

# 15 September THERMODYNAMICS Saturday

Week 37 • Day 255-110

12

→ Quantitative study of energy transformations associated with physical or chemical process.

→ Isolated system : No exchange (Thermosflask)

Closed system : Exchange of energy only  
(cup of tea with cover)

Open system : Both energy and matter  
(cup of tea without cover)

→ Extensive property :

Mass, volume, KE, PE, Heat capacity, U, H, S, G, resistance, conductance

Intensive property :

Density, all concentrations, vapour pressure, viscosity, surface tension, electrode potential, molar conductance, dipole moment, dielectric constant, refractive index, specific heat capacity, molar heat capacity, pressure, temperature etc. chemical potential

## First Law

Change in heat or work is at the expense of 'U'.

$$dU = dq + dw$$

→ state function, exact differential

$$U = f(v, T) \text{ or } f(P, V) \text{ or } f(T, P)$$

→ cyclic process ;  $\oint dU = 0$

Appointment

October 15

Monday	5	12	19	26
Tuesday	6	13	20	27
Wednesday	7	14	21	28
Thursday	1	8	15	22
Friday	2	9	16	23
Saturday	3	10	17	24
Sunday	4	11	18	25

2015

14

Monday

Septe

Week 38 • Day 257-108

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

For perfect differential;

$$z = f(x, y)$$

$$i) \frac{\partial^2 z}{\partial y \partial x} = \frac{\partial^2 z}{\partial x \partial y}$$

$$ii) \left( \frac{\partial x}{\partial y} \right)_z \left( \frac{\partial y}{\partial z} \right)_x \left( \frac{\partial z}{\partial x} \right)_y = -1 \quad (\text{Euler chain reaction})$$

### ● Expansion or compression work

a) free expansion  $\Rightarrow P_{ext} = 0$  (system expands in vacuum)  
 $w = 0$

b) expansion against constant pressure (irreversible)

$$w = \int dw = -P_{ext} \int_{V_1}^{V_2} dv$$

$$c) \text{Reversible expansion: } w = - \int_{V_1}^{V_2} P dV$$

for isothermal  $\rightarrow w = -nRT \ln \left( \frac{V_2}{V_1} \right)$

September'15 if we calculate work

September'15 if we calculate work	1	8	15	22	29
Tuesday	2	9	16	23	30
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Thursday	4	11	18	25	
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Saturday	6	13	20	27	

Notes

done by system

In any process, to perform maxim. work; reversible process must be followed

15

September

Tuesday

Week 38 • Day 258-107

15

● Enthalpy ( $H$ ) =  $f(P, T)$

(generally)

$$\rightarrow dU = dq - pdV$$

at constant  $V$ ,

$$\boxed{dU = dq_v}$$

However, if process is carried out at constant  $P$ , the system changes its volume. Part of energy supplied as heat will be utilized for doing work, so  $dU \neq dq$  (at constant  $P$ ).

$$\boxed{H = U + PV}$$

( $H$  = heat at constant  $P$ )

$\rightarrow$  state function, exact differential,  $\Delta H$  independent of path.

$$dH = du + Pdv + vdp$$

$$dH = dq + dw + Pdv + vdp$$

$$dH = dq_p + dw + Pdv \text{ (at constant } P\text{)}$$

for system performing mechanical work,  
( $dw = -pdv$ )

$$\boxed{dH = dq_p}$$

And

$$\boxed{C_p = \left(\frac{\partial H}{\partial T}\right)_P} ; \quad \boxed{C_v = \left(\frac{\partial U}{\partial T}\right)_v}$$

Also

$$\boxed{C_p - C_v = R}$$

$$\boxed{C_p = a + bT + \frac{c}{T^2}}$$

Notes

Appointment

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2015

16

Wednesday

Week 38 • Day 259-106

Septem



SSP Notes

## • Variations

i)  $U$  vs  $T$  (at const.  $V$ )

$$\boxed{dU = nC_V dT}$$

Keyes - Sears modification

$$\boxed{\pi_T = -C_V \mu_J}$$

ii)  $U$  vs  $V$  (at const.  $T$ )

$$\boxed{dU_T = \left(\frac{\partial U}{\partial V}\right)_T dV}$$

$$\boxed{\mu_J = \left(\frac{\partial T}{\partial V}\right)_U}$$

From Joule's expt. (valid for ideal gas)

$$\boxed{dU_T = 0} \Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = 0$$

$$\Rightarrow \left(\frac{\partial U}{\partial P}\right)_T = 0$$

→  $\pi_T$  = internal pressure (due to intermolecular interactions)

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

→

$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$  = isobaric expansion coefficient

→  $\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$  = isothermal compressibility

September'15

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Sunday	6	13	20	27

Notes

Appointment

15

September

Thursda, SSP Notes

III) H vs T (at const. P)

Week 38 • Day 260-105

17

$$dH = c_p dT$$

IV) H vs P (at const. T)

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

for ideal gas  $\left(\frac{\partial H}{\partial P}\right)_T = 0 \Rightarrow \left(\frac{\partial H}{\partial V}\right)_T = 0$

### • Adiabatic process

→ adiabatic, reversible, ideal gas

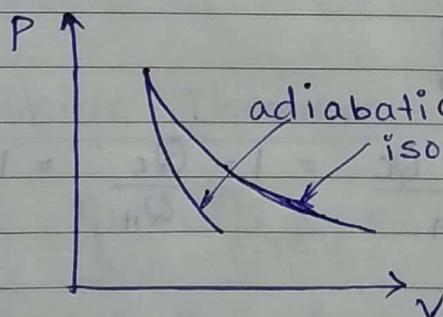
$$PV^\gamma = \text{constant}$$

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

$$T^\gamma P^{1-\gamma} = \text{constant}$$

$$dU = dW$$

$$C_V dT = -pdV = -\frac{RT}{V} dV$$



Notes

Appointment

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2015

18

Friday

Week 38 • Day 261-104

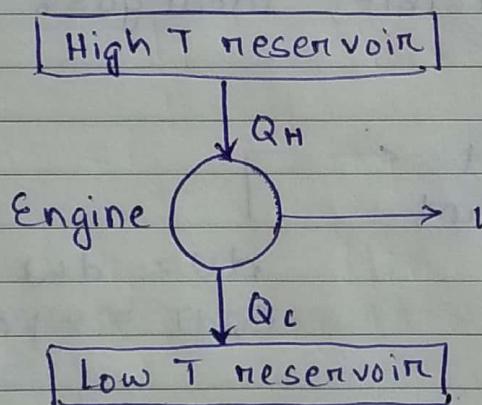
Sept SSP Notes

## Second Law

→ It is impossible to construct an engine, that operating in a cycle will produce no effect other than the extraction of heat from a reservoir and the performance of an equivalent amount of work. (Kelvin-Planck)

→ Entropy of an isolated system always increases

( $\because$  spontaneous processes are irreversible processes)



$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H}$$

## Carnot Cycle

$$\rightarrow \Delta U_{CY} = 0$$

September '15

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Sunday	6	13	20	27

Notes

Appointment

15

September

Saturday

Week 38 • Day 262-103

19

$$W_{CY} = -q_{CY} = -(q_1 + q_2)$$

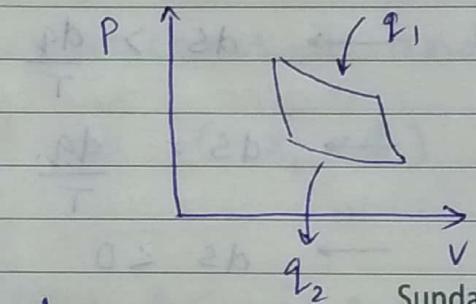
$$W_{CY} = -R(T_1 - T_2) \ln\left(\frac{V_2}{V_1}\right)$$

$$\eta = \frac{|W_{CY}|}{q_{\text{rev}}} = \frac{W_{CY}}{q_1}$$

$$\Rightarrow \frac{W_{CY}}{(-q_1)} = 1 - \frac{T_2}{T_1}$$

$$\Rightarrow \eta = \frac{|q_1 + q_2|}{q_1} = 1 + \frac{q_2}{q_1}$$

$$\Rightarrow \oint \frac{dq}{T} = 0$$



### • Entropy (S)

Sunday 20

$$dS = \frac{dq_{\text{rev}}}{T}$$

$$S = k_B \ln W$$

### • Clausius Theorem

$W$  = no. of ways  
in which energy

$$\eta_V \leq \eta_{\text{rev}} \quad (\text{cannot theorem})$$

of system  
can be  
arranged  
(no. of  
microstates)

$$1 + \frac{q_2}{q_1} \leq 1 - \frac{T_2}{T_1} = 1 + \frac{q_{2,\text{rev}}}{q_{1,\text{rev}}}$$

$$\oint \frac{dq}{T} \leq 0$$

(Clausius Theorem)

October '15

Notes

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2015

21

Monday

Week 39 • Day 264-101

September

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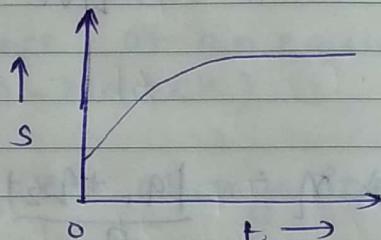
→  $\oint \frac{dq}{T} < 0$ ; if any part of cyclic process is irreversible.

→  $\oint \frac{dq}{T} = 0$ , if reversible cyclic process.

→  $\oint \frac{dq}{T} > 0$ , impossible

### • Clausius Inequality

$$\boxed{ds \geq \frac{dq}{T}}$$



→  $ds > \frac{dq}{T}$ ; spontaneous process

→  $ds = \frac{dq}{T}$ ; reversible process

→  $ds < 0$ ; impossible

→ Entropy increases for a spontaneous process in an isolated system; maximum at equilibrium.

### • $\Delta S^\circ$ of an ideal gas

$$\rightarrow \Delta S = nC_V \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{V_2}{V_1}\right) \quad \left. \begin{array}{l} \text{for reversible} \\ \text{process} \end{array} \right\}$$

$$\rightarrow \Delta S = nC_P \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{P_1}{P_2}\right) \quad \left. \begin{array}{l} \text{as} \\ \frac{dq}{T} = ds \text{ (we take} \\ \text{in derivative)} \end{array} \right\}$$

$$\left. \begin{array}{l} \Delta S_{\text{sum.}} = -\Delta S_{\text{syst.}} \text{ for reversible process} \\ \Delta S_{\text{sum.}} = 0 \text{ for irreversible process} \end{array} \right. \quad \begin{array}{l} \text{Notes} \\ \text{Appointment} \end{array}$$

September'15

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Saturday	5	12	19	26
Sunday	6	13	20	27

15

September

Tuesday

Week 39 • Day 265-100

- $\Delta S$  of phase transitions  
(isothermal & reversible)

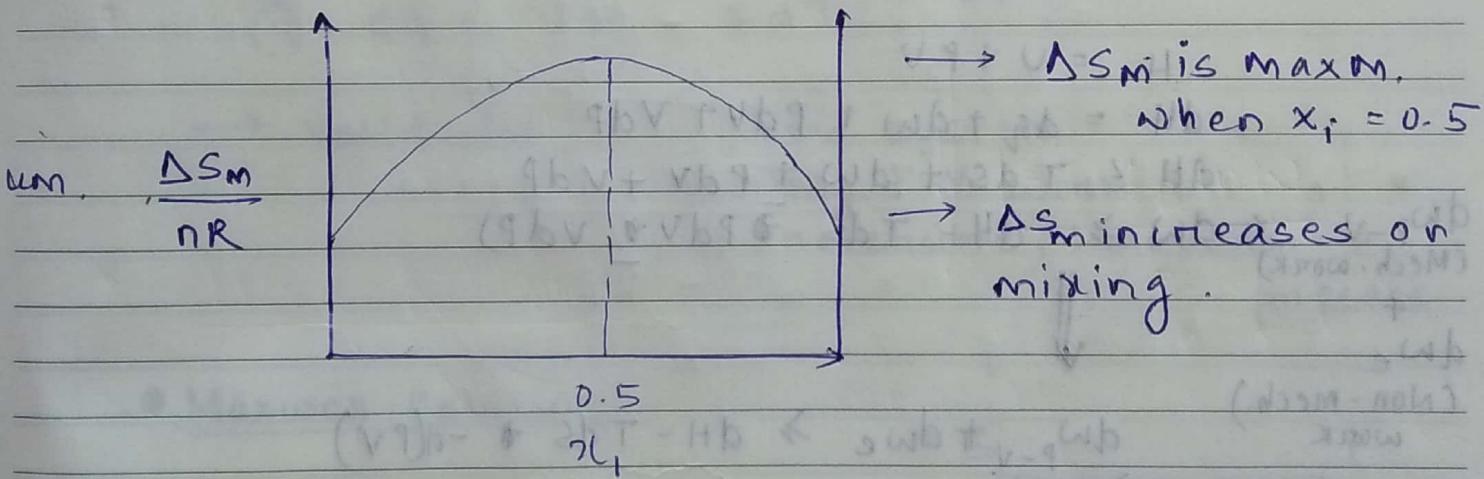
$$\boxed{\Delta S_{tr} = \frac{\Delta H_{tr, H}}{T_{tr, H}}}$$

$$\Delta S \text{ (isothermal)} = \Delta S \text{ (isothermal)} \\ \text{reversible exp.} \quad \text{irreversible exp.}$$

- $\Delta S$  for mixing of gases

$n_1$ , gas 1 and  $n_2$ , gas 2 (at const. T and P)

$$\boxed{\Delta S_m = -nR \sum x_i \ln x_i} > 0 \quad (\because x_i < 1)$$



- Helmholtz energy (A)

$$TdS \geq dq \quad (\text{Clausius Inequality})$$

October'15

Notes

Appointment

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Thursday	1	8	15	22	29
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Saturday	3	10	17	24	31
Sunday	4	11	18	25	

2015

23

Wednesday

Septe SSP Notes

Week 39 • Day 266-099

$$dU \leq Tds + dw$$

$$dw > dU - Tds \quad (*)$$

$dw$  is  $\Theta$ ve  $\rightarrow$  energy obtained from system as work.

For an isothermal, reversible process -

$$\boxed{dw_{\text{max.}} = d(U - TS)} = dA \quad (1)$$

$\rightarrow A$  is such a thermodynamic property, whose change for an isothermal reversible process gives maxm. work available during the process.

### • Gibb's Energy (G)

$$H = U + PV$$

$$dH = dq + dw + PdV + Vdp$$

$$dH \leq Tds + dw + PdV + Vdp$$

$$dw_{p-V} \leftarrow dw \geq dH - Tds - PdV - Vdp$$

(Mech. work)

+  
dwe  
(Non-mech.)  
work



$$dw_{p-V} + dwe \geq dH - Tds - d(PV)$$

$$-PdV + dwe \geq dH - Tds - PdV - Vdp$$

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Sunday	6	13	20	27

Notes

Appointment

15

September

Thursday

24

at constant P, isothermal change, Week 39 Day 267-098

$$\boxed{(dW_e)_{\max.} = d(H - TS) = dG} \quad \text{--- (2)}$$

$$G = H - TS$$

→ G is such a thermodynamic property of the system, whose change at constant T and P provides the maximum external (non-PV) work available during the process.

### • Fundamental Equations

$$(1) \quad dU = Tds - pdV$$

$$(2) \quad dH = Tds + pdV$$

$$(3) \quad dA = -pdV - SdT$$

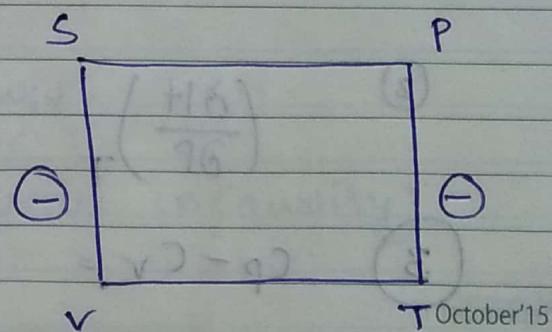
$$(4) \quad dG = Vdp - SdT$$

→ Valid for : (I) closed system  
 (II) Only P-V work  
 (III) reversible / irreversible process

### • Maxwell Relations

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

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



Notes

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2015

25

Friday

Week 39 • Day 268-097

Sept



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

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

Ex.

$$dU = Tds - PdV$$

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \text{and} \quad \left(\frac{\partial U}{\partial V}\right)_S = -P$$

$$\Rightarrow \frac{\partial^2 U}{\partial V \partial S} = \left(\frac{\partial T}{\partial V}\right)_S \quad \text{and} \quad \frac{\partial^2 U}{\partial S \partial V} = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$\Rightarrow \boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V}$$

### • Thermodynamic Equation of state

$$\textcircled{1} \quad \left(\frac{\partial U}{\partial V}\right)_T = \frac{\alpha T - kP}{k}$$

$$\textcircled{2} \quad \left(\frac{\partial H}{\partial P}\right)_T = V(1 - \alpha T)$$

September 15

$$\textcircled{3} \quad C_P - C_V = \frac{\alpha^2 PV}{K}$$

$$\textcircled{4} \quad \pi_T + P = T \left(\frac{\partial P}{\partial T}\right)_V$$

( $U = f(S, V)$ )  
Appointment

	Monday	7	14	21	28
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Notes

15

September

Saturday

- Temperature dependence of Gibb's energy

Week 39 • Day 269-096

20

$$\left[ \frac{\partial \left( \frac{\Delta G}{T} \right)}{\partial T} \right]_P = \Delta H \left[ \frac{\partial \left( \frac{1}{T} \right)}{\partial T} \right]_P = - \frac{\Delta H}{T^2}$$

(Gibb's - Helmholtz equation)

- Pressure dependence of Gibb's Energy

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

$$\Delta G = nRT \ln \left( \frac{f}{P_i} \right)$$

case I (Liquid OR Solid)

$$\boxed{\Delta G = V \Delta P}$$

$$\boxed{\frac{f}{P} = \phi}$$

Sunday 27

f = fugacity coefficient

case II (Gases) → ideal

$$\Delta G = nRT \ln \left( \frac{P_2}{P_1} \right) = nRT \ln \left( \frac{V_1}{V_2} \right)$$

- Spontaneity of a change

$$dU = dq_{rx} + dw_{rx} = dq_{irx} + dw_{irx}$$

$$dq_{irx} - dq_{rx} < 0 \text{ (Clausius inequality)}$$

$$dw_{rx} > dw_{irx}$$

$$\rightarrow |-10| > |-9|$$

Notes

Appointment

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2015

28

Monday

$$G = H - TS$$

Septem

Week 40 • Day 271-094

$$G = U + PV - TS$$

$$dG = \underbrace{dU + PdV}_{dq} + VdP - TdS - SdT$$

$$= dq + VdP - TdS - SdT$$

At const. T and P

$$dG_{P,T} = dq - TdS < 0$$

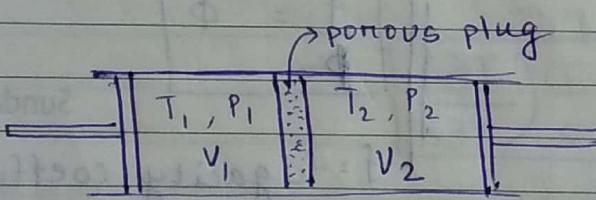
(dq - dq<sub>rev.</sub>)

$\rightarrow \Delta G < 0$  : Spontaneous change

$\Delta G = 0$  : Equilibrium

$\Delta G > 0$  : Non-spontaneous change

● Joule - Thomson effect (Application: cooling of gas)



$$\begin{aligned} P_1 &> P_2 & (dp = \text{Ex}) \\ T_1 &> T_2 \\ V_1 &< V_2 \end{aligned}$$

$\rightarrow$  Isenthalpic cooling ( $\Delta H = 0$ )

$\mu_{JT}$  = Joule - Thomson coefficient

$$= \left( \frac{\partial T}{\partial P} \right)_{\text{H}}$$

$$\mu_T = \left( \frac{\partial H}{\partial P} \right)_T$$

$$\boxed{\mu_T = \mu_{JT} C_p}$$

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Notes

Appointment

15

September

Tuesday

Week 40 • Day 272-093

$$\rightarrow U_{JT} = \frac{1}{4} C_p \left[ T \left( \frac{\partial V}{\partial T} \right)_p - V \right]$$

$$U_{JT} = \frac{1}{C_p} \left[ \frac{2a}{RT} - b \right] \quad (\text{van der waal's})$$

 $\rightarrow$  Inversion temperature

$$\boxed{U_{JT} = 0} \Rightarrow \boxed{\frac{2a}{Rb} = T_i} \quad \checkmark$$

NOTE:

 (a) isothermal reversible expansion

$$\rightarrow \Delta S_{\text{gas}} = -\Delta S_{\text{sumn.}} = nR \ln \left( \frac{V_2}{V_1} \right)$$

$$\rightarrow \Delta S_{\text{total}} = 0$$

 (b) isothermal irreversible expansion

$$\rightarrow \Delta S_{\text{gas}} = nR \ln \left( \frac{V_2}{V_1} \right) \quad \left\{ \text{as } S \text{ is a state function} \right\}$$

$$\rightarrow \Delta S_{\text{sumn.}} < 0$$

$$\rightarrow \Delta S_{\text{total}} = \Delta S_{\text{gas}}$$

 (c) an adiabatic reversible expansion

$$\rightarrow \Delta S_{\text{gas}} = 0$$

$$\rightarrow \Delta S_{\text{total}} = 0$$

Notes

$$\rightarrow \Delta S_{\text{sumn.}} = 0$$

Appointment

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2015



30

Wednesday

Septem

Week 40 • Day 273-092

SSP Notes

NOTE :

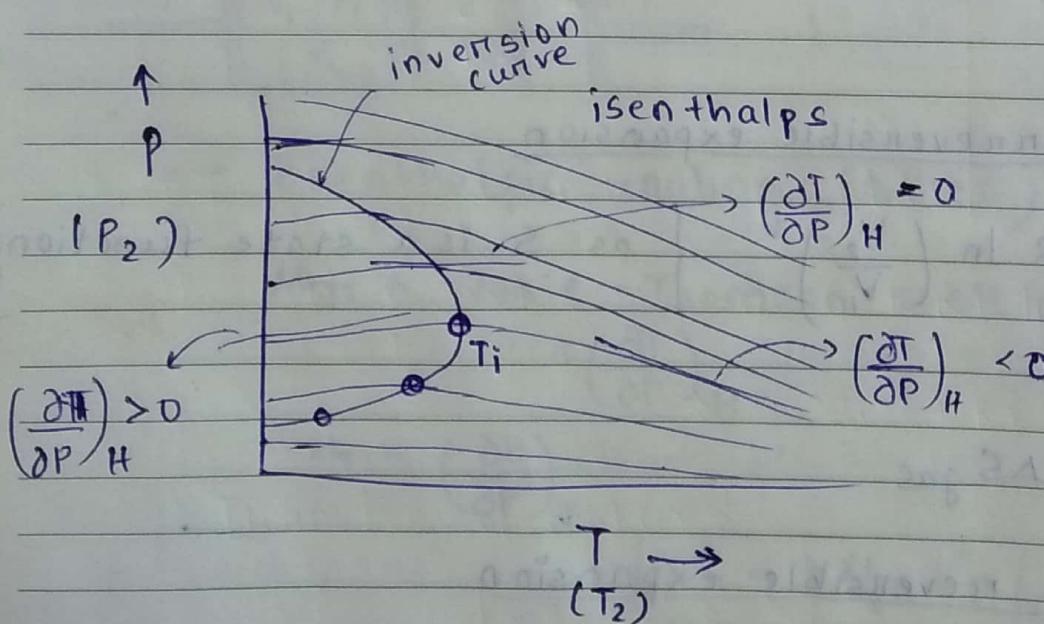
$$k_T = \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

The small isothermal compressibility tell us that we can expect a small change in volume from even a large change (increase) in pressure. So we can make following approximations :

$$k_T \approx \frac{1}{V} \left( \frac{V - V_i}{P - P_i} \right) \approx \frac{1}{V_i} \left( \frac{V - V_i}{P} \right)$$

so  $V = V_i (1 - k_T P)$   $V_i$  = volume at 1 atm

$$\rightarrow \Delta G = \int V dP = \int \frac{M}{P} (1 - k_T P) dP$$



September'15

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Saturday	5	12	19	26
Sunday	6	13	20	27

Below and above inversion curve, heating occurs only.

Notes

Appointment

15 October Open - Systems Thursday  
 ● Partial molar quantities Week 40 • Day 274-091

### (a) Partial molar volume

$$V_J = \left( \frac{\partial V}{\partial n_J} \right)_{P, T, n'}$$

$$dV = V_A dn_A + V_B dn_B$$

### (b) Partial Molar Gibb's Energy

$$\rightarrow \mu_J = \left( \frac{\partial G}{\partial n_J} \right)_{P, T, n'} = \text{chemical potential} \quad (\text{a state function})$$

$$\rightarrow dG = V dP - S dT + \mu_A dn_A + \mu_B dn_B + \dots$$

$$\underbrace{\frac{\partial G}{\partial P}_{T, V}}_{= (dW_e)_{\max.}} = \mu_A dn_A + \mu_B dn_B + \dots = \text{Max. non-PV work}$$

Fundamental equation of chemical thermodynamics

→ Further,

$$\mu_J = \left( \frac{\partial U}{\partial n_J} \right)_{S, V, n'} = \left( \frac{\partial H}{\partial n_J} \right)_{S, P, n'} = \left( \frac{\partial A}{\partial n_J} \right)_{T, V, n'}$$

Notes

Appointment

November'15

Monday	30	2	9	16	23
Tuesday	3	10	17	24	
Wednesday	4	11	18	25	
Thursday	5	12	19	26	
Friday	6	13	20	27	
Saturday	7	14	21	28	
Sunday	1	8	15	22	29

2015

02

Friday

Week 40 • Day 275-090

October

20

### Gibbs - Duhem equation

$$\left| \sum_{i=1}^N n_i d\mu_i = 0 \right|$$

Also,  
 $G = \bar{n}_A M_A + \bar{n}_B M_B + \dots$

⇒ Chemical potential of one component of a mixture cannot change independently of the chemical potentials of the other components.

In a binary mixture,

$$\left| d\mu_A = - \frac{\bar{n}_B}{\bar{n}_A} d\mu_B \right|$$

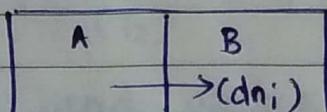
III<sup>ly</sup>  $\sum_{i=1}^N n_i^o dV_i = 0$   $V_i = \text{partial-molar volume of } i\text{-th component}$

### \* Properties of chemical potential

1) For n-moles :  $G = G^\circ + nRT \ln\left(\frac{P}{P^\circ}\right)$   
 (ideal gas)

$$\Rightarrow \mu = \mu^\circ + RT \ln\left(\frac{P}{P^\circ}\right) \quad \{ \text{per mole} \}$$

2) Transfer of matter



$\mu_{i,A}^o \quad \mu_{i,B}^o$

\* Chemical potential is an intensive property (does not depend on no. of moles)

October'15

Monday	5	12	19	26
Tuesday	6	13	20	27
Wednesday	7	14	21	28
Thursday	1	8	15	22
Friday	2	9	16	23
Saturday	3	10	17	24
Sunday	4	11	18	25

Notes

Appointment

**15**
**October**
**Saturday**

Week 40 • Day 276-089

$$dG^A = \mu_{i,A} (-dn_i)$$

$$dG^B = \mu_{i,B} (dn_i)$$

$$dG = dG^A + dG^B = (\mu_{i,B} - \mu_{i,A}) dn_i$$

⇒ Spontaneous transfer of matter occurs from region of high  $\mu$  to region of low  $\mu$ ; at equilibrium  $\mu$  of a component is same in every phase.

### 3) Mixture (mixing) of ideal gas:

$$\mu_i = \mu_i^\circ + RT \ln \left( \frac{P_i}{P_0} \right) \xrightarrow{\text{partial pressure } (= x_i P)}$$

$$\Rightarrow \mu_i = \mu_i^\circ + RT \ln \left( \frac{x_i P}{P_0} \right)$$

$$\Rightarrow \mu_i = \left[ \mu_i^\circ + RT \ln \left( \frac{P}{P_0} \right) \right] + RT \ln x_i$$

$$\Rightarrow \boxed{\mu_i = \mu_i^* + RT \ln x_i}$$

chemical potential of pure gas  $i$  under same pressure  $P$ .

$$\Rightarrow \boxed{\mu_i < \mu_i^*}$$

(ch. pot. of gas  $i$  in mixture < ch. pot. of pure gas  $i$  at a given  $T$  and  $P$ )

Notes

Appointment

November'15

Monday	30	2	9	16	23
Tuesday		3	10	17	24
Wednesday		4	11	18	25
Thursday		5	12	19	26
Friday		6	13	20	27
Saturday		7	14	21	28
Sunday	1	8	15	22	29

2015

05

Monday

Week 41 • Day 278-087

October 20

Also  $G = \sum_{i=1}^N n_i \mu_i$

$$G = \sum_{i=1}^N n_i \mu_i^* + RT \sum_{i=1}^N n_i \ln x_i$$

$$\Rightarrow G = G^* + nRT \sum_{i=1}^N x_i \ln x_i$$

pure state

Gibb's energy

$$\Rightarrow \boxed{\Delta G_m = nRT \sum_{i=1}^N x_i \ln x_i}$$

$$n = \sum n_i$$

$$\Delta S_{\text{mix.}} = - \left[ \left( \frac{\partial (\Delta G)}{\partial T} \right)_{p, N} \right] ; \Delta Y_{\text{mix.}} = \left( \frac{\partial (\Delta G_{\text{mix.}})}{\partial P} \right)_{T, n}$$

$$\text{Ans, } dG = Vdp - SdT$$

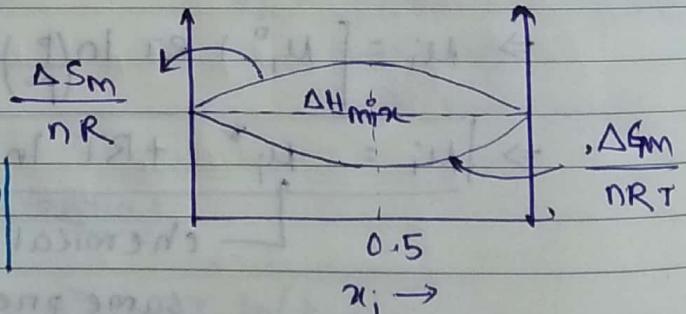
$$\left( \frac{\partial G}{\partial P} \right)_T = Y$$

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

$$\boxed{\Delta S_{\text{mix.}} = -nR \sum x_i \ln x_i}$$

$$\boxed{\Delta H_{\text{mix.}} = 0}$$

Similarly,  $\Delta U_{\text{mix.}} = \Delta Y_{\text{mix.}} = 0$   
for ideal gases



### \* Real Systems

For ideal gas :  $\mu_i = \mu_i^0 + RT \ln \left( \frac{p_i}{p_0} \right)$

For real gas :  $\mu_i = \mu_i^0 + RT \ln(f_i)$

October'15

$f_i$  = fugacity (effective pressure)

Monday	5	12	19	26
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Notes

Appointment

↳ state function

15 October Tuesday

→ ideal gas :  $f_i = p_i$ ; real gas :  $\frac{f_i}{p_i} = \gamma_i$  Week 41 • Day 279-086

$\gamma_i$  = fugacity / activity coefficient  
(measure deviation from ideality)

→  $\lim_{p_i \rightarrow 0} \frac{f_i}{p_i} = 1 \Rightarrow$  real gas behaves ideally at low pressure

→ at low pressure, attraction dominates

$f_i < p_i \Rightarrow |\gamma_i| < 1$   
think molecules  
beating

→ at high pressure, repulsion dominates

$f_i > p_i \Rightarrow |\gamma_i| > 1$

### • for solution phase

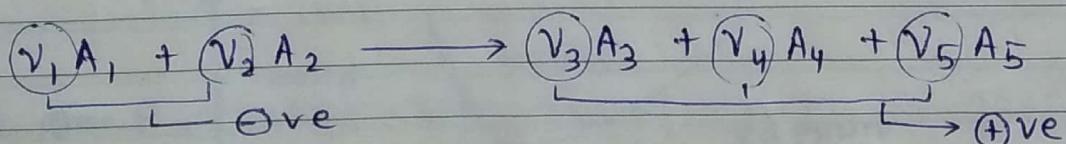
For ideal solution :  $M_i = M_i^\circ + RT \ln \gamma_i$

For real (non-ideal) :  $M_i = M_i^\circ + RT \ln \alpha_i$

$\alpha_i$  = activity. =  $\gamma_i$ ;  $\gamma_i$  = effective concentration

$\lim_{\alpha_i \rightarrow 0} \frac{\alpha_i}{x_i} = 1 \Rightarrow$  Real solution behaves ideally  
under an extremely dilute solution's  
concentration.

### \* Chemical Equilibrium



$$\left[ \sum v_i A_i = 0 \right] \quad \left\{ \begin{array}{l} \rightarrow \text{single phase reaction} \\ \rightarrow \text{At constant T and P.} \end{array} \right.$$

Appointment

November'15

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Tuesday	3	10	17	24	
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Thursday	5	12	19	26	
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2015



SSP Notes

07

Wednesday

Week 41 • Day 280-085

→ If reaction advances by  $\xi$  moles, then,  
no. of moles of  $i$ -th species at any time:

$$n_i = n_i^{\circ} + v_i \xi$$

$$\Rightarrow dn_i = v_i d\xi$$

$$dG_{p,T} = \sum u_i dn_i = \sum (u_i v_i) d\xi$$

$$\left[ \frac{(\partial G)}{(\partial \xi)} \right]_{p,T} = \Delta G_g^{\circ} = \sum v_i M_i$$

At equilibrium,  $\Delta G_g = 0$

$$\Rightarrow \boxed{\Delta G_g^{\circ} = -RT \ln K_a}$$

$$(\because \Delta G_g = \Delta G_g^{\circ} + RT \ln K_a) \quad (K_a = K_p \text{ or } K_c \text{ etc.})$$

October'15

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Notes

Appointment

15

October

Thursday

Week 41 • Day 281-084

08

## ● Phase Equilibrium

Phase: Part of a system that is uniform throughout w.r.t. chemical composition and physical properties.

Constituents: Different chemical species present in a system.

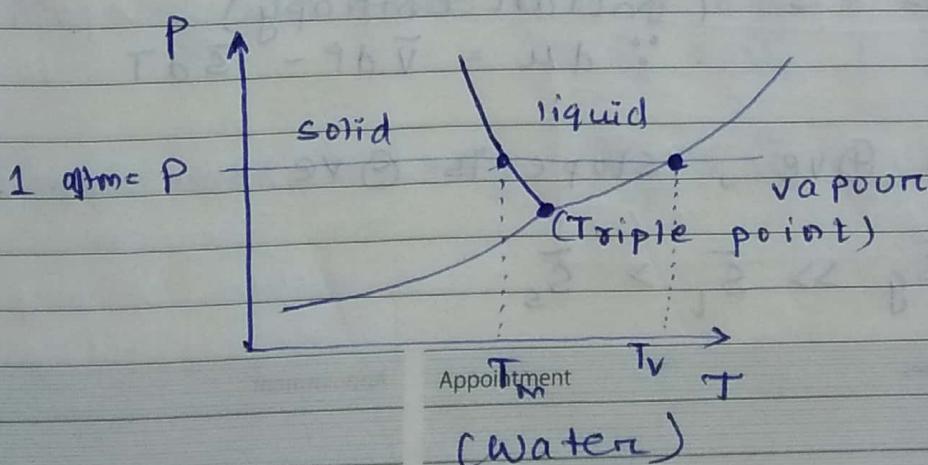
Components: Minimum number of constituents (independent species) necessary to define the composition of all the phases present in the system.

→ Constituents = components (No.) (if no reaction occurs)

## Phase rule:

If  $F$  is no. of degrees of freedom (intensive variables) that must be specified to describe the state of a system completely, then it is related to no. of components ( $C$ ) and phase ( $P$ ) of system of any composition,

$$F = C - P + 2$$



November '15

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2015

09

Friday

Week 01 • Day 000-000

October

2015

- single phase represented by area. ( $F = 1$ ) (invariant)
- When 2 phases are in equilibrium ( $F = 3 - 2$ )
  - $F = 1 \rightarrow$  one independent variable ( $P_{inj}$ ) represented by a line in phase diagram
- When 3 phases are in equilibrium
  - $F = 0 \rightarrow$  system is invariant represented by a point in phase diagram (triple point)
- When two phases are in equilibrium =

$p$	$T_p, P_p, u_p$	$\alpha = p$	$T_w, T_p$
$\alpha$	$T_w, P_w, u_w$		$P_w = P_p$

### ● Phase stability of a pure substance

#### (a) dependence on $T$

$$\left(\frac{\partial u}{\partial T}\right)_p = -\bar{s} \quad (\text{molar entropy})$$

$\therefore du = \bar{V}dT - \bar{s}dT$

$\bar{s}$  is  $\text{Ove}$ , slope is  $\text{Ove}$

$$\bar{s}_g > \bar{s}_l > \bar{s}_s$$

October 15

Month	5	12	19	26
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Thursday	2	9	16	23
Friday	3	10	17	24
Saturday	4	11	18	25

Name

Appointment

Notes

15

October

Saturday

10

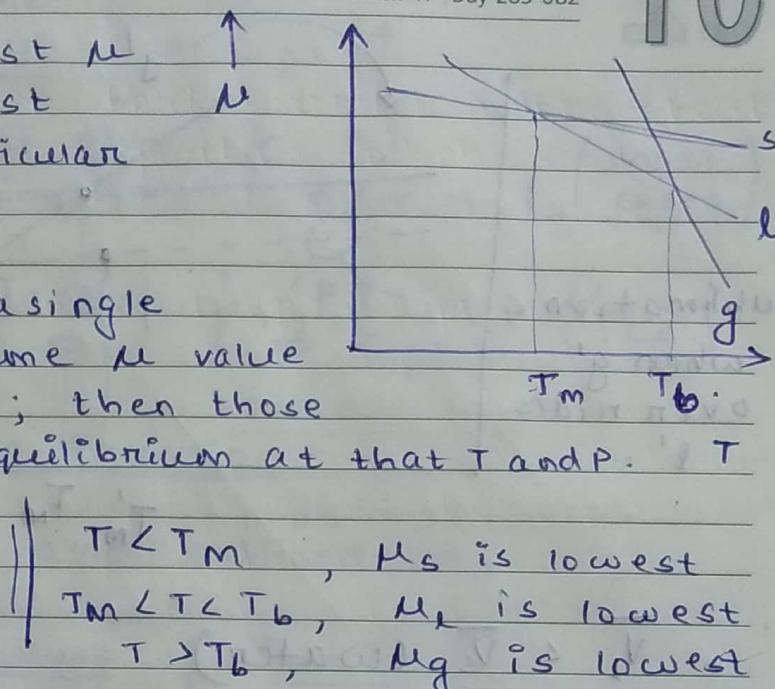
Week 41 • Day 283-082

→ Phase with lowest  $\mu$  value is the most stable at a particular  $T$  and  $P$ .

→ If two phases of a single component have same  $\mu$  value at a given  $T$  and  $P$ ; then those phases coexist at equilibrium at that  $T$  and  $P$ .

$$T = T_m, \mu_s = \mu_l$$

$$T = T_b, \mu_s = \mu_g$$



$T < T_m$ ,  $\mu_s$  is lowest

$T_m < T < T_b$ ,  $\mu_l$  is lowest

$T > T_b$ ,  $\mu_g$  is lowest

### • dependence on $P$

$$\left(\frac{\partial \mu}{\partial P}\right)_T = \bar{V} \text{ (molar volume)}$$

Sunday 11

$\bar{V}$  is positive  $\Rightarrow \mu \downarrow$  as  $P \downarrow$ ;  $T = \text{const.}$

Effect of decreasing  $P$  (depends on  $\bar{V}_s$ ,  $\bar{V}_l$  &  $\bar{V}_g$ )

Melting :  $s \leftrightarrow l \begin{cases} \bar{V}_l > \bar{V}_s : \text{decrease in } T_m \\ \bar{V}_l < \bar{V}_s : \text{increase in } T_m \end{cases}$

Vaporization :  $l \leftrightarrow g : \bar{V}_g > \bar{V}_l : \text{decrease large in } T_b.$

Notes

Appointment

November'15

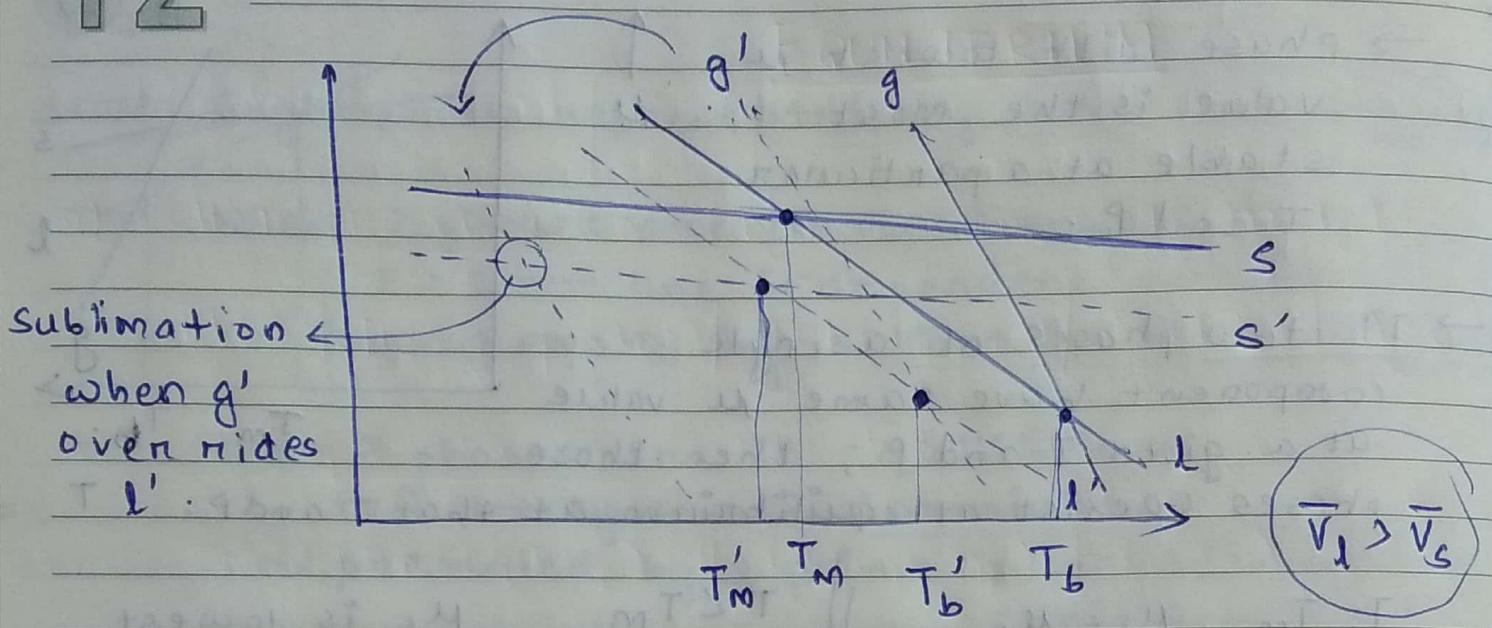
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2015

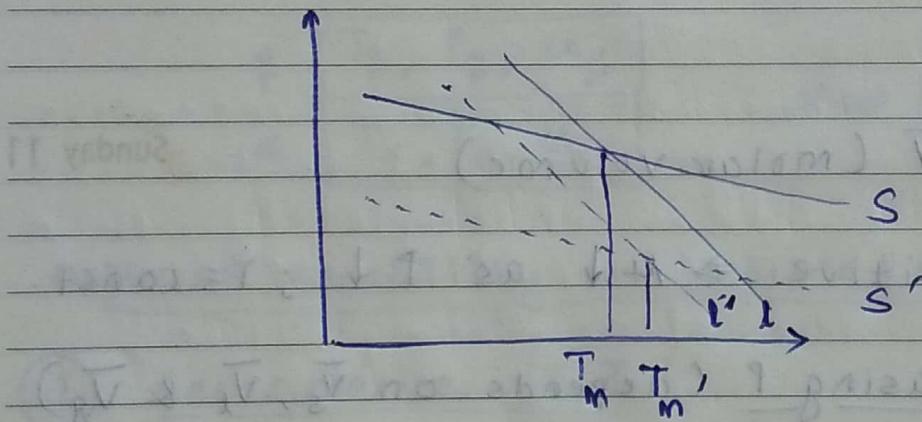
12

Monday

Week 42 • Day 285-080



$$\bar{V}_l < \bar{V}_s \text{ (water)}$$



\* Clapeyron Equation (1 component, 2 phases in eqn.)

Slope of P-T curve

$$\frac{dP}{dT} = \frac{\Delta \bar{S}}{\Delta \bar{V}} = \frac{\Delta \bar{H}}{T \Delta \bar{V}}$$

→ can be applied for any phase eqn. of a pure substance.

October'15

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Notes

Appointment

15

October

Tuesday

Week 42 • Day 286-079

(i) vaporization:  $\Delta \bar{H} \text{ } (+\text{ve})$  }  $P \uparrow$   
 $\Delta \bar{V} \text{ } (+\text{ve})$  }  $\Rightarrow b.p.t. \uparrow$

(ii) Melting: (a)  $\Delta \bar{H} \text{ } (+\text{ve})$  }  $P \uparrow$  (most cases)  
 $\Delta \bar{V} \text{ } (+\text{ve})$  }  $\Rightarrow m.p.t. \uparrow$

(b)  $\Delta \bar{H} \text{ } (+\text{ve})$  }  $P \uparrow$   
 $\Delta \bar{V} \text{ } (-\text{ve})$  }  $\Rightarrow m.p.t. \downarrow$  (ice)

### \* Clausius - Clapeyron Equation

✓  
For vaporization and sublimation,

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

Notes

Appointment

November'15

Monday	30	2	9	16	23
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2015

14

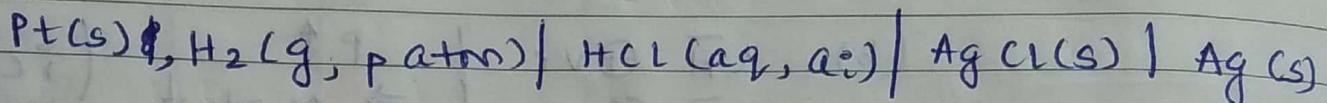
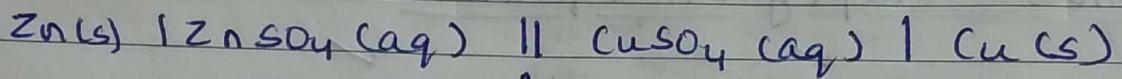
Wednesday

Week 42 • Day 287-078

ELECTROCHEMICAL

Oct

SSP Notes

EQUILIBRIUMa) Cell representation (single common electrolyte)b) Cell representation (different electrolytes)

↑  
salt bridge ( $\text{KCl}/\text{NH}_4\text{NO}_3$  soln.)  
↑  
eliminates junction  
potential

$$\text{Now } dWe = \phi dQ \quad (\phi = \text{potential diff.})$$

$dN_i = \text{no. of moles of ion } i \text{ with charge } z_i$   
 $|dQ = z_i F dN_i|$

$$dWe = \sum_{i=1}^N z_i F \phi_i dN_i$$

$\phi_i$  = electric potential of the phase containing species  $i$

October'15

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Notes

Appointment

15

October

Thursday

SSP Notes

15

Week 42 • Day 288-077

$$dG = -SdT + VdP + \sum_{i=1}^N \mu_i d\sigma_i + dw_e$$

(open system)

$$dG = -SdT + VdP + \sum_{i=1}^N [\mu_i + z_i F \phi_i] d\sigma_i$$

electrochemical potential =  $\tilde{\mu}_i$

Electrochemical equilibrium:

$$\sum_{i=1}^N [v_i \tilde{\mu}_i]_{eq} = \sum_{i=1}^N [v_i (\mu_i + z_i F \phi_i)]_{eq} = 0$$

coefficient

$$\rightarrow \boxed{\Delta G_f = -nFE}$$

NERNST EQN.

$$E = E^\circ - \frac{RT}{nF} \ln \prod a_i^{v_i}$$

$$\Delta G = -nFE = \sum v_i \mu_i$$

$$\text{At eqm., } E = 0 \Rightarrow \Delta G = \sum v_i (RT \ln a_i + \mu_i^\circ)$$

$$E^\circ = \frac{RT}{nF} \ln K_a$$

$$\Rightarrow \boxed{K_a = e^{-nFE^\circ/RT}}$$

Notes

Appointment

November'15

Monday	30	2	9	16	23
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16

Friday

Oct

$$\textcircled{1} \quad \Delta H^\circ = nRT \left[ \frac{\partial \ln P}{\partial T} \right]_P$$

$$\textcircled{2} \quad \Delta H_m^\circ = \Delta H^\circ + nRT \left[ \frac{\partial \ln P}{\partial T} \right]_P$$

$$\textcircled{3} \quad K_{T, P} = \frac{\Delta H_m^\circ}{nRT} \left( \frac{\partial \ln P}{\partial T} \right)_P$$

$$\textcircled{4} \quad \Delta G_m^\circ_{\text{standard}} = -Z_1^2 e^2 \frac{n}{R} \left( 1 - \frac{1}{Z_1} \right)$$

$Z_1$  = charge no. of the ion

$R$  = radius of ion

$G_m^\circ$  = standard relative permeability

### \* Activity of Electrolytes



$$\boxed{\mu = \mu^0 + \nu_A RT \ln \frac{P_A}{P_A^0}}$$

$$\Rightarrow \left( \mu = \mu^0 + RT \ln \frac{P_A}{P_{A_1} P_{B_1}} \right)$$

$$\frac{P_A}{P_A^0} = \frac{P_A}{P_A^0}$$

$$P_A = P_A^0$$

$$\boxed{P_A = P_A^0}$$

Standard

Molecule	S	D	B	B'
Acetone	8	11	25	37
Propane	12	14	25	38
Butane	1	8	15	28
Toluene	12	9	25	38
Styrene	8	16	27	38
Tetrahydrofuran	8	13	28	35

Molar

Concentration

$$\boxed{\frac{m_A}{V_A} = \frac{m_B}{V_B} = M}$$

15

October

Saturday

Week 42 • Day 290-075

17

where,

$$\alpha_{A\gamma^+ B\gamma^-} = (\gamma_{\pm} M_{\pm})^{\nu_{\pm}} \quad \left[ \begin{array}{l} \alpha_{A\gamma^+} = \gamma_{+} M_{+} \\ \alpha_{B\gamma^-} = \gamma_{-} M_{-} \end{array} \right]$$

$$\gamma_{\pm} = (\gamma_{+}^{\gamma_{+}} \gamma_{-}^{\gamma_{-}})^{\frac{1}{\nu_{\pm}}} \quad \left[ \begin{array}{l} \gamma_{\pm} = \nu_{+} + \nu_{-} \\ M_{\pm} = (M_1^{\gamma_{+}} M_2^{\gamma_{-}})^{\frac{1}{\nu_{\pm}}} \end{array} \right]$$

### Debye - Hückel Theory

$$\log \gamma_{\pm} = -AZ_{\pm}z_{\pm} I^{1/2} \quad | \quad A \approx 0.51 \text{ (aq. soln, } 25^\circ\text{C)}$$

$I$  = ionic mobility

$$= \frac{1}{2} \sum M_i z_i^2 = \frac{1}{2} (M_1 z_1^2 + M_2 z_2^2 + \dots) \quad \text{Sunday 18}$$

⇒ Ions with higher charges have larger effect on activity coefficients.

⇒ Ionic strength is a measure of effective influence of ions present in an electrolyte.

Important:

$$E + \frac{2RT}{F} \ln b = E^{\circ} + C b^{1/2} \quad |$$

$b = \text{Molarity}$

and  $\ln \gamma_{\pm} = \frac{E^{\circ} - E}{2RT/F} - \ln b$

November'15

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19

Monday

Week 43 • Day 292-073

pH calculation

$$E - E_{\text{cal}} = 0.0591 \text{ pH} \quad (\text{Better derive})$$

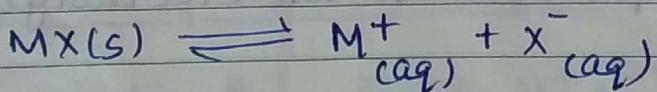
In practice:

- ① A solution of known pH is used ( $\text{pH}_1$ ), with cell potential  $E$ ,
- ② Unknown solution is used; measured potential,  $E$ .

$$\Delta E = (E_{\text{Unknown}} + E_{\text{Known}}) = 0.0591 (\text{pH}_{\text{Known}} - \text{pH}_{\text{Unknown}})$$

Use 
$$\text{pH} = \text{pH}(s) - \frac{E}{0.0591}$$

pH of standard solution

Solubility product

$$\begin{aligned} K_a &= \alpha_M + \alpha_{X^-} \\ &= S^2 \gamma_t^2 \end{aligned}$$

$$K_s = S^2 \quad (\text{for dilute solution})$$

$$\gamma_t = 1$$

October'15

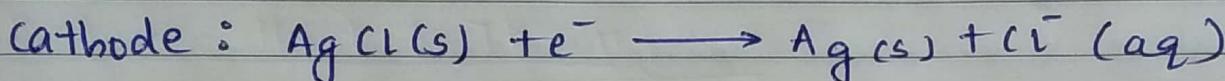
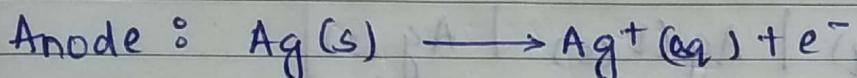
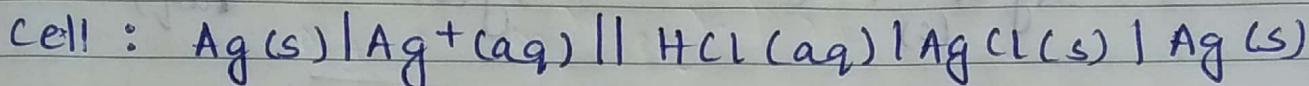
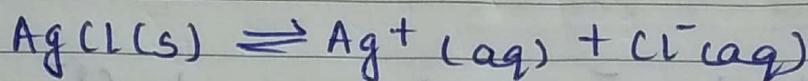
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Notes

Appointment

$$\Rightarrow K_s = e^{-\frac{\Delta F^\circ}{RT}}$$

setup a cell; where the cell reaction reproduces solubility equilibrium.



$$E^\circ_{\text{cell}} = E^\circ_R - E^\circ_L = -0.58$$

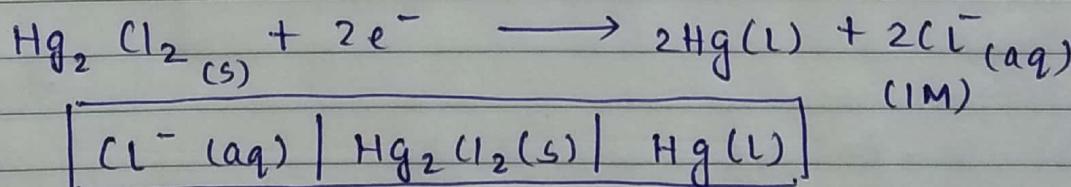
$$K_S = e^{-nFE^\circ/RT} = e^{-22.6} \quad (\text{at } 25^\circ\text{C})$$

$$K_S = 1.53 \times 10^{-10}$$

$$S = \sqrt{K_S} = 1.24 \times 10^{-5} \text{ mol kg}^{-1}$$

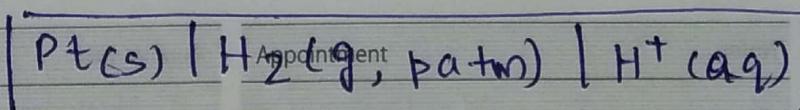
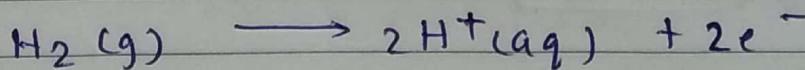
①

### Calomel electrode



②

### Standard Hydrogen electrode



November'15

Notes

Monday	30	2	9	16	23
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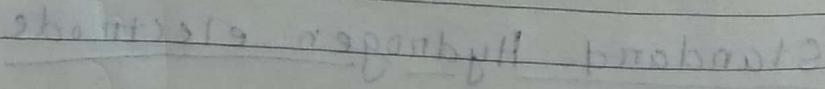
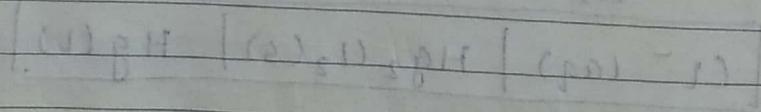
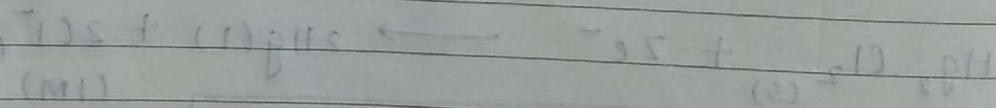
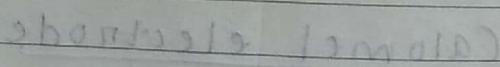
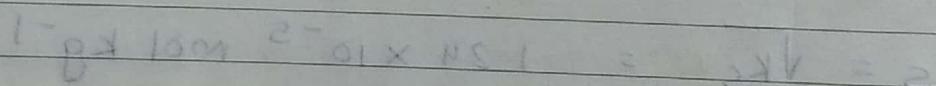
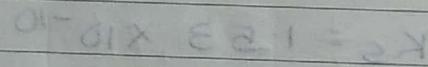
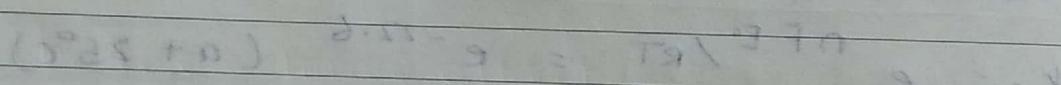
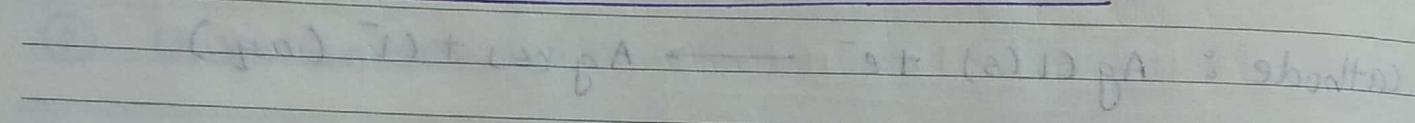
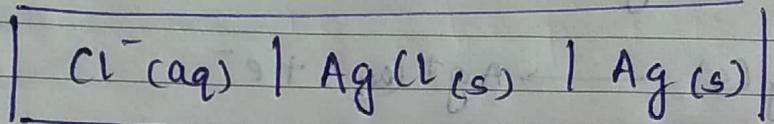
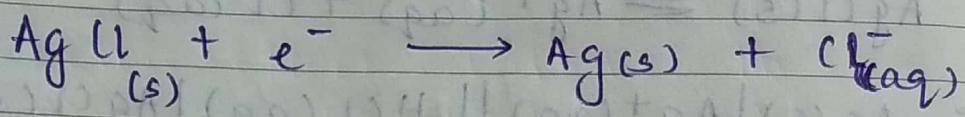
2015

21

Wednesday

Week 43 • Day 294-071

(3)

Silver Electrode

October'15

Monday	5	12	19	26
Tuesday	6	13	20	27
Wednesday	7	14	21	28
Thursday	1	8	15	22
Friday	2	9	16	23
Saturday	3	10	17	24
Sunday	4	11	18	25

Notes

Appointment

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