

Entropy

Entropy is a measure of the randomness or disorder in a system, commonly used in thermodynamics and other scientific fields to quantify how dispersed or unavailable energy becomes within a system.

How entropy changes

Entropy increases in a system

when heat energy is added, which makes the molecules more disordered and energy more spread out.

when heat energy is removed, entropy decreases, making the system more ordered. However,

according to the 2nd law of thermodynamics, in an isolated system (one that does not exchange energy or matter with its surroundings), entropy can

SUNDAY 12

13

January

MONDAY

013-352 25
3rd Week

Tue	4	11	18	25			
Wed	5	12	19	26			
Thu	6	13	20	27			
Fri	7	14	21	28			
Sat					2	9	16
					15	23	30
					3	10	17
					24	31	

only increase or remain constant
 it never naturally decreases

source and loss of entropy

Entropy increases as energy is added as heat to the system making more microscopical arrangements (microstates) accessible to the particles.

Entropy decreases if energy is removed (such as by cooling), causing particles to move less randomly, leading to fewer possible microstates and increased order.

Notes

SUN	MON	TUE	WED	THU	FRI	SAT
2 9 16 21	3 10 17 24	4 11 18 25	5 12 19 26	6 13 20 27	7 14 21 28	1 8 15 22 29

* In an isolated system, while entropy can decrease in one part (eg by energy being concentrated or organized), then it will increase by an even greater amount elsewhere, ensuring the total entropy does not decrease.

eg when ice melts in room

temp water, heat of fusion from the surrounding to the ice. The ice molecule, which were more ordered, now behave more randomly

If you want to live a happy life, tie it to a goal, not to people or things

as water so entropy of the system increases

* The surroundings (room)

09.00

lose some energy \rightarrow

10.00

become slightly more

11.00

ordered but the increase

12.00

entropy in the air-water

13.00

system outweighs the decrease

14.00

in the room, resulting in

15.00

a net increase in the

16.00

total energy, entropy

17.00

~~total energy, entropy~~

18.00

~~total energy, entropy~~

~~total energy, entropy~~

Wed	5	12	19	26	Wed	5	12	19	26
Thu	6	13	20	27	Thu	6	13	20	27
Fri	7	14	21	28	Fri	7	14	21	28
Sat	1	8	15	22	Sat	1	8	15	22

January
'25 007-358
2nd Week

TUESDAY

Gibb's free energy (ΔG)

It determines whether a process or chemical reaction will occur spontaneously at constant temp & pressure. ΔG is calculated using formulae

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

$\Delta H \rightarrow$ enthalpy change

$T \rightarrow$ Temp

$\Delta S \rightarrow$ Entropy change

$\Delta G = -ve \rightarrow$ Spontaneous

$\Delta G = +ve \rightarrow$ non spontaneous

$\Delta G = 0 \rightarrow$ equilibrium

(i) a) $\Delta H = -ve$ exothermic

If ΔS is +ve (entropy increases)

Notes

Both terms favours spontaneity

ΔG always -ve

A good plan violently executed now is better than a perfect plan next week.

e.g. \rightarrow Combustion

OO

January

WEDNESDAY

008-357

2nd Week

25

Mon	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
Tue	3	10	17	24	31	1	8	15	22	29										
Wed	4	11	18	25		2	9	16	23	30										
Thu	5	12	19	26																
Fri	6	13	20	27																
Sat	7	14	21	28																
Sun																				

(b) If ΔS is -ve (entropy decreases)

whether ΔG° is -ve depends on

the temp r, low T may make

$\Delta G^\circ = \text{VC}$ but high T the

$-T\Delta S$ term may not compensate.

(2) ΔH is +ve

(a) If ΔS is positive

At high temp r the entropy term dominates and

ΔG° can become -ve

Notes

making the process spontaneous

e.g melting of ice
 $\Delta H > 0$ $\Delta S > 0$

No one can keep a committed person from succeeding

5	12	19	26
6	13	20	27
7	14	21	28
8	15	22	29
9	16	23	30

January

25 009-356
2nd Week

THURSDAY

* If $\Delta S < 0$ both terms oppose spontaneity
 ΔH_f always +ve
 (Non spontaneous)

(3) Temperature influence

* when ΔS is +ve increasing temp^r increases the magnitude of $-T\Delta S$, making ΔG_f more -ve (more spontaneous)

* when ΔS is -ve increasing temp^r makes ΔG_f more positive reducing spontaneity

Notes

10

January

FRIDAY

11A.355 '25
2nd Week

SUN	1	15	17	28	31	TUE	7	14	21	28
TUE	2	16	18	29		WED	8	15	22	29
WED	3	17	19	30		THU	9	16	23	
THU	4	18	20	31		FRI	10	17	24	
FRI	5	19	21	22		SAT	11	18	25	

8:00

~~cryob.~~

10:00

① melting of ice (0°C)

11:00

$$\Delta H = +6.01 \text{ kJ/mol}$$

12:00

(endothermic, heat absorbed)

13:00

$$\Delta S = +22.05 \text{ J/mol K}$$

14:00

entropy increases

15:00

At ② low temp^r

16:00

$$\Delta G > 0 \text{ (no melting)}$$

17:00

$$\text{at. } T > 273, \Delta G = 0$$

18:00

equilibrium

③ combustion of CH_4

Notes

* ΔH is large and-ve ΔS is +ve

Courage is the ladder in which all other virtues mount

 ΔG always -ve, Spontaneous

13

February

THURSDAY

044-321
7th Week 25

JANUARY 2025

Sun	5	12	19	26
Mon	6	13	20	27
Tue	7	14	21	28
Wed	8	15	22	29
Thu	9	16	23	30
Fri	10	17	24	31
Sat	11	18	25	

FEBRUARY 2025

Sun	2	9
Mon	3	10
Tue	4	11
Wed	5	12
Thu	6	13
Fri	7	14
Sat	8	15

09:00

Temperature Dependence Thermodynamics function

10:00

Enthalpy Dependence on Temperature

11:00

$$\text{Enthalpy, } H = U + PV \quad \textcircled{1}$$

13:00

 $H \rightarrow \text{Enthalpy}$ $U \rightarrow \text{Internal energy}$ $P \rightarrow \text{Pressure}$

14:00

 $V \rightarrow \text{volume}$

15:00

Enthalpy represents the heat content of a system at constant pressure.

16:00

 $\textcircled{1} \Rightarrow \text{differential form}$

17:00

$$dH = dU + PdV + VdP$$

18:00

From thermodynamics 1st Law

$$dU = dq - PdV \quad \textcircled{II}$$

At constant pressure, $dP = 0$

Notes

$$\textcircled{1} \& \textcircled{II} \Rightarrow dH = dq_p$$

Thus, the change in enthalpy equals the

The aim of the wise is not to secure pleasure, but to avoid pain

February

25 045-320
7th Week

14

FRIDAY

Mon	11	8	10	17	24
Tue	12	9	11	18	25
Wed	13	10	12	19	26
Thu	14	11	13	20	27
Fri	15	12	14	21	28
Sat	16	13	15	22	29

heat absorbed at constant constant.

By definition,

$$\text{Heat capacity}, C_p = \left(\frac{dH}{dT} \right)_P$$

So,

$$dH = C_p dT \quad \text{(II)}$$

Integrating between two temp^r T_1 & T_2
of equation (III)

$$\Delta H = H(T_2) - H(T_1) = \int_{T_1}^{T_2} C_p dT \quad \text{(IV)}$$

equation (IV) shows enthalpy depends on temperature through the heat capacity

For an ideal gas, C_p is often considered constant in a limited temperature range

Notes

$$\Delta H = C_p (T_2 - T_1)$$

For a real system, C_p is a function of T . A common polynomial form

Unless commitment is made, there are only promises and hopes, but no plans

15

February

SATURDAY

046-319 25
7th Week

Mon	6	13	20	27	Mon	3	10	17	24
Tue	7	14	21	28	Tue	4	11	18	25
Wed	1	8	15	22	Wed	5	12	19	26
Thu	2	9	16	23	Thu	6	13	20	27
Fri	3	10	17	24	Fri	7	14	21	28
Sat	4	11	18	25	Sat	1	8	15	22

is

$$C_p = a + bT + cT^2 + dT^{-2}$$

Then

$$\Delta H = \int_{T_1}^{T_2} (a + bT + cT^2 + dT^{-2}) dT$$

$$\Delta H = a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) + \frac{c}{3}(T_2^3 - T_1^3)$$

$$- d \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Enthalpy - Temp relationship for ideal gas

For 1 mole of an ideal gas

$$H(T) = H^\circ + \int_{T^\circ}^T C_p(T) dT$$

where H° is the enthalpy at reference temp16 SUNDAY Thus, enthalpy increases with temperature, the rate of increase being determined by C_p .

Notes

For solids and liquids, C_p is nearly constant over moderate temp ranges

Creativity is allowing yourself to make mistakes

So, ΔH or ΔH ΔH or ΔT

SUN	5	12	19	26	WED	2	9	16	23	30
MON	6	13	20	27	THU	3	10	17	24	
TUE	7	14	21	28	FRI	4	11	18	25	
WED	1	8	15	22	SAT	5	12	19	26	

February

25 DEB-317
8th Week

MONDAY

for gases

C_p varies significantly with T . At higher temperatures, vibrational modes contribute, increasing C_p .

Since ~~enthalpy~~ enthalpy is a function of state variables: T & P

$$dH = C_p dT + \left[v - T \left(\frac{\partial v}{\partial T} \right)_P \right] dP$$

at constant pressure

$$dH = C_p dT$$

Reaction enthalpy and temperature

Kirchhoff's law,

The enthalpy of reaction varies with temperature

Notes

$$\Delta H_T = \Delta H_{T_0} + \int_{T_0}^T \Delta C_p dT$$

where $\Delta C_p = \sum v_i C_{p,i}$ (stoichiometric heat capacities)

The greatest test of courage on earth is to bear defeat without losing heart

In summary

09.00

- enthalpy depends only on temperature and pressure

10.00

At constant pressure,

11.00

ΔH depends solely on C_p and ΔH

12.00

For solids and liquids, C_p is nearly constant \rightarrow linear dependence

13.00

For gases, C_p increases with temp

14.00

(due to rotational and vibrational modes)

15.00

For reactions, enthalpy correction

16.00

with temperature is made using Kirchhoff's law.

17.00

Actual standard molar enthalpies of formation

Sun	10	2	9	16	23	Sun	6	11	20	27
Mon	11	3	10	17	24	Mon	7	14	21	28
Tue	4	11	18	25		Tue	1	8	15	22
Wed	5	12	19	26		Wed	2	9	16	23
Thu	6	13	20	27		Thu	3	10	17	24
Fri	7	14	21	28		Fri	4	11	18	25
Sat	1	8	15	22	29	Sat	5	12	19	26

Entropy Variation with temperature

Entropy (S) is a state function and is defined for a reversible process as

$$dS = \frac{dq_{rev}}{T} \quad \text{--- (1)}$$

$T \rightarrow \text{temp}^{\circ}$.

where dq_{rev} is the reversible heat absorbed by the system at temp $^{\circ}$ T .

Entropy changes with temperature can be expressed in terms of heat capacity

$$dq_{rev} = \frac{C}{dT} \quad \text{--- (II)}$$

when C is the heat capacity (C_p at const. pressure or C_v at constant volume)

Substituting

$$(I) \& (II) \Rightarrow dS = \frac{C}{T} dT \quad \text{--- (III)}$$

Integrating

Notes If the temperature changes from T_1 to T_2

$$\Delta S = \int_{T_1}^{T_2} \frac{C}{T} dT$$

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February

THURSDAY

051-314 25
6th Week

JANUARY 2025

Sun	5	12	19	26
Mon	6	13	20	27
Tue	7	14	21	28
Wed	8	15	22	29
Thu	9	16	23	30
Fri	10	17	24	31
Sat	11	18	25	

FEBRUARY 2025

Sun	2	9	16	23
Mon	3	10	17	24
Tue	4	11	18	25
Wed	5	12	19	26
Thu	6	13	20	27
Fri	7	14	21	28
Sat	8	15	22	29

Change of entropy with respect to

temp r at different conditions —

- For constant heat capacity

$$\Delta S = C \ln \left(\frac{T_2}{T_1} \right)$$

- At constant volume

$$\Delta S = C_v \ln \left(\frac{T_2}{T_1} \right)$$

- At constant pressure

$$\Delta S = \bar{C}_p \ln \left(\frac{T_2}{T_1} \right)$$

General case

Heat capacity depends on temperature

For solids and gases we can express it as

$$C = a + bT + cT^2 + \dots$$

Notes So entropy change becomes

$$\Delta S = \int_{T_1}^{T_2} \frac{a + bT + cT^2 + \dots}{T} dT$$

$$\Delta S = a \ln\left(\frac{T_2}{T_1}\right) + b(T_2 - T_1) + \frac{c}{2}(T_2^2 - T_1^2)$$

This is useful for real systems where C is not constant

Summary

At very low temp^r ($T \rightarrow 0$)

According to the Third Law of thermodynamics, entropy approaches a constant minimum value and taken as zero for perfectly crystalline substance.

$$S \rightarrow 0 \text{ as } T \rightarrow 0$$

At high temperature

Entropy increases because more molecular states (microstates) become accessible.

Notes Thus entropy is a monotonically increasing function of temp^r.

22

February

SATURDAY

093-012 25
8th Week

JANUARY 2025

Sun	5	12	19	26	Sun	2	9	16	23
Mon	6	13	20	27	Mon	3	10	17	24
Tue	7	14	21	28	Tue	4	11	18	25
Wed	1	8	15	22	Wed	5	12	19	26
Thu	2	9	16	23	Thu	6	13	20	27
Fri	3	10	17	24	Fri	7	14	21	28
Sat	4	11	18	25	Sat	8	15	22	29

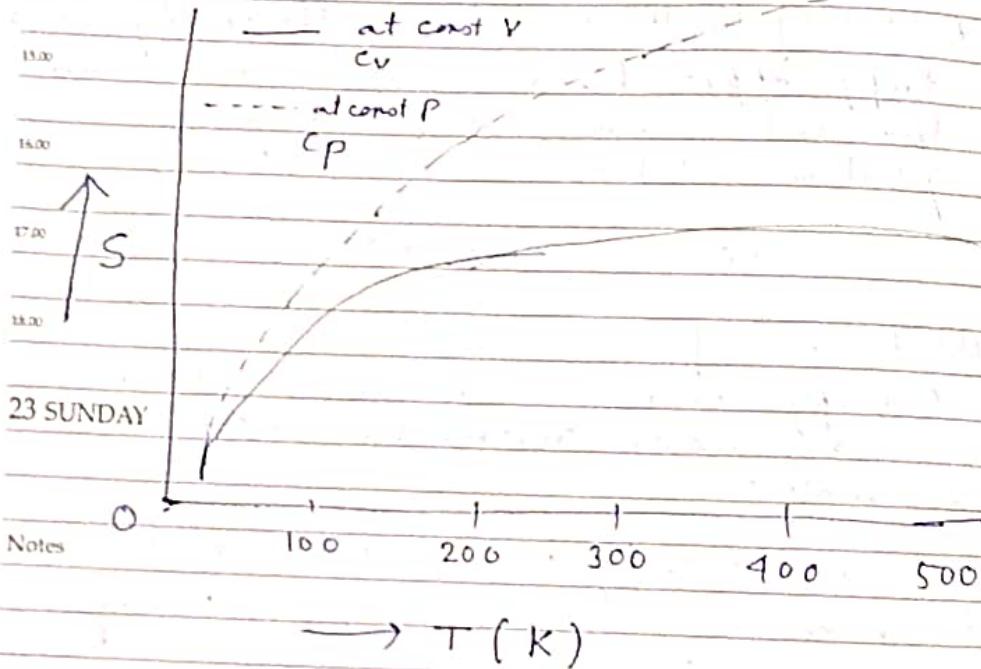
FEBRUARY 2025

Graphical representationS vs T curve

- starts near zero at absolute zero (for perfect crystal)

- Increases smoothly with temperature

$$\text{slope} = \frac{ds}{dT} = \frac{C}{T}$$



23 SUNDAY

Wed	5	12	19	26	Wed	2	9	16	23	30
Thu	6	13	20	27	Thu	3	10	17	24	
Fri	7	14	21	28	Fri	4	11	18	25	
Sat	1	8	15	22	Sat	5	12	19	26	

February

25
9th Week

MONDAY

9:00 Variation of Gibb's free energy with temperature

10:00 Gibb's free energy (G_f)

$$G_f = H - TS \quad \text{--- (i)} \quad \begin{aligned} H &\rightarrow \text{Enthalpy} \\ T &\rightarrow \text{Absolute Temp} \\ S &\rightarrow \text{Entropy} \end{aligned}$$

13:00 G_f is thermodynamics potential that determines the spontaneity of a process at constant P & T .

15:00 Differential form of eq (i)

$$dG_f = dH - TdS - SdT \quad \text{--- (ii)}$$

$$17:00 \text{ At const. Pressure, } dH = TdS + VdP \quad \text{--- (iii)}$$

$$18:00 (ii) \& (iii) \Rightarrow dG_f = VdP - SdT$$

At const pressure $dP = 0$

$$(dP = 0)$$

Notes

$$\left(\frac{dG_f}{dT} \right)_P = -S \quad \text{--- (iv)}$$

26

February

TUESDAY

25

24	1	14	21	28
25	2	15	22	29
26	3	16	23	30
27	4	17	24	31
28	5	18	25	

Integrating eq (iv)

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

$$U(T) = U(T_0) - \int_{T_0}^T S dT$$

q.f. S is approximately constant over the temp range

$$U(T) = U(T_0) - S(T - T_0)$$

This shows that U decreases linearly with T if S is constant.

For a chemical reaction

$$\Delta U = \Delta H - T \Delta S$$

- AT low T, the ΔH term dominates

- AT high temp, the $-T \Delta S$ term dominates

- If $\Delta S > 0$, the reaction becomes more spontaneous as T increases
- If $\Delta S < 0$, the reaction becomes less spontaneous with rise in T.

Notes

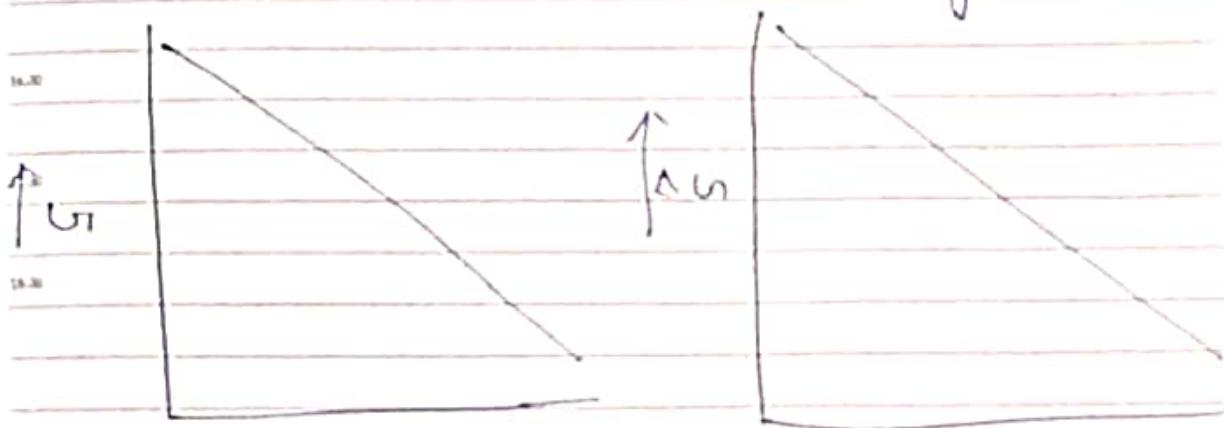
Conclusion

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

- Gibbs free energy always decreases with ~~size~~ temp at constant pressure

- For reactions

• $\Delta U = \Delta H - T\Delta S$ explains temp dependence of spontaneity



Notes

Graph I

ΔU vs T

ΔU decreases linearly with T at constant pressure

Slope = $-S$

$\rightarrow T$

Graph II

ΔH vs T

For a reaction
 Intercept = ΔH
 Slope = $-\Delta S$

Determination of Enthalpy Experimentally

Enthalpy change (ΔH) is determined experimentally using a calorimeter, where the heat absorbed or evolved during a process is measured at constant pressure. The (reaction mixture) is placed in the calorimeter and the temperature change (ΔT) of the surrounding water or solution is recorded using the relation

$$q_p = \Delta H = m c \Delta T$$

where m = mass of solution
 c = specific heat capacity
 ΔT = Temperature rise / fall, the enthalpy change is calculated.

For reactions where direct measurement is not possible; Hess's Law or bond enthalpies are used.

At constant pressure, the heat evolved or absorbed in chemical reaction is equal to the enthalpy change (ΔH)

$$\Delta H = qp$$

Apparatus.

- i) calorimeter vessel (thermally insulated)
- ii) Thermometers
- iii) Stirrer
- iv) Known mass of water or solution

Procedure

A known mass (volume) of solution / H_2O is taken in the calorimeter.

The initial temperature is measured initially.

The reaction (neutralization, dissolution or combustion) is carry out inside the calorimeter.

The maximum or minimum temperature attained is recorded.

The temperature change (ΔT) is calculated

with help of following relation

$$Q = m C \Delta T$$

At constant, $\Delta H = Q_p$

$$\Delta H_{\text{molar}} = \frac{Q_p}{n}$$

The in this way enthal (molar) is calculated.

Corrections & Accuracy

Heat loss to surroundings should be minimized.

Calorimeter constant may be determined using a standard reaction

SUNDAY Stirring ensures uniform temperature

Determination of entropy experimentally

Entropy of a system can not be measured directly but it is determined from reversible heat changes.

Entropy change (ΔS) is obtained using following relation experimentally

$$\Delta S = \frac{dq_{rev}}{T}$$

The heat absorbed or evolved (dq) during a reversible process is measured calorimetrically.

For isothermal processes, entropy change is calculated as

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p}{T} dT$$

Entropy is measured from heat capacity measurements as mentioned above

- Entropy of Phase Transitions

During a reversible Phase change (fusion, vaporisation etc) at constant T .

$$\Delta S = \frac{\Delta H_{\text{trans}}}{T}$$

- Absolute entropy (Third Law method)

According to the third law of Thermodynamics, entropy of a perfectly crystalline substance at absolute zero is zero.

$$S_0 = 0 \text{ at } T = 0 \text{ K}$$

$$S(T) = \int_0^T \frac{C_p}{T} dT + \left[\sum \frac{\Delta H_{\text{trans}}}{T} \right]$$

Experimental Tools used

Calorimetry - To measure heat capacities and enthalpy of transitions.

Cryogenic techniques - For low temp^r entropy measurements.

Entropy is determined experimentally by calorimetric measurements of heat capacities and enthalpy change.

Coming together, sharing together, working together, succeeding together

05

March

WEDNESDAY

064-301
10th Week 25

of Phase transitions and applying
 the relation

$$\Delta S = \int \frac{C_P}{T} dT + \underline{\Delta H_{\text{trans}}}$$

FEBRUARY 2025				
Sun	2	9	16	23
Mon	3	10	17	24
Tue	4	11	18	25
Wed	5	12	19	26
Thu	6	13	20	27
Fri	7	14	21	28
Sat	1	8	15	22

MARCH				
Sun	30	2		
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Tue		4		
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Fri		7		
Sat	1	8	15	15

Wed	2	9	16	23	30
Thu	3	10	17	24	
Fri	4	11	18	25	
Sat	5	12	19	26	

Mon	1	8	15	22	29
Tue	2	9	16	23	30
Wed	3	10	17	24	31
Thu	4	11	18	25	

March
'25 065-300
10th Week

THURSDAY

Gibbs Free Energy Determination (Experimental)

Gibbs Free energy change (ΔG_f) is determined experimentally from equilibrium measurements.

At equilibrium, the relationship is

$$\Delta G_f = -RT \ln K \quad \textcircled{1}$$

$R \rightarrow$ gas constant

$T \rightarrow$ Absolute temp'

$K \rightarrow$ equilibrium constant of the reaction

Measuring concentrations or partial pressures of reactants and products of reactants and products at equilibrium K value is calculated. The calculated value of K is put into eqn $\textcircled{1}$ to obtain the value of ΔG_f .

Alternatively, ΔG_f can be calculated from electrochemical cell experiments using following relations

$$\Delta G_f = -nFE$$

$n \rightarrow$ No. of electrons

$F \rightarrow$ Faraday

Successful leaders have the courage to take action where others hesitate

$E \rightarrow$ EMF of cell

FRIDAY

March

Date 200 25
10th Week

Tue	4	11	18	25	Tue	4	11	18	25
Wed	5	12	19	26	Wed	5	12	19	26
Thu	6	13	20	27	Thu	6	13	20	27
Fri	7	14	21	28	Fri	7	14	21	28
Sat	1	8	15	22	Sat	1	8	15	22

A galvanic cell is constructed and EMF of cell is measured accurately and ΔG° value is calculated.

- Van't Hoff method (Temperature dependence)

Gibb's free energy is related to enthalpy (ΔH) and entropy (ΔS)

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

By calorimetric experiments

ΔH and ΔS are measured then

ΔG° is calculated at given temperature.

Sun	5	12	19	26
Mon	6	13	20	27
Tue	7	14	21	28
Wed	8	15	22	
Thu	9	16	23	
Fri	10	17	24	
Sat	11	18	25	

January

25 016-349
3rd Week

THURSDAY

Chemical Potential

Chemical potential is a fundamental thermodynamic property that measures the change in a system energy when the quantity of a substance is increased by one unit while temp^r and pressure remain constant.

Partial derivative of Gibbs's free energy with respect to the no of particles of a substance symbolized as $\mu = \left(\frac{\partial U}{\partial N} \right)_{T, P}$ at constant temp^r and pressure.

If μ represents the energy required to add one mole of particles to the system and is a measure of the chemical energy intensity of a system.

Courage is resistance to fear, mastery of fear not absence of fear

Mrs. Jane

within a syste

17

January

FRIDAY

017-348 25
3rd Week

DECEMBER 2024

Sun	1	8	15	22	29
Mon	2	9	16	23	30
Tue	3	10	17	24	31
Wed	4	11	18	25	
Thu	5	12	19	26	
Fri	6	13	20	27	
Sat	7	14	21	28	

Sun	5	12	19	26
Mon	6	13	20	27
Tue	7	14	21	28
Wed	1	8	15	22
Thu	2	9	16	23
Fri	3	10	17	24
Sat	4	11	18	25

Role of chemical potential in thermodynamics

chemical potential plays a crucial role in

- Equilibrium: At chemical or phase equilibrium, the chemical potential of a substance are equal across all phases or parts of the system, ensuring no net spontaneous change occurs. For example: In a liquid-vapour system, equilibrium is reached when chemical potential of the liquid equals that of the vapour.

Sun	3	10	17	24
Mon	4	11	18	25
Tue	5	12	19	26
Wed	6	13	20	27
Thu	7	14	21	28
Fri	1	8	15	22
Sat	2	9	16	23

January

'25 018-347
3rd Week

18

SATURDAY

(*) Phase transition: It helps determine

the conditions under which phases

co-exist or transform, such as

m.pt. vaporization or crystallization

(*) Chemical reactions

It influences reaction spontaneity

and direction by affecting the

system free energy landscape

(*) Separation process

It guides processes like distillation where substances separate based

on differences in chemical potential

Notes

FEB

MAR

APR

SUNDAY 19

20

January

MONDAY

020-345 '25
4th Week

Wed	4	11	18	25
Thu	5	12	19	26
Fri	6	13	20	27
Sat	7	14	21	28

Thu	2	9	15	22	29
Fri	3	10	17	24	31
Sat	4	11	18	25	

09.00 Examples of μ

10.00 consider a liquid vapour equilibrium system. The chemical potential of the substance in

11.00 a liquid phase equals the chemical potential in the

12.00 vapor phase at equilibrium.

13.00 If the chemical potential in the vapour is lower, molecules tend to

14.00 evaporate from the liquid to

15.00 vapour to increase energy

16.00 stability until equilibrium is established. This equality

Notes

of chemical potential prevents further net transfer of molecules between phases.

FEBRUARY		Sun	Mon	Tue	Wed	Thu	Fri	Sat
Sun	2	9	16	23				
Mon	3	10	17	24	Mon	31	3	10
Tue	4	11	18	25	Tue	4	11	18
Wed	5	12	19	26	Wed	5	12	19
Thu	6	13	20	27	Thu	6	13	20
Fri	7	14	21	28	Fri	7	14	21
Sat	8	15	22	Sat	1	8	15	22

January

[25] 021-344
4th Week

21

TUESDAY

The chemical potential is defined as the change in a system Gibbs free energy when one mole of a component is added at constant P & T. moreover other components constant. of a state function. It represents partial molar Gibbs free energy of a component in a mixture. Chemical potential determines how the Gibbs energy and other thermodynamics potential change with the number of particles and it plays a key role in establishing phase and chemical equilibria. Identity is such a crucial affair that one should not miss it.

22

January

WEDNESDAY

022-343 25
4th Week

Mon	5	12	19	26	1	8	15	22	29
Tues	6	13	20	27	2	9	16	23	30
Fri	7	14	21	28	3	10	17	24	31

At equilibrium, chemical potentials of components are equal across phases or uniform within a homogeneous system and the sum of chemical potentials multiplied by stoichiometric coefficients in a reaction equals zero. It is fundamental in understanding how mixtures behave thermodynamically, as changes in composition directly affect the system's free energy via chemical potential.

Notes

7 14 21 28
7 14 21 28
8 15 22 Sat 1 8 15 22 29

- Pure gases A and B have chemical potentials in mixt at standard pressure
- In the mixture, each component's chemical potential changes according to its partial pressure
- The change in chemical potential reflects changes in Gibbs free energy on mixture
- * equilibrium in mixtures requires equality of chemical potentials in same phases or components

FRIDAY

January

024-341 25
4th Week

Wed	4	11	18	25	Wed	1	8	15
Thu	5	12	19	26	Thu	2	9	16
Fri	6	13	20	27	Fri	3	10	17
Sat	7	14	21	28	Sat	4	11	18

09.00

Other example

10.00

The Cribbo - Duhem equation at constant temp'r and pressure is

13.00

$$n_A d\mu_A + n_B d\mu_B = 0$$

14.00

where

- n_A , n_B are the mole nos of components A & B

16.00

- $d\mu_A$, $d\mu_B$ are the infinitesimal changes in their chemical potential

Notes

If we express mole numbers as mole fractions

$$x_A + x_B = 1$$

$$x_A \partial \mu_A + x_B \partial \mu_B = 0$$

Let for binary mixture at.

a certain composition, the mole fraction of A is $x_A = 0.4$

$$\text{L B is } x_B = 0.6$$

If the change in chemical potential for A with respect to composition is

known as

$$\partial \mu_A = 2 k_J / \text{mol}$$

MONDAY

January
027-338 '25
5th WeekFri 6 13 20 27
Sat 7 14 21 28
Fri 3 10 17 24
Sat 4 11 18 25

Using the Cribb's Duhem

equation calculate $\Delta \mu_B$

$$0.4 \times 2 + 0.6 \times d \mu_B = 0$$

$$\therefore 0.8 + 0.6 d \mu_B = 0$$

$$\therefore 0.6 d \mu_B = -0.8$$

$$d \mu_B = \frac{-0.8}{0.6}$$

$$= -1.33 \text{ kJ/mol}$$

This result tells us that the change in chemical

Notes

potential of component B

is -1.33 kJ/mol

SUN	3	10	17	24
MON	4	11	18	25
TUE	5	12	19	26
WED	6	13	20	27
THU	7	14	21	28
FRI	8	15	22	29
SAT	1	8	15	22

when compound A changes by $\frac{1}{2} \text{ kJ/g/mol}$ in

chemical potential at this composition, maintaining the equilibrium constant

Given by Cribbs - Tuhey

equation.

* Another example

when mixing ethanol and water the chemical potential helps explaining the behaviour of the mixture. Ethanol and water form

29

January

WEDNESDAY

029-336 '25
5th Week

Sun	1	8	15	22	Mon	6	13	19	26
Mon	2	9	16	23	30	7	14	21	28
Tue	3	10	17	24	31	Wed	1	8	15
Wed	4	11	18	25	Thu	2	9	16	23
Thu	5	12	19	26	Fri	3	10	17	24
Fri	6	13	20	27	Sat	4	11	18	25
Sat	7	14	21	28					

a two component system

where the chemically potential of each component depends on its concentration. Mixing ethanol

and H₂O results in interation that change the partial

molar volumes \rightarrow chemical potentials of both components

e.g. total vol^m of equal volumes

of ethanol & water becomes less than the sum of their separate volumes due to favourable molecular interactions & hydrogen bonding

Exothermic result -

chemical potential changes for both ethanol & water in the mixture compared to pure substances.

01

January

WEDNESDAY

001-364 25
1st Week

Mon	2	9	16	23	30	Tue	7	14	21	28
Tue	3	10	17	24	31	Wed	8	15	22	29
Wed	4	11	18	25		Thu	2	9	16	23
Thu	5	12	19	26		Fri	3	10	17	24
Fri	6	13	20	27		Sat	4	11	18	25

09:00 Thermodynamics description of mixtures in details 10:00

Mixtures in thermodynamics are

11:00 described by examining how
their properties differ from
12:00 pure substances, especially when multiple
components are combined to form
13:00 a single phase such as a solution
or gas mixture. The main focus is on
14:00 how mixing affects key thermodynamic
quantities.

15:00 Gibbs free energy, entropy and
enthalpy.

16:00 Thermodynamics quantities for mixtures 17:00

18:00 When two or more substances mix,
their molecules interpose changing
the system's molecular environments
and the thermodynamic properties,
which are especially dynamic in
Notes mixture.

Mon	4	11	18	25	Tue	5	12	19	26
Wed	5	12	19	26	Thu	6	13	20	27
Thu	6	13	20	27	Fri	7	14	21	28
Fri	7	14	21	28	Sat	1	8	15	22
Sat	1	8	15	22					

January

'25 002-363
1st Week

THURSDAY

* Gibbs' free energy of mixing

The change in Gibbs' energy describes the spontaneity of mixing. For two ideal gases

$$\Delta_{\text{mix}} G = nRT (\chi_1 \ln \chi_1 + \chi_2 \ln \chi_2)$$

$\chi_1 \rightarrow$ mole fraction of 1

$\chi_2 \rightarrow$ " 2

This value is -ve, meaning mixing happens spontaneously

under constant pressure and temperature as system moves towards higher disorder (entropy)

* Entropy of mixing: Mixing increases randomness and thus entropy for ideal gases.

$$\Delta_{\text{mix}} S = -nR (\chi_1 \ln \chi_1 + \chi_2 \ln \chi_2)$$

Since mole fraction can be in

Talent wins games, but teamwork and intelligence wins championships

between 0 & 1, the entropy change

US

January

FRIDAY

003-362 25
1st Week

Mon	2	9	16	23	30	Mon	6	13	20	27
Tue	3	10	17	24	31	Tue	7	14	21	28
Wed	4	11	18	25		Wed	1	8	15	22
Thu	5	12	19	26		Thu	2	9	16	23
Fri	6	13	20	27		Fri	3	10	17	24
Sat	7	14	21	28		Sat	4	11	18	25

09.00

always +ve, reflecting the increased disorder

10.00

* Enthalpy of mixing! For

11.00

ideal mixtures (especially gases)
the enthalpy change is zero

13.00

$$\Delta_{\text{mix}} H = 0$$

14.00

this holds because ideal gas molecules do not interact

15.00

significantly mixing does not absorb or release heat

16.00

Partial molar properties

Notes

In mixtures, the properties of each component depend on the composition of the mixture because the

SUN	5	12	19	26	MON	7	14	21	28
MON	6	13	20	27	TUE	8	15	22	29
TUE	7	14	21	28	WED	9	16	23	30
WED	8	15	22	29	THU	10	17	24	31
THU	11	18	25		FRI	12	19	26	
FRI	13	20	27		SAT	14	21	28	
SAT	15	22	29		SUN	16	23	30	

January

25 004-361
1st Week**SATURDAY**

molecular environment varies

Partial Molar Volume:

The partial molar volume of a component describes how adding more of it changes the total volume of the mixture, factoring in interactions with other components.

Let 1 mole of N_2 and 1 mole

of H_2 are mixed at constant P.

Let $n = 2$ mole Total mole.

$$H_2 \Rightarrow \text{mole fraction} = .5$$

SUNDAY 05

$$N_2 \Rightarrow .5 \quad .5 = .5$$

$$\Delta S_{\text{mix}} = (2 \text{ mol}) \times R \ln 2$$

$$= 11.5 \text{ J,}$$

Strength lies in differences, not in similarities

The value means reflects both increase in randomness i.e. in gases

MONDAY

January
006-359 '25
2nd WeekThu 5 12 19 26
Fri 6 13 20 27
Sat 7 14 21 28Thu 2 9 16
Fri 3 10 17
Sat 4 11 18

distribute throughout the containers

09.00

10.00

11.00

12

13.00

4.00

5.00

00

10

0

es

* Enthalpy change, $\Delta_{\text{mix}} H = 0$

- No heat is produced or absorbed during mixing

* Gibbs energy change

$$\Delta_{\text{mix}} G = -n R T \left(\ln x_1 + x_2 \ln \frac{x_2}{x_1} \right)$$

~~negative~~

Exothermic

Want T ~~low~~ and x_1 ~~high~~ for $\Delta_{\text{mix}} G$ to be

~~negative~~

Want T ~~high~~ and x_1 ~~low~~ for $\Delta_{\text{mix}} G$ to be

~~positive~~

Want T ~~high~~ and x_1 ~~high~~ for $\Delta_{\text{mix}} G$ to be

~~positive~~

Want T ~~low~~ and x_1 ~~low~~ for $\Delta_{\text{mix}} G$ to be

~~negative~~

Want T ~~high~~ and x_1 ~~low~~ for $\Delta_{\text{mix}} G$ to be

~~positive~~

VII.32. Chemical Potential: Gibbs-Duhem Relations

The free energy (G) of a given system as a state function depends upon the parameters (P, T, V). Since these three are interrelated, we may write, for a system of fixed composition, $G = f(P, T)$.

But if we take an open system in which the quantities of the components may also vary, the free energy will depend upon the amounts of the components. Suppose we have a system containing n_1 moles of A_1 , n_2 moles of A_2 , n_3 moles of A_3 , etc, then its free energy,

$$G = f(P, T, n_1, n_2, n_3, \dots)$$

If all the variables undergo change, the total differential will be given by,

$$dG = \left(\frac{\partial G}{\partial P} \right)_{T, n_1} dP + \left(\frac{\partial G}{\partial T} \right)_{P, n_1} dT + \left(\frac{\partial G}{\partial n_1} \right)_{P, T, n_2, n_3, \dots} dn_1 + \left(\frac{\partial G}{\partial n_2} \right)_{P, T, n_1, n_3, \dots} dn_2 + \dots$$

Remembering $\left(\frac{\partial G}{\partial P} \right)_{T, n_1} = V$, and $\left(\frac{\partial G}{\partial T} \right)_{P, n_1} = -S$,

$$dG = VdP - SdT + \left(\frac{\partial G}{\partial n_1} \right)_{P, T, n_2, n_3, \dots} dn_1 + \left(\frac{\partial G}{\partial n_2} \right)_{P, T, n_1, n_3, \dots} dn_2 + \dots \quad \dots \quad \dots \quad \text{(VII.80)}$$

The terms like $\left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_1,n_2\dots}$ means that P, T and all other mole numbers except n_i have been kept constant during differentiation. It is called the partial molal free energy of that component (A_i).

The partial molal free energy expressed as $\left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j}$ for the i th component is called its chemical potential and is denoted by the symbol, μ_i .

The chemical potential (μ_i) is thus the rate of increase in Gibbs free energy per mole of the component (i) added. We may say, μ_i is the free energy increase of the system when 1 mole of this component is added to an infinitely large amount of the system so as to keep the composition practically unaltered.

Expressing partial molal free energies in terms of μ , we can rewrite equation (VII.80) at constant temperature and pressure,

$$dG_{P,T} = \mu_1 dn_1 + \mu_2 dn_2 + \mu_3 dn_3 + \dots = \sum \mu_i dn_i \quad \dots \text{ (VII.81)}$$

Next imagine that at constant P and T , all the constituents are increased in the same proportion (Δx). That is, A_1 is increased by an amount $n_1 \Delta x$ moles, A_2 is increased by $n_2 \Delta x$ moles, ... A_i is increased by $n_i \Delta x$ moles. Hence,

$$dn_1 = n_1 \Delta x, \quad dn_2 = n_2 \Delta x, \quad dn_i = n_i \Delta x, \text{ etc.}$$

Since G is an extensive property, this will also increase by an amount $G \cdot \Delta x$, i.e.,

$$dG = G \Delta x$$

Now, applying equation (VII.81),

$$dG = \mu_1 n_1 \Delta x + \mu_2 n_2 \Delta x + \dots + \mu_i n_i \Delta x + \dots$$

$$\text{or } G \Delta x = \mu_1 n_1 \Delta x + \mu_2 n_2 \Delta x + \dots + \mu_i n_i \Delta x + \dots$$

$$\text{Hence, } G = \mu_1 n_1 + \mu_2 n_2 + \dots + \mu_i n_i + \dots = \sum \mu_i n_i.$$

Now complete differentiation of this equation gives us,

$$\begin{aligned} dG &= (\mu_1 dn_1 + \mu_2 dn_2 + \mu_3 dn_3 + \dots) \\ &\quad + (n_1 d\mu_1 + n_2 d\mu_2 + n_3 d\mu_3 + \dots) \quad \dots \text{ (VII.82)} \end{aligned}$$

Subtracting equation (VII.81) from (VII.82),

$$n_1 d\mu_1 + n_2 d\mu_2 + n_3 d\mu_3 + \dots = 0$$

We have thus three useful relations for chemical potentials with the composition of the system.

$$\left. \begin{array}{l} (i) \quad G = \mu_1 n_1 + \mu_2 n_2 + \mu_3 n_3 + \dots = \sum \mu n \\ (ii) \quad dG = \mu_1 dn_1 + \mu_2 dn_2 + \mu_3 dn_3 + \dots = \sum \mu dn \\ (iii) \quad 0 = n_1 d\mu_1 + n_2 d\mu_2 + n_3 d\mu_3 + \dots = \sum n d\mu \end{array} \right\} \quad \dots \text{ (VII.83)}$$

These are commonly known as Gibbs-Duhem relations.

APRIL 2025

	SUN	M	TUE	WED	THU	FRI	SAT		
SUN	6	13	20	27	Sun	4	11	18	25
Mon	7	14	21	28	Mon	5	12	19	26
TUE	1	8	15	22	TUE	6	13	20	27
WED	2	9	16	23	WED	7	14	21	28
THU	3	10	17	24	THU	1	8	15	22
FRI	4	11	18	25	FRI	2	9	16	23
SAT	5	12	19	26	SAT	3	10	17	24

MAY 2025

	SUN	M	TUE	WED	THU	FRI	SAT		
SUN	4	11	18	25	SUN	4	11	18	25
Mon	5	12	19	26	Mon	5	12	19	26
TUE	6	13	20	27	TUE	6	13	20	27
WED	7	14	21	28	WED	7	14	21	28
THU	1	8	15	22	THU	1	8	15	22
FRI	2	9	16	23	FRI	2	9	16	23
SAT	3	10	17	24	SAT	3	10	17	24

March

25 06-2025
10th Week

SATURDAY

08

Thermodynamic Description of Phase transitions.

A phase transition is the transformation of a system from one (solid, liquid, gas, plasma) to another, accompanied by abrupt changes in certain thermodynamics properties.

Thermodynamics provides a rigorous framework to describe these transitions in terms of free energy, entropy, enthalpy and Gibb's potential.

Classification of phase transitions.

1. First order Phase transitions

(a) Characterized by discontinuity in 1st derivatives of Gibb's free energy (eg. entropy, volume)

e.g. melting, boiling and sublimation

SUNDAY 09

(b) Latent heat is absorbed or released

Notes: (c) Clapeyron equation describes slope of phase boundary

APR

10

March

MONDAY

06-9-296
11th Week 25

FEBRUARY 2025

Sun	2	9	16	23
Mon	3	10	17	24
Tue	4	11	18	25
Wed	5	12	19	26
Thu	6	13	20	27
Fri	7	14	21	28
Sat	1	8	15	22

Sun	30	2	9	16	23
Mon	31	3	10	17	24
Tue	4	11	18	25	1
Wed	5	12	19	26	8
Thu	6	13	20	27	15
Fri	7	14	21	28	22
Sat	1	8	15	22	29

(2) Second-order Phase transitions

(a) First derivatives of G_f are continuous but second derivatives (heat capacity, compressibility, expansion coefficient) are discontinuous.

(b) No latent heat

(c) e.g.: Superconducting transition,

Ferromagnetic to paramagnetic transition (Curie point)

(3) At constant T and P , the stable phase is determined by the lowest Gibbs's free energy (G_f)

Condition for phase equilibrium between two phases α & β :

$$G_{f\alpha} = G_{f\beta}$$

$$\mu_\alpha = \mu_\beta$$

Notes

1	8	15	22	29
2	9	16	23	30
3	10	17	24	
4	11	18	25	
5	12	19	26	

Wed 7 14 21 28
 Thu 8 15 22 29
 Fri 9 16 23 30
 Sat 10 17 24 31

25 070-295
 11th Week

TUESDAY

④ clausius - clapeyron Equation (For 1st order transitions)

clausius - clapeyron equation describes
 the slope of the phase boundary in P-T diagram

$$\frac{\partial P}{\partial T} = \frac{\Delta S}{\Delta V} = \frac{L}{T \Delta V}$$

- L = Latent heat of transition
- ΔS = entropy change
- ΔV = volume change

This equation is fundamental in
 describing vapour - liquid equilibrium
 solid - liquid equilibrium etc.

12

March

WEDNESDAY

071-291 '25
11th Week

Mon	3	10	17	24	Mon	30	2
Tue	4	11	18	25	Tue	31	3
Wed	5	12	19	26	Wed	4	11
Thu	6	13	20	27	Thu	5	12
Fri	7	14	21	28	Fri	6	13
Sat	1	8	15	22	Sat	7	14
						8	15
						9	16

(5) Entropy and Enthalpy changes

09.00

10.00

11.00

12

13.00

14.00

15.00

16.00

17.00

18.00

otes

In first-order transitions, entropy (ΔS) and enthalpy (ΔH) undergo finite discontinuities.

In second-order transitions, entropy changes continuously but heat capacity (C_p) diverges at transition.

temp²

(6) Stability of a phase is determined by second derivatives of G_f .

$$\left(\frac{\partial^2 G_f}{\partial T^2}\right)_P = -\frac{C_p}{T} \leftarrow 0$$

At phase boundaries, these stability conditions change character leading to transition.

Mon	1	8	15	22	29	Tue	6	13	20	27
Tue	2	9	16	23	30	Wed	7	14	21	28
Wed	3	10	17	24		Thu	1	8	15	22
Thu	4	11	18	25		Fri	2	9	16	23
Fri	5	12	19	26		Sat	3	10	17	24
Sat							31			

March

25 072-293
11th Week

THURSDAY

① At the critical point

(eg liquid - gas) $\Delta V \rightarrow 0$

and distinction phases vanishes

Thermodynamics response functions

(eg compressibility, heat capacity)

often diverge.

In short,

Thermodynamics describes phase

transitions through Gibbs free energy
chemical potential, entropy

enthalpy and stability conditions.

VII.29. Change of Phase: Clapeyron-Clausius equation

In the study of changes of phase in a system such as freezing, vaporisation etc. thermodynamic relations are quite useful. In such phase-changes, there is a correlation between the pressure and the temperature at which the change takes place.

(a) Let G_1 and G_2 be the free energies of a liquid and its vapour which are in equilibrium in a system at temperature T . Imagine a virtual change of a small amount of liquid vaporising at equilibrium. The drop in free energy of the liquid is $-\Delta G_1$ and the gain in the same for the vapour is $+\Delta G_2$. Since the system is in equilibrium, net $\Delta G = 0$,

$$\therefore -\Delta G_1 + \Delta G_2 = 0$$

$$\text{or} \quad \Delta G_1 = \Delta G_2$$

$$\text{i.e.,} \quad V_1 \Delta P - S_1 \Delta T = V_2 \Delta P - S_2 \Delta T$$

$$\text{or} \quad \frac{\Delta P}{\Delta T} = \frac{S_2 - S_1}{(V_2 - V_1)} = \frac{\Delta S}{(V_2 - V_1)}$$

$$\text{i.e.,} \quad \frac{dP}{dT} = \frac{T \Delta S}{T(V_2 - V_1)} = \frac{L}{T(V_2 - V_1)}$$

where L is the latent heat of the process.

This is called the Clapeyron-Claudius equation. It may also be written in other ways.

(b) From Maxwell's relations, we have

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

When two phases are in equilibrium, say a solid and a liquid or a liquid and a vapour, the vapour pressure is independent of the mass and hence, of the volume. Therefore, in such cases, we may write,

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

Further, if we consider the latent heat of the change, L , as nearly constant and independent of temperature, we have

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T} \left(\frac{\partial Q}{\partial V}\right)_T = \frac{L}{T(V_2 - V_1)}$$

$$\text{Thus, } \frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}, \quad \dots \text{ (VII.63)}$$

V_2 and V_1 being the final and initial volumes of the system. The equation is applicable to all phase-changes.

The sign of $\frac{dP}{dT}$ depends on the signs of L and ΔV . Thus, if L is positive and $V_2 > V_1$, there would be a rise in pressure with increase in temperature. In the evaporation of a liquid these conditions prevail, and as such, the vapour pressure increases with rise in temperature. In the melting of a solid, L is positive and if $V_2 > V_1$, melting temperature would increase with pressure as in the case of paraffin. But if $V_2 < V_1$, higher pressure will lower the melting temperature, as in the case of ice.

This relation would also apply to the transformation of one modification of a solid to another, say α -sulphur to β -sulphur; L would, of course, mean the heat of transformation.

The Clapeyron-equation may be simplified in the case of vaporisation of a substance. In such a case, the relation is,

$$\frac{dP}{dT} = \frac{L}{T(V_g - V_l)}, \quad (V_g = \text{volume of gas}, \\ V_l = \text{volume of liquid}).$$

Since $V_l \ll V_g$, so approximately,

$$\frac{dP}{dT} = \frac{L}{TV_g} = \frac{L}{T(RT/P)} = \frac{L \cdot P}{RT^2}, \quad (\text{for one mole})$$

assuming the vapour to behave as a perfect gas,

$$\frac{1}{P} \frac{dP}{dT} = \frac{L}{RT^2} \quad \dots \text{ (VII.64)}$$

$$\therefore \frac{d \ln P}{dT} = \frac{L}{RT^2}, \quad \dots \text{ (VII.65)}$$

or

where L is the latent heat per gm-mole.

If we further assume that the latent heat practically remains constant in the temperature range T_1 to T_2 , the integration of this relation gives,

$$I = \frac{L}{R} \ln \left(\frac{P_2}{P_1} \right) + C \quad \dots \text{ (VII.66)}$$

or

$$\ln \frac{P_1}{P_2} = -\frac{L}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \quad \dots \text{ (VII.67)}$$

i.e.,

$$\log \frac{P_1}{P_2} = -\frac{L}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \quad \dots \text{ (VII.68)}$$

It is needless to mention that this relation is also applicable to sublimation processes where L would be the latent heat of sublimation.

Application etc.

Application of clausius - clapeyron equation in phase diagram of water

The clausius - clapeyron equation gives the slope of the phase boundary lines in a P-T phase diagram :

$$\frac{dP}{dT} = \frac{\Delta H_{\text{trans}}}{T \Delta V_m}$$

where $\frac{dP}{dT}$ = slope of co-existence curve
(phase boundary)

ΔH_{trans} = enthalpy change of transition
(fusion, vaporization,
sublimation)

$\Delta V = V_2 - V_1$ = change in molar

Expect the best, plan for the worst and prepare to be surprised

volume during transition

1	8	15	22	29
2	9	16	23	30
3	10	17	24	
4	11	18	25	
5	12	19	26	

Tue	6	13	20	27
Wed	7	14	21	28
Thu	1	8	15	22
Fri	2	9	16	23
Sat	3	10	17	24

March

25 074-291
11th Week**SATURDAY**

$T \rightarrow \text{Temp}^*$ at which transition occurs

Water has three main phase boundaries
solid-liquid, liquid-vapour and $S \rightleftharpoons V$

1. Fusion curve Solid-Liquid boundary

For most substances

$$V_{\text{liq}} > V_{\text{solid}} \quad \text{So}$$

$$\Delta V_{\text{fusion}} > 0$$

So slope $\frac{dP}{dT}$ is +ve

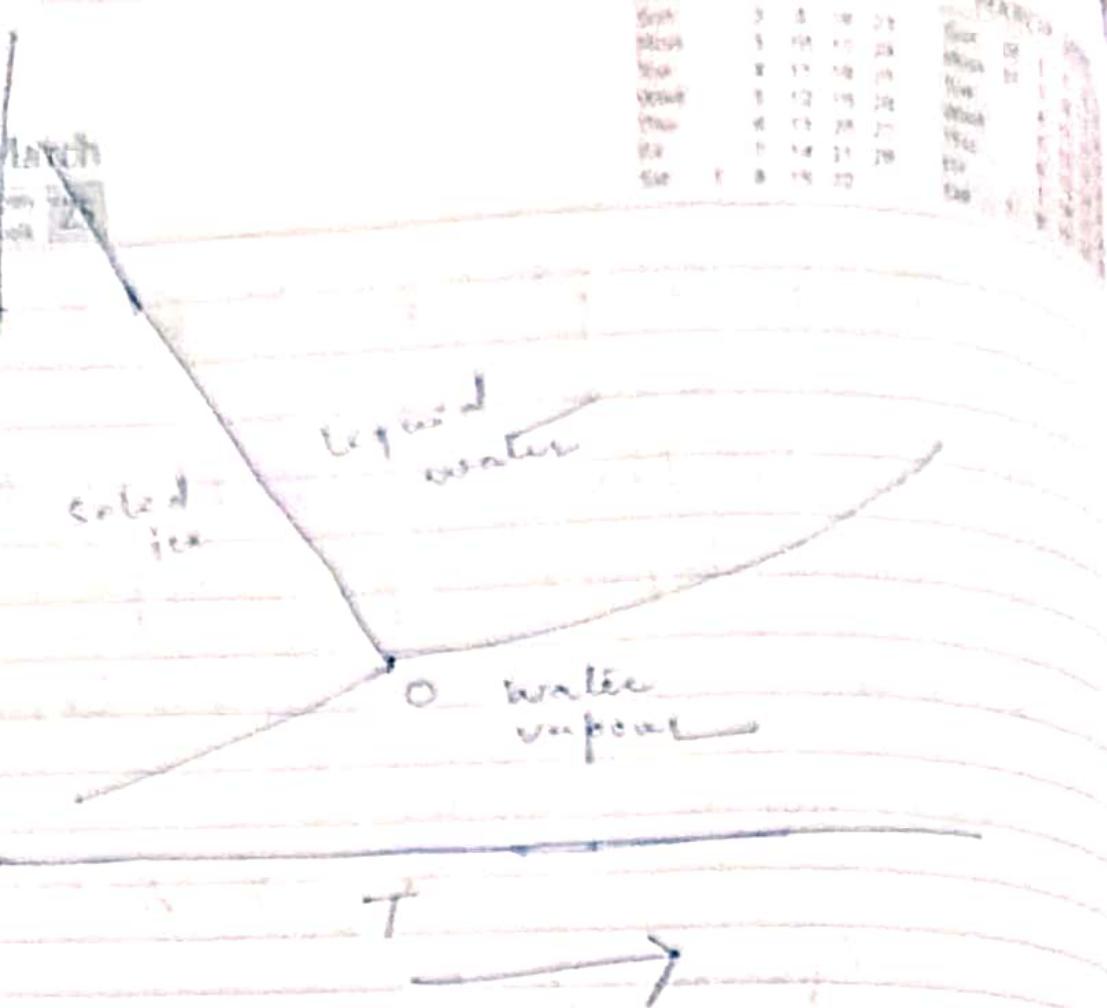
But in water, however, ice is less dense than liquid water (due to hydrogen-bonded structure)

SUNDAY 16

So, $V_{\text{liq}} < V_{\text{solid}}$

$$\Rightarrow V_{\text{fusion}} < 0$$

So slope $\frac{dP}{dT}$ is negative



solid - liquid line water phase
curve tilts to the left. This
is applying pressure lowers the
melting point of ice.

by skating is possible - Pressure
on ice under the skate blade

Sun	2	5	10	15	20
Mon	3	10	17	24	
Tue	4	11	18	25	
Wed	5	12	19	26	
Thu	6	13	20	27	

2. Liquid-vapour Boundary (vaporization curve)

$\Delta H_{\text{vap}} > 0$ (endothermic) and ΔV_{vap} is very large (since $V_{\text{gas}} \gg V_{\text{liq}}$)

Therefore, slope $\frac{dP}{dT}$ is +ve but small

This gives the steeply rising vapour pressure curve.

3. Solid-vapour Boundary (sublimation curve)

Here $\Delta H_{\text{sub}} > 0$ and $\Delta V_{\text{sub}} \approx \text{gas volume}$

Slope is +ve

Notes

explains how ice can sublime directly at low pressure.

WEDNESDAY

March

17th Week 25

Mon	1	10	17	24	Mon	1	12	2	9	15
Tue	2	11	18	25	Tue	2	13	3	10	16
Wed	3	12	19	26	Wed	3	14	4	11	17
Thu	4	13	20	27	Thu	4	15	5	12	18
Fri	5	14	21	28	Fri	5	16	6	13	19
Sat	6	15	22	Sat	6	17	7	14	20	26
Sun	7	16	23	Sun	7	18	8	15	21	27

Thermodynamics of Non-ideal systems

In real systems, deviations from the ideal behaviour occur due to molecular interactions and finite molecular sizes. The study of thermodynamics of non-ideal systems helps in understanding phase equilibria, solution behavior and chemical reactions under realistic conditions.

① Ideal vs Non-Ideal system

- Ideal system: No intermolecular forces obeys ideal gas law ($PV=nRT$) or Raoult's law in solutions
- Non-ideal system

Shows deviation due to intermolecular attractions / repulsions and finite volume of molecules.

② Equation of state for Non-Ideal gases

	Mon	Tue	Wed	Thu	Fri	Sat
Sun	6 13 20 27	Sun	4 11 18 25			
Mon	7 14 21 28	Mon	5 12 19 26			
Tue	8 15 22 29	Tue	6 13 20 27			
Wed	9 16 23 30	Wed	7 14 21 28			
Thu	10 17 24	Thu	8 15 22 29			
Fri	11 18 25	Fri	9 16 23 30			
Sat	12 19 26	Sat	10 17 24 31			

March

25
12th Week

20

THURSDAY

For real gases, ideal gas law is modified using corrections.

Van-der-Waals Equation

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

- $a \rightarrow$ attractive forces
- $b \rightarrow$ excluded volume.

③ Fugacity and Activity

Since pressure and concentration alone can not describe non-ideal system, New thermodynamic functions are introduced

• Fugacity (f): effective pressure of a real gas replacing actual pressure

$$\mu = \mu^\circ + RT \ln f$$

Our greatest Strength as a human race is our ability to acknowledge our differences

Activity (a) : effective concentration
in solution.

$$\mu = \mu^\circ + RT \ln a$$

(ii) Activity co-efficient (γ)

$$a_i = \gamma_i x_i$$

$\gamma_i \rightarrow$ activity co-efficient

(measures deviation from ideal)

$\gamma = 1$ for ideal solution

SUN	6	13	20	27
MON	7	14	21	28
TUE	8	15	22	29
WED	9	16	23	30
THU	10	17	24	
FRI	11	18	25	
SAT	12	19	26	

March

25 081-284
12th Week**SATURDAY**

22

(5) Excess functions

To quantify non-ideality in mixtures, excess properties are defined.

$$M^E = M^{\text{real}} - M^{\text{ideal}}$$

These are crucial for predicting phase diagrams and solution thermodynamics.

(6) Thermodynamics Description of Non-ideal solution

- Positive deviation from Raoult's law

Weak solute - solvent interaction

Henry's law becomes more

NT

March

MONDAY

06.30 25
1st. week

Sun	5	12	19	26
Mon	6	13	20	27
Tue	7	14	21	28
Wed	8	15	22	29
Thu	9	16	23	30

- Negative deviation

Strong solution - solvent interaction then vapour pressure is less.

Modified Raoult's law

$$P_i = \chi_i \gamma_i P_i^*$$

⑦ Partial molar quantities

For Non-ideal mixtures, partial molar properties (eg \bar{G} , \bar{H} , \bar{V}) describe how thermodynamic functions vary with composition

⑧ Cribb's - Duhem equation

Links activity co-efficient

Components in a mixture

$$\sum_i n_i d\mu_i = 0$$

Conclusion

The thermodynamics of non-ideal systems introduces concepts like fugacity, activity and activity

co-efficients to correct

deviations from ideality.

These corrections are essential for practical applications in solution chemistry, chemical engineering and materials science.

Notes

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WEDNESDAY

March

095-240
13th Week 25

Tue	4	11	18	25	100	4	11	18	25
Wed	5	12	19	26	100	5	12	19	25
Thu	6	13	20	27	100	6	13	20	27
Fri	7	14	21	28	100	7	14	21	28
Sat	1	8	15	22	100	1	8	15	22

Activity and Activity co-efficient

In thermodynamics and solution chemistry of activity is introduced to account for deviations from ideal behaviour. For ideal solutions, the concentration is sufficient to describe the system. However, in non-ideal systems, interactions among particles cause deviations, which are corrected by using activity (α) and activity co-efficient (γ).

Activity is the effective concentration of a species in a system, which accounts for non-ideal interactions.

For ideal system:

$$\text{activity} = \text{actual concentration}$$

For Non-ideal systems:

$$\text{Activity} = \text{concentration} \times \text{correction factor}$$

$$\alpha_i = \gamma_i C_i$$

α_i = activity of species

γ_i = activity co-efficient

 There are two things to aim at to get what you want and enjoy it

C_i = molar concentration
(For solution)

Notes

	APRIL 2014
SUN	6 13 20 27
MON	7 14 21 28
TUE	8 15 22 29
WED	9 16 23 30
THU	10 17 24 31
FRI	11 18 25
SAT	12 19 26

March

'25 ORG-279
13th Week

27

THURSDAY

Activity Co-efficient (γ)

The activity co-efficient is a dimensionless factor that measures the deviation of a real solution from ideal behaviour.

 a_i

$$\gamma_i = \frac{a_i}{c_i / c^\circ}$$

For ideal system $\gamma_i = 1$ so activity equals to concentration

For non ideal system

- If $\gamma_i > 1$, +ve deviation
(repulsion dominates)

- If $\gamma_i < 1$, -ve deviation
(attraction dominates)

- In chemical equilibria concentration is represented by activity

$$K = \prod (a_i)^{\nu_i}$$

- In electrochemistry: Nernst equation uses activity instead of concentration
- In colligative properties: Activity explains deviations from Raoult's law.

The factors affecting activity

Co-efficient

① Concentration — deviation increases with higher solution concentration

② Ionic strength — In ionic solutions, γ depends on ionic atmosphere

③ Temperature and pressure affect intermolecular forces, thus γ

To map out a course of action and follow it to an end requires courage

1	12	21	29
2	13	22	30
3	14	23	31
4	15	24	
5	16	25	
6	17	26	
7	18	27	
8	19	28	
9	20	29	
10	21	30	
11	22	31	
12	23	24	
13	25	26	
14	27	28	
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31			

25 MAR 27
13th Week

SATURDAY

(11) Nature of solute and solvent

Polarity, hydrogen bonding etc.

Debye - Huckel limiting law

For dilute ionic solutions

$$\log \gamma_{\pm} = - A z^2 \sqrt{I}$$

where

γ_{\pm} = mean ionic activity co-efficient

z = charge of ion

I = Ionic strength

A = constant depending on temperature and dielectric constant.

SUNDAY 30

Applications.

- Calculation of equilibrium constants in real systems
- To measure electrode potentials in electrochemistry
- To study colligative properties and osmotic pressure studies
- In electrolytic solⁿ metallurgy and chemical engineering process.

Fugacity and fugacity co-efficient

In thermodynamics of real gases, deviations from ideal behaviour occur due to molecular interactions and finite molecular volume. To account for this non-ideality, the concept of fugacity is introduced, which replaces pressure in equations applicable to real gases. Fugacity allows us to extend the Gibbs free energy relations and equilibrium criteria of ideal gases to real gases.

For an ideal gas, fugacity equals to pressure

$$f = P$$

$$f \neq P$$

Thus, fugacity is a corrected pressure that accounts for non-ideal interactions.

MAY 2025

Sun	1	8	15	22	29
Mon	2	9	16	23	30
Tue	3	10	17	24	
Wed	4	11	18	25	
Thu	5	12	19	26	
Fri	6	13	20	27	
Sat	7	14	21	28	

April

25 092-273
14th Week

WEDNESDAY

02

The fugacity is related to chemical potential (μ). For one mole of gas

$$d\mu = RT d(\ln f)$$

$$d\mu = RT d(\ln P)$$

For real gases

$$\mu(T, P) = \mu^\circ(T) + RT \ln f$$

Fugacity co-efficient

To measure how much fugacity deviates from pressure, the fugacity co-efficient (ϕ) is introduced.

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

- For ideal gases, $f = P$, hence

$$\phi = 1$$

- For real gases

$$\phi \neq 1$$

Ordinary people while working together can perform extraordinary feats

If expresses the degree of non-ideality of the gas.

Notes

THURSDAY

April

093-272 '25
14th Week

Wed	5	12	19	26	Wed	2	9	15	21
Thu	6	13	20	27	Thu	3	10	17	24
Fri	7	14	21	28	Fri	4	11	18	25
Sat	1	8	15	22	Sat	5	12	19	26

09.00

Using a real gas equation of state i.e. Van der waals Virial fugacity can be calculated.

12

From thermodynamics :

$$\ln \phi = \frac{1}{RT} \int_0^P (z-1) \frac{dP}{P}$$

where

$z = \frac{P/V}{RT}$ is the compressibility factor

if $z = 1$ (ideal gas) then

$$\ln \phi = 0 \text{ and hence } \phi = 1$$

Fugacity represents the escaping tendency of a substance from one phase to another.

We all need past that's where our sense of life

TUE	7	14	21	28
WED	1	8	15	22
THU	2	9	16	23
FRI	3	10	17	24
SAT	4	11	18	25

THU	5	12	19	26
FRI	6	13	20	27
SAT	7	14	21	28
SUN	8	15	22	29
MON	9	16	23	30

25 094-271
14th Week

FRIDAY

9) is useful in phase equilibrium calculations (L - V equilibrium
S - V equilibrium)

In chemical reactions involving real gases fugacity replaces pressure in the equilibrium constant expression

$$K = \prod_i v_i^{\nu_i}$$

Applications

① Phase equilibria

Fugacity helps predict V-L equilibrium

more accurately

② Chemical equilibrium

Expressions of equilibrium constant

for real gases require fugacity

05
31

SATURDAY

April
095-270 14th Week 25

Thermodynamic

Property relations

MARCH 2025

Sun	30	2	9	16	23
Mon	31	3	10	17	24
Tue	4	11	18	25	
Wed	5	12	19	26	
Thu	6	13	20	27	
Fri	7	14	21	28	
Sat	8	15	22	29	

APRIL 2025

Sun	6	13	20
Mon	7	14	21
Tue	8	15	22
Wed	9	16	23
Thu	10	17	24
Fri	11	18	25
Sat	12	19	26

Fugacity links equations of state
with gibb's free energy

①

Petrochemical and environmental system

Used in calculation of
non-ideal gas mixtures