -0.00163 \text{ K} \right]$$

8 Find the pressure at which water would boil at 150°C if the change in specific volume when 1 kg of water is converted into steam is 1.676 m^3 . $1 \text{ atm} = 10^5 \text{ Nm}^{-2}$, $L = 2.268 \times 10^6 \text{ Jkg}^{-1}$.

$$\left[V_2 - V_1 = 1.676, \quad dT = 50^{\circ}\text{C}, \quad T = 373 \text{ K} \quad dP = \frac{L}{T(V_2 - V_1)} dT = 1.814 \times 10^5, \quad P = (1 + 1.814) \times 10^5 = 2.814 \times 10^5 \text{ Nm}^{-2} \right]$$

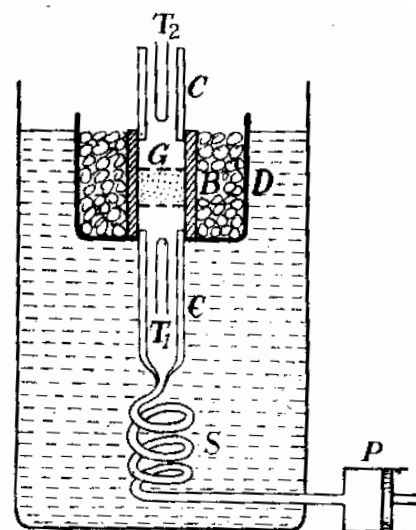
Syllabus : Low Temperature Physics : Methods of producing low temperatures: (i) Joule Thomson (Joule Kelvin / Throttling / Porous plug) experiment, Joule Thomson Coefficient, inversion temperature (ii) Adiabatic demagnetization - working and theory

Liquefaction of gases : Regenerative cooling coupled with Joule Thomson cooling; Adiabatic expansion with Joule Thomson cooling (qualitative)

Low Temperature Physics : The various experimental methods to produce very low temperatures are 1) by adding salt to ice, 2) cooling by evaporation of a liquid under reduced pressure (cascade process), 3) by adiabatic expansion of a gas, 4) by Joule - Thomson effect, 5) by regenerative cooling and 6) adiabatic demagnetisation of a paramagnetic salt.

Joule - Kelvin (Thomson) effect

Principle When a gas is made to expand without doing external work and without allowing any heat to enter or leave it during the expansion, then, if the molecules of the gas attract one another, internal work will have to be done in pulling them apart. This can be



achieved at the expense of heat energy of the gas. This results in cooling. This is called **Joule Thomson effect**. If the molecules of the gas repel each other, then there is heating. If there is no intermolecular forces, there is no change in temperature.

The porous plug experiment The principle of this experiment is to drive a gas by a compressor at a constant pressure through a porous plug and measure the temperature of the gas as it enters and leaves the plug.

Construction :The porous plug G consists of a porous material, such as cotton, wool, silk, etc., having a number of fine holes or pores and is thus equivalent to a number of narrow orifices in parallel.

The porous plug is positioned between two perforated brass plates and enclosed in a boxwood tube B. The plug is surrounded by a non-conducting jacket to prevent any heat from entering or leaving the gas. B is surrounded by a brass case D full of cotton wool, which serves as a thermal insulator. The box-wood tube is fitted on both sides with copper tubes CC. The lower of these is connected to a compression pump P through a copper spiral S. The whole apparatus is placed in a water bath to ensure constant temperature

Experiment :The compressed gas is allowed to suffer *throttle expansion* through the porous plug G. The temperature of the gas on the two sides of the plug are measured with platinum resistance thermometers T_1 and T_2 . The gas is allowed to flow for about an hour in order to obtain the steady state.

The experiment is repeated for various differences of pressure on the two sides of the porous plug. The initial pressure of the gas is measured by a manometer at the entrance into the lower copper tube, while its final pressure is that of the atmosphere. Different gases are investigated over a wide range of temperatures.

Joule and Thomson experimented on air, oxygen, nitrogen and carbon dioxide between 4°C and 100°C , the initial and final pressures being 4.5 and 1 atmosphere respectively.

The results of the experiment

- 1) At sufficiently low temperature all gases show a cooling effect in passing through the porous plug. But at ordinary temperatures most gases show a cooling effect, while hydrogen shows a heating effect.
- 2) The fall in temperature is proportional to the difference of pressure on the two sides of the porous plug. The greater the difference of pressure, the greater the drop in temperature.
- 3) The fall in temperature per atmosphere difference of pressure decreases as the initial temperature of the gas is raised, becomes zero at a particular temperature, which is different for each gas, and above this

temperature there is no more fall but rise in temperature. The temperature, at which the Joule-Thomson effect changes sign, *i.e.*, the cooling effect becomes heating effect, is called the **temperature of inversion**.

Theory of the experiment

Let P_1 , V_1 and U_1 be the initial pressure, volume and internal energy of the gas. After undergoing the throttling process (passing through porous plug) let P_2 , V_2 and U_2 be the final values respectively. ($P_2 < P_1$)

The net work done by the gas on the piston $W = P_2V_2 - P_1V_1$

As no heat enters or leaves the system, work has to be done at the expense of internal energy. $U_1 - U_2 = P_2V_2 - P_1V_1$ or $U_1 + P_1V_1 = U_2 + P_2V_2$

or $H_1 = H_2$ where $H = U + PV$ called enthalpy or total heat of the system which is a constant. Thus Joule Kelvin expansion is **isenthalpic**.

Let H be a function of temperature and pressure, Thus $H = H(T, P)$

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \dots\dots(1)$$

but $\left(\frac{\partial H}{\partial T}\right)_P = C_p$, specific heat at constant pressure.

$$\text{Thus } dH = C_p dT + \left(\frac{\partial H}{\partial P}\right)_T dP \dots\dots(2)$$

But $H = U + PV$, $dH = dU + P dV + V dP$ Also $dQ = dU + PdV = T dS$

Comparing the two equations $dH = T dS + V dP$

$$\text{Differentiating with respect to pressure, } \left(\frac{\partial H}{\partial P}\right)_T = T \left(\frac{\partial S}{\partial P}\right)_T + V \dots\dots(3)$$

$$\text{From Maxwell's fourth relation } \left(\frac{\partial S}{\partial P}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_P \dots\dots(4)$$

$$\text{From (3) and (4) we get } \left(\frac{\partial H}{\partial P}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_P + V \dots\dots(5)$$

$$\text{Substituting (5) in (2) we get } dH = C_p dT + \left[-T \left(\frac{\partial V}{\partial T}\right)_P + V\right] dP \dots\dots(6)$$

Since Joule - Thomson expansion is isenthalpic, $dH = 0$,

$$\text{Thus } 0 = C_p dT + \left[-T \left(\frac{\partial V}{\partial T}\right)_P + V\right] dP \text{ or } C_p dT = \left[T \left(\frac{\partial V}{\partial T}\right)_P - V\right] dP$$

$$\text{Or } \mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T}\right)_P - V\right] \dots\dots(7)$$

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{T^2}{C_p} \left[\frac{\partial}{\partial T} \left(\frac{V}{T}\right)_P\right] \dots\dots(8)$$

where $\mu = \left(\frac{\partial T}{\partial P}\right)_H$ is called the **Joule Thomson coefficient** which is the measure of change in temperature with pressure at constant enthalpy.

Since $P_2 < P_1$, dP is negative. Thus, if μ is positive, then dT is negative implying cooling effect. Similarly if μ is negative, then dT is positive implying heating effect. If μ is zero, then no heating or cooling effect.

The physical reason for the above is the following

From equation (1), since $dH = 0$,

$$0 = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \quad \text{or} \quad \left(\frac{\partial H}{\partial T}\right)_P dT = - \left(\frac{\partial H}{\partial P}\right)_T dP \quad \text{or} \quad \left(\frac{\partial T}{\partial P}\right)_H = - \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial T}{\partial H}\right)_P$$

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = - \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial T}{\partial H}\right)_P = - \left(\frac{\partial H}{\partial P}\right)_T \frac{1}{C_P}$$

Since $H = U + PV$,
$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T + \left\{ \frac{\partial}{\partial P}(PV) \right\}$$

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = - \frac{1}{C_P} \left[\left(\frac{\partial U}{\partial P}\right)_T + \left\{ \frac{\partial}{\partial P}(PV) \right\} \right]$$
 In this equation it is observed that Joule Thomson coefficient is made up of two terms – the first term is the measure of deviation from Joule’s law and the second term is the deviation from the Boyles’ law.

For the perfect gas, both the terms are zero. Thus $\mu = 0$. For real gases, the first term produces cooling effect and the second term may produce cooling or heating effect depending on the temperature and pressure.

Expression for Inversion temperature

The temperature, at which the Joule-Thomson effect changes sign, i.e., the cooling effect becomes heating effect, is called the **temperature of inversion**.

The van der waals equation of state is
$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \quad \dots(1)$$

Simplifying
$$PV + \frac{a}{V} - Pb - \frac{ab}{V^2} = RT$$

$$PV = RT - \frac{a}{V} + Pb + \frac{ab}{V^2} \quad \text{or} \quad V = \frac{RT}{P} - \frac{a}{PV} + b + \frac{ab}{PV^2}$$

Replacing PV by RT , we get
$$V = \frac{RT}{P} - \frac{a}{RT} + b + \frac{abP}{R^2T^2} \quad \dots\dots(2)$$

Differentiating with respect to T ,
$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + \frac{a}{RT^2} - \frac{2abP}{R^2T^3} \quad \dots\dots(3)$$

From (2)
$$\frac{RT}{P} = V - b + \frac{a}{RT} - \frac{abP}{R^2T^2} \quad \text{or} \quad \frac{R}{P} = \frac{V-b}{T} + \frac{a}{RT^2} - \frac{abP}{R^2T^3} \quad \dots\dots(4)$$

Substituting (4) in (3) and simplifying
$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{V-b}{T} + \frac{2a}{RT^2} - \frac{3abP}{R^2T^3}$$

Or
$$T \left(\frac{\partial V}{\partial T}\right)_P = V - b + \frac{2a}{RT} - \frac{3abP}{R^2T^2}$$

or
$$T \left(\frac{\partial V}{\partial T}\right)_P - V = \frac{2a}{RT} - b \quad \dots\dots(5)$$
 The term involving the product of a and b is neglected.

The $J - T$ coefficient is
$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P} \left[T \left(\frac{\partial V}{\partial T}\right)_P - V \right] \quad \dots\dots(6)$$

Substituting (5) in (6) $\mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_p} \left[\frac{2a}{RT} - b\right] \dots\dots(7)$

For the real gases, the cooling or heating effect depends on van der waals constants a and b.

Case 1 If the intermolecular forces are very strong i.e., $a \gg b$ then $\frac{2a}{RT} > b$.

Hence $\mu > 0$. Thus cooling effect takes place.

Case 2 If the intermolecular forces are weak i.e., $b > a$ then $\frac{2a}{RT} < b$. Hence $\mu < 0$. Thus heating effect takes place.

Case 3 If $\frac{2a}{RT} = b$ then $\mu = 0$, there is no heating or cooling

Thus Joule – Thomson effect changes sign at the temperature T_i called **inversion temperature** given by $T_i = \frac{2a}{Rb}$.

Thus, it is clear that if the initial temperature of a real gas is more than inversion temperature, heating effect is produced. If the initial temperature is less than inversion temperature and then passed through porous plug, cooling effect is produced. It is called **regenerative or Joule Thomson cooling**.

Relation between inversion temperature and critical temperature

The inversion temperature is $T_i = \frac{2a}{Rb} \dots\dots(1)$

The critical temperature is $T_c = \frac{8a}{27Rb} \dots\dots(2)$

Dividing (1) by (2) $\frac{T_i}{T_c} = \frac{2a}{Rb} \times \frac{27Rb}{8a} = \frac{27}{4} = 6.75$ or $T_i = 6.75 T_c$

Difference between Adiabatic expansion and Joule Thomson effect

S. No.	Adiabatic expansion	Joule Thomson effect
1	Work is done by the gas.	Work is done by the gas or on the gas.
2	Larger cooling of gas is produced.	Smaller cooling of gas is produced.
3	Reversible process	Irreversible process
4	Cooling is produced even in an ideal gas	Joule Thomson effect is zero. i.e., no heating or cooling is produced in an ideal gas
5	Real gases produce only cooling effect.	It can be cooling or heating effect in case of real gases.

Adiabatic demagnetisation

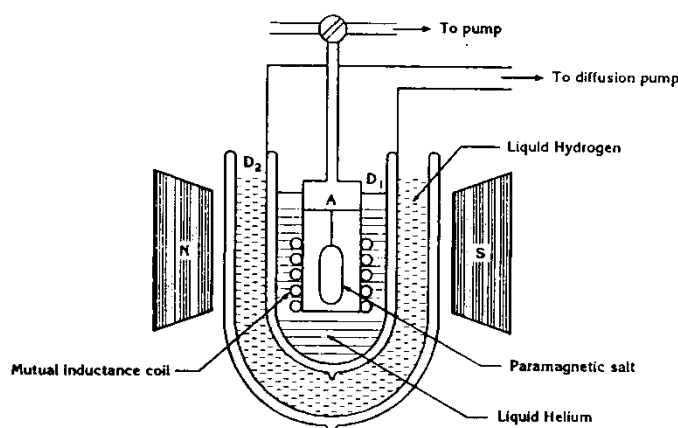
It is a process of cooling. The principle is that a paramagnetic salt heats up when placed in a magnetic field and cools down when removed from the magnetic field adiabatically. This is called adiabatic demagnetisation.

Principle The process of magnetising a substance involves doing work on the substance, which will slightly heat the substance. This work done in aligning the elementary magnets (atoms of the substance) in the field direction is stored in the substance in the form of magnetic energy. If such a substance is demagnetised adiabatically, it has to do work and the energy required for this is drawn from within. This results in the cooling of the substance.

Experimental setup :The experimental arrangement is as shown. The sample Gadolinium sulphate which is a paramagnetic salt is suspended in a vessel surrounded by liquid helium taken in the dewar flask D_1 . It is surrounded by liquid hydrogen taken in the dewar flask D_2 . The whole arrangement is kept between the poles of a strong electromagnet.

The magnetic field is switched on so that the specimen is magnetised. The heat generated during this process is removed by introducing hydrogen gas into the chamber A and then pumping it out using a high vacuum pump so that the specimen is thermally isolated. The specimen attains the temperature of the liquid helium which is being pumped so that it boils under reduced pressure. This temperature is in the range of 1 K. When the magnetic field is switched off, adiabatic demagnetisation of the specimen takes place and its temperature falls.

According to Curie law the magnetic susceptibility of a substance is inversely proportional to the absolute temperature. By measuring the magnetic susceptibility of the substance using a mutual inductance coil, before and after the demagnetisation, the final temperature is computed. Temperature in the range of 0.001 K was attained by many researchers by using this method.



Theory :According to Curie's law $\chi T = \text{constant}$ or $\frac{\chi_1}{\chi_2} = \frac{T_2}{T_1}$ where χ_1 and χ_2 are the susceptibility of the salt at temperatures T_1 and T_2 respectively. Or $T_2 = \frac{\chi_1}{\chi_2} T_1$ (1)

From first law of thermodynamics $dQ = dU + dW = dU + P dV$

From second law $dQ = T dS$. Thus $T dS = dU + P dV$ (2)

When a paramagnetic salt is placed in a magnetic field of flux density B, intensity of magnetisation increases (dl). Thus work done on the salt is $dW = B dl$.

Thus equation (2) becomes $T dS = dU + P dV - B dl$

As the process is carried out at constant pressure, $dV = 0$.

Thus $T dS = dU - B dl$ (3)

Comparing (2) and (3) – B corresponds to P and I corresponds to V .

From Maxwell thermodynamic equation $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$, Replacing P by $-B$ and V by I we get $-\left(\frac{\partial T}{\partial B}\right)_S = \left(\frac{\partial I}{\partial S}\right)_B = \left(\frac{\partial I}{\partial T}\right)_B \left(\frac{\partial T}{\partial S}\right)_B$ or $\left(\frac{\partial T}{\partial B}\right)_S = -\left(\frac{\partial I}{\partial T}\right)_B / \left(\frac{\partial S}{\partial T}\right)_B$ (4)

As $dQ = T dS$ or $\partial S = \frac{\partial Q}{T}$. Thus $\frac{\partial S}{\partial T} = \frac{1}{T} \left(\frac{\partial Q}{\partial T}\right)_B$ or $\frac{\partial S}{\partial T} = \frac{m C_B}{T}$ (5)

where m is the mass of the specimen and C_B is the specific heat at constant magnetic field. Hence $\left(\frac{\partial T}{\partial B}\right)_S = -\left(\frac{\partial I}{\partial T}\right)_B / \frac{m C_B}{T}$

or $\left(\frac{\partial T}{\partial B}\right)_S = -\frac{T}{m C_B} \left(\frac{\partial I}{\partial T}\right)_B$ or $\partial T = -\frac{T}{m C_B} \left(\frac{\partial I}{\partial T}\right)_B \partial B$ (6)

This gives the fall in temperature due to adiabatic demagnetisation.

Liquefaction of gases

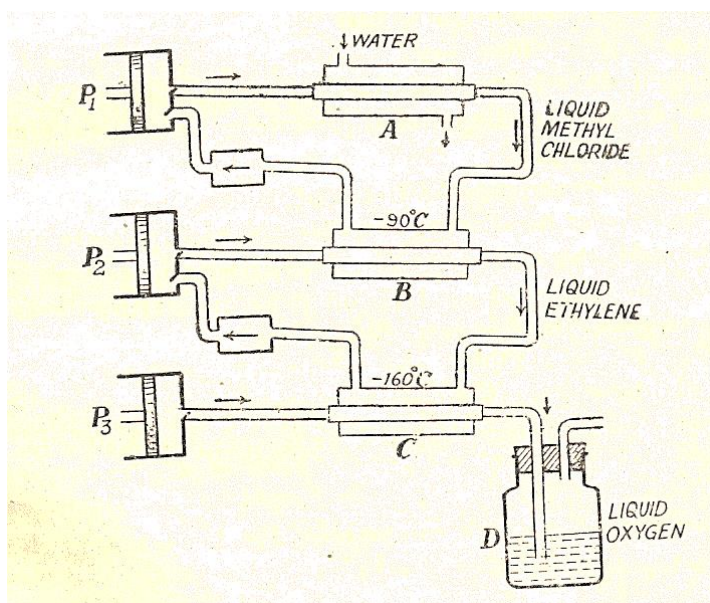
1. Cascade process – It uses series of liquids with successively lower boiling points to reach low temperatures in stages.

The apparatus used by Kamerlingh Onnes consists of three units, each of which comprises of a compression pump and a condenser. In the first unit methyl chloride is liquefied. Since the critical temperature of methyl chloride is -143°C , it can be liquefied at the room temperature with a pressure of a few atmospheres.

Compressed methyl chloride gas from pump P_1 , is passed through the spiral tube (shown straight in the figure) inside the condenser A , while cold water is circulated through the outer jacket

of A . Liquid methyl chloride thus obtained is made to circulate the jacket of the condenser B of the second unit, which is connected to the suction side of P_1 , this enables the liquid methyl chloride, which normally boils at -24°C to evaporate under reduced pressure

and produce a fall of temperature to about -90°C in B .



Compressed ethylene from pump P_2 is passed through the spiral tube inside B . since it has a critical temperature of 10°C , it is readily liquefied in B maintained at about -90°C by the continuous circulation of liquid methyl chloride through it. Liquid ethylene formed in B is made to flow round the jacket of the condenser C of the third unit at the same time allowed to evaporate under reduced pressure by connecting the

jacket of C to the suction side of P_2 . The temperature of C thereby falls to about -160°C , although the normal boiling point of ethylene is -140°C . Compressed oxygen from the pump P_3 passes through the spiral tube inside C where it is easily liquefied since its critical temperature is only -118°C . Liquid oxygen is collected in a Dewar flask D.

2 Regenerative Joule – Thomson process

The principle involved in this method are Joule-Thomson effect and regenerative cooling.

Liquefaction of air - Linde's Process

Linde's air liquefier makes use of the principle of regenerative cooling. The experimental arrangement is schematically shown in fig.

Pure, dry air is compressed to about 16 atmospheres by the compressor C_1 . This compressed air is cooled by allowing it to pass through a spiral tube immersed in a cold water bath W and then passed through KOH solution taken in a bottle T to remove CO_2 .

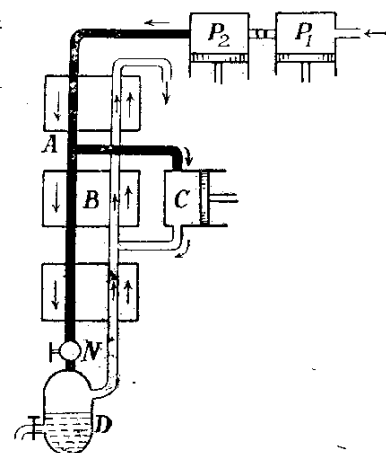
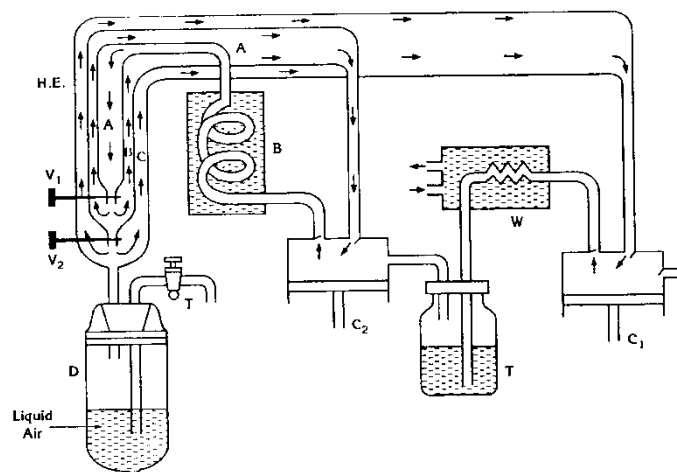
Water vapour present in the air is also removed by passing it over a dehydrating agent which is not shown in the figure. Air free from CO_2 and water vapour enters the compressor C_2 which compresses it to about 200 atmospheres. The heat generated during this compression is removed by passing it through a spiral tube kept immersed in a freezing mixture B.

Air enters into the exchanger through the tube A, expands on passing through the valve V_1 to about 16 atmospheres. This expansion produces cooling and part (4/5 th) of the cooled air returns to the compressor C_2 through the tube B. This will reduce the temperature of the air in the tube A. The remaining (1/5th) of the air expands from 16 atmosphere to 1 atmosphere through the valve V_2 . This further cools the air and while passing to compressor C_1 through C, it lowers the temperature of the air in B still further.

This regenerative cooling process continues and at one stage a part of the air liquefies which is collected in the Dewar flask D.

3 Adiabatic expansion process based on the cooling produced when a gas expands adiabatically doing external work.

Claude's air liquefier Pure, dry air, compressed by the



pump P_1 and P_2 is divided into two parts at A. One part goes to the expansion cylinder C and suffers adiabatic expansion and consequent cooling. The cooled gas flows upward in the pipe B thereby cooling the second part of the incoming compressed gas in the second heat exchanger. The high pressure gas thus partially liquefies. It then suffers Joule-Thomson expansion at the throttle valve N. The liquid air is collected in a Dewar flask D. The evaporated air is taken to the compressor and again compressed.

1. What is Joule Thomson effect? Explain.
2. Describe the Joule - Thomson Porous plug experiment and discuss the results..
3. Give the theory of Joule-Thomson effect and hence arrive at the expression for the Joule - Thomson coefficient. Explain the physical meaning the equation.
4. What is inversion temperature? Derive an expression for the inversion temperature of a gas obeying Van der Waals' equation.
5. Distinguish between Adiabatic expansion and Joule-Kelvin effect.
6. Explain the phenomenon of adiabatic de-magnetisation. How this phenomenon is employed to produce and measure very low temperature.
7. Explain with theory the adiabatic demagnetisation method for producing very low temperature.
8. Give a brief account of the different methods of producing low temperature.
9. What is meant by liquefaction of gases? Explain.
10. Explain the method of liquefaction of natural gas by the cascade method.
11. What is regenerating cooling? Describe with a diagram Claude's process for liquefying air.
12. Explain Linde's method of regenerative cooling coupled with Joule - Thomson cooling.

1. Calculate the change in temperature produced by adiabatic throttling process of a gmmol of oxygen when the pressure is reduced by 100 atmospheres. The initial temperature of gas is 27°C . Given for oxygen, $C_p = 29.53 \text{ Jmol}^{-1}$, $b = 3.12 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$, $R = 8.3 \text{ J K}^{-1}$.

(Ans: 34.5K)

2. The Van der Waal's constants for hydrogen are $a = 0.0247 \text{ atm litre}^2 \text{ mol}^{-2}$, $b = 2.65 \times 10^{-2} \text{ litre mol}^{-1}$. Find (i) temperature of inversion, (ii) Joule-Thomson cooling for 5 atm, fall of pressure, initial temperature being 100K. Given $R = 8.34 \text{ J K}^{-1} \text{ mol}^{-1}$.

(Ans: 0.568K)

3. Calculate the change in temperature, when helium gas suffers Joule-Thomson expansion at -10°C . The pressure difference on two sides of the plug is 10 atmospheres and Vander Waal's constant for the gas are $a = 0.0341 \times 10^{-1} \text{ Nm}^4 \text{ mole}^{-2}$, $b = 2.37 \times 10^{-5} \text{ m}^3 \text{ mole}^{-1}$ and $R = 8.34 \text{ JK}^{-1} \text{ mol}^{-1}$.

(Ans: -0.9878K)

Questions

1. Write a note on Internal energy, Enthalpy, Helmholtz free energy and Gibbs free energy.
2. Distinguish between internal energy and enthalpy.
3. Derive Maxwell's thermodynamic relations.
4. Arrive at the Maxwell's relations using thermodynamic potentials.
5. Derive the TdS equations from the Maxwell's thermodynamic relations.
6. State and explain third law of thermodynamics (Nernst heat theorem).
7. Write four Maxwell's thermodynamic relations and hence deduce an expression for difference in molar specific heats of a gas and calculate it in case of a real gas.
8. Derive the first and second energy equations using TdS relations.
9. (a) What is Gibbs function? (b) Show that it represents free energy of the system in a reversible isothermal – isobaric process. (c) Derive Maxwell thermodynamic relation between volume and entropy keeping pressure and temperature constant.
10. (a) What is Helmholtz function? (b) Show that it represents free energy of the system in a reversible isothermal – isochoric process, (c) Derive Maxwell thermodynamic relation between entropy and pressure keeping temperature and volume constant.