

Second Law of thermodynamics: derived toward entropy

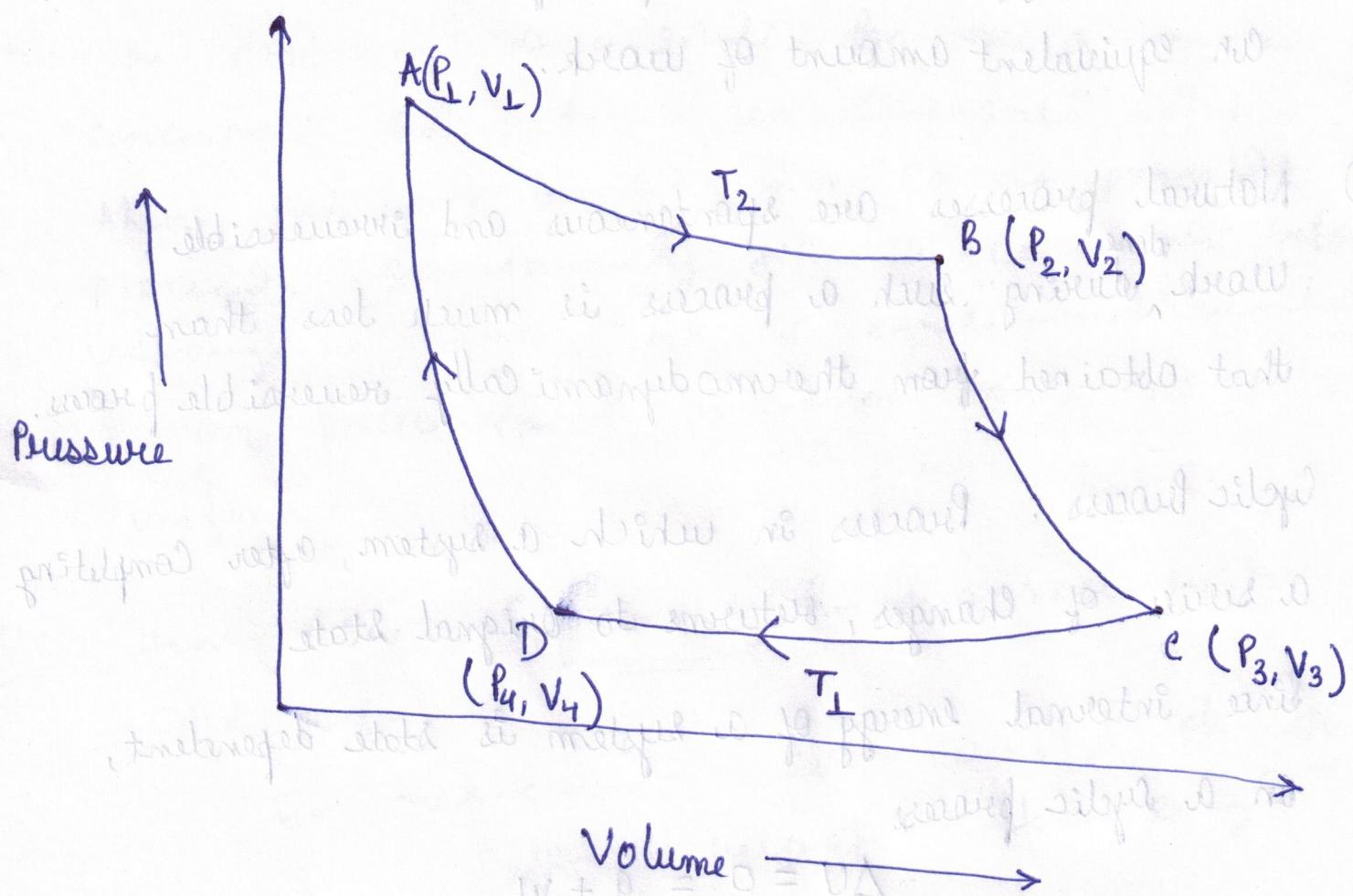
(P1)

- * Limitations of ~~See~~ First Law
 - ① No restriction on the direction of flow of heat
 - ② Does not tell whether a specified change or a process including a chemical reaction can occur spontaneously
 - ③ Heat energy can't be completely converted into an equivalent amount of work.
- * Natural processes are spontaneous and irreversible.
Work ^{done} during such a process is much less than that obtained from thermodynamically reversible process.
- * Cyclic Process: Process in which a system, after completing a series of changes, returns to original state
- * Since internal energy of a system is state dependent, in a cyclic process
$$\Delta U = 0 = q + w$$
$$\Rightarrow q = -w \quad \text{①}$$
- * If cyclic process done at constant temperature \Rightarrow isothermal cycle

(P2)

- * If cyclic process carried out reversibly \Rightarrow reversible cycle.
- * Carnot Cycle - 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 a series of four successive operations (4 strokes).



Stroke 1: Isothermal Expansion at temperature T_2 ($A \rightarrow B$)

$$\therefore \Delta U = 0 \Rightarrow q = -w$$

$$W_L = -RT_2 \cdot \ln\left(\frac{V_2}{V_1}\right) \quad (2)$$

Stroke 2: $(B \rightarrow C)$ Adiabatic Expansion

$$q = 0 \Rightarrow \Delta U = -w \quad (\text{By Convention})$$

$$\Rightarrow -w_2 = -C_V (T_2 - T_1)$$

Stroke 3: $(C \rightarrow D)$ Isothermal Compression at temperature $T_{2\perp}$

$$w_3 = R T_{2\perp} \ln \left(\frac{V_4}{V_3} \right) \quad (4)$$

Stroke 4: $(D \rightarrow A)$ Adiabatic Compression

$$w_4 = C_V (T_2 - T_1) \quad (5)$$

Additionally, in the light of adiabatic expansion of an ideal gas

$$\frac{V_2}{V_1} = \frac{V_3}{V_4} \quad (6)$$

$$\text{Net heat absorbed, } q_r = R (T_2 - T_1) \cdot \ln \left(\frac{V_2}{V_1} \right) \quad (7)$$

$$\text{Net work done by the gas, } W = -w_1 + (-w_2) + w_3 + w_4$$

$$W = R (T_2 - T_1) \cdot \ln \left(\frac{V_2}{V_1} \right) \quad (8)$$

from (7) and (8)

$$\boxed{q = w}$$

Essential Condition for a Cyclic process.

(P4)

* Second Law of Thermodynamics

It is impossible to use a cyclic process to extract heat from a reservoir and to convert it into work without transferring at the same time a certain amount of heat from a hotter to a colder part of the system.

* Efficiency of a Heat Engine : fraction of the heat absorbed by an engine which it can convert into work gives the efficiency (η) of the engine.

$$\eta = \frac{(T_2 - T_1)}{T_2} = \frac{q_2 - q_1}{q_2} \quad (9)$$

* Carnot Theorem:

Efficiency of a machine working reversibly depends only on the temperature of the source and sink and independent of the nature of substance used for operations.

⇒ All periodic machines working reversibly between the same two temperatures have the same efficiency.

(P5)

* Alternate Statement for Second Law of Thermodynamics:

It is impossible to convert heat into work without compensation.

* from eq. ①

$$1 - \frac{T_1}{T_2} = 1 - \frac{q_{21}}{q_{12}}$$

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

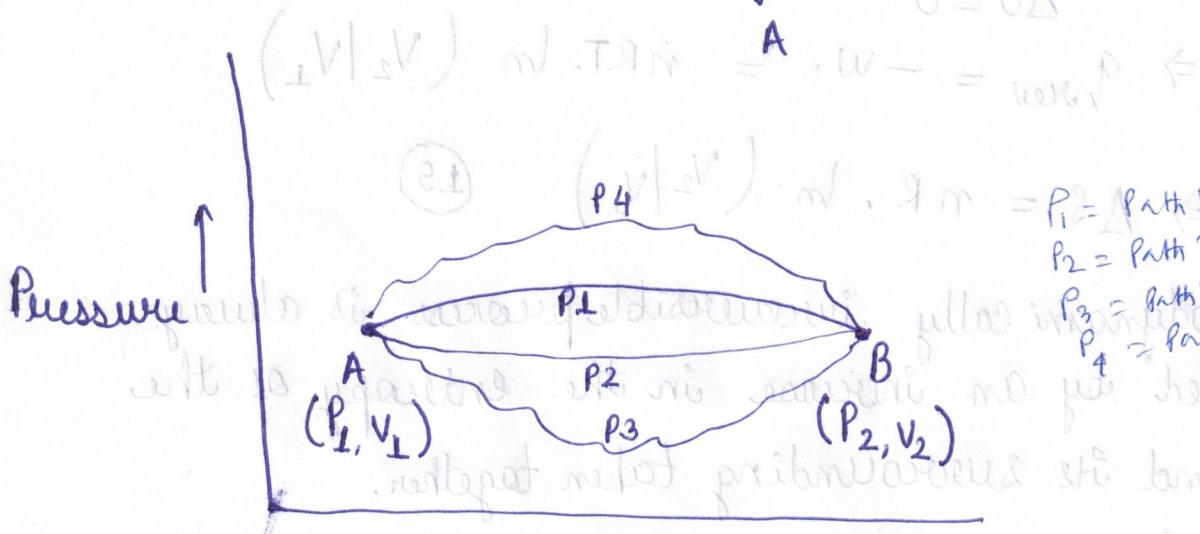
In general form,

$$\frac{q_{\text{rev}}}{T} = \text{Constant}$$

(10)

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

* Entropy, $\Delta S = S_B - S_A = \int_A^B \frac{dq}{T}$ (11)



$$P_1 = P_{\text{Path 1}}$$

$$P_2 = P_{\text{Path 2}}$$

$$P_3 = P_{\text{Path 3}}$$

$$P_4 = P_{\text{Path 4}}$$

$$\text{Volume} \rightarrow (V_1 + V_2)$$

* Entropy is path independent and depends only on initial & final states of the system.

(29) for each infinitesimally small change,

$$ds = \frac{dq}{dT} \quad (12)$$

at constant temperature, $\Delta S = dq/T$ (13)

Note: Equation (11) is only valid when change of state A to state B is reversible.

- (*) Entropy change for a finite change of state of a system at constant temperature,

$$\Delta S = q_{\text{rev}}/T \quad (14)$$

(*) Unit of entropy = J/K

(*) Entropy is an extensive property, ie depends upon the amount of substance involved.

(*) Entropy Change in an Isothermal Expansion of an ideal gas.

$$\Delta U = 0$$

$$\Rightarrow q_{\text{rev}} = -w = nRT \cdot \ln(V_2/V_1)$$

$$\Rightarrow \Delta S = nR \cdot \ln(V_2/V_1) \quad (15)$$

(*) A thermodynamically irreversible process is always accompanied by an increase in the entropy of the system and its surrounding taken together.

$$(\Delta S_{\text{sys}} + \Delta S_{\text{sur}}) = 0 \quad (\text{for reversible process})$$

$$> 0 \quad (\text{for irreversible process})$$

* Alternate - Alternate Statement for Second Law of thermodynamics.

The energy of the universe remains constant ; the entropy of the Universe tends towards a maximum.

* Entropy Changes accompanying changes of phase:

- (a) from solid phase to liquid phase \rightarrow at constant pressure

$$\frac{V_b}{V} + \Delta S_{\text{fus}} = \Delta H_{\text{fus}} / T_{\text{fus}}$$

where ΔH_{fus} \Rightarrow molar heat of fusion

$-T_{\text{fus}}$ \Rightarrow fusion point.

- (b) from liquid phase to vapour phase

$$\Delta S_{\text{vap}} = \Delta H_{\text{vap}} / T_b$$

T_b - boiling point

ΔH_{vap} - molar heat of vaporization

- (c) from one crystalline form to another

$$\Delta S_{\text{tr}} = \Delta H_{\text{tr}} / T$$

* Entropy Change of an Ideal Gas with Change in P, V and T:

- (a) when T and V are two variables

$$\Delta S = n C_v \cdot \ln \left(\frac{T_2}{T_1} \right) + n R \cdot \ln \left(\frac{V_2}{V_1} \right)$$

- (b) when T and P are two variables

$$\Delta S = n C_p \cdot \ln \left(\frac{T_2}{T_1} \right) - n R \cdot \ln \left(\frac{P_2}{P_1} \right)$$

* Entropy Changes of an Ideal Gas in different processes:

- (1) isothermal process $\rightarrow \Delta S_T = R \cdot \ln \left(\frac{P_1}{P_2} \right)$

- (2) isobaric process $\rightarrow \Delta S_p = C_p \cdot \ln \left(\frac{T_2}{T_1} \right)$

$$③ \text{ Isochoric process} - \Delta S_v = C_v \cdot \ln\left(\frac{T_2}{T_1}\right) \quad (P2)$$

* Entropy of a Mixture of Ideal Gases:

for one mole of an ideal gas, $dS = C_v \cdot \frac{dT}{T} + R \cdot \frac{dv}{v}$

for a mixture of ideal gases, $S = \sum n_i (C_p \cdot \ln T - R \cdot \ln P - R \ln x_i + S'_0) \quad (9)$

x_i = mole fraction of a particular gas in the mixture.

P = total pressure

* Entropy of Mixing: at constant pressure P

$$\Delta S_{mix} = -R \cdot \sum n_i \cdot \ln x_i \quad (10)$$

where n_i and x_i represents the number of moles and mole fraction of each constituent of the mixture.

* Standard Entropies: Entropy of one mole of a substance in pure state at one atmospheric pressure and 25°C. denoted as S° .

* Work functions: $A = U - TS \quad (11)$

* Free energy functions: $G = H - TS \quad (12)$

* $\Delta A = \Delta U - T \Delta S$ (Helmholtz free energy / function) (13)

$(-\Delta A)$ gives the maximum work that can be done by the system during the given change.

$-\Delta A = W_{rev}$ (reversible work)

(*) Gibbs free energy, $\Delta G = \Delta H - T\Delta S$ (14) (P3)

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

$$\Rightarrow \Delta G = \Delta U + P\Delta V - T\Delta S$$

$$\Rightarrow \Delta G = \Delta A + P\Delta V \quad (15)$$

$$\Rightarrow \Delta G = -w + P\Delta V$$

$$\Rightarrow -\Delta G = w - P\Delta V$$

\hookrightarrow work done by the gas on expansion against constant external pressure P

$\Rightarrow -\Delta G$ \Rightarrow maximum work obtainable from a system other than that due to change of volume

$$\text{Net Work} = w - P\Delta V = \Delta h = 4.6 \quad (E)$$

$\Rightarrow -\Delta h$ is a measure of the net work that can be obtained from a system at constant temperature and pressure.

(*) Variation of Free energy change with temperature and pressure:

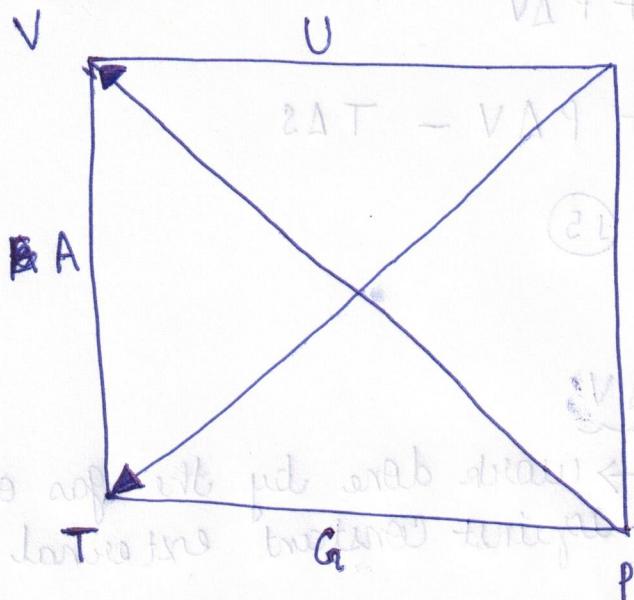
$$dh = VdP - SdT \quad (16)$$

$$\left(\frac{\partial h}{\partial T}\right)_P = -S$$

$$\left(\frac{\partial h}{\partial P}\right)_T = V$$

$$\Rightarrow \Delta h = nRT \cdot \ln\left(\frac{P_2}{P_1}\right) = nRT \cdot \ln\left(\frac{V_2}{V_1}\right) \quad (17)$$

* Maxwell Relations:



$$\textcircled{1} \quad dU = TdS - PdV$$

$$\textcircled{2} \quad dH = TdS + VdP$$

$$\textcircled{3} \quad dA = -SdT - PdV = \left. \begin{array}{l} \text{minimum of } \Delta A \\ \text{at constant } T \text{ and } V \end{array} \right\} \textcircled{18}$$

$$\textcircled{4} \quad dG = -SdT + VdP$$

$$\textcircled{1} \quad \left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P$$

$$\textcircled{2} \quad \left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V$$

$$\textcircled{3} \quad \left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$$

$$\textcircled{4} \quad \left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P$$

\textcircled{19}

Maxwell's Relations.

$$V = \left(\frac{\partial S}{\partial P} \right)$$

$$\left(\frac{\partial S}{\partial P} \right)_{T,V} = \left(\frac{\partial V}{\partial T} \right)_{P,V} = \Delta A \leftarrow$$

* Criteria for reversible and irreversible (spontaneous) process:

$$\therefore dS = dq_{rev}/T = (dU + PdV)/T$$

$$\text{for reversible process } TdS = dU + PdV$$

$$\text{for irreversible process } TdS > dU + PdV$$

(20)

① Criteria in terms of Change of entropy \rightarrow

$$\Delta S > 0 \quad (\text{equality holds in case of reversible process}) \quad (21)$$

② Criteria in terms of $\Delta U \rightarrow$

$$\Delta U \leq 0 \quad (\text{equality holds in case of reversible process}) \quad (22)$$

③ Criteria in terms of change of enthalpy \rightarrow

$$\Delta H \leq 0 \quad (23)$$

④ Criteria in terms of change in work function \rightarrow

$$\text{at constant volume, } \Delta A \leq 0 \quad (24)$$

⑤ Criteria in terms of change of free energy \rightarrow

$$\text{at constant temperature and pressure, } \Delta G \leq 0 \quad (25)$$

* Gibbs Helmholtz equation:

$$\text{at constant pressure } \Delta G = \Delta H + T \cdot \left(\frac{\partial(\Delta G)}{\partial T} \right)_P \quad (26)$$

for a reaction at constant volume, corresponding equation will be

$$\Delta A = \Delta U + T \cdot \left(\frac{\partial(\Delta A)}{\partial T} \right)_V \quad (27)$$

* Chemical Potential:

n_i = number of moles of the constituent i.

$$\left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_i - n_i} = \bar{H}_i = \bar{G}_i + T \bar{s}_i \quad (28)$$

⇒ Chemical Potential of a given substance is the change in free energy of the system that results on the addition of one mole of that substance at a constant temperature and pressure, to such a large quantity of the system that there is no appreciable change in the overall composition of the system.

for an infinitesimal free energy change,

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \left(\frac{\partial G}{\partial P}\right)_{T,N} dP + \mu_1 dn_1 + \mu_2 dn_2 + \dots + \mu_j dn_j \quad (29)$$

if temperature and pressure remain constant

$$(dG)_{T,P} = \mu_1 dn_1 + \mu_2 dn_2 + \dots + \mu_j dn_j \quad (30)$$

if a system has a definite composition having n_1, n_2, \dots, n_j moles of constituents 1, 2, ..., j, respectively, then

$$(G)_{T,P,N} = n_1 \mu_1 + n_2 \mu_2 + \dots + n_j \mu_j \quad (31)$$

⇒ Chemical potential may be defined as the contribution per mole of each particular constituent of the mixture to the total free energy of the system under conditions of constant temperature and pressure.

* Gibbs-Duhem Equation: $\sum n_i \cdot d\mu_i = 0 \quad (32)$

* Variation of chemical potential with temperature:

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,N} = -\bar{s}_i \quad (33)$$

(Partial molar entropy)

(P+) Variation of chemical potential with pressure:

$$\left(\frac{\partial \mu_i}{\partial P} \right)_{T, N} = \bar{V}_i \text{ (partial molar volume)} \quad (34)$$

* Chemical Potential in a System of Ideal Gas:

$$PV = (n_1 + n_2 + \dots + n_j) RT$$

$$\left(\frac{\partial V}{\partial n_i} \right)_{T, P, n_1, n_2, \dots} = \bar{V}_i = RT/P = \left(\frac{\partial \mu_i}{\partial P} \right)_{T, N}$$

$$\Rightarrow d\mu_i = (RT/P) dP = RT \cdot \ln P \quad (35)$$

$$\therefore p_i = \left(\frac{n_i}{n} \right) P = x_i P \quad (\because x_i = \text{mole fraction})$$

$$\Rightarrow \mu_i = \mu_{i(P)}^{\circ} + RT \cdot \ln p_i \quad (36)$$

$$\mu_i = \mu_{i(\infty)}^{\circ} + RT \cdot \ln x_i \quad (37)$$

* Clapeyron Equation: $\frac{dp}{dT} = \frac{q}{T \Delta V} \quad (38)$

\Rightarrow Change in pressure dP must accompany the change in temperature dT and vice versa, in the case of a system containing two phases of a pure substance in equilibrium with each other.

Third law of Thermodynamics :-

(PL)

* from Gibbs-Helmholtz equation

$$\Delta G - \Delta H = T \cdot \left(\frac{\partial \Delta G}{\partial T} \right)_P \quad (1)$$

at absolute zero (ie $T=0$), $\Delta G = \Delta H$

* Nernst heat theorem : (holds only in case of pure solids)

value of $\frac{\partial(\Delta G)}{\partial T} \rightarrow 0$ as temperature is lowered towards absolute zero

$\Rightarrow \Delta G$ and ΔH approach each other asymptotically as $T \rightarrow 0$
and becomes $\Delta G = \Delta H$ at $T = 0$ K.

Mathematically,

$$\lim_{T \rightarrow 0} \left[\frac{\partial \Delta G}{\partial T} \right]_P = \lim_{T \rightarrow 0} \left[\frac{\partial \Delta H}{\partial T} \right]_P = 0. \quad (2)$$

* Third law of Thermodynamics:

At the absolute zero of temperature, the entropy of every substance may become zero and it does becomes zero in the case of a perfectly crystalline solid.

$$\lim_{T \rightarrow 0} S = 0$$

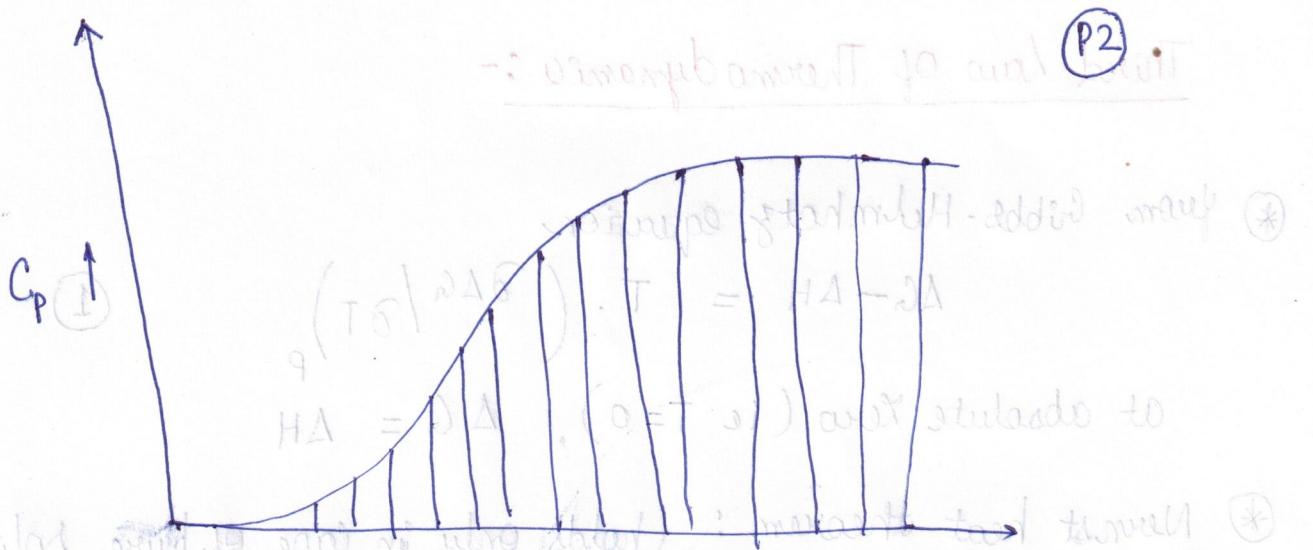
\therefore At constant pressure, $dS = \left(C_p/T \right) dT$

$$\int_0^S dS = \int_0^T \left(C_p/T \right) dT$$

$$\text{absolute entropy, } S = \int_0^T C_p \cdot d(\ln T)$$

(19)

(P2)



- work reversal is equivalent to $T \ln(T_0) - \int_{T_0}^T C_p dT$ for cyclic processes

\Rightarrow absolute entropy = Area under the curve.

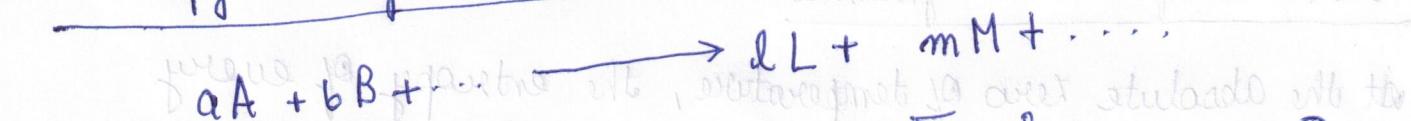
(*) Debye T^3 law: $C_p \propto T^3$ follows the law starting from 0 K to 15 K at very low temperatures

$$C_p \approx C_v \approx aT^3 \quad (4)$$

where a is an empirical constant.

$$\Rightarrow S_p = \int_0^{T^*} aT^3 dT/T + \int_{T^*}^T C_p dT/T = \frac{1}{3} a (T^*)^3 + \int_{T^*}^T C_p \frac{dT}{T}$$

(*) Entropy Changes in Chemical Reactions:



$$\text{Standard entropy change } \Delta S^\circ = \sum_{\text{products}} S^\circ - \sum_{\text{reactants}} S^\circ \quad (5)$$

$$= [dS_L^\circ + mS_M^\circ + \dots] - [aS_A^\circ + bS_B^\circ + \dots]$$

(*) Boltzmann Entropy Equation:

$$S = k \cdot \ln W \quad (7)$$

$W \Rightarrow$ number of microstates corresponding to a given macrostate

$k = \text{Boltzmann Constant.}$

EFFECT OF TEMPERATURE ON GIBBS FUNCTION

For a closed system doing no non-expansion work

$$dG = VdP - SdT$$

At constant pressure

$$dG = - SdT \text{ and } \left(\frac{\partial G}{\partial T}\right)_P = -S \quad (1)$$

$$\text{But } G = H - TS \text{ or } -S = \frac{G - H}{T}$$

$$\text{and } \left(\frac{\partial G}{\partial T}\right)_P = \frac{G}{T} - \frac{H}{T} \quad (2)$$

This is one form of Gibbs-Helmholtz equations. Since it contains both the function G and its derivative, it is not very useful. To eliminate this let us differentiate G/T w.r.t. T

$$\begin{aligned} \left[\frac{\partial(G/T)}{\partial T} \right]_P &= \frac{1}{T} \left(\frac{\partial G}{\partial T} \right)_P + G \frac{\partial}{\partial T} \left(\frac{1}{T} \right) \\ &= \frac{1}{T} \left(\frac{\partial G}{\partial T} \right)_P - \frac{G}{T^2} = \frac{1}{T} \left[\left(\frac{\partial G}{\partial T} \right)_P - \frac{G}{T} \right] \end{aligned}$$

Eliminating G between Eqs 2 and 3

$$\left[\frac{\partial(G/T)}{\partial T} \right]_P = - \frac{H}{T^2} \quad (4)$$

$$\begin{aligned} \left[\frac{\partial(G/T)}{\partial T} \right]_P &= \left[\frac{\partial(G/T)}{\partial(\frac{1}{T})} \right]_P \cdot \frac{d(\frac{1}{T})}{dT} \\ &= \left[\frac{\partial(G/T)}{\partial(\frac{1}{T})} \right]_P \times -\frac{1}{T^2} \end{aligned} \quad (5)$$

Substituting this in Eqn 4 we get

$$\left[\frac{\partial(G/T)}{\partial(\frac{1}{T})} \right]_P = H \quad (6)$$

Eqn 4 and 6 are more useful forms of $G - H$ Eqn.

(2)

For a measurable change

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

and

$$\left[\frac{\partial(\Delta G/T)}{\partial(T^{-1})} \right]_P = \Delta H \quad (3)$$

If equation 2 is integrated from T_1 to T_2 assuming ΔH to be independent of Temperature in the range T_1 to T_2

$$\left[\frac{\partial(\Delta h/T)}{\partial T} \right]_P = -\Delta H \int_{T_1}^{T_2} \frac{1}{T^2} dT$$

~~$\Delta h_2 - \Delta h_1$~~

$$\frac{\Delta h_2}{\Delta T_2} - \frac{\Delta h_1}{\Delta T_1} = \Delta H \left[\frac{1}{T_2} - \frac{1}{T_1} \right] \quad (4)$$

$$\text{or } \Delta G_2 = \Delta G_1 \frac{T_2}{T_1} + \Delta H \left[1 - \frac{T_2}{T_1} \right] \quad (5)$$

EFFECT OF PRESSURE ON G FOR GASES.

$$\Delta G = nRT \int_{P_i}^{P_f} \frac{dp}{p} = nRT \ln P_f/P_i \quad (6)$$

Or

$$G(P_f) = G(P_i) + nRT \ln P_f/P_i \quad (7)$$

If P_i is taken as the standard pressure 1 atm for ideal gases - $G(P) = G^\circ + nRT \ln P/P^\circ \quad (8)$

For real systems, the effective pressure varies from P and is replaced by the "effective" pressure, fugacity, ' f '.

for one mol of a gas

$$G_m^{\circ} = G_m^{\circ} + RT \ln \frac{f}{P^{\circ}} \quad \text{--- (14)}$$

Fugacity is a function of Pressure and Temperature and is related P by the equation $P = \phi P^{\circ}$. Where ϕ is called the fugacity coefficient.

$$\lim_{P \rightarrow 0} \frac{f}{P} = 1 \text{ and } \phi = 1, f = P.$$

ϕ is related to the compression factor 'z' of a gas.

$$\int_{P^{\circ}}^P V_m dP = G_m - G_m^{\circ} = RT \ln \frac{f}{f^{\circ}} \quad \text{--- (15)}$$

If the gas behaved as perfect gas

$$\int_{P^{\circ}}^P V_m, \text{perfect} dP = RT \ln \frac{P}{P^{\circ}} \quad \text{--- (16)}$$

The difference between the two

$$\int_{P^{\circ}}^P (V_m - V_m, \text{perfect}) dP = RT \left[\ln \frac{f}{f^{\circ}} - \ln \frac{P}{P^{\circ}} \right] \quad \text{--- (17)}$$

This can be rearranged as

$$\ln \left[\frac{f}{P} \times \frac{P^{\circ}}{f^{\circ}} \right] = \frac{1}{RT} \int_{P^{\circ}}^P (V_m - V_m, \text{perfect}) dP. \quad \text{--- (18)}$$

When $P^{\circ} \rightarrow 0$, the gas behaves as an ideal gas and $f^{\circ} = P^{\circ}$. Hence $f^{\circ}/P^{\circ} = 1$ as $P \rightarrow 0$. Taking the limits setting $\frac{f^{\circ}}{P^{\circ}} = 1$ and $P^{\circ} = 0$, the equation (18) becomes

$$\ln \frac{f}{P} = \frac{1}{RT} \int_0^P (V_m - V_m, \text{perfect}) dP$$

$$\text{But } f/P = \phi. \therefore \ln \phi = \frac{1}{RT} \int_0^P (V_m - V_m, \text{perfect}) dP \quad \text{--- (19)}$$

For a perfect gas $V_{\text{perfect},m} = \frac{RT}{P}$ and for a real gas $V_m = \frac{RTZ}{P}$. Substituting them in Eqn. 19, we get $\ln \phi = \frac{1}{RT} \int_0^P \left(\frac{RTZ}{P} - \frac{RT}{P} \right) dP$, $\ln \phi = \int_0^P \frac{Z-1}{P} dP. \quad \text{--- (20)}$

Assignment 1

Note: upto Second Law of Thermodynamics and Entropy.

- ① Heat supplied to a Carnot engine is 1897.8 kJ. How much useful work can be done by the engine which works between 0°C and 100°C ?
- ② 5 moles of an ideal gas expand reversibly from a volume of 8 dm^3 to 80 dm^3 at a temperature of 27°C . Calculate the change in entropy.
- ③ Calculate the entropy increase in the evaporation of one mole of water at 100°C . Heat of vaporisation of water at 100°C = 2259.4 J/g .
- ④ Calculate the entropy change accompanying the freezing of one mole of water at 25°C to ice at -10°C .
Given: heat of fusion of ice at its fusion point (0°C) = 6 kJ/mol
heat capacity of ice = 36.82 J/K.mol
heat capacity of liquid water = 75.31 J/K.mol
- ⑤ Calculate ΔS when one mole of steam at 100°C is converted into ice at 0°C .
Given: Average specific heat of water = $4.184 \times 10^3 \text{ J/K.g}$
heat of vaporization at boiling point = 2490.6 J/kg

Assignment 2

Note: upto reversible - irreversible process.

- ① Calculate the change in entropy accompanying the heating of one mole of Helium gas, assumed ideal, from a temperature of 298 K to a temperature of 1000 K at constant pressure. Assume that $C_V = \frac{3}{2} R$.
- ② One mole of an ideal gas expands reversibly from a temperature of 25°C and pressure of 1 atm to a temperature of 0°C and pressure of 500 mmHg. Calculate ΔS for the process. Assume that $C_V = \frac{3}{2} R$.
- ③ One mole of N_2 is mixed with 3 moles of O_2 at 25°C to form a mixture at final pressure of 1 atm, initial pressure of each being also 1 atm. Calculate the molar entropy of mixing.
- ④ Show that for ideal gas
- $$\left(\frac{\partial U}{\partial V} \right)_T = 0$$
 - $$\left(\frac{\partial H}{\partial P} \right)_T = 0$$
 - $$\left(\frac{\partial U}{\partial P} \right)_T = 0$$
 - $$\left(\frac{\partial H}{\partial V} \right)_T = 0$$

Assignment 3

Note: Up to Chemical Potential.

- ① The free energy change (ΔG) accompanying a given process is -85.77 kJ at 25°C and -83.68 kJ at 35°C . Calculate the change in enthalpy (ΔH) for the process at 30°C .
- ② Derive Gibbs - Duhem equation.
- ③ Derive Clapeyron - Clausius equation from Clapeyron equation, when applied to liquid \rightleftharpoons vapour equilibrium.

Clapeyron - Clausius Equation :-

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_{\text{vap}}}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

- ④ Show that in the case of a mixture of ideal gas, the chemical potential of any constituent is given by

$$\mu_i = \mu_{i(p)}^{\circ} + RT \cdot \ln p_i$$

$$\text{Or } \mu_i = \mu_{i(c)}^{\circ} + RT \cdot \ln c_i$$

where p_i and c_i represent the partial pressure and concentration respectively, of the constituent concerned.

Assignment 4

Note: upto Third Law of Thermodynamics.

- ① Determine absolute entropy of a gas at 25°C under atmospheric pressure. Assume substance in solid exist in two allotropic forms α and β .
- ② C_V for Uranium metal is 3.04 J/K mol at 20 K. Calculate the absolute entropy of the metal at 20 K.
- ③ The heat capacity, C_p (in J/K. mol) of a substance is given by :

$$C_p(s) = 16.74 \times 10^{-5} T^3 \quad (0 < T < 50 \text{ K})$$

$$C_p(s) = 20.92 \quad (50 < T < 150 \text{ K})$$

$$C_p(l) = 25.10 \quad (150 < T < 400 \text{ K})$$

At the melting point (150 K), $\Delta H_f = 1255.2 \text{ J/mol}$. Calculate the absolute entropy of the substance in the liquid state at 300 K.

- ④ Calculate the standard entropy change for the reaction



$$S_{\text{N}_2}^\circ = 191 \text{ J/K. mol}$$

$$S_{\text{O}_2}^\circ = 205.0 \text{ J/K. mol}$$

$$S_{\text{NO}}^\circ = 210.45 \text{ J/K. mol.}$$

heat of fusion at freezing point = 333.555×10^3 J/kg.

Required time of evaporation so that heat of fusion

can melt 118.528 kg water toward a cold storage tank (1)

initial storage tank at 0°C with 100 kg water

8001 has 3°A

Required time of evaporation so that heat of fusion is (2)

with storage tank at 0°C & water flow to tank is (3)

appreciable

flow rate is 0.001 kg/m³ sec (4)

3°C to initial 0°C water to tank is (5)

$\sqrt{K P_{\text{base}}}$ =

the required time of evaporation so that heat of fusion is (6)

3°C to 0°C 3°C to initial 0°C water to tank is (7)

$= (3^\circ\text{C})$ time required to 0°C water to tank is (8)

time $\sqrt{K P_{\text{base}}} =$ time of evaporation

time $\sqrt{K P_{\text{base}}} =$ time of evaporation

initial 0°C to 0°C water to tank is (9) (10)

3°C to 0°C water to tank is (11)

$\sqrt{K P_{\text{base}}} =$ time of evaporation

$\sqrt{K P_{\text{base}}} =$ time required to 0°C water to tank

5) Calculate the entropy change accompanying the conversion of 1 mole of ice at 273.1 K and 1 atm pressure into steam at 373.1 K and 1 atm pressure. Given:

$$\text{at } 273.1 \text{ K, } \Delta H_{\text{fus}}(\text{ice}) = 6 \text{ kJ/mol}$$

$$\text{at } 373.1 \text{ K, } \Delta H_{\text{vap}}(\text{water}) = 40.6 \text{ kJ/mol}$$

Assume C_p ($= 75.2 \text{ J/K}$) remains constant ~~at 75.2 J/K~~ in the temperature range $373.1 - 273.1 \text{ K}$.

$$(x_{\text{O}_2} > T > 0) \quad \delta T = \frac{\partial x_{\text{O}_2}}{\partial T} \cdot \delta T = (2) \beta$$

$$(x_{\text{O}_2} > T > 0) \quad \delta T = (2) \beta$$

$$(x_{\text{O}_2} > T > 0) \quad \delta T = (2) \beta$$

$$\text{and } T = 2.37 \text{ K} = 241, \quad (x_{\text{O}_2}) \text{ and partial pressure of oxygen at standard conditions at } 10 \text{ kPa}$$

$$x_{\text{O}_2} = 0.21$$

partial pressure of oxygen standard conditions at standard conditions



$$\text{and } x_{\text{H}_2} = 0.09$$

$$\text{and } x_{\text{N}_2} = 0.70$$

$$\text{and } x_{\text{O}_2} = 0.21$$

e) $\left(\frac{\partial V}{\partial S}\right)_P = nRT/(P, C_p)$ f thermisch
zurück d. Wärmeentz.

f) internal pressure, $\left(\frac{\partial U}{\partial V}\right)_T = 0$ (1)
constant int. pressure \Rightarrow $P = \text{const}$ at const. T
constant int. pressure \Rightarrow constant ΔP
constant ΔP \Rightarrow $P_0 + \Delta P = \text{const}$ at const. T

\Rightarrow many additional steps \Rightarrow last ΔP \Rightarrow dam (2)
constant ΔP \Rightarrow max. time Δt \Rightarrow constant (3)
 \Rightarrow $\Delta t = \Delta P / \text{const}$ \Rightarrow max. time $\Delta t = \Delta P / \text{const}$ (4)
 \Rightarrow $\Delta t = \Delta P / \text{const}$ \Rightarrow max. time $\Delta t = \Delta P / \text{const}$ (5)

\Rightarrow $\Delta t = \Delta P / \text{const} \Rightarrow$ max. time $\Delta t = \Delta P / \text{const}$ (6)
 \Rightarrow set to $\Delta t = \Delta P / \text{const}$ \Rightarrow max. time $\Delta t = \Delta P / \text{const}$ (7)
last, $\Delta t = \Delta P / \text{const}$ \Rightarrow max. time $\Delta t = \Delta P / \text{const}$ (8)
 \Rightarrow $\Delta t = \Delta P / \text{const}$ \Rightarrow max. time $\Delta t = \Delta P / \text{const}$ (9)

my ticket \Rightarrow take back (10)

$$0 = \left(\frac{V_0}{V_0}\right) e^{t/t_{max}}$$

$$0 = \left(\frac{V_0}{V_0}\right) e^{t/t_{max}}$$

$$0 = \left(\frac{V_0}{V_0}\right) e^{t/t_{max}}$$

$$0 = \left(\frac{V_0}{V_0}\right) e^{t/t_{max}}$$

Solutions to Assignment 1

$$\textcircled{1} \quad T_2 = 100 + 273 = 373 \text{ K}$$

$$T_1 = 273 \text{ K}$$

$$q_2 = 1897.8 \text{ J/K}$$

$$\omega = q_2 (T_2 - T_1) / T_2 = 508.7 \text{ kJ}$$

$$\textcircled{2} \quad \Delta S = n R \ln (V_2/V_1) = 95.73 \text{ J/K}$$

$$\textcircled{3} \quad \Delta S_{\text{vap}} = \Delta H_{\text{vap}} / T_b = \frac{2259.4 \times 18 \text{ g/mol}}{373 \text{ K}} = 109.03 \text{ J/K mol}$$

$$\textcircled{4} \quad \text{i) } \text{H}_2\text{O(l)} \text{ at } 25^\circ\text{C} \rightarrow \text{H}_2\text{O(l)} \text{ at } 0^\circ\text{C} \quad \Delta S = \int_{298}^{273} C_p(T) \frac{dT}{T}$$



$$\Delta S = -\Delta H_{\text{fus}} / T$$



$$\Delta S = \int_{273}^{263} C_p(T) \frac{dT}{T}$$

$$\Delta S_{\text{total}} = (75.31) \ln \left(\frac{273}{298} \right) - \frac{6000}{273} + 36.86 \times \ln \left(\frac{263}{273} \right)$$

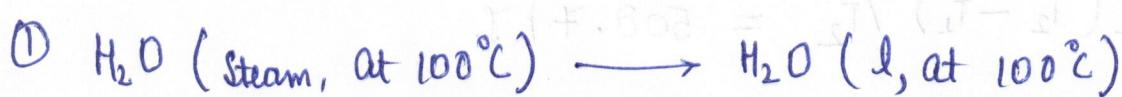
$$= -29.96 \text{ J/K mol}$$

$$\textcircled{5} \quad \rho = 4.184 \times 10^3 \times 10 \times 10^{-3} \text{ J}$$

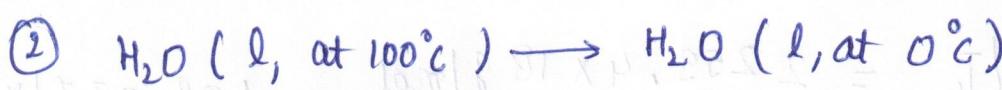
$$⑤ C_p = (4.184 \times 10^3 \text{ J/K.kg}) (18 \times 10^{-3} \text{ g/mol}) \\ = 75.31 \text{ J/K.mol}$$

$$\Delta H_{\text{vap}} = (2490 \times 10^3 \times 18 \times 10^{-3}) = 44831.56 \text{ J/mol}$$

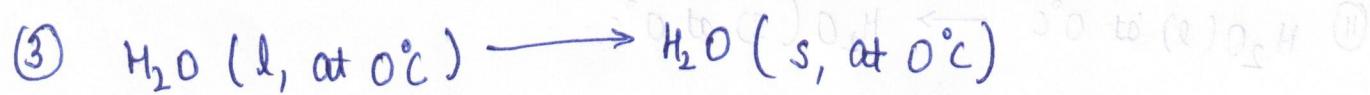
$$\Delta H_{\text{fus}} = (333.555 \times 10^3 \times 18 \times 10^{-3}) = 6004 \text{ J/mol}$$



$$\Delta S_1 = -\Delta H_{\text{vap}} / T_b = -44831.56 / 373 = 119.24 \text{ J/mol}$$



$$\Delta S_2 = \int_{373}^{273} C_p dT / T = -21.24 \text{ J/mol}$$



$$\Delta S_3 = -\Delta H_{\text{fus}} / T_{\text{fus}} = -6004 / 273 = -22.04 \text{ J/mol}$$

$$\Delta S_{\text{total}} = \Delta S_1 + \Delta S_2 + \Delta S_3 = -165.73 \text{ J/K.mol}$$

Solutions to Assignment 2

① for an ideal gas

$$C_p - C_v = R$$

$$C_p = 2.5R$$

$$\Delta S = C_p \ln \left(\frac{T_2}{T_1} \right) = 25.17 \text{ J/K.mol.}$$

②

$$\Delta S = C_p \cdot \ln \left(\frac{T_2}{T_1} \right) + R \ln \left(\frac{P_1}{P_2} \right)$$

for an ideal gas

$$C_p - C_v = R$$

$$\Rightarrow C_p = 5/2 R$$

$$\Delta S = 1.66 \text{ J/K.}$$

$$③ x_1 = 1/(1+3) = 0.25$$

$$x_2 = 1 - x_1 = 0.75$$

$$\Delta S_{\min} = -R \sum x_i \cdot \ln x_i$$

$$= -R (x_1 \ln x_1 + x_2 \ln x_2)$$

$$= 4.676 \text{ J/K.mol.}$$

④ ① for an ideal gas, $P = nRT/V$

$$\left(\frac{\partial P}{\partial T} \right)_V = P/T = nR/V$$

$$\therefore dU = TdS - PdV$$

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial S}{\partial V} \right)_T - P = T \left(\frac{\partial P}{\partial T} \right)_V - P = T \cdot \frac{P}{T} - P = 0$$

$$\textcircled{b} \quad V = nRT/p \quad \text{for ideal gas.}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = nR/P = V/T.$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_P = 0 \quad \left\{ \begin{array}{l} \text{Hint: } dH = Tds + Vdp \\ \therefore \left(\frac{\partial H}{\partial P}\right)_T = T \left(\frac{\partial S}{\partial P}\right)_T + V \\ \left(\frac{\partial H}{\partial P}\right)_T + \left(\frac{\partial U}{\partial P}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_P \end{array} \right.$$

$$\textcircled{c} \quad H = U + PV \Rightarrow U = H - PV = H - nRT$$

$$\left(\frac{\partial U}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T - \left(\frac{\partial (nRT)}{\partial P}\right)_T = 0 - 0 = 0$$

$$\textcircled{d} \quad H = U + PV = U + nRT$$

$$\left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T + \left(\frac{\partial (nRT)}{\partial V}\right)_T = 0 + 0 = 0$$

$$\textcircled{e} \quad \left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S \quad (\text{Maxwell rule}).$$

$$\because \left(\frac{\partial T}{\partial P}\right)_S \cdot \left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_P = -1 \quad (\text{cyclic rule}).$$

$$\left(\frac{\partial T}{\partial P}\right)_S = - \frac{(\partial S / \partial P)_T}{(\partial S / \partial T)_P}$$

$$\therefore ds = C_p dT/T$$

$$\left(\frac{\partial S}{\partial T}\right)_P = C_p/T$$

$$Q = \theta + \frac{1}{T} \cdot T = 1 - \left(\frac{10}{T_0}\right) T = \theta + \left(\frac{20}{V_0}\right) T = \left(\frac{V_0}{T}\right)$$

$$\therefore \left(\frac{\partial S}{\partial P}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_P \quad (\text{from Maxwell reln})$$

$$\Rightarrow \left(\frac{\partial T}{\partial P}\right)_S = \frac{(C_V/C_P)P}{C_P/T}$$

$$\therefore PV = nRT \\ \Rightarrow \left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}$$

$$\Rightarrow \left(\frac{\partial V}{\partial S}\right)_P = \frac{nRT}{P \cdot C_P}$$

$$(f) dU = TdS - PdV$$

$$\text{let } S = f(T, V)$$

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

$$dU = T \left[\left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \right] - PdV. \quad \text{---(1)}$$

$$\therefore U = f(T, V)$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad \text{---(11)}$$

equating

~~taking~~ the coeff of (dV) from eq (1) & (11)

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

$$= T \cdot \left(\frac{\partial P}{\partial T}\right)_V - P \quad (\text{Maxwell reln})$$

for ideal gas

$$PV = RT \Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = R/V$$

$$\Rightarrow \left(\frac{\partial u}{\partial v} \right)_T = T(R/V) - P \left(\frac{V_0}{T_0} \right) P - P = 0 \left(\frac{28}{78} \right)$$

$$\frac{T_0 V_0}{T_0 + P_0} = \frac{P_0}{2 \left(\frac{78}{28} \right)} \leftarrow$$

$$T_0 V_0 = T_0 + P_0 \left(\frac{78}{28} \right) \leftarrow T_0 V_0 = V_0 T_0 + \frac{50}{28} V_0 T_0$$

$$\frac{P_0}{T_0} = \frac{(V_0)}{\left(\frac{78}{28} \right)}$$

$$\frac{T_0 P_0}{P_0 + \frac{50}{28} V_0 T_0} = \frac{\left(\frac{V_0}{28} \right)}{\left(\frac{V_0}{28} \right) + \frac{50}{28}}$$

$$V_0 T_0 - 26 T_0 = V_0 \quad \textcircled{1}$$

$$\left(V_0 T_0 \right)_f = 26 \quad \text{lit}$$

$$\frac{V_0}{T_0} \left(\frac{28}{V_0} \right) + T_0 \left(\frac{28}{T_0} \right) = 26$$

$$\textcircled{1} - V_0 T_0 - \left[\frac{V_0}{T_0} \left(\frac{28}{V_0} \right) + T_0 \left(\frac{28}{T_0} \right) \right] T = V_0$$

$$\textcircled{1} \quad \frac{V_0}{T_0} \left(\frac{V_0}{28} \right) + T_0 \left(\frac{V_0}{28} \right) = V_0$$

\textcircled{1} & \textcircled{2} \text{ auf } (V_0) \text{ f\ddot{o}r } T \text{ f\ddot{o}hren}

$$T = \left(\frac{28}{V_0} \right) T = \frac{(V_0)}{V_0}$$

(neu know)

$$T = \left(\frac{98}{T_0} \right) T =$$

$$V_0 T = \left(\frac{16}{T_0} \right) T = T_0 = V_0$$

Solutions to assignment 3

$$\textcircled{1} \quad \left(\frac{\partial(\Delta G)}{\partial T} \right)_P = \frac{-83.68 - (-85.77)}{308 - 298} = 0.209 \text{ kJ/K}$$

ΔG at 30°C may be taken as avg. of values at 25°C & 35°C

$$\Delta G \text{ at } 30^\circ\text{C} = -\left(\frac{85.77 + 83.68}{2} \right) = -84.725 \text{ kJ}$$

$$\Delta G = \Delta H + T \cdot \left(\frac{\partial(\Delta G)}{\partial T} \right)_P$$

$$\Delta H = -148.05 \text{ kJ}$$

$$\begin{aligned} \textcircled{2} \quad dG &= \mu_1 dn_1 + \cancel{\mu_2 dn_2} + \dots + \mu_i dn_i + \eta_j dH_j \\ &= (\underbrace{\mu_1 dn_1 + \mu_2 dn_2 + \dots + \mu_i dn_i}_{\text{constant temp & pressure}}) + (\underbrace{\eta_j dH_j}_{\text{constant temp & pressure}}) \\ &= (dG)_{T, P} \end{aligned}$$

\Rightarrow for const. temp & pressure,

$$\sum n_j dH_j = 0.$$

$\textcircled{3}$ for liquid \rightleftharpoons vapor equilibrium

$$\begin{aligned} \frac{dp}{dT} &= \frac{\Delta H_{\text{vap}}}{T(V_g)} \quad (\text{assuming } V_g \gg V_{\text{vapor}}) \\ &= \frac{\Delta H_{\text{vap}}}{T} \cdot \frac{P}{RT} \end{aligned}$$

$$\frac{1}{P} \times \frac{dP}{dT} = \frac{\Delta H_{\text{vap}}}{RT^2}$$

$$\frac{d(\ln P)}{dT} = \frac{\Delta H_{\text{vap}}}{RT^2}$$

$$\int d(\ln P) = \frac{\Delta H_{\text{vap}}}{R} \int \frac{1}{T^2} dT = \frac{\Delta H_{\text{vap}}}{R} \left[-\frac{1}{T} \right]_T^{T_2} = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\frac{P_2}{P_1} = e^{-\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)}$$

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_{\text{vap}}}{R} \left[\frac{(T_2 - T_1)}{T_1 T_2} \right]$$

④ In an ideal gas $PV = nRT$

Let a system consisting of a number of ideal gases with

n_1, n_2, \dots be the no. of moles of constituent gases.

$$V = (n_1 + n_2 + \dots) RT/P$$

$$\left(\frac{\partial V}{\partial n_i} \right)_{T, P, n_1, n_2, \dots} = \bar{V}_i = RT/P$$

$$\therefore \left(\frac{\partial \mu_i}{\partial P} \right)_{T, N} = \bar{V}_i$$

$$\Rightarrow \left(\frac{\partial \mu_i}{\partial P} \right)_{T, N \text{ (in stat)}} = RT/P$$

$$\Rightarrow d\mu_i = RT d\ln P$$

$$\therefore \mu_i = \left(\frac{n_i}{n} \right) P$$

$$\Rightarrow d\mu_i = RT d\ln p_i$$

$$\Rightarrow \mu_i = \mu_{i(P)}^{\circ} + RT \ln p_i$$

$$\because p_i = \left(\frac{n_i}{V}\right) RT$$

$$\Rightarrow p_i = C_i^{\circ} RT$$

$$\mu_i = \mu_{i(P)}^{\circ} + \underbrace{RT \cdot \ln RT}_{\text{constant}} + RT \ln C_i$$

$$\mu_i^{\circ} = \mu_{i(C)}^{\circ} + RT \ln C_i$$

Solutions to Assignment 4

① Heating solid from $T=0^\circ\text{C}$ to $T=15^\circ\text{K}$:

$$\Delta S_1 = \int_0^{15} aT^3 \frac{dT}{T} \left(= \frac{1}{3} a(T^*)^3 \right)$$

Heating solid from T^* to T_{tr} (transition temp):

$$\Delta S_2 = \int_{T^*}^{T_{tr}} C_{p,s}(\alpha) dT \ln T$$

Transition from α to β form:

$$\Delta S_3 = \Delta H_{tr}/T_{tr}$$

Heating solid in β form to fusion temp:

$$\Delta S_4 = \int_{T_{tr}}^{T_{fus}} C_{p,s}(\beta) d \ln T$$

Changing β form to liquid state:

$$\Delta S_5 = \Delta H_{fus}/T_{fus}$$

Heating liq. to boiling point:

$$\Delta S_6 = \int_{T_{fus}}^{T_b} C_{p,l} d \ln T$$

Changing liq. to gas at T_b :

$$\Delta S_7 = \Delta H_{vap}/T_b$$

Heating gas from T_b to 25°C :

$$\Delta S_8 = \int_{T_b}^{298.15} C_{p,g} d \ln T$$

$$S_{\text{total}} = \sum_{i=1}^8 \Delta S_i$$

② at low temp ($0 < T < 20\text{ K}$) $C_p = C_v = aT^3$

$$a = C_v/T^3 = 38.03 \times 10^{-5} \text{ J/K}^4 \cdot \text{mol}$$
$$(ds = (C_p/T) dT)_{T_0}^{T_2} = 21$$

$$S_{20} - S_0 = aT^2 \cdot dT$$

$$S_{20} = \int_{T_0}^{T_2} aT^2 \cdot dT = \left[\frac{aT^3}{3} \right]_{T_0}^{T_2} = \left(\frac{aT_2^3 - aT_0^3}{3} \right) \quad (\because S_0 = 0)$$

$$S_{20} = 1.01 \text{ J/K.mol.}$$

③ $\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4$

$$= \int_0^{50} \frac{C_{p,s}}{T} dT + \int_{50}^{150} \frac{C_{p,s}}{T} dT + \frac{\Delta H_f}{T_f} + \int_{150}^{300} \frac{C_{p,l}}{T} dT$$

↓
dilute solution

$$= 55.73 \text{ J/(K.mol)} = 21$$

④ $\Delta S^\circ = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$

$$= 2 \times 210.45 - 1 \times 191.62 + 1 \times 205.01$$

$$= 24.27 \text{ J/K.}$$

⑤ $\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$

$$= \frac{\Delta H_{fus}}{T_{fus}} + \int_{273.1}^{73.1} \frac{C_p}{T} dT + \frac{\Delta H_{vap}}{T_{vap}}$$

$$= 154.3 \text{ J/K.mol}$$

21
↓
total