STUDY MATERIAL

Dumkal College, Basantapur

Subject: Chemistry

Course Code- CHEMHT-3
Topic: Chemical Thermodynamics-II

Name of the Teacher: Delwar Ansary

Course Title- a) Need for a Second law; statement of the second law of thermodynamics Concept of heat reservoirs and heat engines; Carnot cycle.
 b) Joule-Thomson experiment and its consequences; inversion temperature,Joule-Thomson coefficient for a van der Waals gas.

$\boxed{\text{2nd Sem}}$

① From 1st law of thermodynamic, we are enables to compute the energy changes. The energy changes and enthalpy changes for different types of physical and chemical transformation. Also from the 1st law we established definite relation between heat absorb or evolve and work perform by the system in a given process.

But 1st law is not capable of predicting the direction of a process.

$-5°c$ ⟶

30°C   20°C
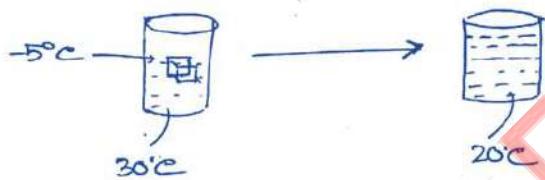
Chem @ DA Sir

* Energy is quantised.

From the 1st law of thermodynamic we can't answer the following —

i) why do change take place in a particular direction.

ii) How and why system are aware to process in a particular direction.

iii) what are the driving forces.

iv) which leads the process in a particular direction.

Therefore the answer of such types of question, we need the 2nd law of thermodynamics.

..> walls of piston of the container are perfect non conducting and bottom is the perfectly conducting.

..> Source and sink are the infinite heat capacity.

...> Piston's are frictionless.
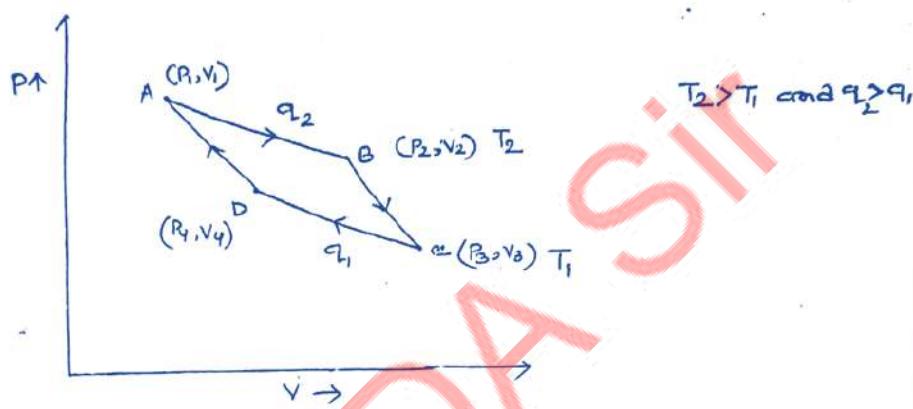
Step-1: Isothermal reverssible expansion $(A \rightarrow B)$. In this step ΔT is zero and volume change from V_1 to V_2 at temperature T_2.

from the 1st law of thermodynamics we know that $\Delta U = q + \omega$ or $0 = q + \omega \Rightarrow q = -\omega$.

$$\therefore q_2 = -\omega_1 = nRT_2 \ln \frac{V_2}{V_1} \qquad (\because \Delta U = 0)$$

Step-2: Adiabatic reverssible expansion $(B \rightarrow C)$:
Here, $\Delta q = 0$ so, that $\Delta U = \omega$.

$$\therefore \omega_2 = nC_v(T_1 - T_2)$$

Step-3: Isothermal reverssible compression $(C \rightarrow D)$:

$$\therefore q_1 = -\omega_3 = nRT_1\left(\ln \frac{V_4}{V_3}\right).$$

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Step-4: Adiabatic reversible compression (D→A)

here, $q = 0$, $\therefore \omega_4 = nC_v(T_2 - T_1)$

$\therefore$ Total work done $= \omega_1 + \omega_2 + \omega_3 + \omega_4$

$$= nRT_2 \ln \frac{V_2}{V_1} + nC_v(T_1 - T_2) + nRT_1 \ln \frac{V_4}{V_3} + nC_v(T_2 - T_1)$$

$$= nRT_1 \ln \frac{V_4}{V_3} + nRT_2 \ln \frac{V_2}{V_1}$$

We know that for adiabatic process —

$$TV^{\gamma-1} = constant.$$

⊚ for B→C step:

$$T_2 V_2^{\gamma-1} = T_1 V_3^{\gamma-1}$$

$$\Rightarrow \frac{T_2}{T_1} = \left(\frac{V_3}{V_2}\right)^{\gamma-1} \underline{\hspace{1cm}} (a)$$

⊚ for D→A steps:

$$T_1 V_4^{\gamma-1} = T_2 V_1^{\gamma-1}$$

$$\Rightarrow \frac{T_2}{T_1} = \left(\frac{V_4}{V_1}\right)^{\gamma-1} \underline{\hspace{1cm}} (b)$$

From the equation (a) and (b) we get—

$$\left(\frac{V_3}{V_2}\right)^{\gamma-1} = \left(\frac{V_4}{V_1}\right)^{\gamma-1}.$$

$$\Rightarrow \frac{V_3}{V_2} = \frac{V_4}{V_1}$$

$$\Rightarrow \frac{V_1}{V_2} = \frac{V_4}{V_3}$$

$\therefore$ Total work done $= nRT_1 \ln \frac{V_1}{V_2} + nRT_2 \ln \frac{V_2}{V_1}$

$$= nR \ln \frac{V_2}{V_1}(T_2 + T_1)$$

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∴ Efficiency $(\eta) = \dfrac{\omega_{Total}}{q_2} = \dfrac{nR(T_2 - T_1) \ln \frac{V_2}{V_1}}{nRT_2 \ln \frac{V_2}{V_1}}$

$$\therefore \eta = \frac{T_2 - T_1}{T_2} = \left(1 - \frac{T_1}{T_2}\right)$$

⦿ Efficiency of heat energy :

The fraction of heat absorbed by the system which it can convert into work, gives efficiency.

• The efficiency of heat engine is depends only temperature, not to the other nature of substances. If T_1 and T_2 are equal; no work done occurs.

T_1 must zero or T_2 must be ∞, to obtain efficiency 100%. This is not possible because neither two situation are physically relizable. So, efficiency always less than 1.

⦿ Kelvin's statements :

It is impossible to use a cyclic process to extract heat from a single reservoir and to convert into work without transfering at the time to certain amount of heat from warmer body to colder body.

In carnot cycle net heat absorb = $(q_2 - q_1) = \omega_{total}$.

$$\therefore \omega_{total} = q_2 - q_1$$

$$\frac{\omega_{total}}{q_2} = \frac{q_2 - q_1}{q_2} \Rightarrow \frac{T_2 - T_1}{T_2} = \frac{q_2 - q_1}{q_2}$$

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

$$\therefore \boxed{\frac{q_{rev}}{T} = \text{constant}}$$

Q. Heat supplied to a carnot cycle 1897.8 kJ. How much useful work can be done by the engine which works between 0°C and 100°C?

We know,

$$\frac{\omega_{Total}}{q_2} = \frac{T_2 - T_1}{T_2}$$

here, $q_2 = 1897.8$ kJ

$T_2 = 100°C = 373K$

$T_1 = 0°C = 273K$

$$\therefore \omega_{total} = 1897.8 \left(\frac{373 - 273}{373}\right) kJ$$

$$\therefore = 508.79 \ kJ$$

▨ <u>Working of carnot cycle in reverse direction (heat pump):</u>

Step-1: Adiabatic reverssible expansion. V_1 change into V_4 and temperature $T_2 \to T_1$
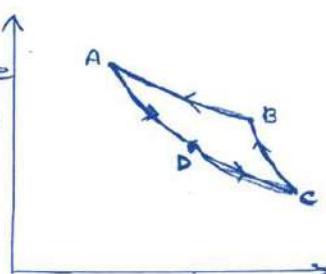
Step-2: Isothermal reverssible compression. $V_4 \longrightarrow V_3$ at T_1 temperature.

Step:3 Adiabatic reverssible compression. $(c \to B)$

Step-4: Isothermal reverssible compression $(B \to A)$ $V_2 \longrightarrow V_1$ and T_2 temperature. constant.

The amount of heat will absorb by the system $= q_1'$ at the lower temperature T_1 in step-2. and amount of heat q_2' transfer to the reserver at the higher temperature T_2 in step-4.

And at the same time net work done on the system will be done. This cycle is call Refrigirator - cycle.

▨ <u>Diagramme of composite cycle:</u>
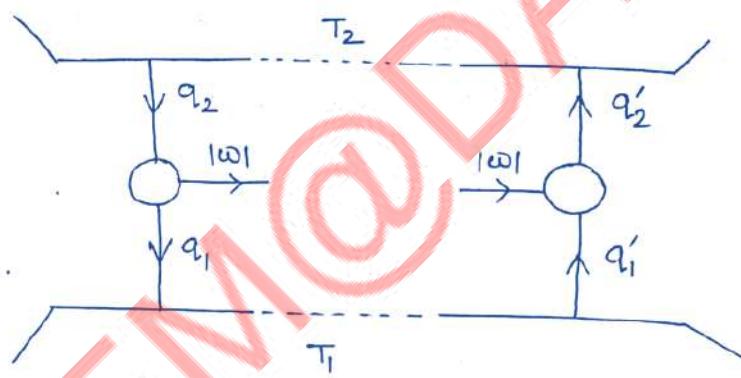
⊚ <u>The co-efficient of prrformence:</u>

$$\eta' = \frac{T_1}{T_2 - T_1}$$

⊛ Comparison of efficiency of reverssible & irreverssibe cornot cycle:

The efficiency of reverssible engine is theoritically gives maximum value. since all the process reverssible so that it is not practically realistic.

Let hs have two cycles. one operates reverssibly and another operates irreverssibly.

Step-01: isothermal expansion from vol^m V_1 to V_2.

$$-\omega_{1(rev)} = q_{2(rev)} = nRT_2 \ln \frac{V_2}{V_1}$$

$$-\omega_{1(rev)} = q_{2(rev)} = P_{ext}(V_2-V_1)$$

let,

$$|\omega_{1(rev)}| > |\omega_{1(irr)}|$$

$$\therefore |q_{rev}| > |q_{irr}|$$

Step-02: Isothermal compression from vol^m $V_3 \to V_4$ at temperature T_1.

$$-\omega_{3(rev)} = q_{1(rev)} = nRT_1 \ln \frac{V_4}{V_3}$$

$$-\omega_{3(irr)} = q_{1(irr)} = P_{ext}(V_4-V_3)$$

let,

$$|\omega_{3(irr)}| > |\omega_{3(rev)}|$$

$$\therefore |q_{1(irr)}| > |q_{1(rev)}|$$

We know that,

$$\eta_{rev} = 1 - \frac{q_1(rev)}{q_2(rev)}$$

$$\eta_{irr} = 1 - \frac{q_1(irr)}{q_2(irr)}$$

Now, since,

$$\frac{q_1(rev)}{q_2(rev)} < \frac{q_1(irr)}{q_2(irr)}$$

$$\therefore \quad \eta_{(rev)} > \eta_{(irr)}$$

● **Joule-Thomson effect:**
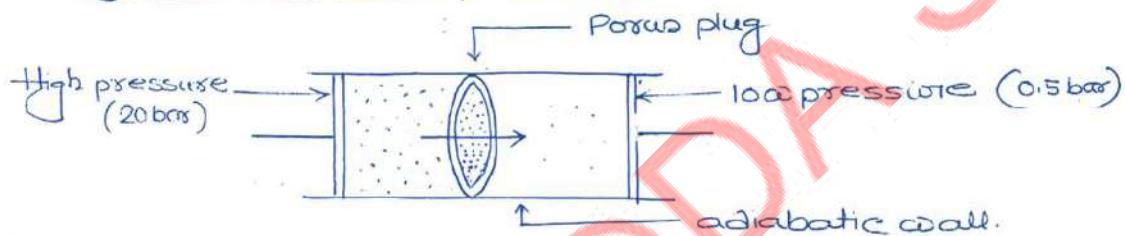
The phenomenon of change of temperature (most of gases, temperature fall down) when a gas is made to expand adiabitically from a region of high pressure to extreamly low pressure region, know as Joule-Thomson effect.

Gas are liquidfied by appling Joule-Thomson effect. Throtting device is used to decrease the fluid.

Suppose a certain amount of gas is passes through porous plug —

Net work done —

$$\omega = P_1 V_1 - P_2 V_2$$

$$\cdot \cdot = 0 \quad \therefore \Delta U = P_1 V_1 - P_2 V_2$$

$$\Rightarrow U_2 - U_1 = P_1 V_1 - P_2 V_2$$

$$\Rightarrow U_2 + P_2 V_2 = U_1 + P_1 V_1$$

$$\Rightarrow H_2 = H_1$$

$$\therefore \Delta H = 0$$

$\therefore$ Isoenthalpic pro or isenthalpic pro it is.

Joule-Thomson experiments:

co-efficient: The ratio of temperature change with change of pressure is called Joule Thomson co-efficient.

$$\mu_{JT} = \left(\frac{\Delta T}{\Delta P}\right)_H$$

$$\boxed{\mu_{JT} = \lim_{\Delta T \to 0} \left(\frac{\Delta T}{\Delta P}\right)_H = \left(\frac{\partial T}{\partial P}\right)_H}$$

Joule-Thomson co-efficient can be converted to easily determinable derivatives.

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

as, $dH = 0$ for Joule-Thomson effect.

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

$$\Rightarrow \left(\frac{\partial H}{\partial T}\right)_P dT = - \left(\frac{\partial H}{\partial P}\right)_T dP$$

$$\Rightarrow \left(\frac{dT}{dP}\right)_H = - \frac{(\partial H/\partial P)_T}{(\partial H/\partial T)_P}$$

$$\Rightarrow \boxed{\left(\frac{dT}{dP}\right)_H = - \frac{1}{C_P}\left(\frac{dH}{dP}\right)_T}$$

Joule-Thomson co-efficient for ideal gas:

$$PV = nRT$$

$$V = \frac{nRT}{P}$$

$$\left(\frac{dV}{dT}\right)_P = \frac{nR}{P}$$

$$\therefore \left(\frac{dT}{dP}\right)_H = -\frac{1}{C_P}\left[-T\left(\frac{nR}{P}\right) + V\right]$$

$$\Rightarrow \left(\frac{dT}{dP}\right)_H = -\frac{1}{C_P}\left[-\frac{nRT}{P} + V\right]$$

$$\Rightarrow \boxed{\left(dT/dP\right)_H = 0}$$

◎ Prove that $(dT/dP)_H = 0$ for ideal gas and explain why the value is zero.

▨ **Another form of Joule-Thomson experiment:**

$$\mu_{JT} = -\frac{1}{C_P}\left(\frac{dH}{dP}\right)_T$$

$$= -\frac{1}{C_P}\left(\frac{d(U+PV)}{dP}\right)_T \qquad \text{as } H = U + PV$$

$$= -\frac{1}{C_P}\left[\left(\frac{\partial U}{\partial P}\right)_T + \left\{\frac{d(PV)}{dP}\right\}_T\right]$$

$$= -\frac{1}{C_P}\left[\left(\frac{dU}{dV}\right)_T\left(\frac{dV}{dP}\right)_T + \left\{\frac{d(PV)}{dP}\right\}_T\right] ----①$$

$\Rightarrow$ for ideal gas we know $\left(\frac{dU}{dV}\right)_T = 0$
so, from the equation-① the 1st part will be
equal to zero , also for ideal gas the
term $\left\{\frac{d(PV)}{dP}\right\}_T = 0$.

$$\therefore \boxed{\mu_{JT} = 0}$$

Joule-Thomson co-efficient for real gas:
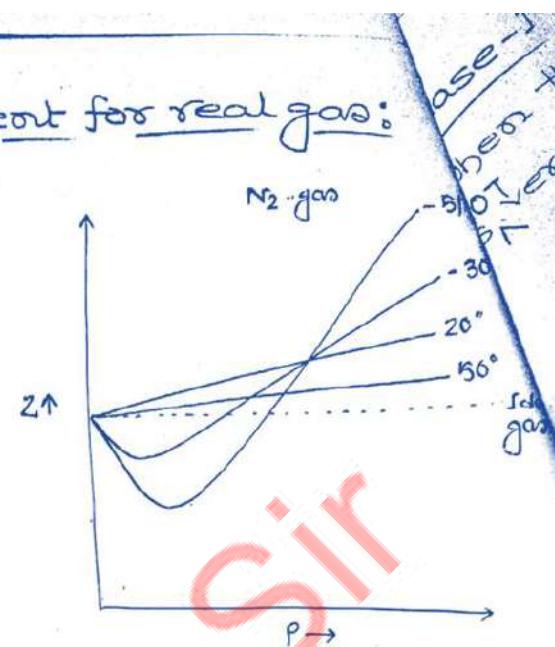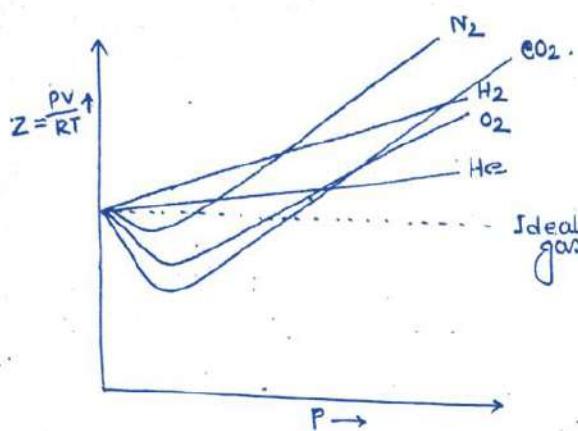
For real gases it gets cooled appreciably H_2 and He are exception and they warmed up during Joule-Thomson experiments but at very low temperature they also show usual behavior. This cooling effect is due to the decrease in Kinetic energy of real gas. Since a part of energy is used up in overcoming the vanderwalb force of attraction existing between the molecules during expansion.

We discuss this, very nearly with the help of this equation –

$$\mu_{JT} = -\frac{1}{C_P}\left[\left(\frac{\partial u}{\partial v}\right)_T\left(\frac{dv}{dP}\right)_T + \left\{\frac{d(PV)}{dP}\right\}_T\right]$$

for, real gas, $\left(\frac{du}{dv}\right)_T$ = always possitive and

$\left(\frac{dv}{dP}\right)_T$ = always negetive.

since, $P \propto 1/v$, and the value of $\left\{\frac{d(PV)}{dP}\right\}_T$ of real gases there may be three cases possible.

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Case-I : In some real gases P-V decrease when the pressure increases (The pressure is NOT very high) at ordinary temperature.

Thus we have –

$$\mu_{jT} = -\frac{1}{C_p}\left[\left(\frac{du}{dv}\right)_T\left(\frac{dv}{dP}\right)_T + \left\{\frac{d(PV)}{dP}\right\}_T\right]$$

$$= -\frac{1}{C_p}\left((-)ve + (-)ve\right)$$

$$= (+)ve.$$

$$\therefore \mu_{jT} = \left(\frac{\Delta T}{\Delta P}\right)_H = \frac{(-)ve}{(-)ve} = (+)ve.$$

$$\therefore \boxed{\Delta T \text{ must be } (-)ve.}$$

Since ΔP is always negative so $\Delta T = (-)ve$ that is the gas is undergoes cooling during expansion.

Case-2 : when the pressure is very high and temperature is very high – PV of all gases increases with pressure. Thus the equation–

$$\mu_{jT} = -\frac{1}{C_p}\left[\left(\frac{du}{dv}\right)_T\left(\frac{dv}{dP}\right)_T + \left\{\frac{d(PV)}{dP}\right\}_T\right]$$

$$= -\frac{1}{C_p}\left[(-)ve + (+)ve\right] - \text{here } (+ > -)$$

$$= (-)ve$$

Thus, $\mu_{jT} = \left(\frac{\Delta T}{\Delta P}\right)_H = \frac{(+)ve}{(-)ve} = (-)ve.$

$\therefore \Delta T$ must be $(+)ve$ value.

Thus the gas undergoes heating during expansion.

<u>case-2:</u> When the pressure is very high and also temperature is very high. PV of all gases increases with pressure. Thus the equation is.

$$\mu_{J-T} = -\frac{1}{C_P}\left[\left(\frac{\partial u}{\partial v}\right)_T \left(\frac{\partial v}{\partial P}\right)_T + \left(\frac{\partial(PV)}{\partial P}\right)_T\right]$$

$$= -\frac{1}{C_P}\left[(+ve)+(+ve)\right] + \left[\left(\frac{\partial(PV)}{\partial P}\right)_T\right]$$

$$= -ve \quad \left[When \left(\frac{\partial(PV)}{\partial P}\right)_T > \left(\frac{\partial u}{\partial v}\right)_T\right]$$

Thus we have,

$$\boxed{\mu_{J-T} = -ve}$$

$$\mu_{J-T} = \left(\frac{\partial T}{\partial P}\right)_H = \frac{+ve}{-ve} = -ve$$

$$\therefore \partial T = +ve \quad \boxed{T_2 > T_1}$$

I.e, the gas under goes heating during expansion

μ_{J-T}	$\left(\frac{\partial H}{\partial P}\right)_T$	Heating/cooling	e.g
+ve	-ve	Cooling, $T_2 < T_1$	most gases at ordinary temperature, H_2 and He at low temperature.
-ve	+ve	Heating occur	most gases at high temperature, H_2 and He at ordinary temperature
0	0	$T_2 = T_1$	ideal gas

⊘ <u>Joule-Thomson co-efficient for Van der Waals equation</u> :

for 1 mol of gas, the Van der Waals equation is.

$$\left(P+\frac{a}{v^2}\right)(v-b) = RT$$

$$\Rightarrow Pv + \frac{a}{v} - Pb - \frac{ab}{v^2} = RT$$

as the value of a and b are very low so we neglected the value of $\frac{ab}{v^2}$: term.

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$$\Rightarrow PV + \frac{a}{V} - Pb = RT \quad -(1)$$

$$\Rightarrow PV = RT + Pb - \frac{a}{V} \qquad \left[\begin{array}{l} PV = RT \\ V = \frac{RT}{P} \end{array}\right]$$

$$\Rightarrow PV = RT + Pb - \frac{aP}{RT} \quad -(2) \text{ Replacing the value of } V \text{ from}$$

$$\Rightarrow V = \frac{RT}{P} + b - \frac{a}{RT} \quad -(3) \quad PV = RT.$$

diff^n w.r. to T at constant P.

$$\left(\frac{\partial V}{\partial P}\right)_P = \frac{R}{P} + \frac{a}{RT^2} \quad -(4)$$

$$\Rightarrow RT = PV + \frac{a}{V} - Pb$$

dividing equation -1 by PT we get,

$$\frac{RT}{PT} = \frac{PV}{PT} + \frac{a}{PTV} - \frac{Pb}{PT}$$

$$\Rightarrow \frac{R}{P} = \frac{V}{T} + \frac{a}{PTV} - \frac{b}{T}$$

$$\Rightarrow \frac{R}{P} = \frac{V}{T} + \frac{aP}{PRT^2} - \frac{b}{T}$$

$$\Rightarrow \frac{R}{P} = \frac{V}{T} + \frac{a}{RT^2} - \frac{b}{T} \quad --- (5)$$

Put the value of equation -5 in equation 4 we get,

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

$$\Rightarrow \left(\frac{\partial V}{\partial T}\right)_P = \frac{V}{T} + \frac{2a}{RT^2} - \frac{b}{T} \quad ---(6)$$

We know that,

$$\mu_{J-T} = -\frac{1}{C_P}\left[-T\left(\frac{\partial V}{\partial T}\right)_P + V\right]$$

Put the value of $\left(\frac{\partial V}{\partial T}\right)_P$ from equation-6 we have,

$$\mu_{J-T} = \frac{1}{C_P}\left[T\left\{\frac{V}{T} + \frac{2a}{RT^2} - \frac{b}{T}\right\} - V\right]$$

$$\boxed{\therefore \mu_{J-T} = \frac{1}{C_P}\left[\frac{2a}{RT} - b\right]} \quad \text{Unit } \frac{2a}{RT} \ldots -2$$

⊘ **Inversion temperature:**

The temperature at which $\mu_{J-T} = 0$ for any real gas, this temperature is called 'inversion temperature'.

$$\frac{2a}{RT} - b = 0$$

$$\Rightarrow \boxed{T_i = \frac{2a}{Rb}}$$

We also get inversion temperature from the following equation,

$$\mu_{J-T} = \frac{1}{C_P}\left[T\left(\frac{\partial v}{\partial T}\right)_P - v\right]$$

$$\Rightarrow T = \frac{v}{\left(\frac{\partial v}{\partial T}\right)_P}$$

$$\Rightarrow T_i = \frac{v}{\frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P} \equiv \frac{1}{\alpha_i}$$

Reference Books:

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