Metallurgical Thermodynamics & Kinetics
(B.Tech 3rd Semester)

Course Instructor

Gourahari Behera

DEPARTMENT OF METALLURGICAL & MATERIALS ENGINEERING
VEER SURENDRA SAI UNIVERSITY OF TECHNOLOGY
BURLA

Metallurgical Thermodynamics and Kinetics

Module I

Importance of Thermodynamics, Definition of Thermodynamics; concept of state and path functions, Equation of states, thermodynamic processes, Phase diagram of a single component system, Internal energy, heat capacity, enthalpy.

Module II

First law of thermodynamics, Second law of thermodynamics, entropy, and entropy changes for various processes, free energy and its significance, free energy change as a function of temperature, reversible and irreversible process, criteria of equilibrium, auxiliary functions, combined statements, Maxwell's relations, transformation formula, Gibbs-Helmoltz equation, Concept of standard state.

Module III

Fugacity, activity, equilibrium constant, Concept of Third law of thermodynamics, temperature dependence of entropy, statistical interpretation of entropy, relation between C_p and $C_{v,}$ consequences of third law, Ellingham – Richardson diagrams.

Module IV

Solutions: partial molal quantities, ideal and non-ideal solutions, Roult's law; Henry's law, Gibbs – Duhem equation, regular solution, Chemical potential, Free energy – composition diagrams for binary alloy systems, determination of liquidus, solidus and solvus lines.

Module V

Introduction of metallurgical kinetics: heterogeneous reaction kinetics: gas-solid, solid-liquid, liquid-liquid and solid-solid systems, Concept of Johnson-Mehl equation, thermal analysis, Thermodynamics of electrochemical cells, solid electrolytes.

LECTURE-1

<u>THERMODYNAMICS :</u> It is the subject which dealing with the relation between heat and motion. Development of metallurgical Thermodynamic occurs due to the application of chemical thermodynamics to the metals & materials which later on known as Thermodynamics of materials.

Importance of Thermodynamics:

- It gives the idea about feasibility of the process.
- It gives the idea about end product & its stability.
- It is useful in calculation of heat values.

Continued…

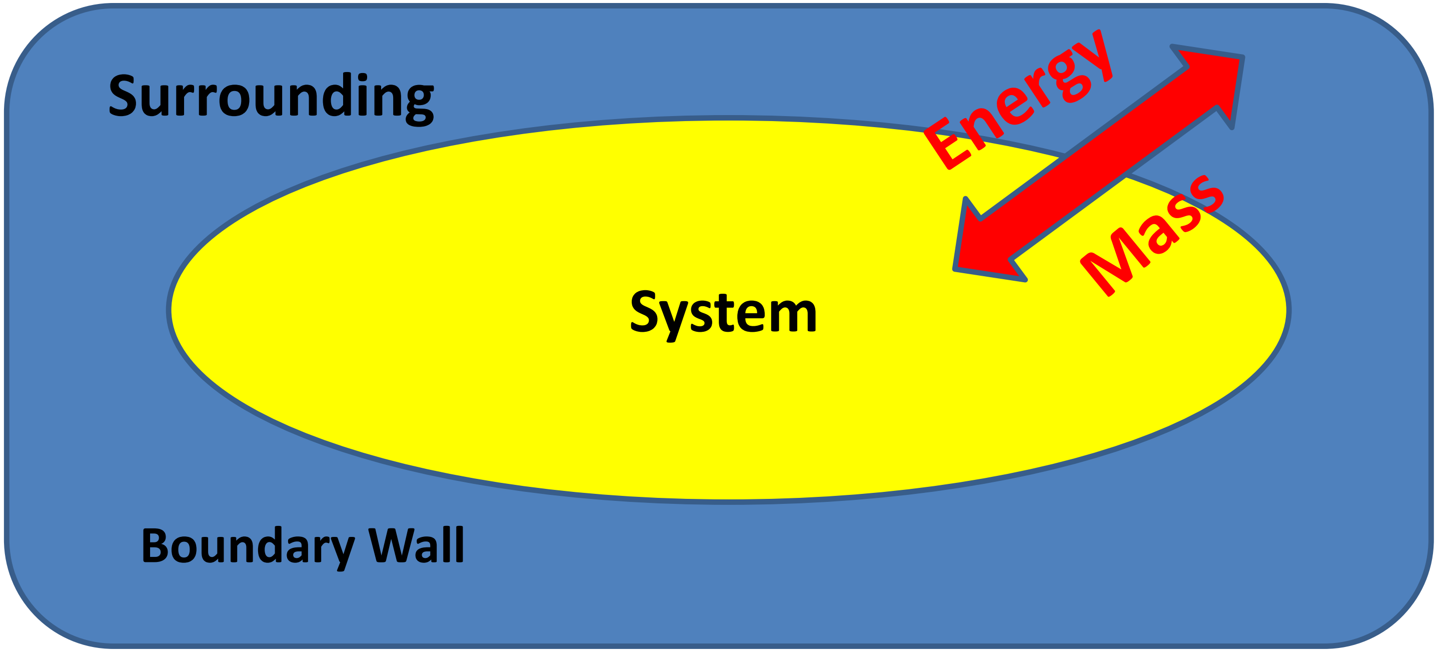
Sl. No.	Endothermic reaction	Exothermic reaction
1	Heat absorbed into the system	Heat released from the system
2	Temperature of the surrounding increases	Temperature of the surrounding decreases
3	Enthalpy of the reactant is lower than the product, i.e., ΔH of reaction = +ve	Enthalpy of the reactant is greater than the product, i.e., ΔH of reaction = -ve
4	Ex: Calcium carbonate decomposition	Ex: Combustion reactions like C+O2=CO2

Continued…

Sl. No.	Thermodynamics	Kinetics
1	Tells whether or not a process or a reaction can occur.	How fast or slow a process or a reaction can occur.
2	Applicable to the systems in stable or metastable equilibrium.	Applicable to the systems in transition from non-equilibrium to equilibrium or between two equilibrium states.
3	Sufficient driving force is needed to enforce a favorable transformation.	Kinetics of a process generally about how overcome the energy barrier to finish the phase transformation.
4	It gives the idea about the reaction as ○ Its Feasibility. ○ Its stability. ○ Its end product. ○ Heat involved in it.	It gives the idea about ○ Reaction rate. ○ Reaction controlling step.

Continued…

System: It is defined as any portion of the universe or the quantity of matter that chosen separately from the rest of the universe & closed by boundary surface.



Schematic of system, surrounding and boundary

Continued…

Surrounding: Except the system the rest of the universe is known as surrounding. The ***previous schematic*** is showing how system and surrounding separated by a boundary layer and also different showing what are different interactions involved in it.

Boundary Wall: This is the wall which separated system from the surrounding.

- Adiabatic Wall: Not allow to any transparent.
- Diathermic Wall: Allow to any transparent.

Continued…

Definition of Thermodynamic Terms:

Types of System: Depending on various parameters system can be classified as follows

1. Nature of Interaction

- **Open system:** Both heat & mass transfer possible. **Example:** Water vaporization in the open atmosphere
- **Closed system:** Only heat transfer possible. **Example:** Water vaporization in a closed chamber
- **Isolated system:** Neither heat nor mass transfer possible. **Example:** Thermo flask

2. Number of components

- **Unary component system:** System consists of single component. **Example:** Water system

Continued…

- **Multi component system:** System consists of more than one component. **Example:** Fe-C (binary component) system

3. Reactiveness

- Reactive system: System is chemically reactive. **Example:** Fe-C system
- Non-reactive system: System is chemically non-reactive. **Example:** SiO_2-Water system

4. Phase

- Homogeneous system: System consists of single phase. **Example:** Water system in single phase like solid or liquid or vapour.
- Heterogeneous system: System consists of more than one phase. **Example:** Chemical reactions in various metallurgical processes.

LECTURE-2

State and Path Function

Sl. No.	State Function	Path Function
1	Independent of path followed and dependent on the initial and final state of the system	Dependent of path followed and independent on the initial and final state of the system
2	Can be integrated using initial and final values.	Need multiple integrals and limits to integrate.
3	Usually expressed by an uppercase letter.	Usually expressed by a lowercase letter.
4	Examples: Internal energy, enthalpy etc.	Work done, heat change

Continued…

Example: From state A to B

- ☐ Work done is different for all the three different paths

- ☐ Internal energy is same for all the three different paths

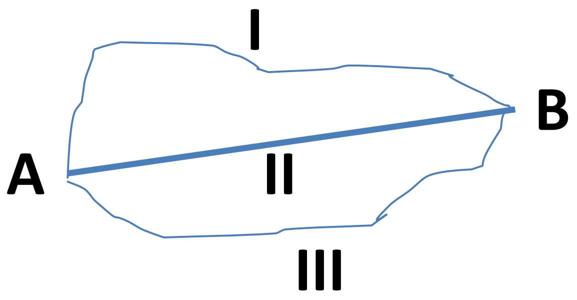
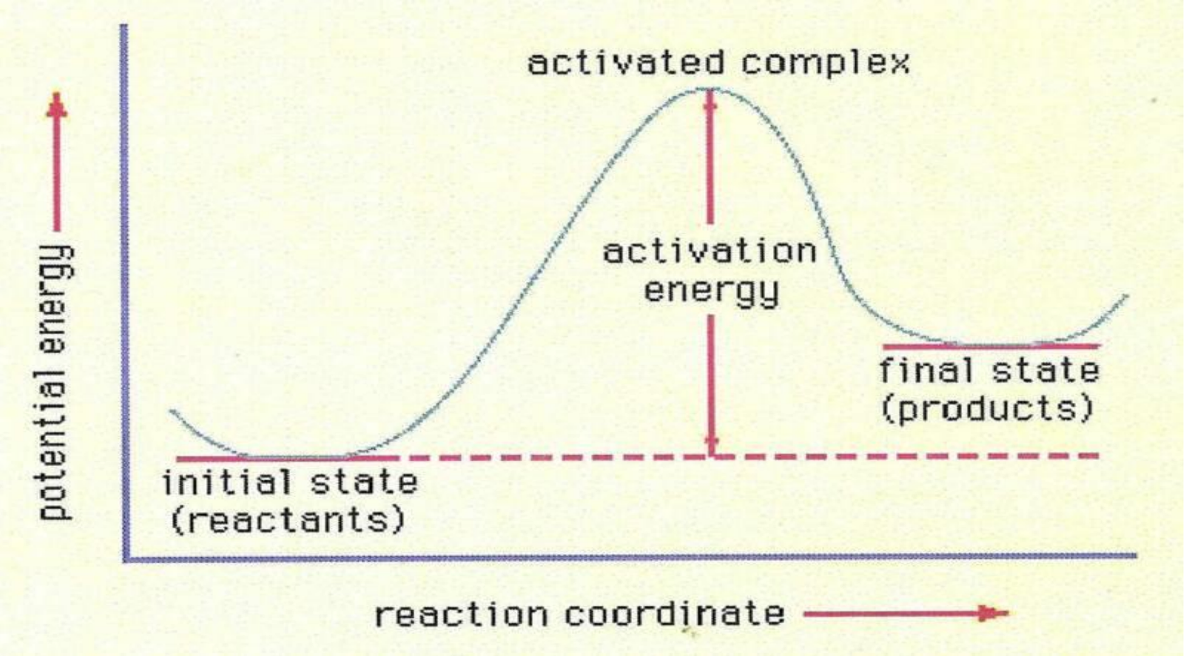


Fig-Schematic of thermodynamic process occurs from state A to state B through three different paths

Continued…

Activated Complex

- As the chemical reaction is progressed, the reactant is converted into product as shown in the figure, where a metastable complex is also observed.



Potential energy vs Reaction coordinate diagram for above reaction

[Ref:https://chemistry.stackexchange.com/questions/6486/how-exactly-is-activation-energy-defined]

Continued…

- An activated complex is the transient unstable complex structure that results at the maximum energy point during the reaction progress in between the reactants and products of the reaction.

- The potential and/or free energy of the activated complex is always higher than the both reactants or product.

- Activated complex is unstable complex that is temporary in nature.

Continued…

MOLECULARITY AND ORDER OF THE REACTION:

Sl. No.	Molecularity	Order of Reaction
1	It is the number of reacting species undergoing collisions the reactions.	It is the sum of the power of the conc. terms in the rate law expression.
2	It is a theoretic value.	It is determined experimentally
3	It has positive integral value 1, 2,3…n.	It can have negative & fractional value also.
4	It does not change with change in temperature and pressure.	It may change with change in temperature and pressure.

Continued…

EQUATION OF STATES: Equations which depend on the state variables like P, V, T, n are known as equation of states.

Universal Gas Law: $$PV = nRT \tag{1}$$

Dieterici Model: $$P(V_m - b) = RTexp(\frac{-a}{V_mRT} \tag{2}$$

PROPERTY: Generally properties (or state variables) are either extensive or intensive.

Sl. No.	Extensive Property	Intensive Property
1	The properties which depends on the size or mass of the system.	The properties which independent of size or mass of the system.
2	**Example:** Mass, Area, Volume, Length, Entropy, Enthalpy etc.	**Example:** Density, Specific volume, Molar volume etc.

Continued…

THERMODYNAMIC EQUILIBRIUM: If in a system both thermal & mechanical equilibrium exists simultaneously. Then it is known as in thermodynamic equilibrium.

- **Thermal Equilibrium:** Uniform temperature throughout the system.
- **Mechanical Equilibrium:** Uniform pressure throughout the system.
- **Chemical Equilibrium:** Uniform chemical potential throughout the system.

LECTURE-3

PROCESS: When in a system there is two or more than two parameters get changed then it is known as system gets changed and process occurs.

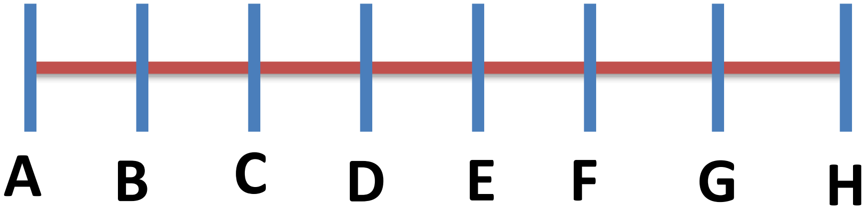
- **Cyclic Process:** Sequence of processes which return back to its initial point.
- **Adiabatic Process:** Process in which net heat change (Δq) is equal to zero.
- **Isothermal Process:** Process in which net temperature change (ΔT) is equal to zero.

Continued…

- **Isobaric Process:** Process in which net pressure change (ΔP) is equal to zero.

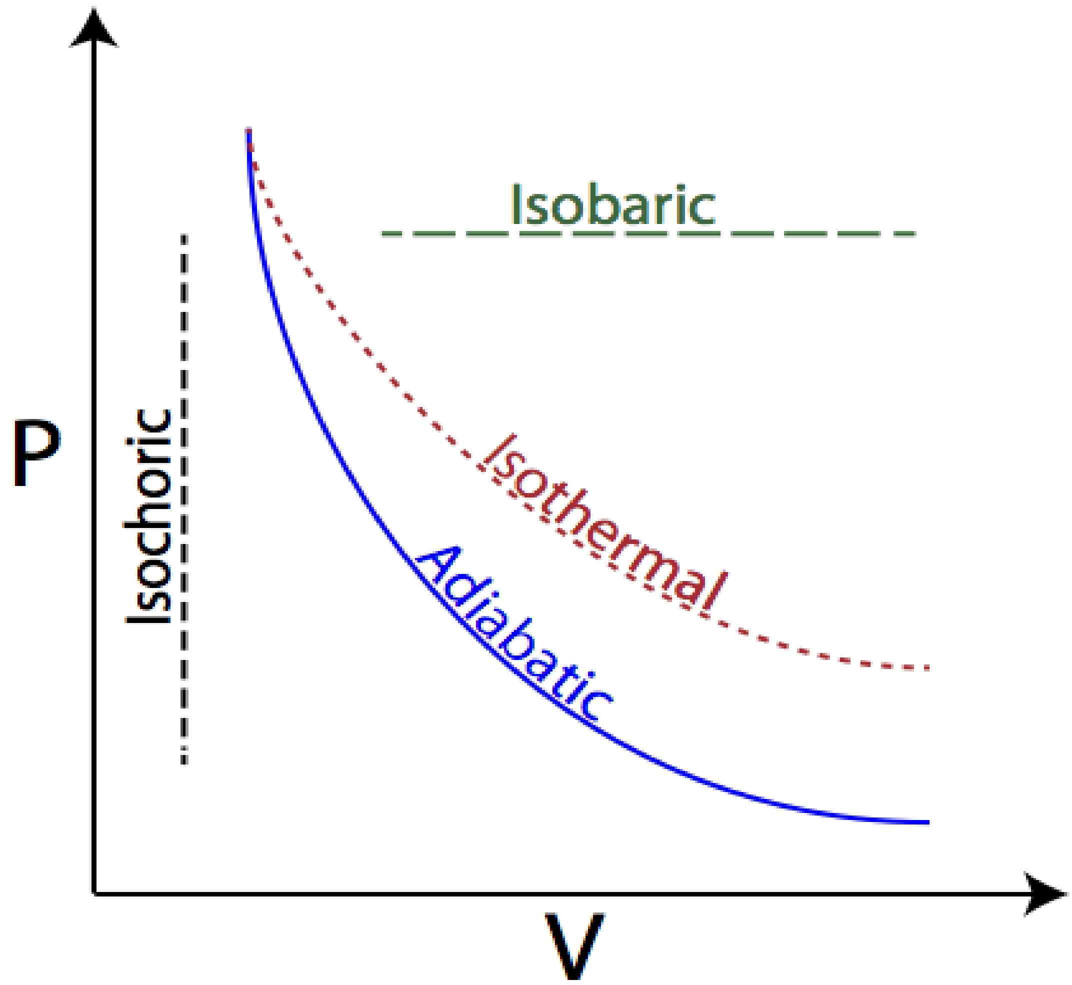
- **Isochoric Process:** Process in which net volume change (ΔV) is equal to zero.

- **Quasi-static Process:** It is the process in which every small steps are in equilibrium, so that entire process is in equilibrium.



$$\boldsymbol{Process_{A\rightarrow H} = \sum_{I=A}^{j=H} Process_{i\rightarrow j}}$$

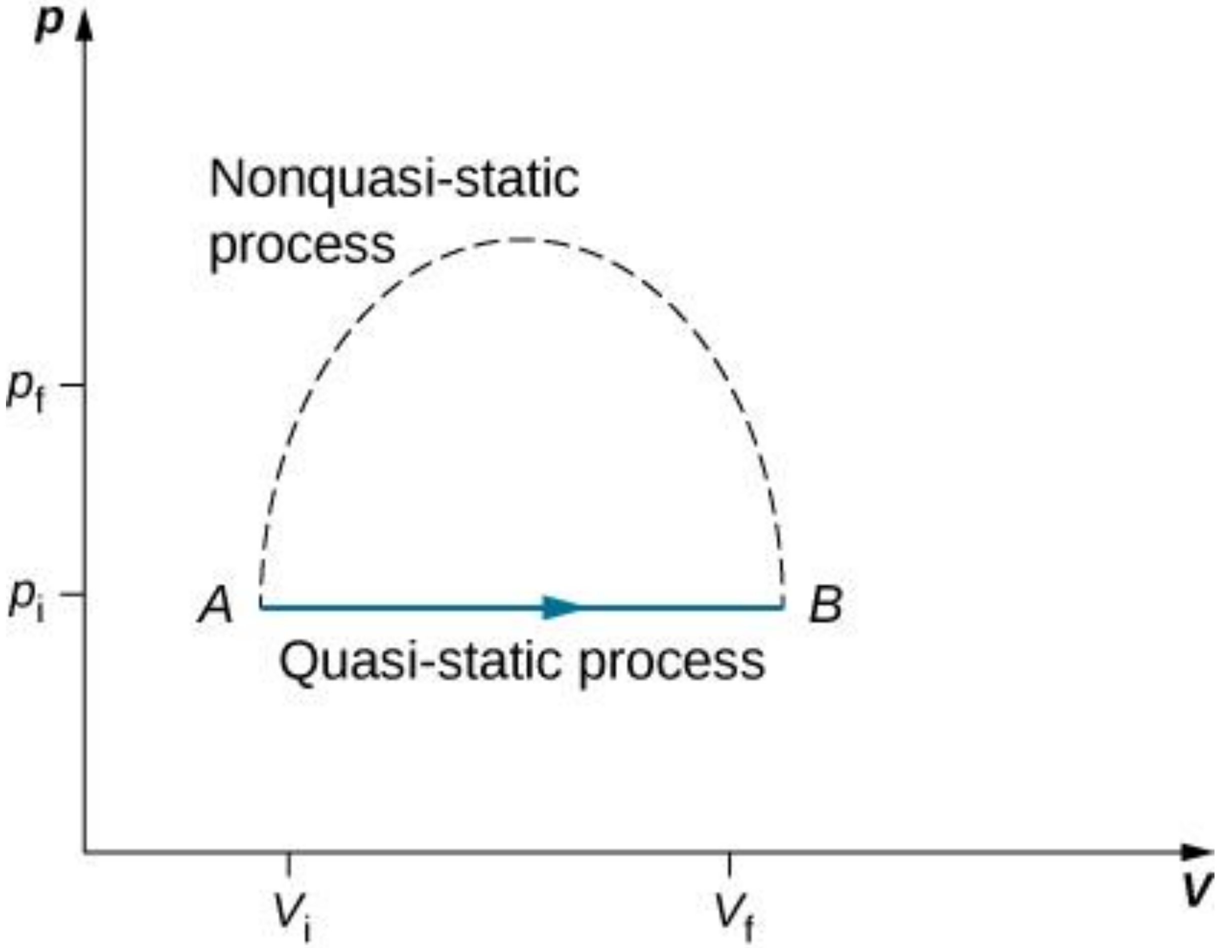
Continued…



P-V graph for different thermodynamic processes

Ref: https://in.pinterest.com/pin/550705860678462036/?nic_v2=1a4vsVIc2

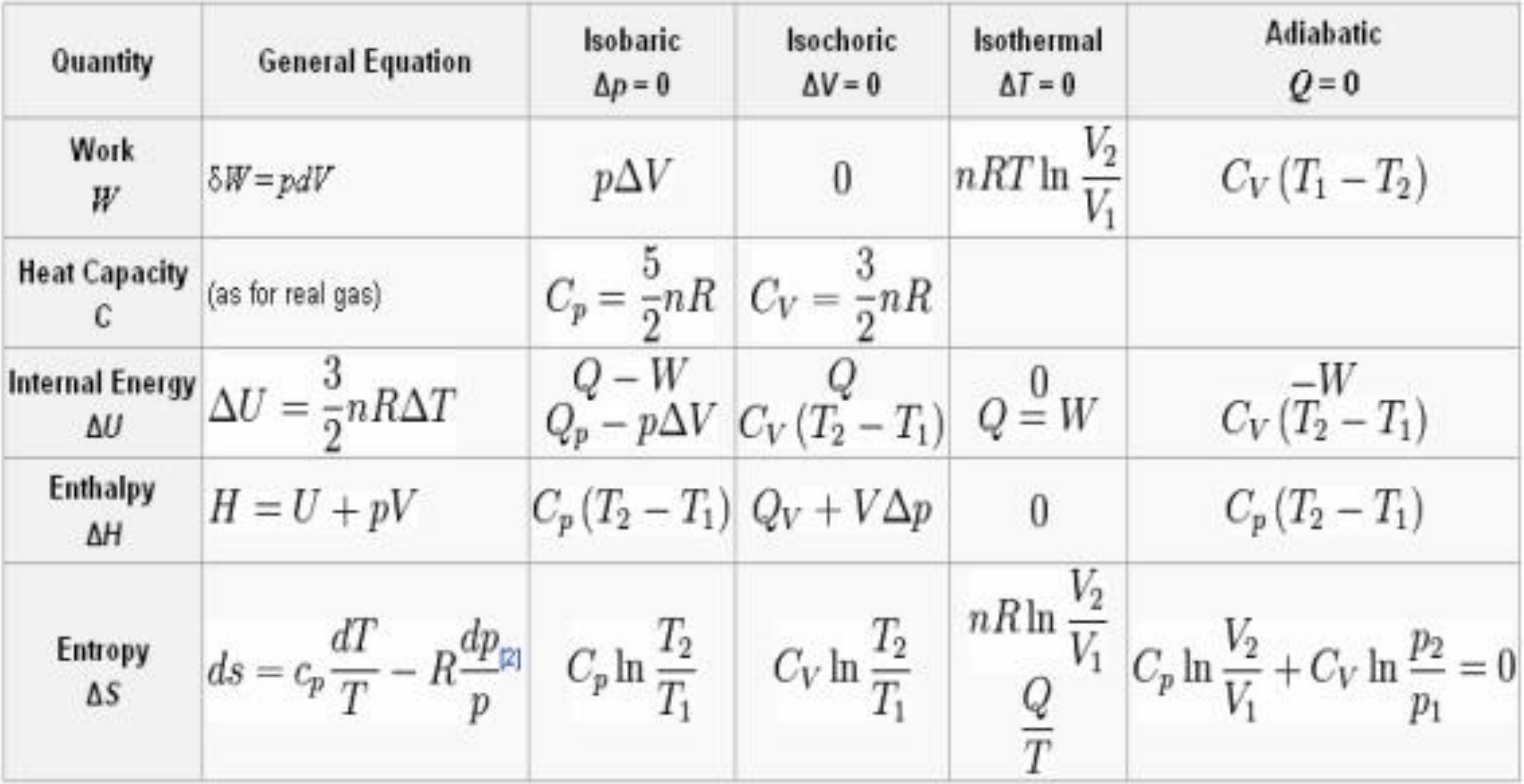
Continued…



P-V graph for quasi-static and non-quasi-static process

Ref: https://www.jobilize.com/physics2/course/3-4-thermodynamic-processes-the-first-law-of-thermodynamics-by-opensta?qcr=www.quizover.com&page=1&=

Continued…



Quantity	General Equation	Isobaric $\Delta p = 0$	Isochoric $\Delta V = 0$	Isothermal $\Delta T = 0$	Adiabatic $Q = 0$
Work W	$\delta W = p dV$	$p\Delta V$	0	$nRT \ln \frac{V_2}{V_1}$	$C_V (T_1 - T_2)$
Heat Capacity C	(as for real gas)	$C_p = \frac{5}{2} nR$	$C_V = \frac{3}{2} nR$		
Internal Energy ΔU	$\Delta U = \frac{3}{2} nR\Delta T$	$Q - W$ $Q_p - p\Delta V$	Q $C_V (T_2 - T_1)$	0 $Q = W$	$-W$ $C_V (T_2 - T_1)$
Enthalpy ΔH	$H = U + pV$	$C_p (T_2 - T_1)$	$Q_V + V\Delta p$	0	$C_p (T_2 - T_1)$
Entropy ΔS	$ds = c_p \frac{dT}{T} - R\frac{dp}{p}$[2]	$C_p \ln \frac{T_2}{T_1}$	$C_V \ln \frac{T_2}{T_1}$	$nR \ln \frac{V_2}{V_1}$ $\frac{Q}{T}$	$C_p \ln \frac{V_2}{V_1} + C_V \ln \frac{p_2}{p_1} = 0$

Equation table for different processes of an Ideal gas

Ref: https://www.brainkart.com/article/Ideal-and-Real-Gases,-Thermodynamic-Relations_5474/

Continued…

ARRHENIUS EQUATION:

Arrhenius' equation represents the relationship between the rate constant, k of the chemical reaction on the absolute temperature, T (in Kelvin) as given by

$$k = Ae^{-\left(E_a/_{RT}\right)} \tag{3}$$

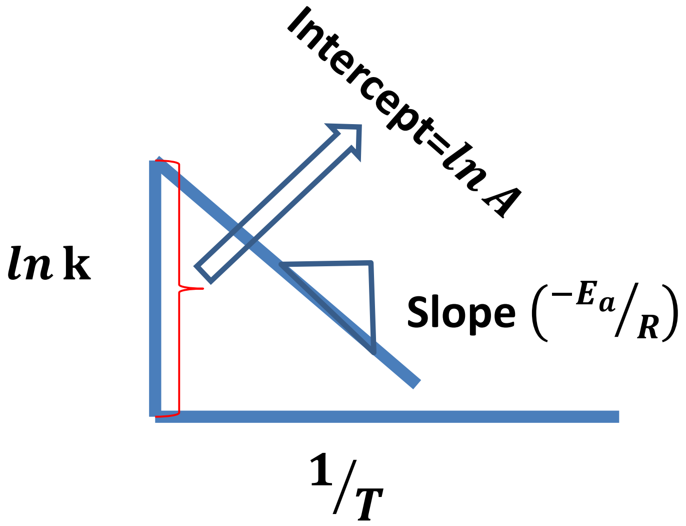
where A is the pre-exponential factor, Ea is the activation energy and R is the universal gas constant

Arrhenius equation can also be represented as

$$\ln k = \ln A - \left(E_a/_{RT}\right) \tag{4}$$

Continued…

Comparing equation (4) with the linear equation,



$$ln\,k_1 = ln\,A - \left({}^{E_a}/_{RT_1}\right) \qquad (5)$$

$$ln\,k_2 = ln\,A - \left({}^{E_a}/_{RT_2}\right) \qquad (6)$$

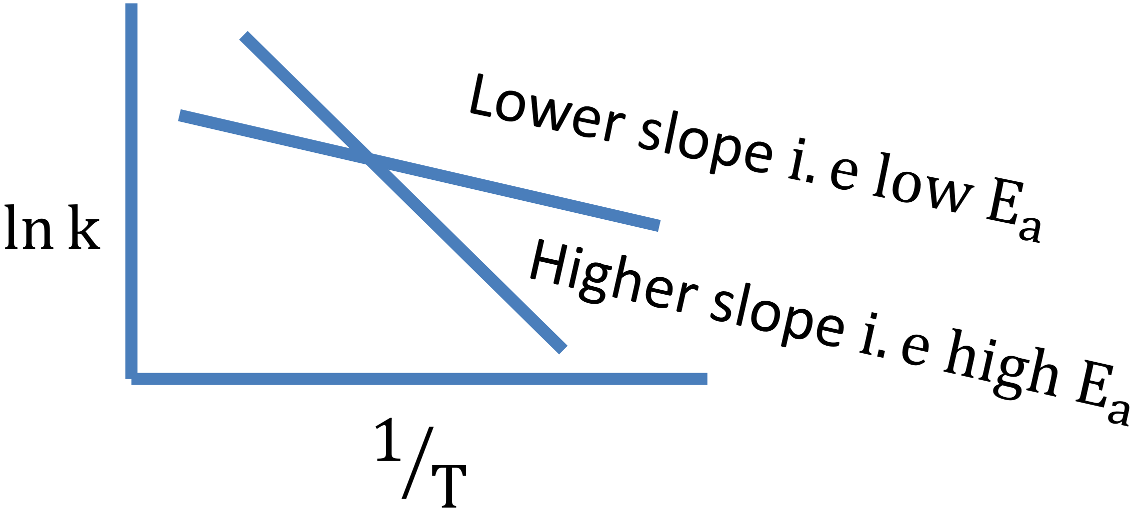
Equation (5) – Equation (6) => $\ln\left(\frac{k_1}{k_2}\right) = \left({}^{\mathrm{E_a}}/_{\mathrm{R}}\right)\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$

Continued…

At constant rate constant:

$E_1 < E_2$ with $k_1=k_2$

=> Temp decrease from T_1 to T_2



Activation energy (Ea): It is defined as the minimum energy required activate the reacting species to produce the product.

LECTURE-4

PHASE DIAGRAM / CONSTITUTION DIAGRAM OF SINGLE COMPONENT SYSTEM

Phase: It is defined as a finite volume in the physical system within which the properties are uniformly constant i.e. do not experience any abrupt change in passing from one point in the volume to another.

Phase Diagram: The graphical representation of equilibrium states of existence of a system is known as phase diagram/constitution diagram.

- The complexity of a phase diagram is primarily determined by a number of components which occur in the system, where components are chemical species of fixed composition.
- Phase Diagram for one-component System is a two dimensional representation of the dependence of the equilibrium state of existence of the two independent variables.
- Temperature & pressure are normally chosen as the two independent variables

Continued…

GIBBS PHASE RULE: It is used to find out the number of independent variables associated with a system. At invariant point degree of freedom is zero.

Mathematically, Gibbs phase rule is given by

$$\mathrm{f} = \mathrm{C} - \mathrm{P} + 2 \tag{7}$$

Where f – Degree of freedom, C – Number of components, P – Number of phases

- **Components:** It refers to the independent chemical species that constitute an alloy.

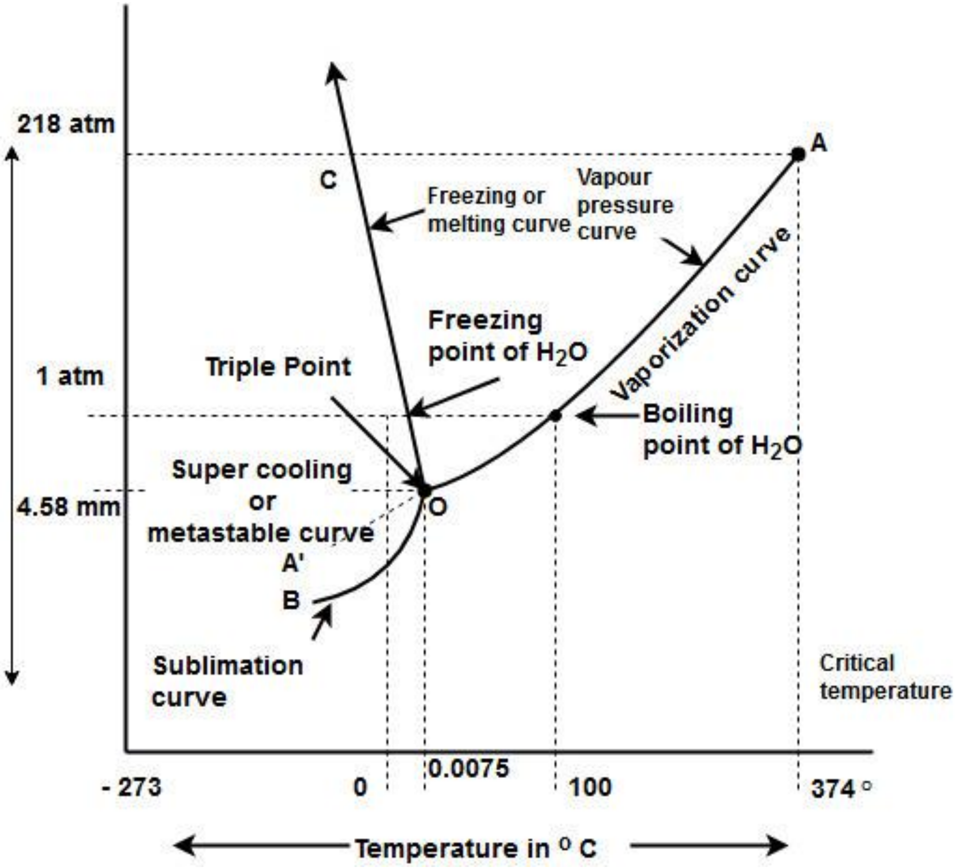
  Example: In Al-Cu system, there is two components involved as Al and Cu.

- **Degree of Freedom**: It refers to the number of independent variables associated with the system.

Continued…

In the above figure represents

- ☐ Three areas BOC (solid), COA (liquid), BOC (vapour) represents single phase. Any one out of this three phase areas of the phase diagram is said to be homogeneous system and if more than one phase then it is said to be heterogeneous system.



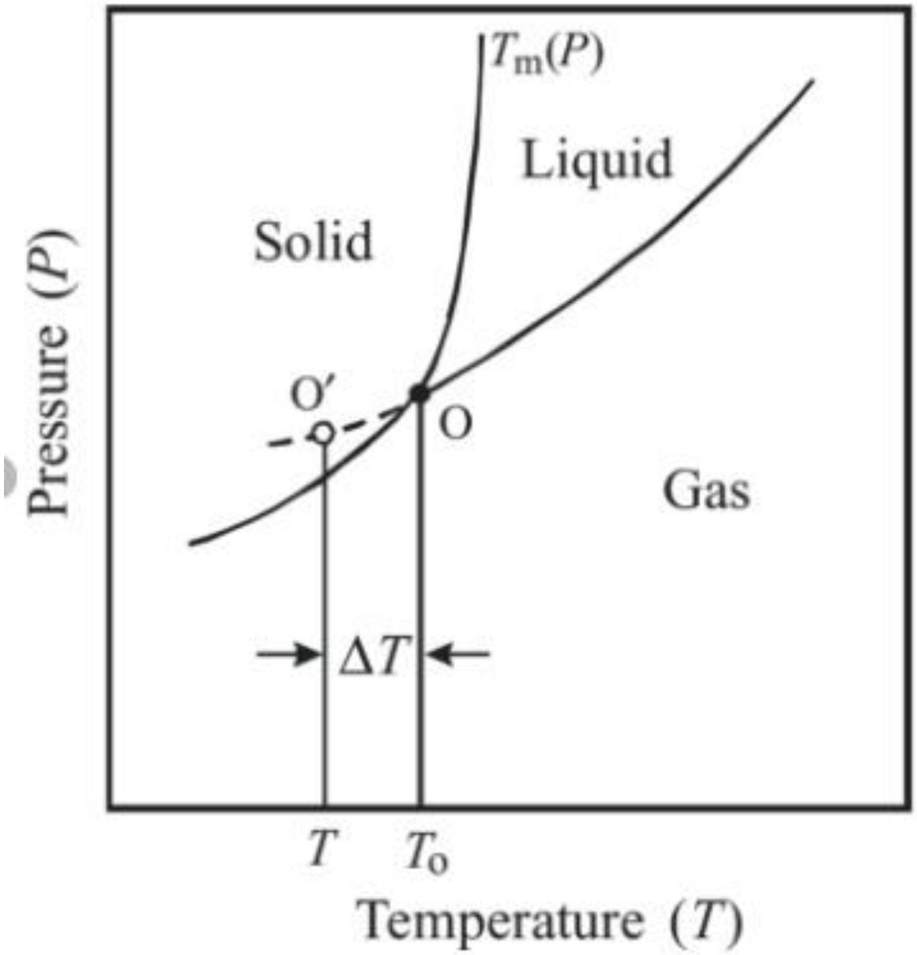
Schematic representation of part of phase diagram for H_2O

Ref: https://www.ques10.com/p/29668/draw-and-explain-neat-labeled-phase-diagram-for-wa/

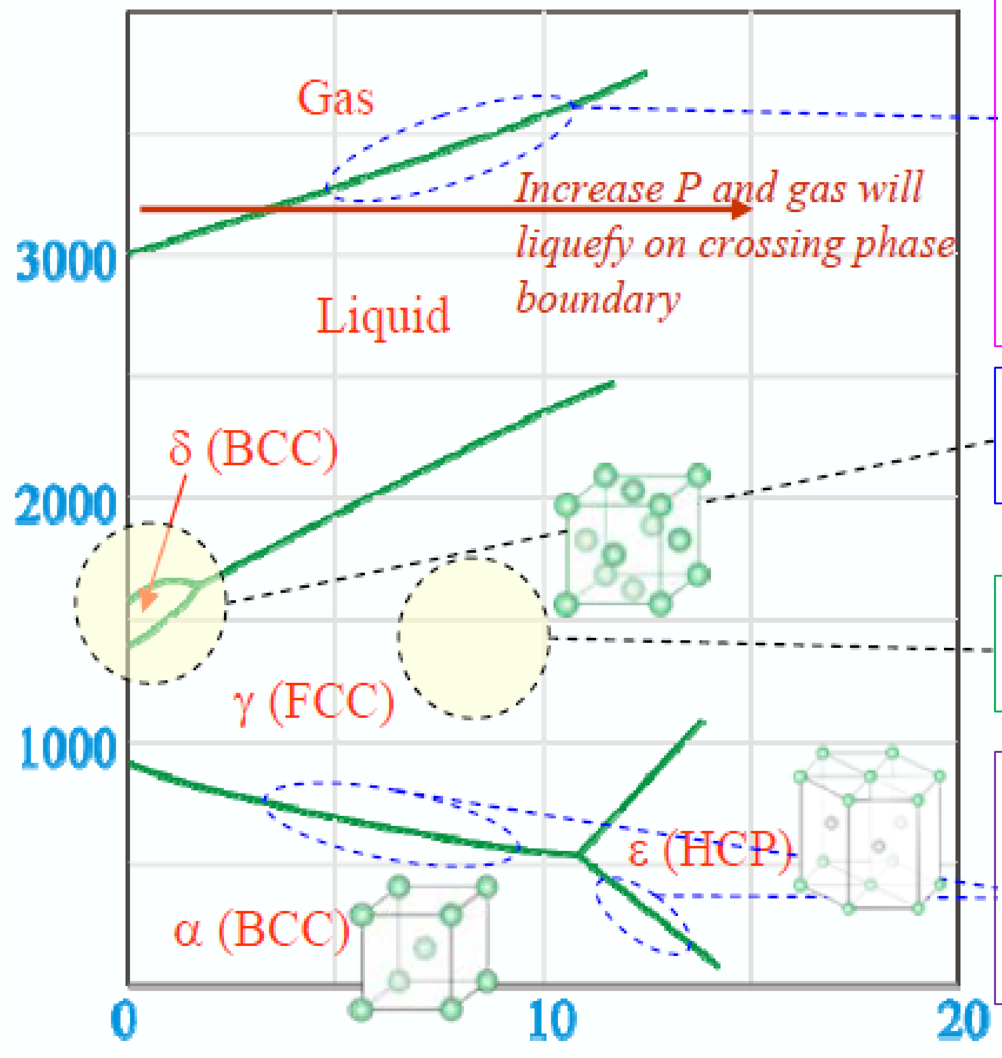
Continued…

- The lines OA – (Solid-Liquid) line, OB – (Liquid-Vapour) line, OC – (Solid-Vapour) line represents the simultaneously variations of P & T required for maintenance of equilibrium between two phase.

- Point 'O' known as triple point where equilibrium lines meet which thus represents the unique values of P & T required for the establishment of three-phase equilibrium. It is central point that represents all the three phases i. e. solid, liquid, vapour.



Schematic phase diagram of pure metal as function of pressure and temperature. T_m : melting temperature; O : triple point; T_0 : the temperature of triple point; O : point reached by super-cooling; and T : degree of supercooling.



Increase P and gas will liquefy on crossing phase boundary

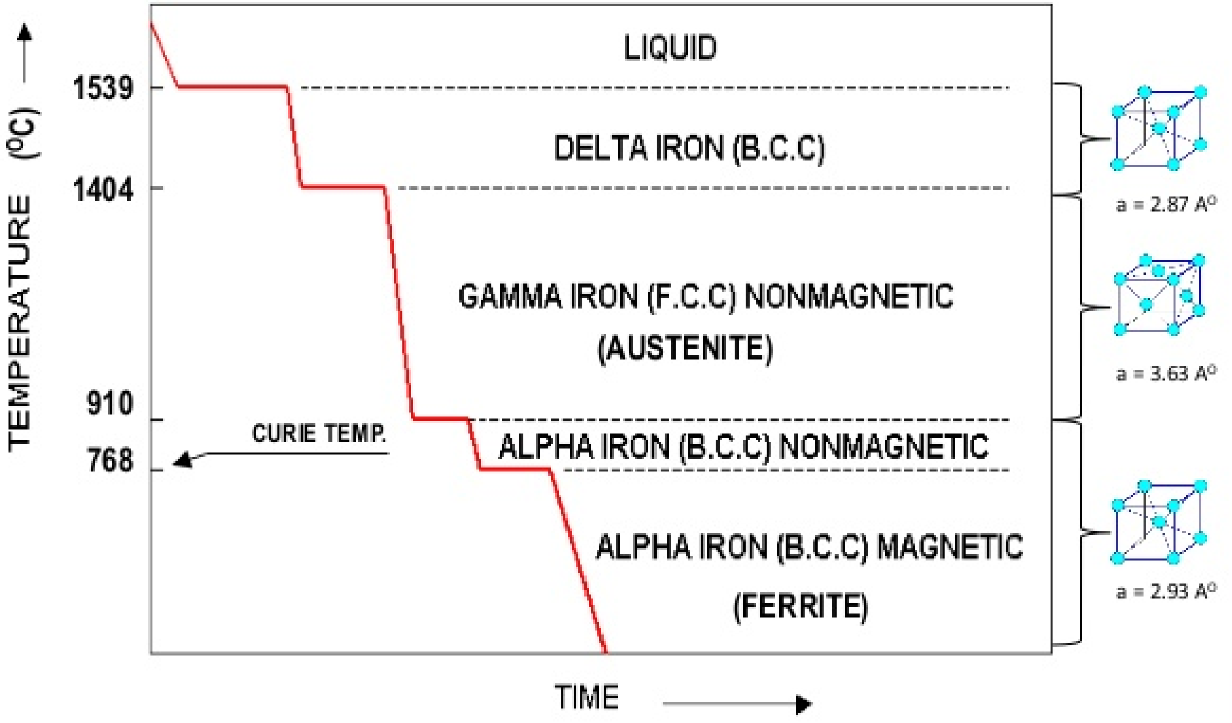
This line slopes upward as at constant T if we increase the P the gas will liquefy as liquid has lower volume (similarly the reader should draw horizontal lines to understand the effect of pressure on the stability of various phases- and rationalize the same).

Phase fields of non-close packed structures shrink under higher pressure

Phase fields of close packed structures expand under higher pressure

These lines slope downward as: Under higher pressure the phase with higher packing fraction (lower volume) is preferred

Allotropy of Pure Iron



Continued…

Phase diagram and allotropes: Iron represents an example of allotropy in a metal. There are at least four allotropic forms of iron, known as α, γ, δ, and ε; at very high pressures and temperatures, some controversial experimental evidence exists for a stable β phase.

- Low-pressure phase diagram of pure iron
- As molten iron cools past its freezing point of 1538 °C, it crystallizes into its δ allotrope, which has a BCC crystal structure.

$$\mathrm{Fe}\ (\mathrm{L},\ 1538\ {}^{0}\mathrm{C}) \rightarrow \mathrm{Fe}\ (\mathrm{S},\ 1538\ {}^{0}\mathrm{C})$$

$$\Delta H_{\text{freezing (L}\rightarrow\text{S)}} = H_{\text{solid}} - H_{\text{liquid}} = -\Delta H_{\text{fusion}}$$

- As it cools further to 1394 °C, it changes to its γ-iron allotrope (austenite), a FCC crystal structure

$$\Delta H_{(\delta \rightarrow \gamma)} = H_{\gamma\text{-iron}} - H_{\delta\text{-iron}}$$

Continued…

- At 912 °C and below, the crystal structure again becomes the bcc α-iron allotrope,

$$\Delta H_{(\gamma \rightarrow \alpha)} = H_{\alpha\text{-iron}} - H_{\gamma\text{-iron}}$$

- At pressures above approximately 10 GPa and temperatures of a few hundred kelvin or less, α-iron changes into a HCP crystal structure,

$$\Delta H_{(\alpha \rightarrow \varepsilon)} = H_{\varepsilon\text{-iron}} - H_{\alpha\text{-iron}}$$

The higher-temperature γ-phase also changes into ε-iron, but does so at higher pressure.

$$\Delta H_{(\gamma \rightarrow \varepsilon)} = H_{\varepsilon\text{-iron}} - H_{\gamma\text{-iron}}$$

- The β phase, if it exists, would appear at pressures of at least 50 GPa and temperatures of at least 1500 K and have an orthorhombic or a double hcp structure.

$$\Delta H_{(\gamma \rightarrow \beta)} = H_{\beta\text{-iron}} - H_{\gamma\text{–iron}}$$

LECTURE-5

INTERNAL ENERGY: It is defined as the inbuilt energy that responsible for the existence of the matter.

Characteristics:

- It depends on state variables P, T, V, n.

- It is a state property and since the state of internal energy is same as the state of the dependent parameters. So it is known as single valued function.

- Internal energy is the sum of the energy associated with translation motion, vibration motion and electronic configuration.

Continued…

- For a cyclic process, change in internal energy (**Δ**U) becomes zero.
- Internal energy is perfect differential i.e. $U_i = f(P_{i,}V_{i,}T_i)$

At constant temperature,

$$\Delta U = \left(\frac{\partial U}{\partial V}\right)_P dV + \left(\frac{\partial U}{\partial V}\right)_P dV = f(V,P)_T$$

At constant volume,

$$\Delta U = \left(\frac{\partial U}{\partial P}\right)_T dP + \left(\frac{\partial U}{\partial T}\right)_P dT = f(P,T)_V$$

At constant pressure,

$$\Delta U = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT = f(V,T)_P$$

Continued…

HEAT CAPACITY: Heat capacity(C) is the quantity of heat required to raise the temperature of a substance by 1^0 C. Thus

$$C = \frac{q}{\Delta T} \tag{8}$$

If the temperature change is made vanishingly small, then

$$C = \frac{\delta q}{dT} \tag{9}$$

Heat capacity at constant volume

$$C_V = \left(\frac{\delta q}{dT}\right)_V = \left(\frac{dU+\delta W}{dT}\right)_V = \left(\frac{dU}{dT}\right)_V \tag{10}$$

Heat capacity at constant pressure

$$C_P = \left(\frac{\delta q}{dT}\right)_P = \left(\frac{dU+PdV+VdP}{dT}\right)_P = \left(\frac{dH}{dT}\right)_V \tag{11}$$

Continued…

Factors affecting Heat Capacity :

Heat Capacity mainly depends on three factors

- **Mass (m) of the substance i.e. number of moles of the substance:** As increase in the mass of the substance the heat requirement increases and vice-verse.
- **Temperature change (ΔT):** It is directly proportional to heat requirement. Increase in the Temperature change (ΔT) of the substance increase the heat requirement and vice-verse.
- **Type of substance or matter:** Solid or gas or liquid and further in particular state, the different materials have different heat (c) absorbing capacity.

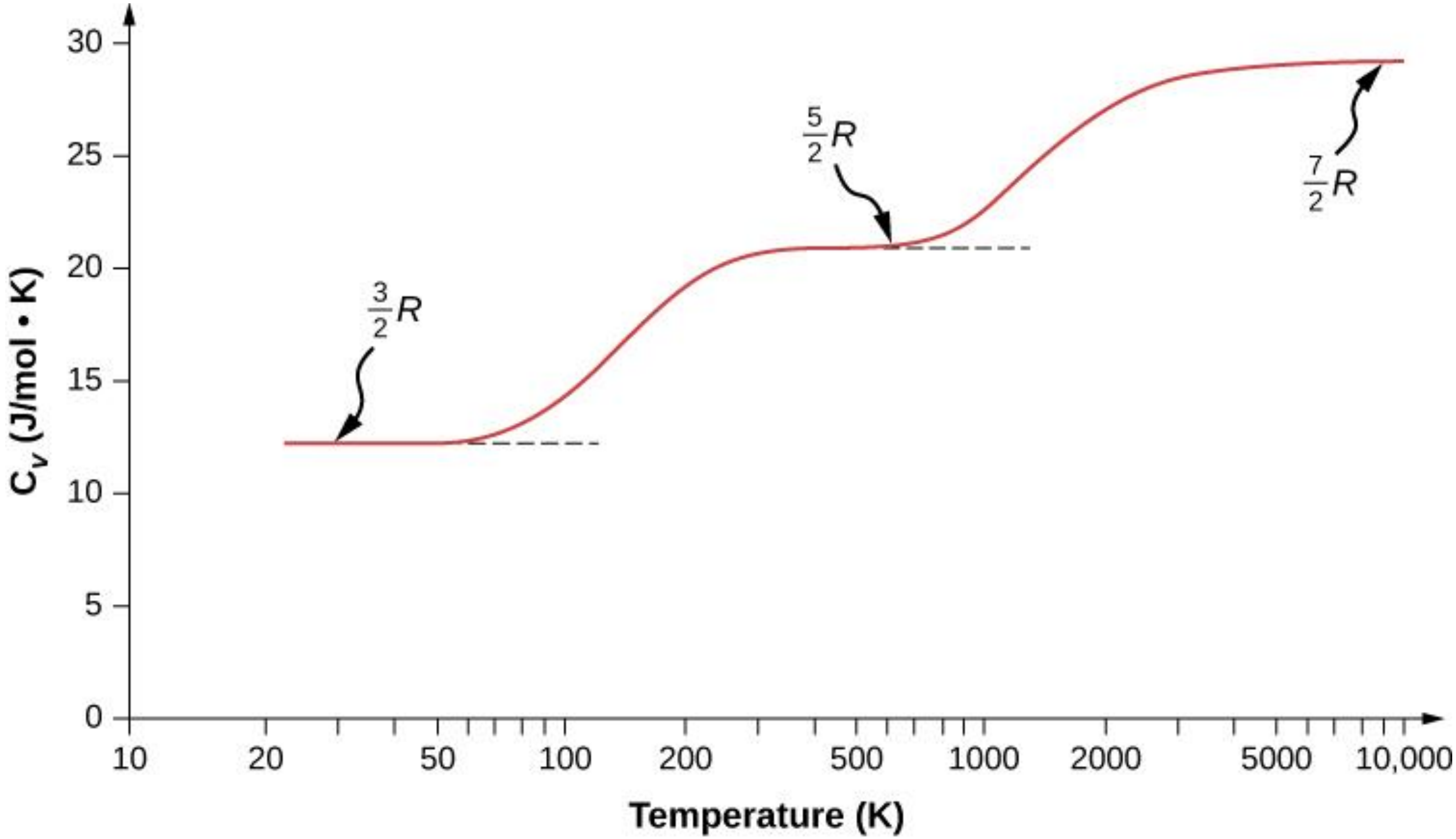
Continued…

Heat Capacity of Ideal Gases:

From the Kinetic theory of gases, we have the following knowledge given below

Types of gases	Examples	c_v value	c_p value
Monatomic	He, Ne, Ar etc.	$\frac{3}{2}R$	$\frac{5}{2}R$
Diatomic	O_2,N_2,H_2 etc.	$\frac{5}{2}R$	$\frac{7}{2}R$
Triatomic	O_3	$\frac{7}{2}R$	$\frac{9}{2}R$

Continued…



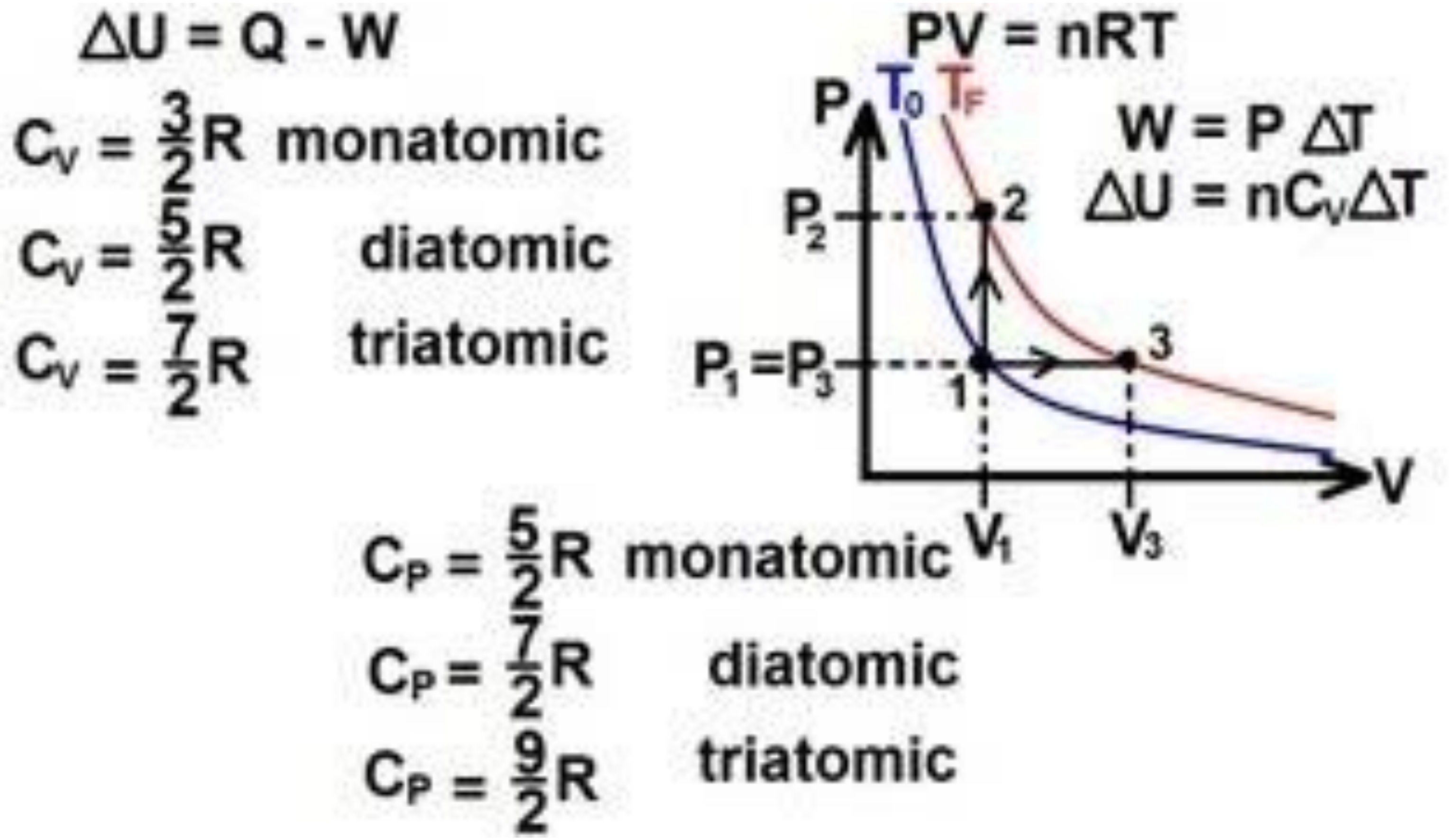
Heat Capacity of Ideal Gases

Ref:

https://phys.libretexts.org/Bookshelves/University_Physics/Book%3A_University_Physics_(OpenStax)/Map%3A_University_Physics_II_Thermodynamics%2C_Electricity%2C_and_Magnetism_(OpenStax)/02%3A_The_Kinetic_Theory_of_Gases/2.04%3A_Heat_Capacity_and_Equipartition_of_Energy

Continued…

Heat capacity involvement in 1st law of Thermodynamics:



$$\Delta U = Q - W$$

$C_V = \frac{3}{2}R$ monatomic

$C_V = \frac{5}{2}R$ diatomic

$C_V = \frac{7}{2}R$ triatomic

$$PV = nRT$$

$$W = P\,\Delta T$$

$$\Delta U = nC_V\Delta T$$

$C_P = \frac{5}{2}R$ monatomic

$C_P = \frac{7}{2}R$ diatomic

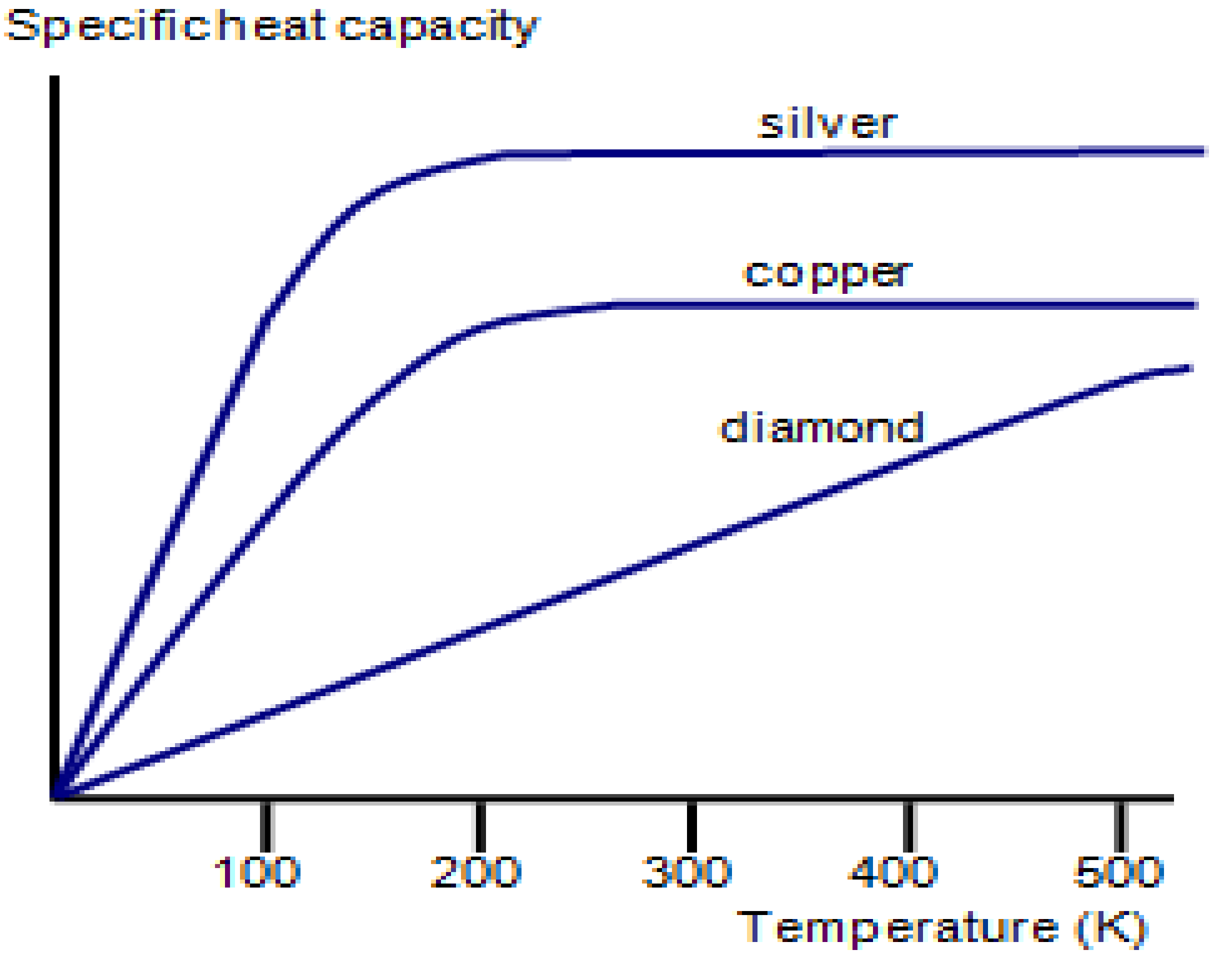
$C_P = \frac{9}{2}R$ triatomic

Heat Capacity of Ideal Gases along with internal energy calculation

Ref: https://www.embibe.com/study/molar-heat-capacities-of-ideal-gas-cv-m-cp-m-concept

Continued…

*Maximum Cp value for solid=3R

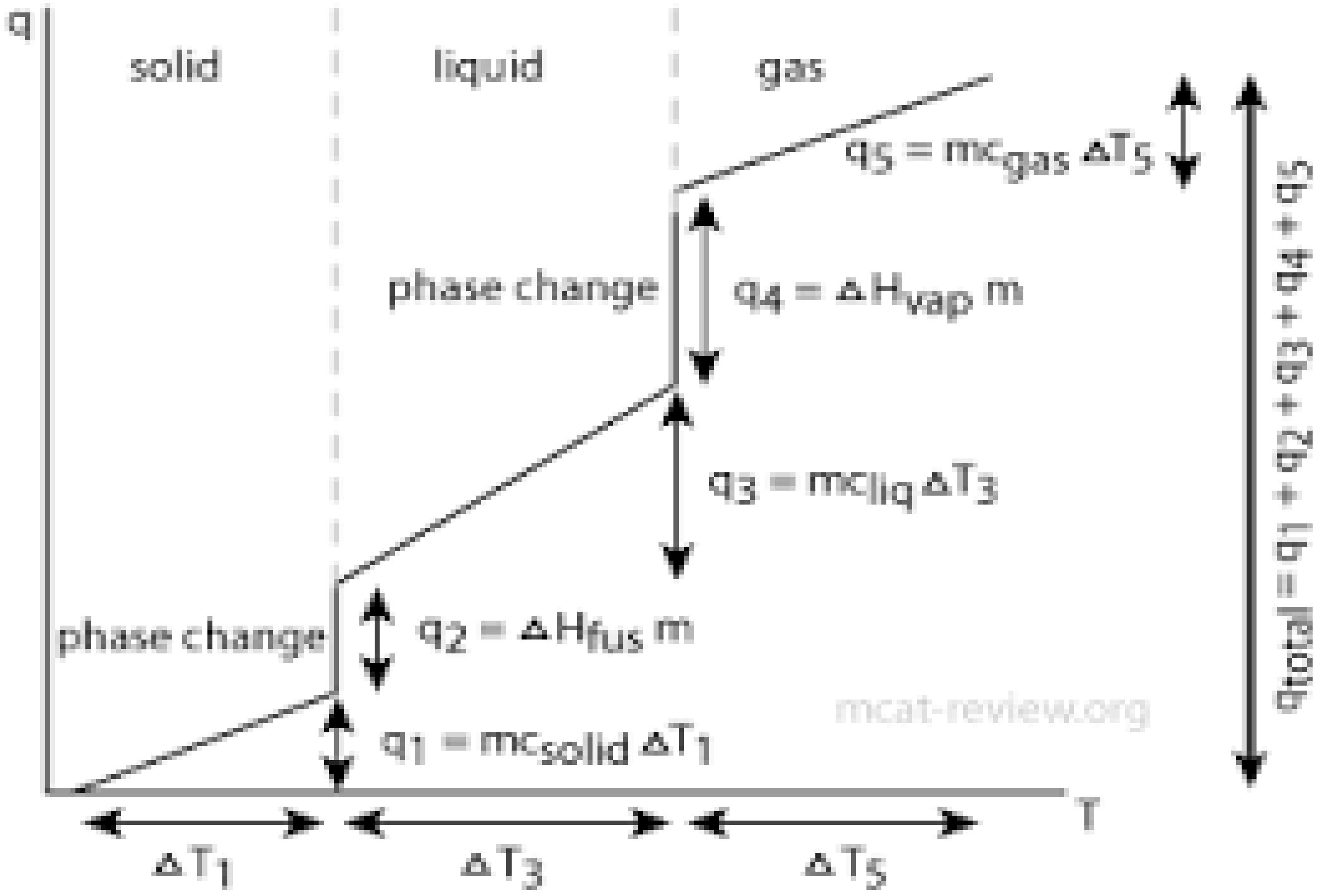


Heat Capacity for different solid materials

Ref: http://www.schoolphysics.co.uk/age16-19/Thermal%20physics/Heat%20energy/text/Heat_energy/index.html

Continued…

- **Molar Heat Capacity:** Heat capacity per unit mol, unit-J/mol. K
- **Specific Heat Capacity:** Heat capacity per unit mass, unit-J/gm. K



Specific Heat Capacity change along with heat change during phase change

Ref: http://mcat-review.org/thermodynamics-thermochemistry.php

QUIZ TEST-1

Q.1 – How the mass and energy are changes for closed and isolated system?

Q.2 – What do you mean by state and path function? Is there any path function which seems to be a state function in certain case, Give example?

Q.3 – Is it possible to vaporize the water below 100^0C, if possible then explain how?

Q.4 –Density is which type of property and how, explain?

Q.5 –Define single valued function with an example.

LECTURE-6

ENTHALPY: It is a defined thermodynamics potential designated by the letter "H", that consists of the internal energy (U) of the system plus the product of the pressure (P) & volume (V) of the system. Mathematically it is given by

$$H = U + PV \tag{12}$$

At constant pressure process

$$\int_{H_1}^{H_2} \Delta H = H_2 - H_1 = (\Delta q)_P = \int_{U_1}^{U_2} \Delta U + P \int_{V_1}^{V_2} \Delta V = (U_2 - U_1) + P(V_2 - V_1) \tag{13}$$

At constant volume process

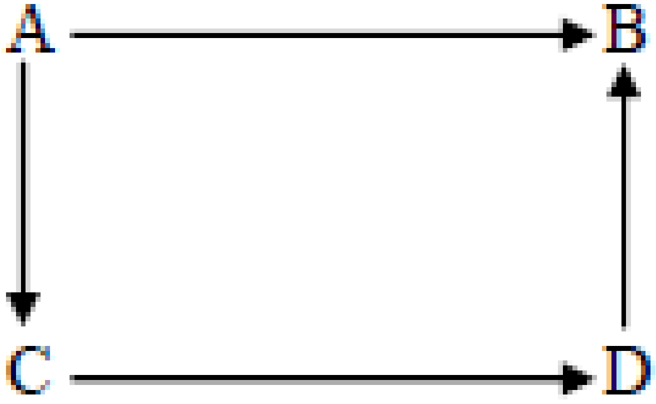
$$\int_{H_1}^{H_2} \Delta H = H_2 - H_1 = (\Delta q)_V = \int_{U_1}^{U_2} \Delta U = U_2 - U_1 \tag{14}$$

(Since at constant volume work done PdV becomes zero)

Continued…

HESS'S LAW: The law states that "The total change of heat in a chemical reaction is same irrespective whether it occurs in a single step or in multiple steps provided that the reaction must be isothermal or isobaric or isochoric."

If a process occur from A to B, then using Hess's law we can write as enthalpy change throughout the path AB is equal to sum of the enthalpies throughout AC, CD and DA.



$$H_{AB} = \Delta H_{AC} + \Delta H_{CD} + \Delta H_{DA} \quad (15)$$

Continued…

<u>Problem-2.1:</u> Calculate the heat of the reaction for the formation of solid WO_3 from solid W and O_2 gas i.e.

Reaction 2.1: $\langle W\rangle + \frac{3}{2}(O_2) = \langle WO_3\rangle$ at 298 K.

Given the following data at 298 K and 1 atm pressure:

Reaction 2.2: $\langle W\rangle + (O_2) = \langle WO_2\rangle\,;\ \Delta H^0_{298} = -134\ kcal$

Reaction 2.3: $3\langle WO_2\rangle + (O_2) = \langle W_3O_8\rangle\,;\ \Delta H^0_{298} = -131.5\ \ kcal$

Reaction 2.4: $\langle W_3O_8\rangle + \frac{1}{2}(O_2) = 3\langle WO_3\rangle\,;\ \Delta H^0_{298} = -66.5\ \ kcal$

<u>Solution:</u> The problem consists of calculation of standard heat of the following reaction (2.1) at 373 K & 1 atm pressure where standard heat of the reaction (2.2), (2.3), (2.4) are given

Reaction 2.1: $\langle \mathrm{W}\rangle + \frac{3}{2}(\mathrm{O_2}) = \langle \mathrm{WO_3}\rangle\,;\ \Delta \mathrm{H}^0_1$

Reaction 2.2: $\langle \mathrm{W}\rangle + (\mathrm{O_2}) = \langle \mathrm{WO_2}\rangle\,;\ \Delta \mathrm{H}^0_2 = \Delta \mathrm{H}^0_{298} = -134\ \mathrm{kcal}$

Reaction2.3: $3\langle \mathrm{WO_2}\rangle + (\mathrm{O_2}) = \langle \mathrm{W_3O_8}\rangle\,;\ \Delta \mathrm{H}^0_3 = \Delta \mathrm{H}^0_{298} = -131.5\ \ \mathrm{kcal}$

Reaction 2.4: $\langle \mathrm{W_3O_8}\rangle + \frac{1}{2}(\mathrm{O_2}) = 3\langle \mathrm{WO_3}\rangle\,;\ \Delta \mathrm{H}^0_4 = \Delta \mathrm{H}^0_{298} = -66.5\ \ \mathrm{kcal}$

Continued…

Let us consider at standard state, heat of reaction of reaction (2.1), (2.2), (2.3) & (2.4) areΔH_1^0,ΔH_2^0, ΔH_3^0 & ΔH_4^0 respectively. Then standard heat of reaction at 298 K can be calculated as

$$\Delta H_1^0 = \Delta H_2^0 + \frac{\Delta H_3^0}{3} + \frac{\Delta H_4^0}{3} = -200 \text{ K Cal.}$$

KIRCHHOFF’S LAW: Kirchhoff’s law states that “If a system undergoes a change from one state to another state then both internal energy & heat occur would alter.”

Mathematically Kirchhoff’s law can be expressed as

$$\int_{T_1}^{T_2} d(\Delta H) = \int_{T_1}^{T_2} (\Delta C_P)_{\text{Reaction}}\, dT \qquad (16)$$

$$\Rightarrow [\Delta H_{T_2} - \Delta H_{T_1}] = \int_{T_1}^{T_2} [(\sum C_P)_{\text{Product}} - (\sum C_P)_{\text{Reactant}}]\, dT$$

$$\Rightarrow [\Delta H_{T_2}] = [\Delta H_{T_1}] + \int_{T_1}^{T_2} [(\sum C_P)_{\text{Product}} - (\sum C_P)_{\text{Reactant}}]\, dT \qquad (17)$$

Continued…

Kirchhoff's law during phase change, solid to liquid state can be expressed as

$$\left[\Delta H_{T_2} - \Delta H_{T_1}\right] = \int_{T_1}^{T_m} \left(\Delta C_{p,reaction}\right)_{solid} dT + L_f + \int_{T_m}^{T_2} \left(\Delta C_{p,reaction}\right)_{solid} dT \qquad (18)$$

Problem-2.2: Calculate the standard heat of formation of PbO from Pb & O_2 at $227^{0}C$ from the following data:

$\Delta H^{0}_{298, \langle PbO \rangle} = -52.4$ Kcal/mol, $C_{P, \langle PbO \rangle} = 10.6 + 4.0 \times 10^{-3} T$ Cal/deg/mol

$C_{P, \langle Pb \rangle} = 5.63 + 2.33 \times 10^{-3} T$ Cal/deg/mol, $C_{P, (O2)} = 7.16 + 1.0 \times 10^{-3} T - 0.4 \times 10^{5} T^{-2}$ Cal/deg/mol

Solution:

For the reaction

Reaction 2.5: $\langle Pb \rangle + \frac{1}{2}(O_2) = \langle PbO \rangle$

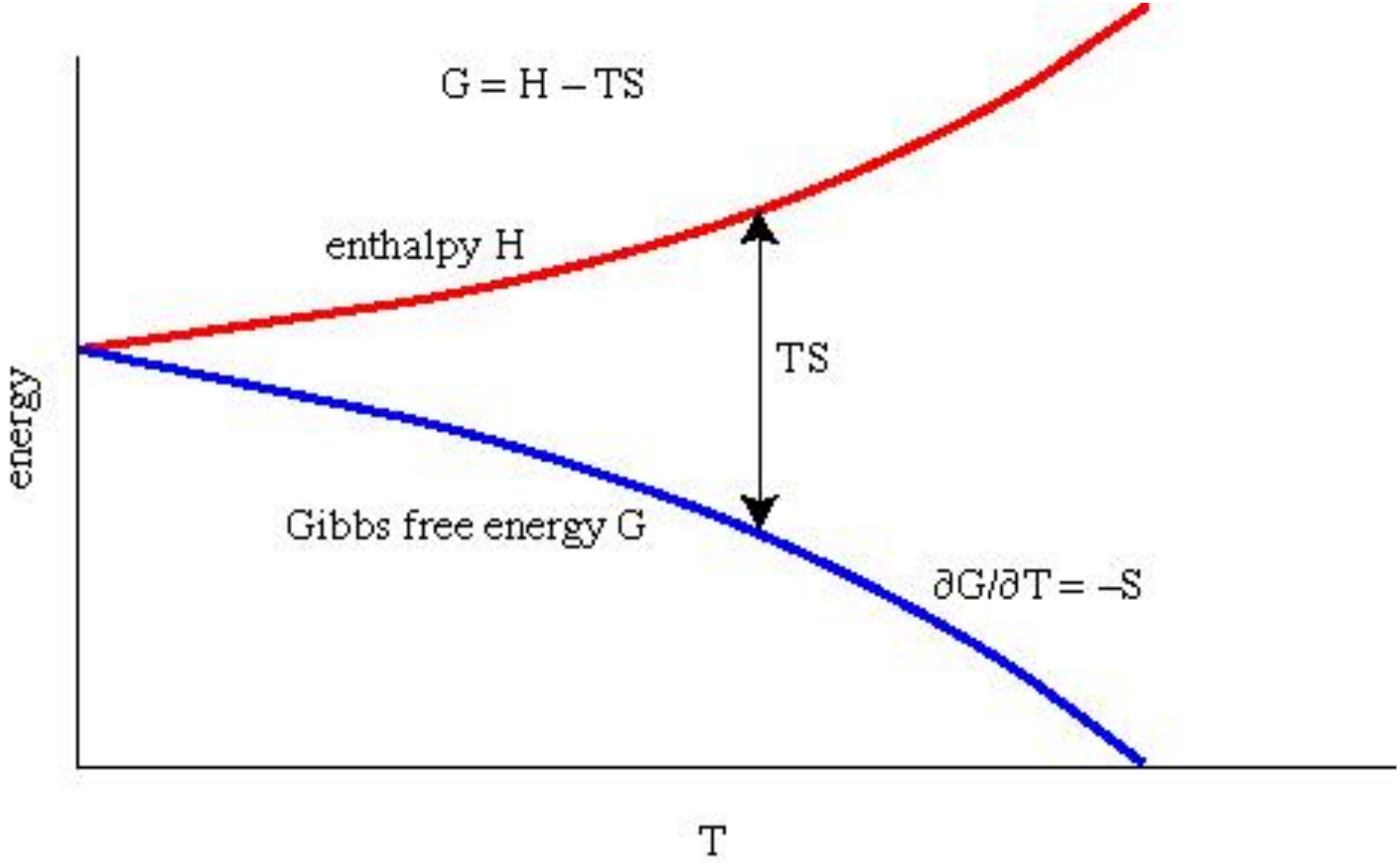
We can calculate the standard heat of formation of PbO by using the equation mentioned below

$$\Delta H^{0}_{500\,K, \langle PbO \rangle} = \Delta H^{0}_{298, \langle PbO \rangle} + \int_{298}^{500} \left(\Delta C_p\right)_{Rea(1)} dT$$

$$= \Delta H^{0}_{298, \langle Pbo \rangle} + \int_{298}^{500} \left[\left(C_p\right)_{\langle PbO \rangle} - \left(C_p\right)_{\langle Pb \rangle} - \frac{1}{2}\left(C_p\right)_{(O_2)}\right] dT$$

$$\Rightarrow \Delta H^{0}_{500, \langle Pbo \rangle} = -51{,}998 \text{ cal}$$

Continued…



Energy vs Temperature graph showing Enthalpy and free energy variation

Ref-http://hacker.faculty.geol.ucsb.edu/geo124T/lecture.html

Continued…

THERMO CHEMISTRY & ITS APPLICATIONS:

It is the study of heat effects accompanying chemical reactions, the formation of solutions & changes in the state of matter such as melting or vaporization & physical-chemical processes.

- ☐ **Heat of Reaction:** It is defined as the heat evolved or absorbed when the reactants react completely to produce products.

Expressed in terms of either per mole of any reactant or any products.

- ☐ **Heat of Formation:** It is defined as the heat evolved or absorbed when one mole of the compound is formed from its constituent elements.
  - Expressed per mole of compound.
  - Depends on temperature.
  - In standard state, heat of formation of a compound out of its constituent elements is called as standard heat of formation.

Continued…

- **Heat of Combustion:** Heat of combustion of a substance is the enthalpy change when one mole of the substance is completely burnt in oxygen.
- **Heat of Solution:** When one substance dissolves in another there will be a change in enthalpy that is known as heat of solution & it depends on the concentration of the solution.

LECTURE-7

FIRST LAW OF THERMODYNAMICS: First law of thermodynamics is also known as **conservation of energy**, which states as the total energy of an isolated system is always constant; energy can neither be created nor be destroyed, it can only be transformed from one form to another.

Let us consider a body in the state A, which performs work W, absorbs heat q & as a consequence moves to the state B. The absorption of heat increase the internal energy of the body by the amount ΔU & the performance of work W by the body decrease its internal energy by the amount W. Thus the total change in the internal energy of the body, ΔU is

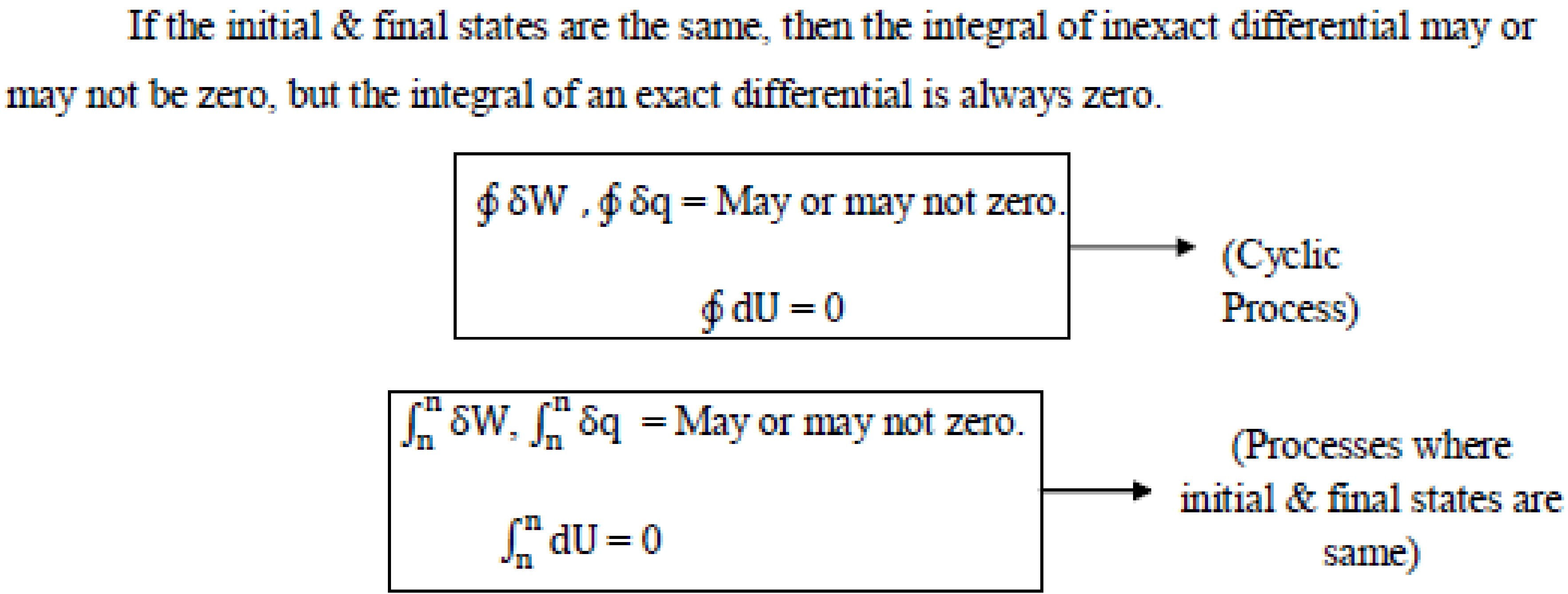
$$\Delta \mathrm{U} = (\mathrm{U_B} - \mathrm{U_A}) = \mathrm{q} - \mathrm{W} \tag{19}$$

Continued…

This is the statement of **1st law of Thermodynamics.**

For an infinitesimal change of state the equation (19) can be written as in differential form as

$$dU = \delta q - \delta W \tag{20}$$



If the initial & final states are the same, then the integral of inexact differential may or may not be zero, but the integral of an exact differential is always zero.

$\oint \delta W$, $\oint \delta q$ = May or may not zero.

$\oint dU = 0$

→ (Cyclic Process)

$\int_n^n \delta W$, $\int_n^n \delta q$ = May or may not zero.

$\int_n^n dU = 0$

→ (Processes where initial & final states are same)

Continued…

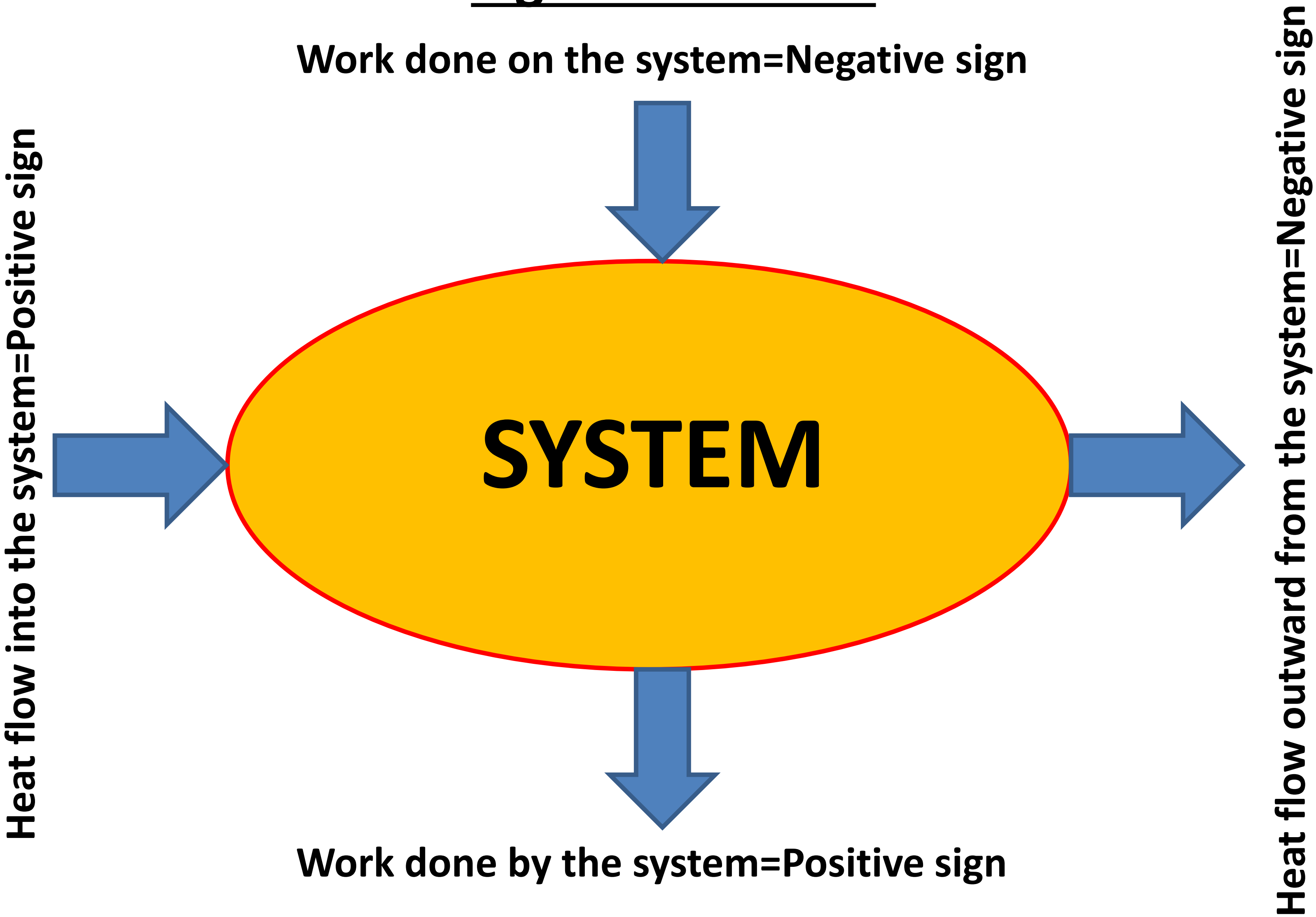
If we have considered that the process taking place in a closed system. In particular, if no work is done on a thermally isolated closed system. We have

$$\Delta\mathrm{U} = 0 \tag{21}$$

This is one aspect of the law of conservation of energy & can be stated as “The internal energy of an isolated system remains constant.”

Continued…

Sign convention



Work done on the system=Negative sign

Heat flow into the system=Positive sign

Heat flow outward from the system=Negative sign

Work done by the system=Positive sign

Continued…

Application of First Law of Thermodynamics:

Isobaric Processes: An isobaric process occurs at constant pressure. Since the pressure is constant, the force exerted is constant and the work done is given as P**Δ**V.

Boundary work is defined as:

$$W_b = \int_1^2 P\, dV$$

For an isobaric process:

$$W_b = P\Delta V = P(V_2 - V_1)$$

- An isobaric gas expansion of gas requires heat transfer to keep the pressure constant.
- Best application of this isobaric process is movable piston in a cylinder, so that pressure inside the cylinder is always at atmospheric pressure, although it is isolated from the atmosphere. In other words, the system is dynamically connected by a movable boundary, to a constant reservoir.

Continued…

- ❑ If a gas is to expand at a constant pressure, heat should be transferred into the system at a certain rate. This process is called an isobaric expansion.

Adiabatic Process:

- ❑ If the system has rigid walls such that work cannot be added ($W = 0$), and the walls of the system are not adiabatic and energy is added in the form of heat ($Q > 0$), the temperature of the system will rise.
- ❑ If the system has rigid walls such that work cannot be added ($W = 0$), and the system boundaries are adiabatic ($Q = 0$), but energy is added as work in the form of friction or the stirring of a viscous fluid within the system, the temperature of the system will rise.

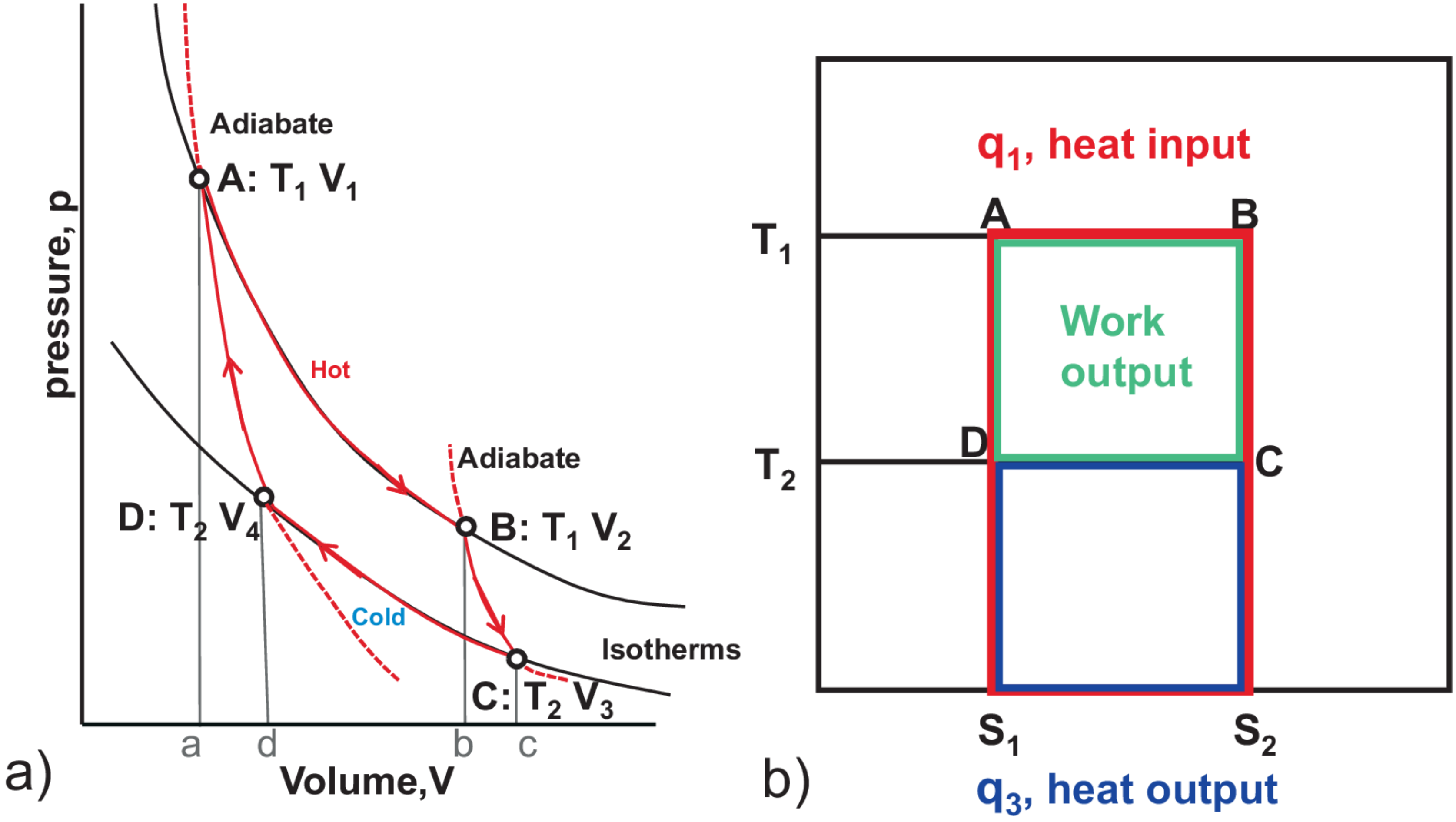
Continued…

- If the system walls are adiabatic (*Q* = 0), but not rigid (*W* ≠ 0), and energy is added to the system in the form of frictionless, non-viscous work, the temperature of the system will rise. The energy added, is stored within the system, and is completely recoverable. Such a process of the frictionless, non-viscous application of work to a system is called an isentropic process.
- If the system contains a compressible gas and is reduced in volume, the uncertainty of the position of the gas is reduced as it is compressed to a smaller volume, and seemingly reduces the entropy of the system, but the temperature of the system will rise as the process is isentropic ($\Delta S = 0$).

Continued…

- The work Should be added in such a way that friction or viscous forces are operating within the system, the process is not isentropic, the temperature of the system will rise, and the work added to the system is not entirely recoverable in the form of work.
- If the walls of a system are not adiabatic, and energy is transferred in as heat, entropy is transferred into the system with the heat. Such a process is neither adiabatic nor isentropic, having $Q > 0$, and $\Delta S > 0$ according to the second law of thermodynamics.
- **Application in Carnot cycle:** The engineer N. L. Sadi Carnot (1796–1832) first proposed an ideal heat engine that operated through a cycle of reversible isothermal and adiabatic steps

Continued…



Carnot cycle representation (a) P-V diagram (b) T-S diagram

Ref- https://www.tf.uni-kiel.de/matwis/amat/td_kin_i/kap_1/pictures/carnot_cycle_pv_ts.png

LECTURE-8

SECOND LAW OF THERMODYNAMICS: According to Clausius & Kelvin & as reformulated by Max Plank, the following statement is significant: “It is impossible to construct a cyclic engine that can convert heat from a reservoir at a uniform temperature completely into mechanical energy without leaving any effect elsewhere.”

The engine must be cyclic i.e. it returns to initial position after each stroke or revolution.

Some Alternative Statements:

i. Heat absorbed at any one temperature can not completely transformed into work without leaving some change in the system or its surrounding.

ii. Spontaneous processes are not thermodynamically reversible.

Continued…

Spontaneous Process: Spontaneous processes are the naturally occurring processes which cannot be reversed without the interruption of external force.

Examples of Spontaneous processes: Flow of heat from higher to lower temperature, diffusion process of a species from higher to lower concentration, mixing of acid-base reactions, all natural processes that occurring in nature without external intervention.

Generally 2nd law of TD mathematically expressed in terms of entropy (S) as

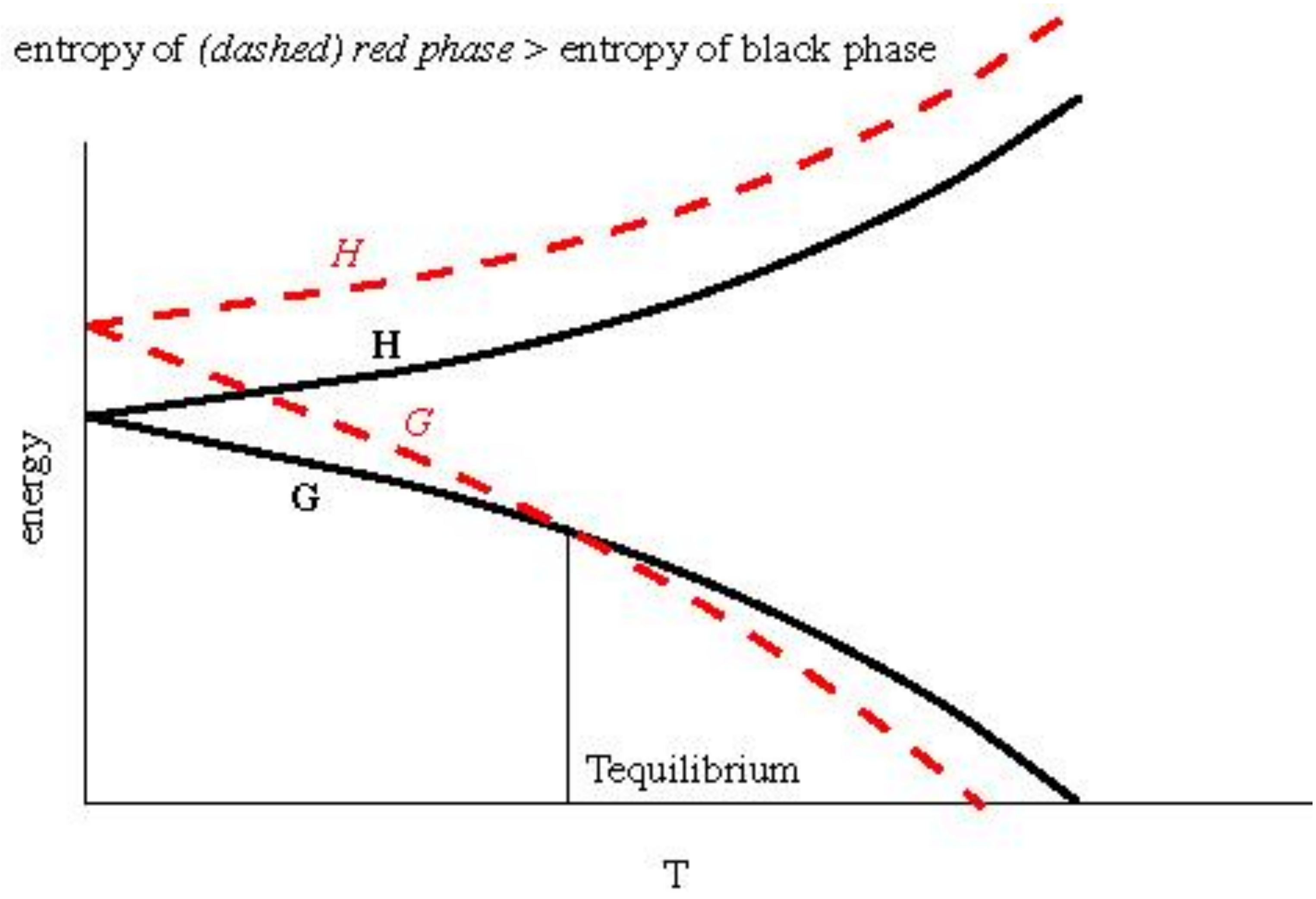
$$\mathrm{dS} = \frac{\delta \mathrm{q_{rev}}}{\mathrm{T}} \qquad (22)$$

Continued…

ENTROPY: Entropy is a measure of randomness of a system. Entropy increases as the number of possible microstates increases where microstate is the microscopic arrangement of atoms or particles.

- Symbolically represented as by "S".
- Standard Entropy (S^0): The absolute entropy of a substance at 1atm pressure and 298 K temperature.
- Unit: J/K.mol.
- Trends for standard entropy values
    a. Entropy of solid < Liquid < Gas
    b. More complexes molecules have higher entropy.

Continued…



Entropy comparison of two different phases using energy vs temperature graph

Ref: http://hacker.faculty.geol.ucsb.edu/geo124T/lecture.html

Continued…

Characteristics of Entropy:

- ☐ It depends on state variables.
- ☐ It is a perfect differential since it is a state property.
- ☐ It is mathematically expressed as $\mathrm{d}S = \frac{\delta q_{rev}}{T}$.
- ☐ For absorption of heat δq is positive. So entropy change $\mathrm{d}S$ is positive. Similarly for release of heat δq is negative. So entropy change $\mathrm{d}S$ is negative.
- ☐ For adiabatic process, δq is equal to zero. Hence $\mathrm{d}S$ is equal to zero. So adiabatic process also known as isotropic process.

Continued…

$\mathbf{Proof\ of\ \delta q\ is\ not\ Perfectly\ Differentiable, but\ \left({}^{\delta q}/_{T}\right)\ is\ Perfectly\ Differentiable}$:

Since, from 1st law of Thermodynamics, we know

$$\delta q = dU + \delta W \tag{23}$$

Again, we know $dU = C_V dT$ & $\delta W = PdV$. So equation (23) becomes

$$\delta q = C_V dT + PdV = C_V dT + RT\frac{dV}{V} \tag{24}$$

(Since molar quantity we have $P = \frac{RT}{V}$)

Now consider the process undergo from state-1 to state-2, we have equation (24) becomes

$$\int_1^2 \delta q = \int_{T_1}^{T_2} C_V\, dT + \int_{V_1}^{V_2} RT\frac{dV}{V} = C_V(T_2 - T_1) + RT(\ln V_2 - \ln V_1) \tag{25}$$

Continued…

$$\Rightarrow \int_1^2 \delta q = \underbrace{C_V \Delta T}_{\boxed{\text{1st Term}}} + \underbrace{RT \ln\left(\frac{V_2}{V_1}\right)}_{\boxed{\text{2nd Term}}} \tag{26}$$

In above equation, we have

- For isothermal process, 1st term is zero. So δq depends on 2nd term.
- For non-isothermal process, both terms are not completely zero. So δq depends on both terms.

Since δq not depends on state variables. So it is not a perfectly differentiable.

Again,

$$\int_1^2 \frac{\delta q}{T} = \int_{T_1}^{T_2} C_V \frac{dT}{T} + \int_{V_1}^{V_2} R \frac{dV}{V} \tag{27}$$

(Dividing equation (26) by T)

$$\Rightarrow \int_1^2 \frac{\delta q}{T} = C_V(\ln T_2 - \ln T_1) + R(\ln V_2 - \ln V_1) \tag{28}$$

Continued…

$$\Rightarrow \int_1^2 \frac{\delta q}{T} = C_V \underset{\underset{\boxed{1^{st}\text{ Term}}}{\Downarrow}}{\ln\left(\frac{T_2}{T_1}\right)} + R \underset{\underset{\boxed{2^{nd}\text{ Term}}}{\Downarrow}}{\ln\left(\frac{V_2}{V_1}\right)} \tag{29}$$

Since, $\frac{\delta q}{T}$ depends on at least one state varies when others remains constant.

- For Isothermal process, $\frac{\delta q}{T}$ depends on 2nd term.

- For Isochoric process, $\frac{\delta q}{T}$ depends on 1st term.

So, $\frac{\delta q}{T}$ is perfectly differentiable.

<u>ENTROPY OF A PERFECT GAS:</u>

Dividing equation of 1st law by temperature (T), we have

$$\int_1^2 \frac{\delta q}{T} = \int_{S_1}^{S_2} dS = \int_{T_1}^{T_2} C_V \frac{dT}{T} + \int_{V_1}^{V_2} R \frac{dV}{V} \tag{30}$$

Continued…

$$\Delta S = S_2 - S_1 = C_V(\ln T_2 - \ln T_1) + R(\ln V_2 - \ln V_1) = C_V \ln\left(\frac{T_2}{T_1}\right) + R\ln\left(\frac{V_2}{V_1}\right) \quad (31)$$

$$\Rightarrow S_2 = C_V \ln\left(\frac{T_2}{T_1}\right) + R\ln\left(\frac{V_2}{V_1}\right) + S_1 \quad (32)$$

Now we know, $C_P - C_V = R \Rightarrow C_V = C_P - R$ & $V = \frac{RT}{P}$ (33)

So using equation (33) in equation (32), it will become

$$S_2 = \left(C_p - R\right)\ln\left(\frac{T_2}{T_1}\right) + R\ln\left(\frac{RT_2/P_2}{RT_1/P_1}\right) + S_1$$

$$= C_P \ln\left(\frac{T_2}{T_1}\right) - R\ln\left(\frac{T_2}{T_1}\right) + R\ln\left[\left(\frac{T_2}{T_1}\right)\left(\frac{P_1}{P_2}\right)\right] + S_1 \quad (34)$$

$$\Rightarrow S_2 = C_P \ln\left(\frac{T_2}{T_1}\right) - R\ln\left(\frac{T_2}{T_1}\right) + R\ln\left(\frac{T_2}{T_1}\right) + R\ln\left(\frac{P_1}{P_2}\right) + S_1$$

$$= C_P \ln\left(\frac{T_2}{T_1}\right) - R\ln\left(\frac{P_2}{P_1}\right) + S_1 \quad (35)$$

Continued…

In general the above equation (35) can be represented as

$$\mathrm{S = C_P \ln T - R \ln P + S_o} \tag{36}$$

Now putting $\mathrm{T = \frac{PV}{R}}$ in above equation (36) we have

$$\mathrm{S = C_P \ln\left(\frac{PV}{R}\right) - R \ln P + S_o = C_P \ln P + C_P \ln V - C_P \ln R - R \ln P + S_o} \tag{37}$$

(Since $\mathrm{C_P \ln R}$ is a constant. So adding with S_o another constant get obtained S_I)

$$\mathrm{\Rightarrow S = C_P \ln P + C_P \ln V - R \ln P + S_I = (C_P - R) \ln P + C_P \ln V + S_I}$$

$$\mathrm{\Rightarrow S = C_V \ln P + C_P \ln V + S_I} \tag{38}$$

So for a process which undergoes from state (1) to state (2) equation (38) can be expressed as

$$\mathrm{\Delta S = S_2 - S_1 = C_V \ln\left(\frac{P_2}{P_1}\right) + C_P \ln\left(\frac{V_2}{V_1}\right)} \tag{39}$$

Continued…

At Isothermal condition (ΔT=0), equation (32) and (35) becomes

$$\mathrm{S_2} = \mathrm{R}\ln\left(\frac{\mathrm{V_2}}{\mathrm{V_1}}\right) + \mathrm{S_1} \tag{40}$$

$$\mathrm{S_2} = -\mathrm{R}\ln\left(\frac{\mathrm{P_2}}{\mathrm{P_1}}\right) + \mathrm{S_1} \tag{41}$$

From equation (40) & (41), we have got

$$\Delta\mathrm{S} = \mathrm{S_2} - \mathrm{S_1} = \mathrm{R}\ln\left(\frac{\mathrm{V_2}}{\mathrm{V_2}}\right) = -\mathrm{R}\ln\left(\frac{\mathrm{P_2}}{\mathrm{P_1}}\right) \tag{42}$$

LECTURE-9

FREE ENERGY: Free energy is defined as the part of energy that available for useful work done & that part of energy which can not available for useful work done is known as bound energy.

- ☐ Total energy (E) is the sum of free energy (A) and bound energy (B).
- ☐ The following two functions are employed in TD, according to the names of the scientists who proposed them.

$$\text{Helmholtz free energy (A)} = U - TS \tag{43}$$

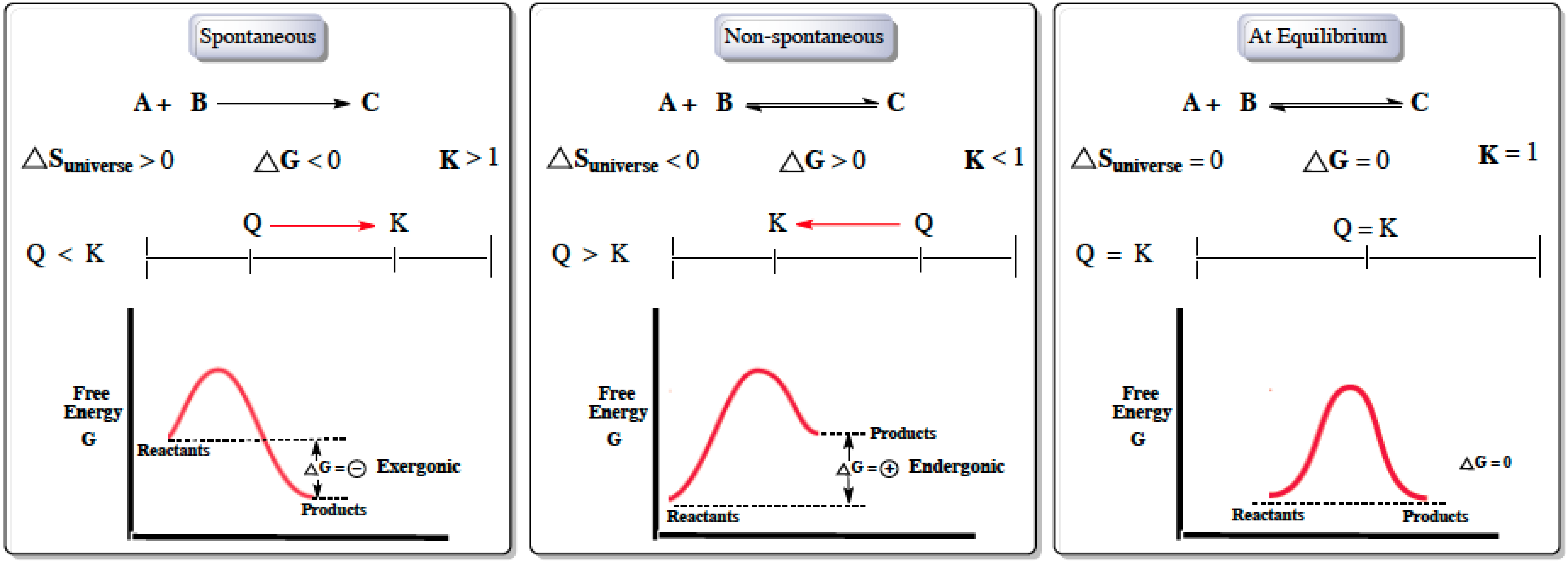
$$\text{Gibbs free energy (G)} = H - TS \tag{44}$$

- ☐ Since U, S, H etc. are the state properties & T is also a state variable. So F and G are also state properties.
- ☐ Below Table is showing, how the nature of the reaction depends on sign of ΔH, ΔS & ΔG.

Continued…

ΔH	**ΔS**	**ΔG**	**Reaction Outcome**
Negative	Positive	Always Negative	Reaction is Spontaneous at all Temperature.
Positive	Negative	Always Positive	Reaction is Non-spontaneous in all Temperature
Negative	Negative	Negative at low Temperature	Reaction is Spontaneous at low Temperature.
		Positive at high Temperature	Reaction is Non-spontaneous in high Temperature
Positive	Positive	Positive at low Temperature	Reaction is Non-spontaneous in low Temperature.
		Negative at low Temperature	Reaction is Spontaneous at high Temperature

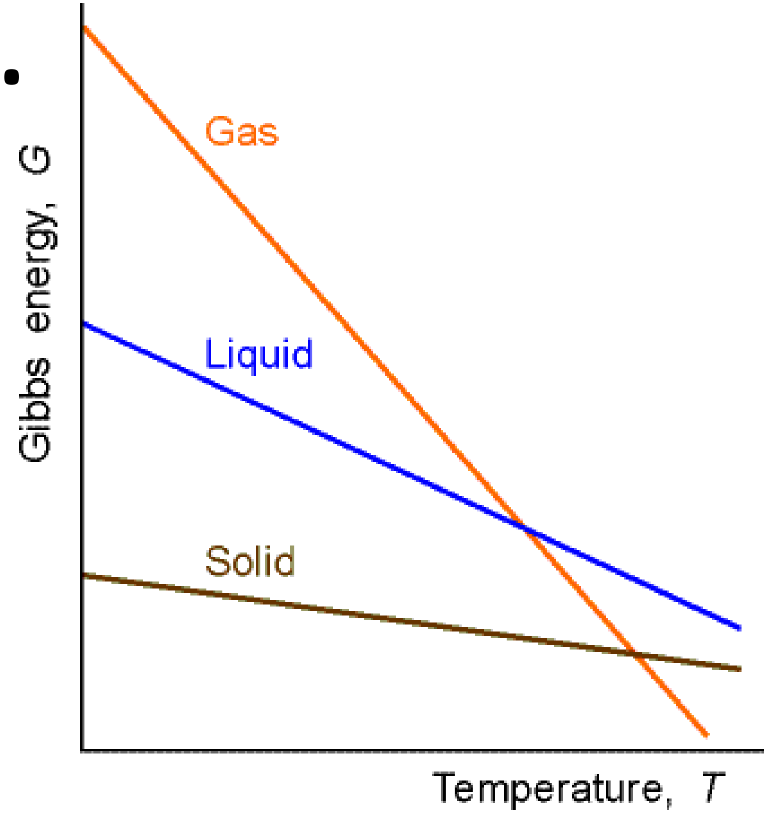
Continued…



Entropy change (ΔS), Gibbs free energy change (ΔG) and rate constant (K) sign and values for different type of chemical reactions and conditions

Ref-https://www.clutchprep.com/analytical-chemistry/chemical-thermodynamics-gibbs-free-energy

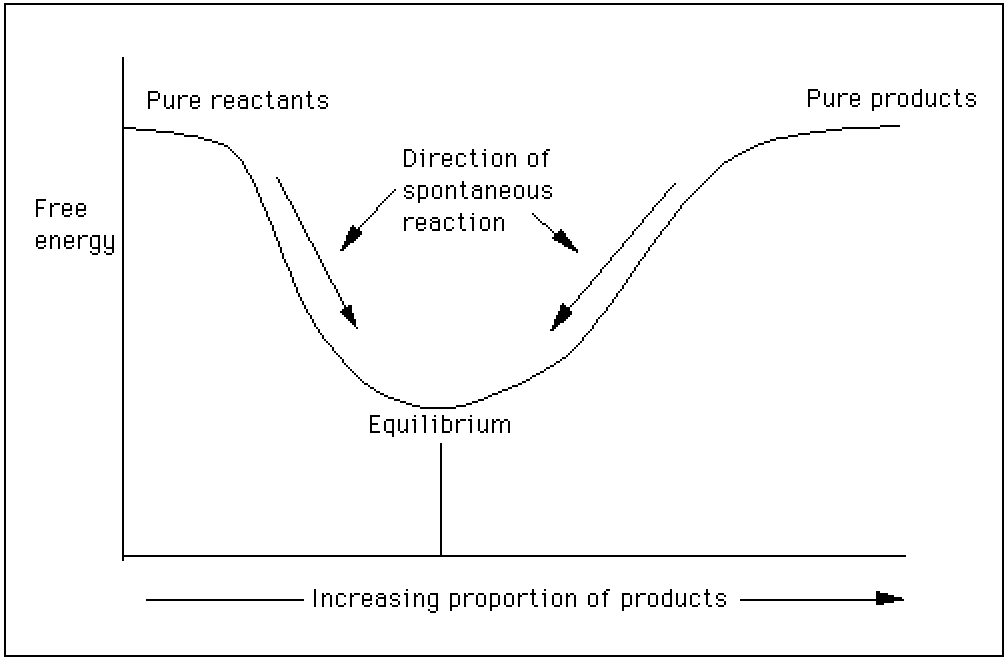
Continued…



Gibbs free energy change (ΔG) for different phases wrt to temperature: Maximum for gaseous state and minimum for solid state.

Ref-http://staff.um.edu.mt/jgri1/teaching/che2372/notes/04/g_props/g_props.html

Continued…



Ref-http://www.shodor.org/unchem/advanced/thermo/index.html

Direction of reaction on the basis of Gibbs free energy

- Forward reaction => Equilibrium energy level is lower than the reactant energy level
- Backward reaction => Equilibrium energy level is lower than the product energy level

Continued…

Free energy change as a function of temperature:

For Isothermal process, the Gibbs free energy change is given by

$$\Delta G = \Delta H - T\Delta S \qquad (45)$$

Therefore

$$\Delta \mathrm{G}_\mathrm{f}^0(\mathrm{T}) = \Delta \mathrm{H}_\mathrm{f}^0(\mathrm{T}) - \mathrm{T}\Delta \mathrm{S}_\mathrm{f}^0(\mathrm{T}) \qquad (46)$$

Now from Kirchhoff’s law

$$\mathrm{H}_\mathrm{T}^0 = \mathrm{H}_{298}^0 + \int_{298}^{\mathrm{T}} \Delta \mathrm{C}_\mathrm{P}^0 \mathrm{dT}$$

Continued…

$$\Rightarrow \Delta \mathrm{H}_{\mathrm{f}}^{0}(\mathrm{T}) = \Delta \mathrm{H}_{\mathrm{f}}^{0}(298) + \int_{298}^{\mathrm{T}} \Delta \mathrm{C}_{\mathrm{P}}^{0}\, \mathrm{dT} \qquad (47)$$

Again

$$\Delta \mathrm{S}_{\mathrm{f}}^{0}(\mathrm{T}) = \Delta \mathrm{S}_{\mathrm{f}}^{0}(298) + \int_{298}^{\mathrm{T}} \frac{\mathrm{C}_{\mathrm{P}}^{0}}{\mathrm{T}}\, \mathrm{dT} \qquad (48)$$

Using equation (47) and (48) in equation (46), we have

$$\Delta \mathrm{G}_{\mathrm{f}}^{0}(\mathrm{T}) = \left[\Delta \mathrm{H}_{\mathrm{f}}^{0}(298) + \int_{298}^{\mathrm{T}} \Delta \mathrm{C}_{\mathrm{P}}^{0} \mathrm{dT}\right] - \mathrm{T}\left[\Delta \mathrm{S}_{\mathrm{f}}^{0}(298) + \int_{298}^{\mathrm{T}} \frac{\Delta \mathrm{C}_{\mathrm{P}}^{0}}{\mathrm{T}}\, \mathrm{dT}\right] \qquad (49)$$

For pure elements, $H_{298}^{0} = 0$, but $S_{298}^{0} \neq 0$.

LECTURE-10

REVERSIBLE & IRREVERSIBLE PROCESS

Sl no.	Reversible Process	Irreversible Process
1	It is defined as the hypothetical passage of a system through a series of equilibrium stages.	The process that can’t be reversed or changed back (permanent damage).
2	Very slow & mostly impractible in nature.	Generally at normal condition it occurs. It may be very fast or fast or slow & practically possible.
3	For isolated system $dS_{sys} = 0$	For isolated system $dS_{sys} > 0$

Continued…

Reversible Process:

Entropy change in a reversible process is given by

$$\Delta S = S_{system} + S_{surr} = S_{surr} \text{ (Since } S_{\text{system}} = 0) \qquad \text{(i)}$$

$$S_{surr} = S_{source} + S_{sink} = \frac{q_1}{T_1} + \frac{q_2}{T_2} \qquad \text{(ii)}$$

Since S_{source} equal and opposite to S_{sink} . So

$$S_{\text{surr}} = 0 \qquad \text{(iii)}$$

So combining equation (i) & (iii), we have

$$(\Delta S)_{rev} = 0$$

Irreversible Process:

- Entropy change in a irreversible process is given by, $(\Delta S)_{Irv} = Positive$
- **Example:** For a cyclic process (Carnot Cycle), net entropy change is always positive.

Continued…

Study of Graphitization of Petroleum Coke:

- ☐ The formation of synthetic graphite from amorphous carbon should theoretically be accompanied by a continuous shrinkage of material. However, in many instances an irreversible volume expansion, commonly referred to as puffing, and is actually observed to occur at some point in the transformation.
- ☐ The addition of certain metals, particularly iron and calcium or their compounds, is known to inhibit or eliminate this expansion. Although "puffing" has generally been associated with the sulfur content of the petroleum coke.
- ☐ Since Graphitization of petroleum coke follows irreversible expansion. So entropy change during this case is same as in case of irreversible process i.e.

$$(\Delta S)_{Grap} = Positive$$

Continued…

Auxiliary Functions: The secondary derived functions as discussed in previous section such as

$$\mathrm{dU = TdS - PdV} \tag{50}$$

$$\mathrm{dH = TdS + VdP} \tag{51}$$

$$\mathrm{dA = -SdT - PdV} \tag{52}$$

$$\mathrm{dG = -SdT + VdP} \tag{53}$$

<u>CRITERIA OF THERMODYNAMICS EQUILIBRIA:</u> Simply it is known as criteria of equilibrium. At equilibrium, there is no change in the system i.e. system remains stable. Again the reversible process occurs through a series of equilibrium stages. Therefore, we keep the independent variables should be fixed to obtained equilibrium criteria. So, in the previous four basic equations to get equilibrium criteria we should have keep the right hand side independent variables as constant.

Continued…

Equilibrium Criteria

Basic Equations	Differential Form	Finite Difference Form
$dU = TdS - PdV$	$(dU)_{S,V} = 0$	$(\Delta U)_{S,V} = 0$
$dH = TdS + VdP$	$(dH)_{S,P} = 0$	$(\Delta H)_{S,P} = 0$
$dA = -SdT - PdV$	$(dA)_{T,V} = 0$	$(\Delta A)_{T,V} = 0$
$dG = -SdT + VdP$	$(dG)_{T,P} = 0$	$(\Delta G)_{T,P} = 0$

N.B.: *Since it is easy to maintain the temperature & pressure constant. So Gibbs free energy criterion achieved which get employ in Chemical & Metallurgical thermodynamics.*

Continued…

MAXWELL’S RELATION

Considering equation (50):

(a) At constant entropy:

$$\partial \mathrm{U} = -\mathrm{P}\partial \mathrm{V} \Rightarrow \left(\frac{\partial \mathrm{U}}{\partial \mathrm{V}}\right)_{\mathrm{S}} = -\mathrm{P} \tag{54}$$

$$\Rightarrow \frac{\partial^2 \mathrm{U}}{\partial \mathrm{S}\, \partial \mathrm{V}} = -\left(\frac{\partial \mathrm{P}}{\partial \mathrm{S}}\right)_{\mathrm{V}} \tag{55}$$

(b) At constant volume:

$$\partial \mathrm{U} = \mathrm{T}\partial \mathrm{S} \Rightarrow \left(\frac{\partial \mathrm{U}}{\partial \mathrm{S}}\right)_{\mathrm{V}} = \mathrm{T} \tag{56}$$

$$\Rightarrow \frac{\partial^2 \mathrm{U}}{\partial \mathrm{S}\, \partial \mathrm{V}} = \left(\frac{\partial \mathrm{T}}{\partial \mathrm{V}}\right)_{\mathrm{S}} \tag{57}$$

Continued…

From equation (55) and (57), we have

$$\left(\frac{\partial \mathrm{T}}{\partial \mathrm{V}}\right)_{\mathrm{S}} = -\left(\frac{\partial \mathrm{P}}{\partial \mathrm{S}}\right)_{\mathrm{V}} \tag{58}$$

In similar way

considering equation (51) at **constant entropy and constant pressure**, it will be found

$$\left(\frac{\partial \mathrm{T}}{\partial \mathrm{P}}\right)_{\mathrm{S}} = \left(\frac{\partial \mathrm{V}}{\partial \mathrm{S}}\right)_{\mathrm{P}} \tag{59}$$

considering equation (52) at **constant temperature and constant volume**, it will be found

$$\left(\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{V}} = \left(\frac{\partial \mathrm{S}}{\partial \mathrm{V}}\right)_{\mathrm{T}} \tag{60}$$

Continued…

considering equation (53) at **constant temperature and constant pressure**, it will be found

$$\left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{P}} = -\left(\frac{\partial \mathrm{S}}{\partial \mathrm{P}}\right)_{\mathrm{T}} \tag{61}$$

So the above equations (58), (59), (60) and (61) are known as **Maxwell's relations**.

QUIZ TEST-2

Q.1 –Write down the mathematical expression for enthalpy changes for the following phase transformation

- Ɛ to β
- ***α*** to ϒ

Q.2 – How the 1st law of Thermodynamics will be mathematically expressed, if in a system heat flow occurs in the outward direction and work done on a system?

Q.3 – Write down the entropy expression for the reaction,

$H_2(g) + 1/2O_2(g) = H_2O(g)$; Temperature varying from 300 K to 400 K

Q.4–What is the condition for free energy change (**Δ**G) in case of forward reaction, backward reaction and at equilibrium condition?

Q.5 –Spontaneous processes are reversible or irreversible, explain it with suitable example.

LECTURE-11

COMBINED EXPRESSIONS OF 1ST & 2ND LAW OF THERMODYNAMICS:

Assumptions:

- Closed System
- Reversible Process
- Work done against pressure

From 1st law of Thermodynamics, we know that

$$\mathrm{dU} = \delta \mathrm{q} - \delta \mathrm{W} = \delta \mathrm{q} - \mathrm{PdV} \tag{62}$$

From 2nd law of Thermodynamics, we know that

$$\delta \mathrm{q} = \mathrm{TdS} \tag{63}$$

Continued…

Combining equation (62) and (63), we got

$$\mathrm{dU = TdS - PdV} \tag{64}$$

Again, we know

$$\mathrm{dH = dU + PdV + VdP} \tag{65}$$

Replacing the term dU from the equation (64) in the equation (65), it will become

$$\mathrm{dH = (TdS - PdV) + PdV + VdP = TdS + VdP} \tag{66}$$

From Helmholtz free energy equation, we know

$$\mathrm{A = U - TS \Rightarrow dA = dU - (TdS + SdT) = (TdS - PdV) - (TdS + SdT)} \tag{67}$$

$$\mathrm{\Rightarrow dA = TdS - PdV - TdS - SdT = -PdV - SdT} \tag{68}$$

Continued…

From Gibbs free energy equation, we know

$$\mathrm{G = H - TS \Rightarrow dG = dH - (TdS + SdT) = (TdS + VdP) - (TdS + SdT)} \tag{69}$$

$$\mathrm{\Rightarrow dG = TdS + VdP - TdS - SdT = VdP - SdT} \tag{70}$$

So, combining 1st & 2nd laws of Thermodynamics with considering the assumptions.

We got the following equations

$$\mathrm{dU = TdS - PdV} \tag{71}$$

$$\mathrm{dH = TdS + VdP} \tag{72}$$

$$\mathrm{dA = -PdV - SdT} \tag{73}$$

$$\mathrm{dG = VdP - SdT} \tag{74}$$

The above four basic differential equations (71-74) are valid under above assumptions i.e. for closed and isolated systems which have fixed mass and composition. The equations are also applicable for open systems provided under a fixed mass and composition.

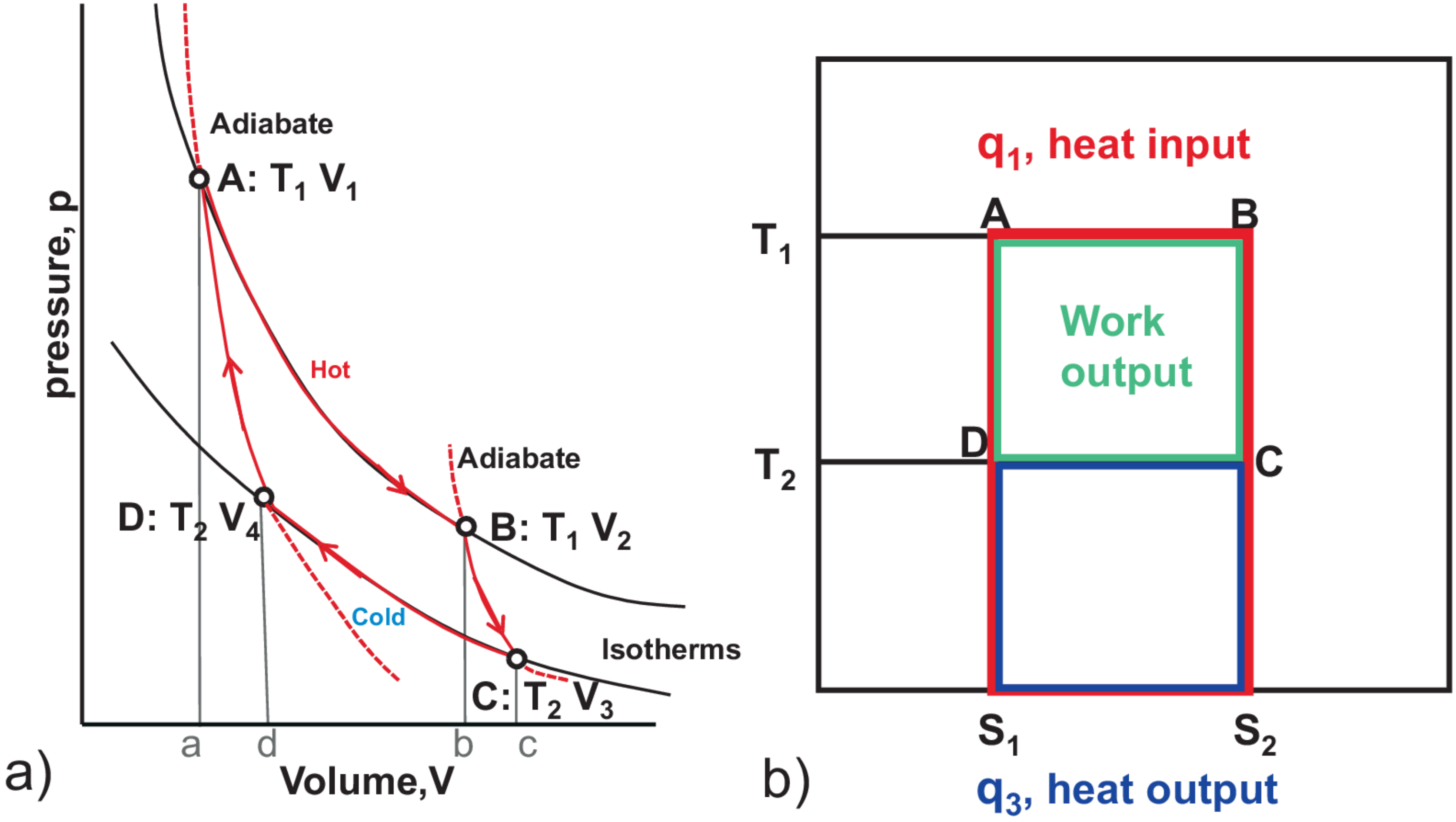
Continued…

Application of both 1st and 2nd law of thermodynamics

Major application in Carnot cycle

- ❑ **Carnot cycle:** During four steps on one down and upward stroke of the piston, visualize the gas and cylinder sitting first on a heat source (heat is added), then on an insulator (no heat exchange), next on a heat sink (heat is removed), and finally back on the insulator.
- ❑ The pressure-volume curve of Figure shows the **Carnot cycle** in the next slide. The gas in the cylinder contains an ideal gas at pressure *(P)*, volume *(V)*, and temperature *(T).*
- ❑ During this isothermal expansion, the gas did work lifting a load. Hence, the work is represented by the area under the A–B segment of the curve

Continued…



Carnot cycle representation (a) P-V diagram (b) T-S diagram

Ref- https://www.tf.uni-kiel.de/matwis/amat/td_kin_i/kap_1/pictures/carnot_cycle_pv_ts.png

Continued…

- ☐ As the gas expands adiabatically from point B to C on the P-V curve. So, the work is done by the gas in terms of expansion on the piston as shown by the area under the BC segment of P-V curve
- ☐ The gas is further isothermally compressed that gives up an heat to the sink. For this, the work is done by the piston on the gas which shown as the area under the CD segment of P-V curve
- ☐ At the end, the gas is compressed adiabatically further to reach at initial state as at point A. For this part, the work is done on the gas, that is shown by the area under the DA segment of P-V curve

Continued…

- The total work done by the gas on the piston is represented as the area under the ABC section of the PV curve, whereas the total work done by the piston on the gas is the area under the CDA section. The difference between these two areas is the interior portion of the ABCD curve in the P-V graph that represents the output of the Carnot engine.

- If the energy absorbed Q_1 heat from the source and given up Q_2 amount of heat to sink , then the work output is expressed as $W_{o/p} = Q_1 - Q_2$.

- The efficiency of the Carnot engine

$$Efficiency = \left[\frac{W_{o/p}}{W_{i/p}} \times 100\right]\% = \left[\frac{Q_1 - Q_2}{Q_1} \times 100\right]\%$$

Continued…

- As per the 2nd law of thermodynamics the efficiency of Carnot reversible cycle depends on the temperatures of two heat reservoirs that operated within the two temperatures in a most efficient way.

- Carnot cycle is the representation of the Carnot heat engine.

- It is operated in between two extreme points that is quasi-static in nature, so that the heat transfer and work done in the Carnot engine always remains in internal equilibrium

- It is equivalent to the second law of thermodynamics that states that "Spontaneous processes are irreversible in nature", and remains valid still yet.

Continued…

TRANSFORMATION FORMULA:

For state property x, y, z. The system X represented as

$$X = f(x, y, z) = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz \tag{75}$$

So for increase in change at constant composition X=0, so equation (75) becomes

$$0 = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz$$

$$\Rightarrow \left(\frac{\partial x}{\partial y}\right)_z dy = -\left(\frac{\partial x}{\partial z}\right)_y dz$$

$$\Rightarrow \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \tag{76}$$

The above equation (76) is known as Transformation formula.

LECTURE-12

GIBBS HELMHOLTZ EQUATION

From Helmholtz free energy equation, we have

$$dA = -PdV - SdT \qquad (77)$$

From Gibbs free energy equation, we have

$$dG = VdP - SdT \qquad (78)$$

1. **Isochoric Process:**

$$dA = -SdT \Rightarrow \left(\frac{dA}{dT}\right)_V = -S \qquad (79)$$

Then as, $A = U - TS \Rightarrow -S = \frac{A-U}{T}$ (80)

From equation (79) and (80), we have

$$\left(\frac{dA}{dT}\right)_V = \frac{A-U}{T} \Rightarrow A - U = T\left(\frac{dF}{dT}\right)_V \qquad (81)$$

$$\Rightarrow A = U + T\left(\frac{dF}{dT}\right)_V \qquad (82)$$

Continued…

2. **For Isobaric Process:**

$$\mathrm{dG} = -\mathrm{SdT} \Rightarrow \left(\frac{\mathrm{dG}}{\mathrm{dT}}\right)_{\mathrm{P}} = -\mathrm{S} \qquad (83)$$

Again we know, $$\mathrm{G} = \mathrm{H} - \mathrm{TS} \Rightarrow -\mathrm{S} = \frac{\mathrm{G}-\mathrm{H}}{\mathrm{T}} \qquad (84)$$

From equation (83) and (84), we got

$$\left(\frac{\mathrm{dG}}{\mathrm{dT}}\right)_{\mathrm{P}} = \frac{\mathrm{G}-\mathrm{H}}{\mathrm{T}} \Rightarrow \mathrm{G} - \mathrm{H} = \mathrm{T}\left(\frac{\mathrm{dG}}{\mathrm{dT}}\right)_{\mathrm{P}} \qquad (85)$$

$$\Rightarrow \mathrm{G} = \mathrm{H} + \mathrm{T}\left(\frac{\mathrm{dG}}{\mathrm{dT}}\right)_{\mathrm{P}} \qquad (86)$$

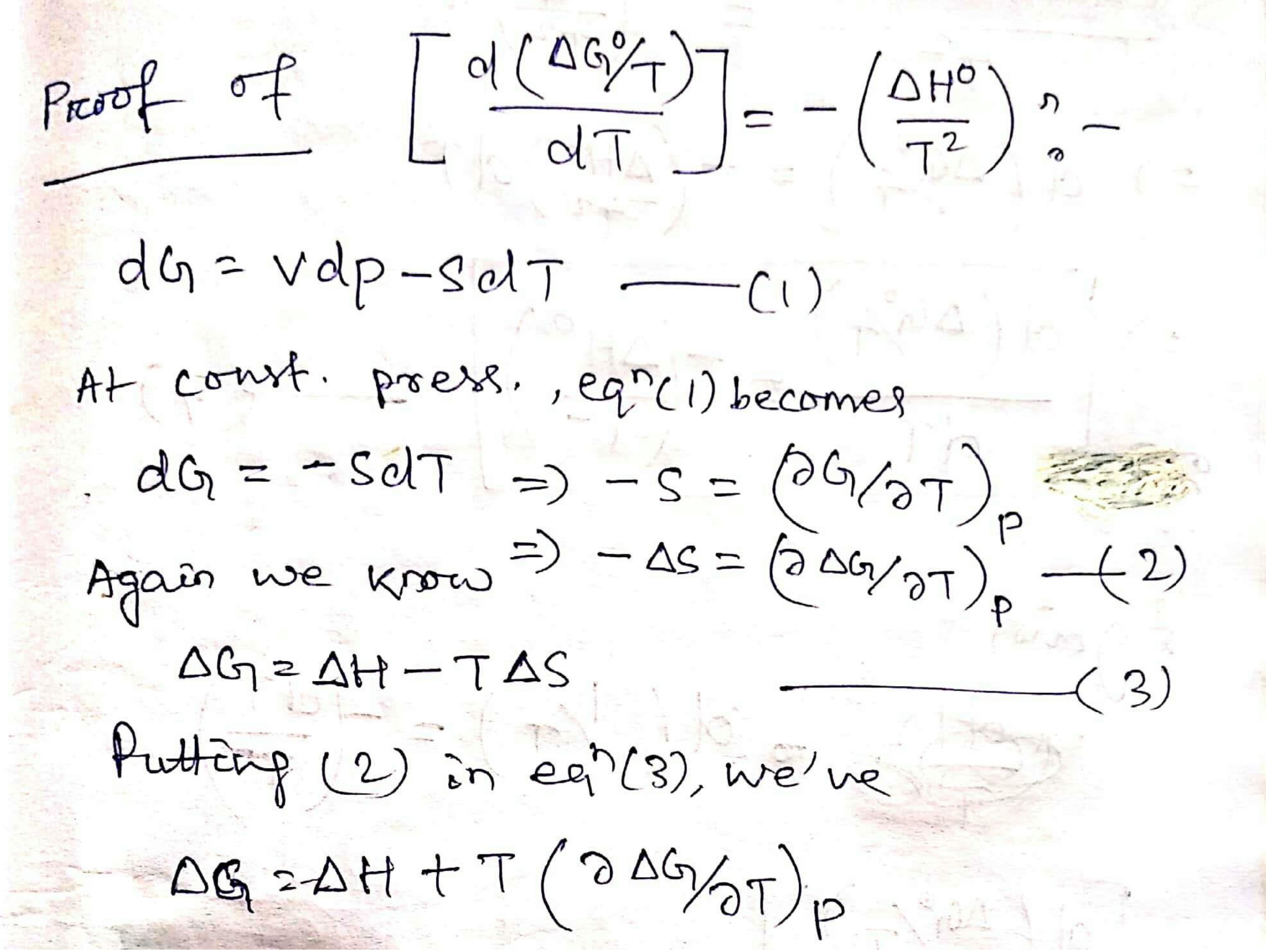
The above equations (82) and (86) are known as Gibbs Helmholtz equation.

Continued…

Importance of Gibbs-Helmholtz Equation:

- ☐ It measures the value of change in Gibbs free energy (ΔG).
- ☐ The measurement of change in Gibbs free energy (ΔG) determines the feasibility & direction of the reaction.
  a) If $\Delta G < 0$, the reaction is feasible & it is a forward reaction.
  b) If $\Delta G > 0$, the reaction is not feasible & it is a backward reaction.
  c) If $\Delta G = 0$, the reaction is at equilibrium position & it is neither a forward nor a backward reaction.

Continued…



Proof of $\left[\frac{d(\Delta G^0/T)}{dT}\right] = -\left(\frac{\Delta H^0}{T^2}\right)$:-

$$dG = Vdp - SdT \quad \text{——} (1)$$

At const. press., eq^n(1) becomes

$$dG = -SdT \Rightarrow -S = \left(\partial G/\partial T\right)_p$$

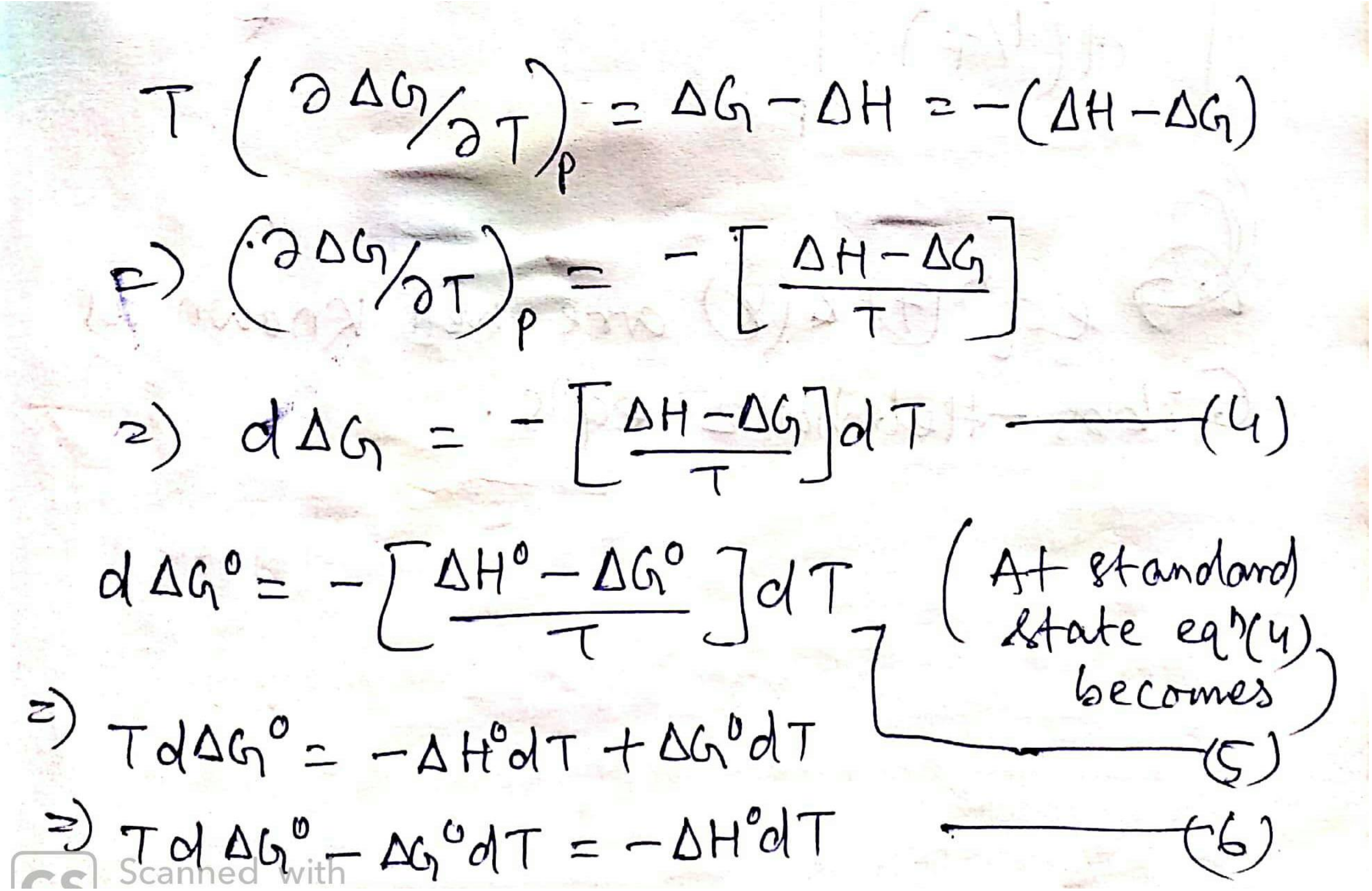
Again we know $\Rightarrow -\Delta S = \left(\partial \Delta G/\partial T\right)_p$ —(2)

$$\Delta G = \Delta H - T\Delta S \quad \text{——} (3)$$

Putting (2) in eq^n(3), we've

$$\Delta G = \Delta H + T\left(\partial \Delta G/\partial T\right)_p$$

Continued…



$$T\left(\frac{\partial \Delta G}{\partial T}\right)_p = \Delta G - \Delta H = -(\Delta H - \Delta G)$$

$$\Rightarrow \left(\frac{\partial \Delta G}{\partial T}\right)_p = -\left[\frac{\Delta H - \Delta G}{T}\right]$$

$$\Rightarrow d\Delta G = -\left[\frac{\Delta H - \Delta G}{T}\right] dT \tag{4}$$

(At standard state eqn(4) becomes)

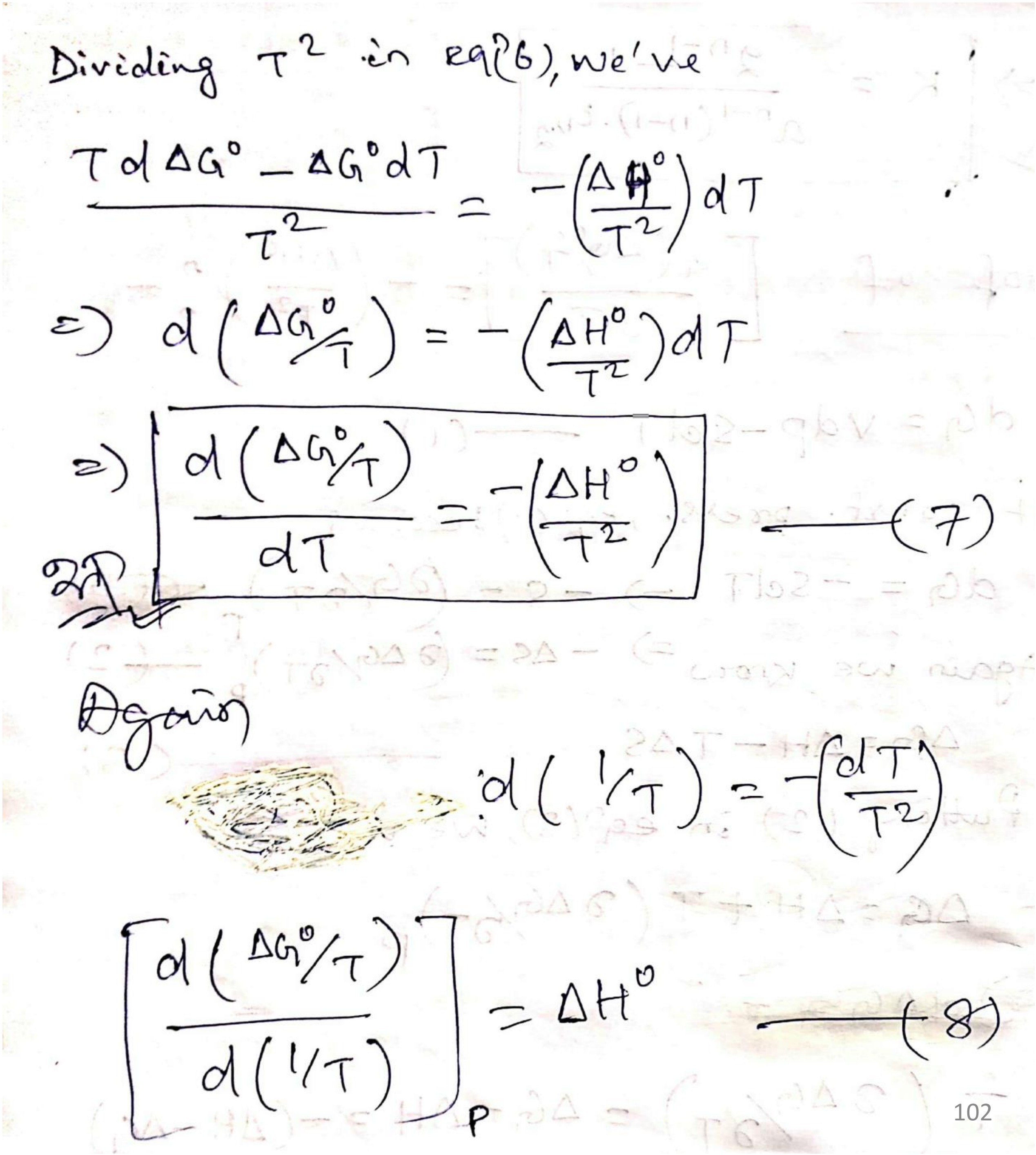
$$d\Delta G^0 = -\left[\frac{\Delta H^0 - \Delta G^0}{T}\right] dT \tag{5}$$

$$\Rightarrow T d\Delta G^0 = -\Delta H^0 dT + \Delta G^0 dT$$

$$\Rightarrow T d\Delta G^0 - \Delta G^0 dT = -\Delta H^0 dT \tag{6}$$

CS Scanned with

Continued…



Dividing T^2 in eq^n(6), we've

$$\frac{T\,d\Delta G^\circ - \Delta G^\circ dT}{T^2} = -\left(\frac{\Delta H^\circ}{T^2}\right)dT$$

$$\Rightarrow d\left(\Delta G^\circ/T\right) = -\left(\frac{\Delta H^\circ}{T^2}\right)dT$$

$$\Rightarrow \boxed{\frac{d\left(\Delta G^\circ/T\right)}{dT} = -\left(\frac{\Delta H^\circ}{T^2}\right)} \longleftarrow (7)$$

Again

$$d\left(1/T\right) = -\left(\frac{dT}{T^2}\right)$$

$$\left[\frac{d\left(\Delta G^\circ/T\right)}{d\left(1/T\right)}\right]_P = \Delta H^\circ \longleftarrow (8)$$

Continued…

Again we know $\Delta G^0 = -RT\ln K$

$\Rightarrow \Delta G^0/T = -R\ln K$ — (9)

Using eq^n(9) in (7) we've

$$\frac{d(-R\ln K)}{dT} = -\left(\frac{\Delta H^0}{T^2}\right) \quad \text{— (10)}$$

$$\Rightarrow \boxed{\frac{d(\ln K)}{dT} = \frac{\Delta H^0}{RT^2}} \quad \text{— (11)}$$

$$\Rightarrow \boxed{\frac{d\ln K}{d(1/T)} = -\left(\frac{\Delta H^0}{R}\right)} \quad \text{— (12)}$$

eq^n(11) & (12) are known as Van't Hoff eq^n.

Continued…

Standard State:

- ☐ The standard state is the stablest state of pure substance at any specified temperature and 1 atm pressure condition.

- ☐ At standard state, the enthalpy of a pure metal is always zero, but the entropy is not equal to zero.

- ☐ At standard state, Gibbs free energy change for a chemical reaction is given by

$$\mathrm{d}G^0 = \mathrm{d}H^0 - TdS^0 \tag{87}$$

- ☐ For any reaction to be spontaneous the Gibbs free energy change should be negative.

LECTURE-13

ESCAPING TENDENCY: It is the tendency of dissolution of one phase to another phase on the measure of thermodynamic potential.

Let’s consider a system consists of liquid phase and a gaseous phase of water. Then to express the escaping tendency or migration of molecules from one phase to another, thermodynamic parameter molar thermodynamic potential is used. In such cases, three cases arise

Case-1: When system is in equilibrium i. e. no migration of molecules from one phase to another, Hence

$$\mathrm{G_{vapour}} = \mathrm{G_{liquid}} \Rightarrow \overline{\Delta \mathrm{G}} = 0 \tag{88}$$

Case-2: Temperature is slightly increased, as a result liquid molecules starts vaporizing then

$$\mathrm{G_{vapour}} < \mathrm{G_{liquid}} \Rightarrow \overline{\Delta \mathrm{G}} = +\mathrm{ve} \tag{89}$$

Continued…

Case-3: Suppose the temperature is lowered, n such case condensation of gas molecules starts. So in that case

$$\mathrm{G_{vapour}} > \mathrm{G_{liquid}} \Rightarrow \overline{\Delta \mathrm{G}} = -\mathrm{ve} \tag{90}$$

FUGACITY: At $\mathrm{P} \to 0, \overline{\mathrm{G}} = -\infty$ in this condition escaping tendency measure by a term known as fugacity.

Fugacity related with pressure under the mathematical expression mentioned below

$$\mathrm{f} = \mathrm{Pe}^{\left(-\mathrm{A}/_{\mathrm{RT}}\right)} \tag{91}$$

Continued…

Graphical Representation of Fugacity:

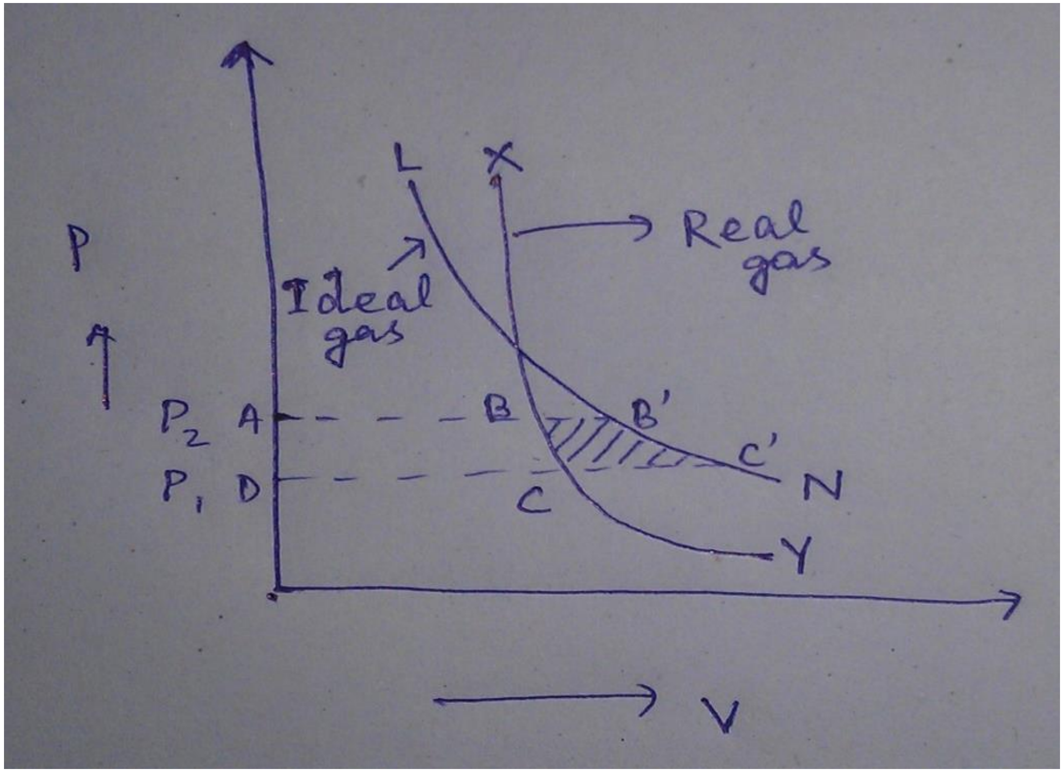


Fig -Combined Pressure vs. Volume graph for Ideal and Real gas

Since we know that

$$dG = VdP - SdP \tag{92}$$

At constant temperature

$$dG = VdP \tag{93}$$

Continued…

Now integrate from P_1 to P_2 pressure change

$$\int_{P_1}^{P_2} dG_{\text{ideal}} = V\int_{P_1}^{P_2} dP = \text{Area A B}'\text{C}'\text{D} \tag{94}$$

$$\int_{P_1}^{P_2} dG_{\text{real}} = V\int_{P_1}^{P_2} dP = \text{Area A BCD} \tag{95}$$

$$\int_{P_1}^{P_2} dG_{\text{ideal}} = \int_{P_1}^{P_2} dG_{\text{real}} - A' \tag{96}$$

For $P_1 \rightarrow 0, P_2 \rightarrow P$ then equation (96) becomes

$$G_{\text{real}}^{P} = G_{\text{ideal}}^{P} - A' \tag{97}$$

$$\Rightarrow RT\ln f = RT\ln P - A' \tag{98}$$

$$\Rightarrow f = Pe^{-A/RT} \tag{99}$$

Continued…

ACTIVITY: The activity of a substance may be defined as the ratio of fugacity of the substance to the fugacity in its standard state.

Mathematically it can be represented as,

$$a = \frac{f}{f^0} \tag{100}$$

At standard state, a=1, since $\mathrm{f} = \mathrm{f}^0$

Again for real gas,

$$\int_{\mathrm{G_i^0}}^{\mathrm{G_i}} \mathrm{dG_{real}} = \mathrm{RT} \int_{\mathrm{f_i^0}}^{\mathrm{f_i}} \mathrm{d\ln f} \tag{101}$$

$$\Rightarrow \mathrm{G_i} - \mathrm{G_i^0} = \mathrm{RT\ln}\left({}^{\mathrm{f_i}}/_{\mathrm{f_i^0}}\right) \tag{102}$$

Since $a_i = \frac{f_i}{f_i^0}$, so equation (102) becomes

$$\mathrm{G_i} - \mathrm{G_i^0} = \mathrm{RT\ln a_i} \tag{103}$$

Continued…

In an ideal gas mixture, $P_i = f_i$. Hence

$$G_i - G_i^0 = RT \ln\left(P_i - P_i^0\right) = RT \ln\left({}^{P_i}/_{P_i^0}\right) \tag{104}$$

Since $P_i^0 = 1\ atm$, So equation (104) becomes

$$G_i - G_i^0 = RT \ln P_i \text{ (Since } \ln P_i^0 = \ln 1 = 0\text{)} \tag{105}$$

From equation (103) and (105), we got

$$\mathrm{RT} \ln \mathrm{a_i} = \mathrm{RT} \ln \mathrm{P_i} \Rightarrow \mathrm{a_i} = \mathrm{P_i} \tag{106}$$

<u>**N. B.:**</u>

- a_i is a dimensionless quantity.
- Value of a_i is numerically equal to the value of P_i (in atm).

Continued…

$$\text{Activity (ith component)} = a_i = \frac{P_i}{P_{\text{reference}}}$$

P_i= partial pressure of the ith gaseous component
$P_{\text{reference}}$= 1 atm (exactly)

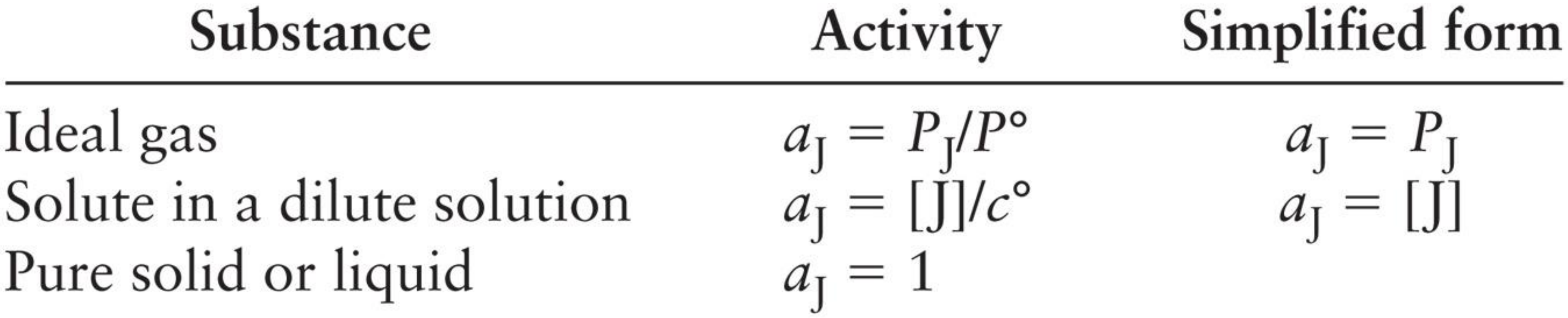
For the reaction: $jA(g) + kB(g) == lC(g) + mD(g)$

$$K = \frac{(a_C)^l\,(a_D)^m}{(a_A)^J\,(a_B)^k} = \frac{\left(\frac{P_C}{P_{ref}}\right)^l \left(\frac{P_D}{P_{ref}}\right)^m}{\left(\frac{P_A}{P_{ref}}\right)^j \left(\frac{P_B}{P_{ref}}\right)^k} = \frac{P_C{}^l P_D{}^m}{P_A{}^j P_B{}^k}$$

Because of the difference in reference states between concentration units and pressure units, unless the numbers of moles of reactant and products are the same, then: $K \neq Kp$

Activity determination in a chemical reaction
Ref- https://slideplayer.com/slide/4213696/

Continued…



Substance	Activity	Simplified form
Ideal gas	$a_J = P_J/P°$	$a_J = P_J$
Solute in a dilute solution	$a_J = [J]/c°$	$a_J = [J]$
Pure solid or liquid	$a_J = 1$	

Activity of different state of matters

Ref- https://people.chem.umass.edu/botch/Chem122S08/Chapters/Ch9/EquilibriumConstant/Activity.html

LECTURE-14

<u>EQUILIBRIUM CONSTANT:</u> Generally Equilibrium constant for a chemical reaction given by ‘K’.

<u>Relationship of K with standard free energy of Reaction:</u>

Consider the following reaction at constant temperature and pressure as

$$lL + mM + \cdots = qQ + rR + \cdots \tag{107}$$

[Where l, m, q, r, …. represents number of moles

(L, M,…) and (Q, R,…) represents reactants and products respectively.]

Then

$$\Delta G = \left(qG_Q + rG_R + \cdots\right) - (lG_L + mG_M + \cdots) \tag{108}$$

$$\Delta G^0 = \left(qG_Q^0 + rG_R^0 + \cdots\right) - (lG_L^0 + mG_M^0 + \cdots) \tag{109}$$

$\Delta G - \Delta G^0$

$$= \left[q\left(G_Q - G_Q^0\right) + r(G_R - G_R^0) + \cdots\right] - [l(G_L - G_L^0) + m(G_M - G_M^0) + \cdots] \tag{110}$$

Continued…

Since we know,

$$G_i - G_i^0 = RT \ln a_i \tag{111}$$

So equation (111) becomes

$$\Delta G - \Delta G^0 = RT\left[\left(q \ln a_Q + r \ln a_R + \cdots\right) - (l \ln a_L + m \ln a_M + \cdots)\right] \tag{112}$$

$$\Rightarrow \Delta G - \Delta G^0 = RT \ln\left[\frac{a_Q^q . a_R^r \ldots.}{a_L^l . a_M^m \ldots.}\right] = RT \ln J \tag{113}$$

Where

$$J = Activity\ quotient\ = \left[\frac{a_Q^q . a_R^r \ldots.}{a_L^l . a_M^m \ldots.}\right] \tag{114}$$

Continued…

At equilibrium,

$$(\Delta G)_{P,T} = 0 \tag{115}$$

So equation (113) becomes

$$-G^0 = RT \ln[J]_{At\ equilibrium} = RT \ln K$$

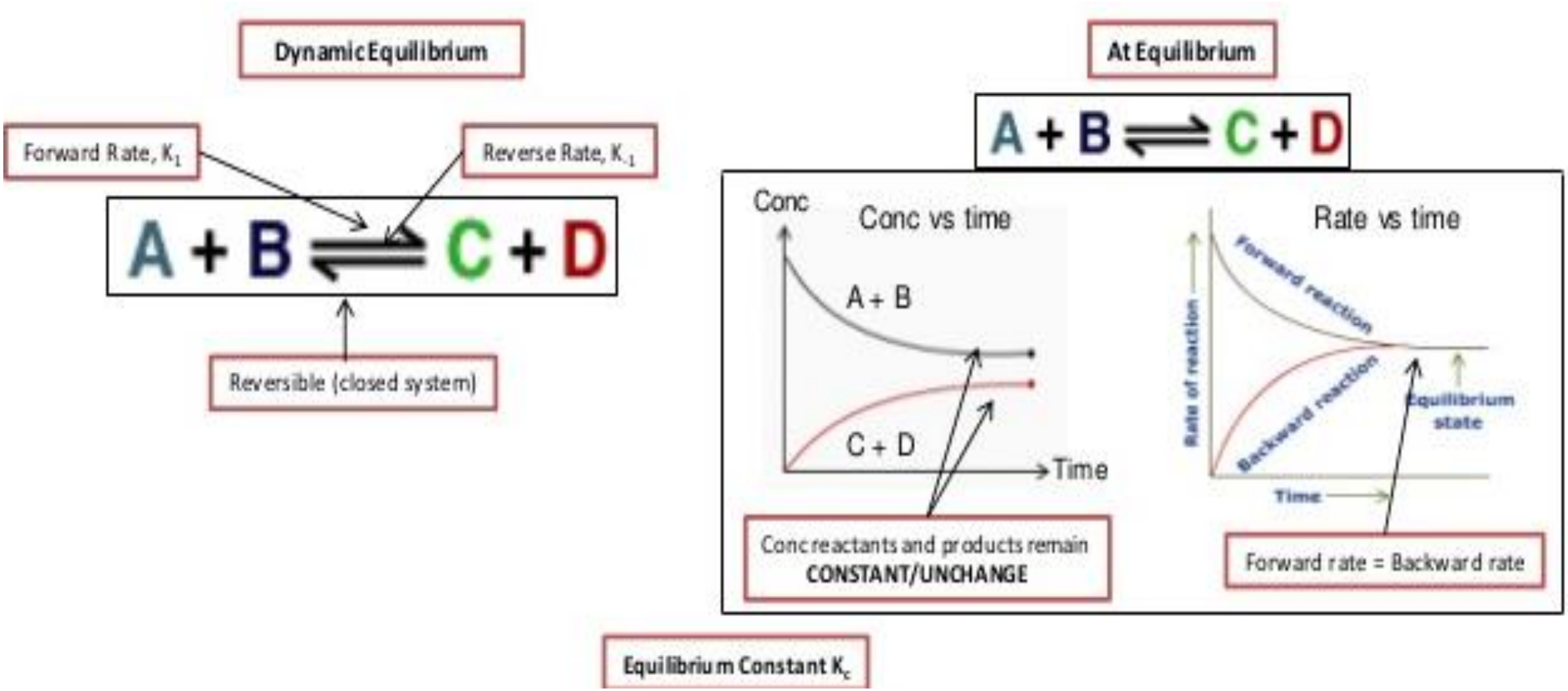
$$\Rightarrow \Delta G^0 = RT \ln K \tag{116}$$

Replacing equation (116) in equation (113) we have

$$\Delta G - (-RT \ln K) = RT \ln J$$

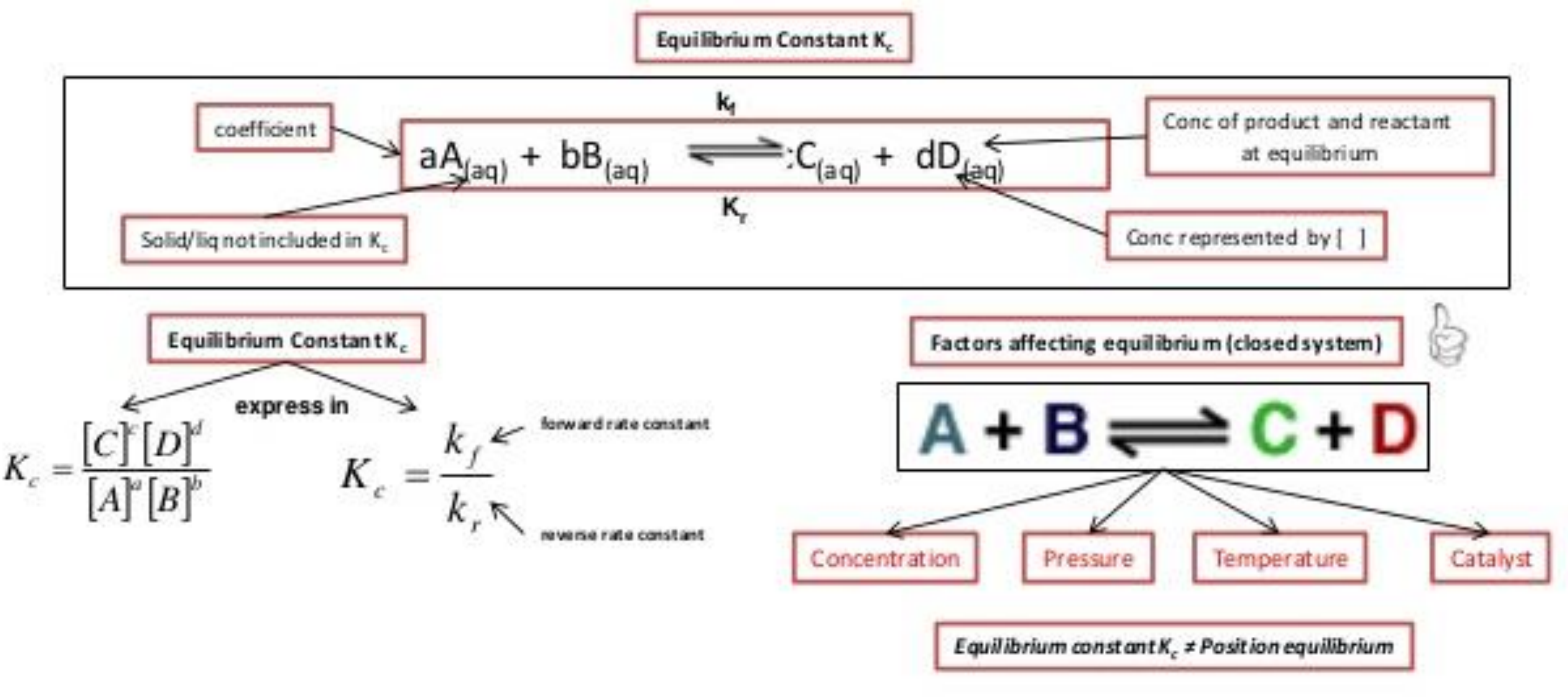
$$\Rightarrow \Delta G = RT \ln J - RT \ln K = RT \ln\left(\frac{J}{K}\right) \tag{117}$$

Continued…



Ref: https://www.slideshare.net/wkkok1957/ib-chemistry-on-gibbs-free-energy-and-equilibrium-constant-kc-52195265

Continued…



Equilibrium Constant K_c

coefficient

$$aA_{(aq)} + bB_{(aq)} \underset{K_r}{\overset{k_f}{\rightleftharpoons}} cC_{(aq)} + dD_{(aq)}$$

Conc of product and reactant at equilibrium

Solid/liq not included in K_c

Conc represented by [ ]

Equilibrium Constant K_c

express in

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$$K_c = \frac{k_f}{k_r}$$

forward rate constant

reverse rate constant

Factors affecting equilibrium (closed system)

$$A + B \rightleftharpoons C + D$$

Concentration

Pressure

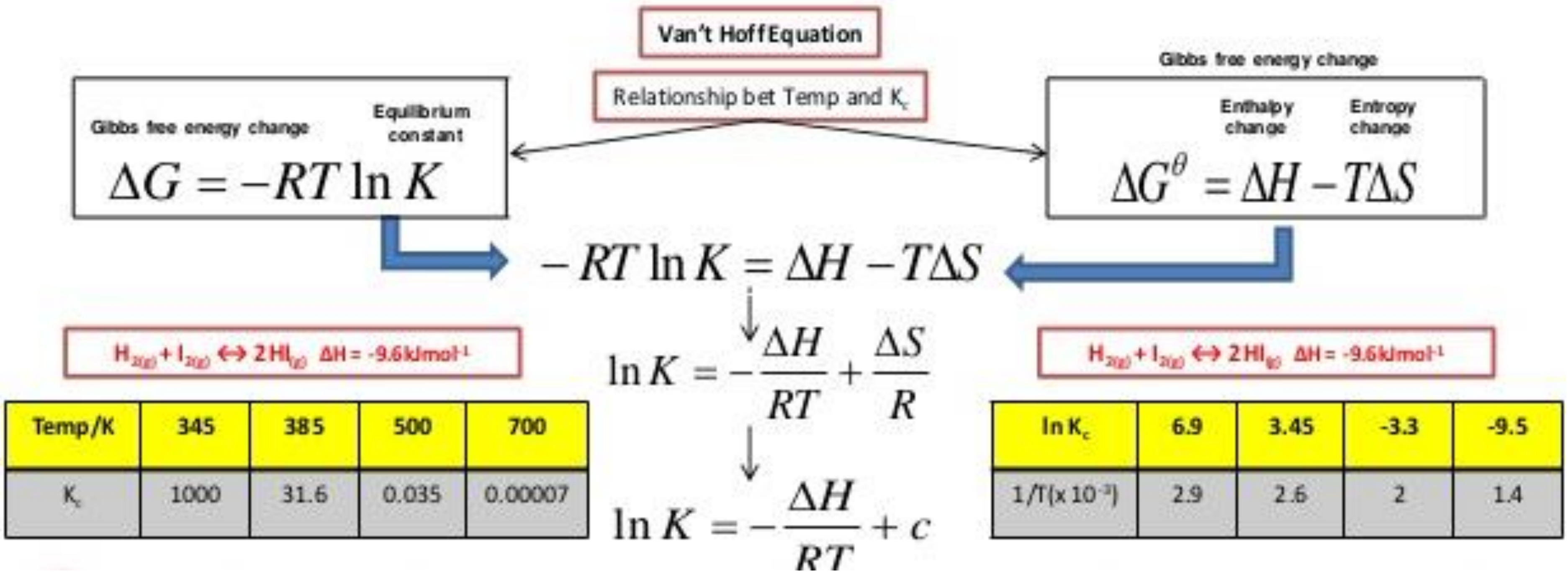
Temperature

Catalyst

Equilibrium constant K_c ≠ Position equilibrium

Ref:
https://www.slideshare.net/wkkok1957/ib-chemistry-on-gibbs-free-energy-and-equilibrium-constant-kc-52195265

Continued…



Van't Hoff Equation

Relationship bet Temp and K_c

Gibbs free energy change

Equilibrium constant

$$\Delta G = -RT\ln K$$

Gibbs free energy change

Enthalpy change

Entropy change

$$\Delta G^{\theta} = \Delta H - T\Delta S$$

$$-RT\ln K = \Delta H - T\Delta S$$

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

$$\ln K = -\frac{\Delta H}{RT} + c$$

$H_{2(g)} + I_{2(g)} \leftrightarrow 2HI_{(g)}$ $\Delta H = -9.6 kJmol^{-1}$

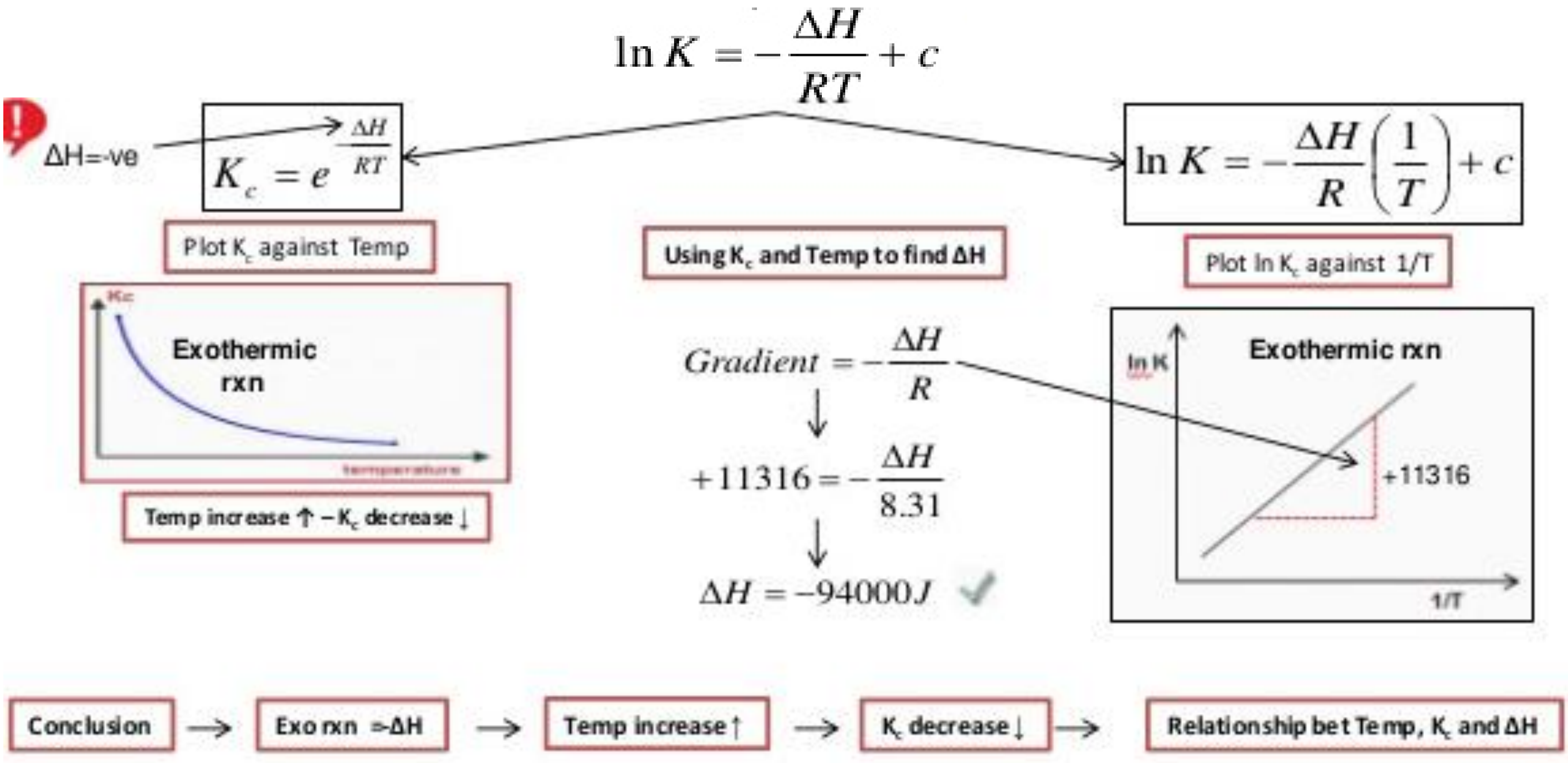
Temp/K	345	385	500	700
K_c	1000	31.6	0.035	0.00007

$H_{2(g)} + I_{2(g)} \leftrightarrow 2HI_{(g)}$ $\Delta H = -9.6 kJmol^{-1}$

$\ln K_c$	6.9	3.45	-3.3	-9.5
$1/T (\times 10^{-3})$	2.9	2.6	2	1.4

Ref:
https://www.slideshare.net/wkkok1957/ib-chemistry-on-gibbs-free-energy-and-equilibrium-constant-kc-52195265

Continued…



$$\ln K = -\frac{\Delta H}{RT} + c$$

ΔH=-ve

$$K_c = e^{-\frac{\Delta H}{RT}}$$

Plot K_c against Temp

Temp increase ↑ – K_c decrease ↓

Using K_c and Temp to find ΔH

$$Gradient = -\frac{\Delta H}{R}$$

$$\downarrow$$

$$+11316 = -\frac{\Delta H}{8.31}$$

$$\downarrow$$

$$\Delta H = -94000J$$ ✓

$$\ln K = -\frac{\Delta H}{R}\left(\frac{1}{T}\right) + c$$

Plot ln K_c against 1/T

Conclusion → Exo rxn =-ΔH → Temp increase ↑ → K_c decrease ↓ → Relationship bet Temp, K_c and ΔH

Ref:
https://www.slideshare.net/wkkok1957/ib-chemistry-on-gibbs-free-energy-and-equilibrium-constant-kc-52195265

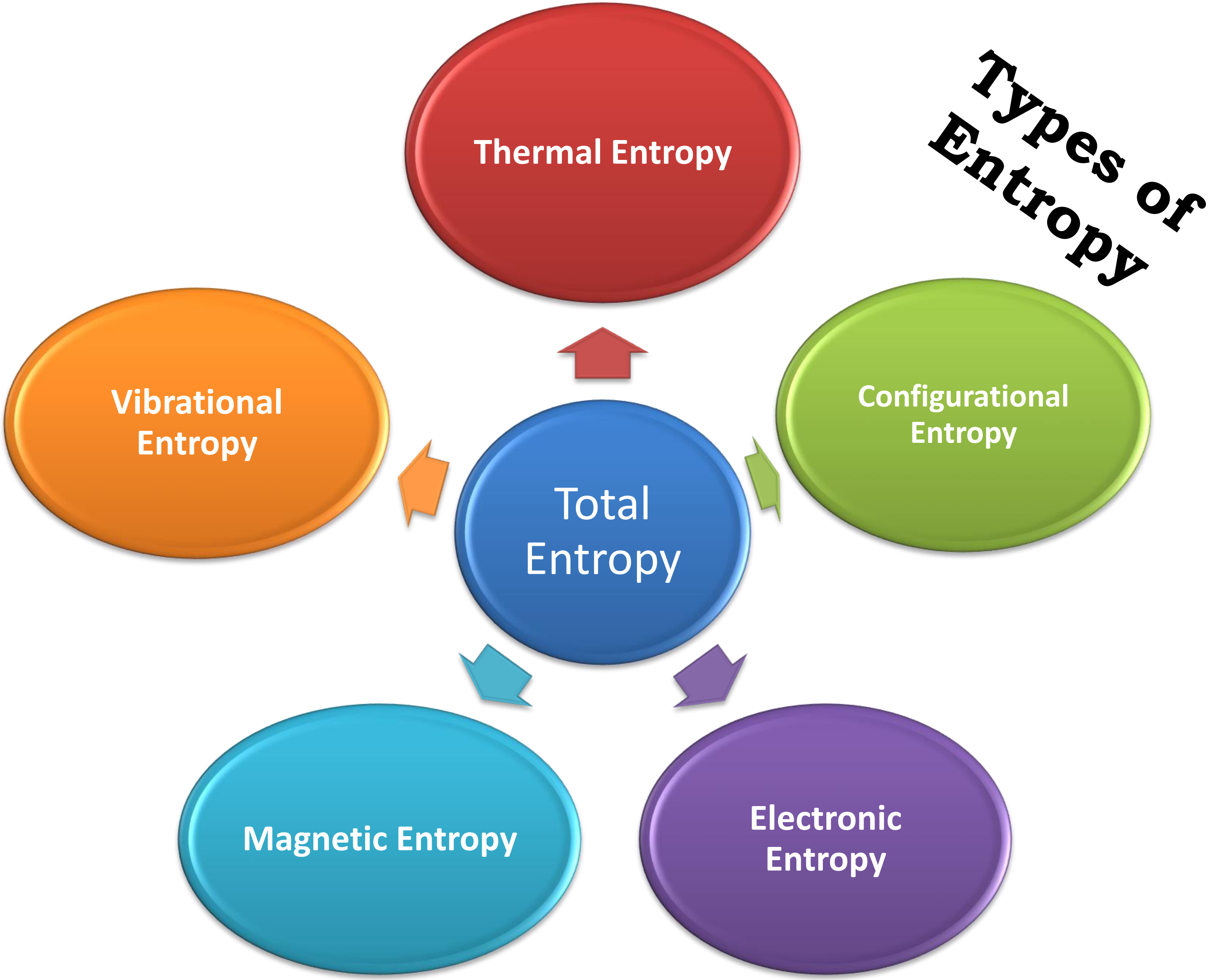
LECTURE-15

THIRD LAW OF THERMODYNAMICS: In 1906, W. Nernst proposed his heat theory on the basis of experimental evidence. It was later generalized by Max Plank as “The entropy of any substance (which is at completely in internal equilibrium) may take as Zero at 0K.” This is known as Third law of Thermodynamics.

- ❑ At T = 0K, thermal energy is zero. Thus this source of disorder gets eliminated. But other sources remain there. In reality it is difficult to achieve exactly zero entropy at T = 0 K.

- ❑ Actually, all disorders are caused by thermal energy which get lowered continuously and vanish at T = 0K provided internal equilibrium exists.

Continued…



Types of Entropy

Total Entropy

Thermal Entropy

Configurational Entropy

Electronic Entropy

Magnetic Entropy

Vibrational Entropy

Continued…

- Out of different contributions towards the total entropy, configurational and thermal entropy are the major contributors.
- Thermal entropy (ΔS_T) is equal to zero at absolute temperature, T = 0 K. However the configurational entropy (ΔS_c) is dependent on configuration not on absolute temperature, so not equals to zero even if at 0 K temperature. So total entropy is not equals to zero at 0 K temperature.
- As per 3rd law of thermodynamics, "The entropy of any substance (which is at completely in internal equilibrium) may take as Zero at 0K." i.e. the total entropy may be zero, if and only it is at complete internal equilibrium => $\Delta S_c =$ R n ln (n) $= 0$;

  $where\ n\ is\ number\ of\ elements\ and\ R\ universal\ gas\ constant.$

Continued…

TEMPERATURE DEPENDENCE OF ENTROPY:

We know

$$\mathrm{H} = \mathrm{U} + \mathrm{PV} \tag{118}$$

$$\Rightarrow \mathrm{dH} = \mathrm{d(U + PV)} = \mathrm{dU} + \mathrm{PdV} + \mathrm{VdP} = \delta \mathrm{q} + \mathrm{VdP} \tag{119}$$

Now putting $\delta \mathrm{q} = \mathrm{T}dS$ & $\mathrm{dH} = \mathrm{C_P dT}$ in equation (119) we have

$$\mathrm{C_P dT} = \mathrm{TdS} + \mathrm{VdP} \tag{120}$$

Now dividing the equation (120) by T we have

$$\mathrm{C_P}\left(\frac{\mathrm{dT}}{\mathrm{T}}\right) = \mathrm{dS} + \frac{\mathrm{VdP}}{\mathrm{T}} \tag{121}$$

At constant pressure the above equation becomes

$$\mathrm{C_P}\left(\frac{\mathrm{dT}}{\mathrm{T}}\right) = \mathrm{dS} \tag{122}$$

Continued…

Integrating equation (122) from state 1 to state 2, we have got

$$\int_1^2 dS = C_P \int_{T_1}^{T_2} \frac{dT}{T}$$

$$\Rightarrow \Delta S = S_2 - S_1 = C_P(\ln T_2 - \ln T_1)$$

$$\Rightarrow \Delta S = C_P \ln\left(\frac{T_2}{T_1}\right) \tag{123}$$

Again, we know

$$\delta q = dU + PdV = C_V dT + PdV \tag{124}$$

Dividing equation (124) by T at constant volume, the equation becomes

$$\frac{\delta q}{T} = C_V \frac{dT}{T} \Rightarrow dS = C_V \frac{dT}{T} \tag{125}$$

Integrating equation (125) from state-1 to state-2, we got

$$\int_{S_1}^{S_2} dS = C_V \int_{T_1}^{T_2} \frac{dT}{T} \Rightarrow \Delta S = S_2 - S_1 = C_V \ln\left(\frac{T_2}{T_1}\right) \tag{126}$$

Continued…

STATISTICAL THERMODYNAMICS: It is originated from kinetic Theory of gases, which related to average kinetic energy of molecules in an ideal gas. The application of probability theory, quantum theory and statistical mechanics allowed it to arrive at microscopic thermodynamics relations from atomistic (i. e. microscopic) point of view.

Statistical interpretation of Entropy measurement follows as

- ☐ Entropy is additive in nature i.e. $\mathrm{S} = \mathrm{S_A} + \mathrm{S_B}$
- ☐ *Probability function is multiplicative in nature i.e.*

$$f(w) = f(w_A . w_B)$$

- ☐ *Entropy can be represented as*

$$S = f(w) = f(w_A . w_B) = f(w_A) + f(w_B)$$

Continued…

Micro-State of a system:

- Consider a system consisting of gas where particles are in a constant state of motion which may be translational, rotational or vibrational.
- Due to these motions particles inside the system occupy different positions in different instant of time. On the other hand due to collision among themselves and wall of the container, velocities change with time.
- Thus particles inside a system has six different coordinates as (x, y, z) and three are velocity co-ordinates as (V_X, V_Y, V_Z).
- If at any instant of time all these six co-ordinates are well-defined for each particle present inside the system then such a complete specification define a micro-state of a system.

Continued…

Ensemble: An Ensamble of a system can be defined by a set which consists of all the possible micro-state of a system. This is because with the passage of time a system passes from one micro-state to other as a result of which individual particles within the system attains different set of position as well as velocity co-ordinates.

Micro-Cannonical Ensamble: Micro-state of an isolated system having constant volume is called micro-Cannonical Ensamble.

Macro-state of a System: The different macro-state of Ensamble can be arranged into a no. of subset in a way that any one of the subset consists of such micro-state which have same number of particles lying between the co-ordinates (X, Y, Z, V_X, V_Y, V_Z) and $(X + \delta X, Y + \delta Y, Z + \delta Z, V_X + \delta V_X, V_Y + \delta V_Y, V_Z + \delta V_Z\ )$. Thus subsets are called macro-state of a system.

Continued…

Let us assume without any restriction n_i particles are allowed to move in g_i sections. So the n_i particles arranged among themselves and that (g_i+1) partitions are among themselves in $n_i!$ and $(g_i-1)!$ Ways respectively. Then the particles and partitions internally arranged among themselves in $(n_i+g_i-1)!$ Ways.

So the number in which n_i particles get allocated in g_i state of degeneracy can be expressed as

$\text{Total possible no. of degenration to accomodate } n_i \text{ particles}$

$$=\left(\frac{(n_i+g_i-1)!}{n_i!(g_i-1)!}\right) \tag{127}$$

Number of microstates in a macrostate of an isolated system of constant volume

$$=\left(\frac{(n_i+g_i-1)!}{n_i!(g_i-1)!}\right) \tag{128}$$

QUIZ TEST-3

Q.1 –Write down all the derived auxiliary equations from combined 1st and 2nd law of thermodynamics.

Q.2 – What is the importance of Gibbs-Helmoholtz equation in deciding the feasibility of a chemical reaction?

Q.3 –How the escaping tendency is related with fugacity?

Q.4–Is it possible to predict the reaction direction and feasibility from rate constant value? If yes, explain it how?

Q.5 –State the 3rd law of thermodynamics?

Assignment-1

With the help of mathematical derivation proof the statement “The entropy of a system in isolation can never decrease”.

LECTURE-16

POSTULATES OF STATISTICAL THERMODYNAMICS:

First Postulate: It stated as “The time average of a mechanical variable such as average energy of a system is equal to the Ensamble average representing the Ensamble, provided the number of microstate representing the system are infinitely large. ”

Derivation: Let the isolated system consists of n number of particles out of which n_1 particles having energy U_1. Similarly n_2 particles having U_2 ... up to n_i particles having U_i. Hence the total energy U which is constant for the system can be expressed as

$$U = U_1 n_1 + U_2 n_2 + \cdots + U_i n_i = \sum U_i n_i \tag{129}$$

As the total number of particles in the system is also constant i.e.

$$n = n_1 + n_2 + \cdots + n_i = \sum_{i=1}^{i} n_i \tag{130}$$

Continued…

If ω be the number of microstate present in a macrostate

$$w = \frac{n!}{n_1!\, n_2! \ldots\ldots n_i!} = \frac{n!}{\prod_i n_i!} \tag{131}$$

Second Postulates: It is stated as "All microstate are equally probable therefore the probability of a system to represent in a particular microstate is directly proportional to the number of microstate present in the macrostate." Hence macrostate of higher number of microstate well define the macroscopic properties of the system.

Maxwell-Boltzmann Statistics: It stated as "Particles in a microstate are distinguished from each other on the basis of the total energy content by each particle."

Limitation: If there is an isolated system of constant volume then two or more particles have same energy level. Then it is difficult to distinguish the particles from each other. This problem gets solved under Boltzmann- Einstein statistics.

Continued…

Boltzmann-Einstein Statistics: It stated as “Particles of same energy and size get distinguished from each other on the basis of orientation or degeneracy principle.”

Suppose there are n_i number of particles with energy U_l in which there are g_i states of energy (degenerate state energy). To place n_i particles in g_i sections we need (g_i+1) partitions.

RELATIONSHIP BETWEEN STATISTICAL INTERPRETATIONS OF ENTROPY:

Entropy is additive in nature. For example, if we will take two particles A and B which have entropy S_A and S_B. Then net entropy

$$\mathrm{S} = \mathrm{S_A} + \mathrm{S_B} \tag{132}$$

Probability function is multiplicative in nature i.e.

$$\mathrm{f(w)} = \mathrm{f(w_A.\, w_B)} \tag{133}$$

Entropy can be represented as

$$\mathrm{S} = \mathrm{f(w)} = \mathrm{f(w_A.\, w_B)} = \mathrm{f(w_A)} + \mathrm{f(w_B)} \tag{134}$$

Continued…

Now taking the derivative of equation (134) w.r.t. w_B, we got

$$\frac{df(w)}{dw_B} = \frac{df(w_A)}{dw_B} + \frac{df(w_B)}{dw_B} \tag{135}$$

$$\Rightarrow \frac{df(w_A.w_B)}{d(w_A.w_B)} \times \frac{d(w_A.w_B)}{dw_B} = \frac{df(w_B)}{dw_B} \tag{136}$$

$$\Rightarrow w_A \frac{df(w_A.w_B)}{d(w_A.w_B)} = \frac{df(w_B)}{dw_B} \tag{137}$$

Now taking derivative of equation (137) w.r.t. w_A, we got

$$\left[w_A \frac{d\left(\frac{df(w_A.w_B)}{d(w_A.w_B)}\right)}{d(w_A.w_B)} \times \frac{d(w_A.w_B)}{dw_A}\right] + \left[\frac{df(w_A.w_B)}{d(w_A.w_B)} \times \frac{dw_A}{dw_A}\right] = \frac{d\left(\frac{df(w_B)}{dw_B}\right)}{dw_A} \tag{138}$$

$$\Rightarrow w_A.\,w_B\ \frac{d^2f(w_A.w_B)}{d(w_A.w_B)^2} + \frac{df(w_A.w_B)}{d(w_A.w_B)} = 0 \tag{139}$$

Putting $w_A.\,w_B = w$ in equation (139), we got

$$w\frac{d^2f(w)}{dw^2} + \frac{df(w)}{dw} = 0 \tag{140}$$

Continued…

So, equation (140) became a 2nd order differential equation.

For 2nd order differential equation the solution is

$$\mathrm{f(w)} = \mathrm{c_1 \ln w + c_2} \Rightarrow \mathrm{S} = \mathrm{c_1 \ln w + c_2} \qquad (141)$$

Now for no disorderness , S=0, equation (141) will become

$$\mathrm{c_1 \ln w + c_2} = 0 \qquad (142)$$

Again as we have S=0 i.e. there is only one microstate is possible,$\mathrm{w} \cong 1 \Rightarrow \ln \mathrm{w} = 0$.

Hence equation (142) will become, $\mathrm{c_2} = 0$ (143)

Now taking $$\mathrm{c_1} = \frac{\mathrm{R}}{\mathrm{N_0}} = \mathrm{k} \qquad (144)$$

[Where, R = Universal gas constant, N_0= Avogadro’s number,

K = Boltzmann’s constant]

Now using the equation (143) and (144) in equation (5.25), we got

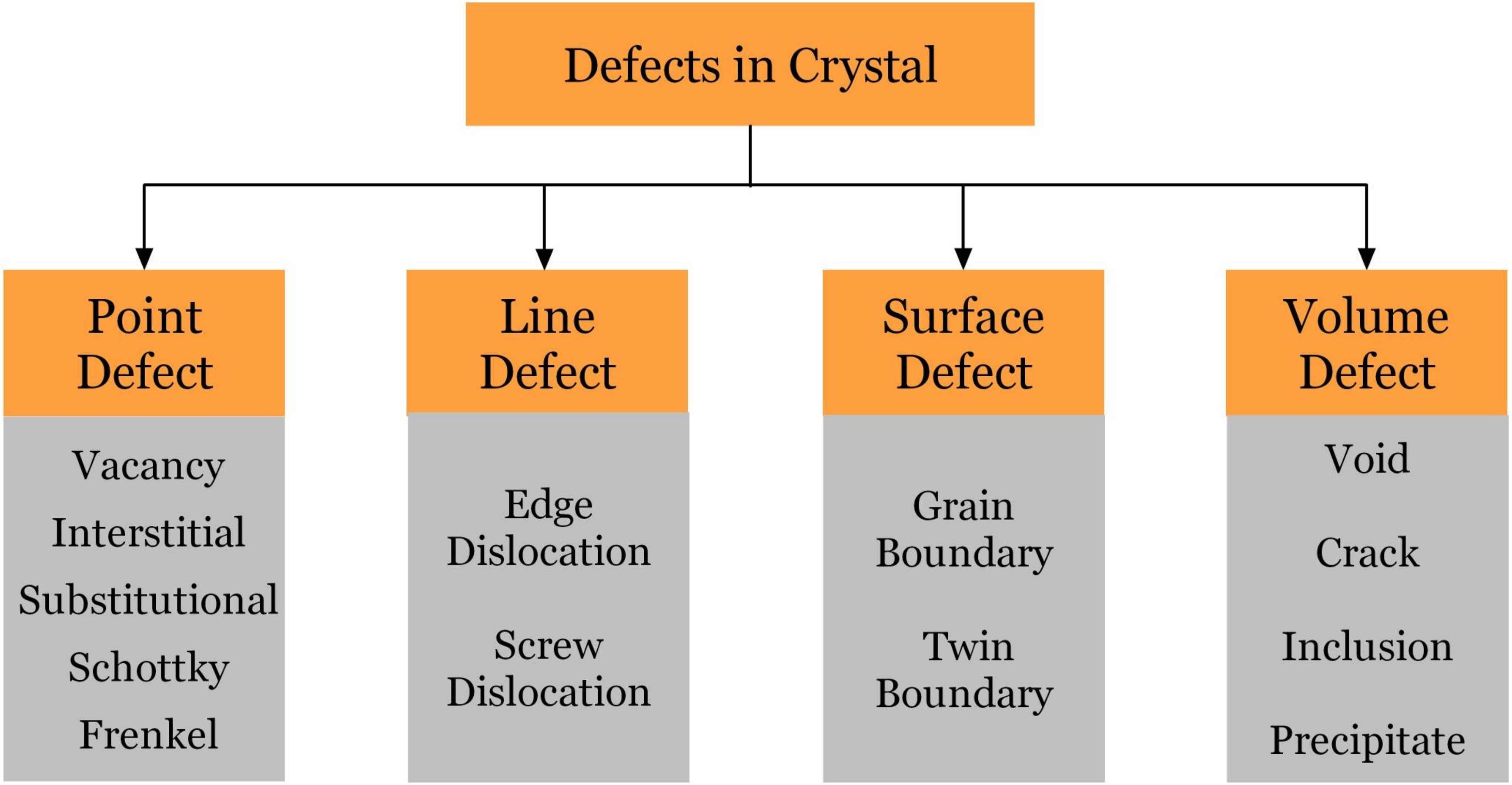
$$\mathrm{S} = \mathrm{k \ln w} \qquad (145)$$

LECTURE-17

Consequences of 3rd Law of Thermodynamics: When disorderness in a substance completely vanishes, it becomes perfectly ordered and has only one possible arrangement of atoms. Then and only then, a complete internal equilibrium is established. The causes for deviation from perfect order are

- Thermal energy and resulting motion of atoms and molecules (at T = 0K).
- Non-crystallinity, as in amorphous solids and liquids.
- Crystal defects-vacancies, interstitial atoms, dislocation.
- Disordered compound structure.
- Disordered solid solution.

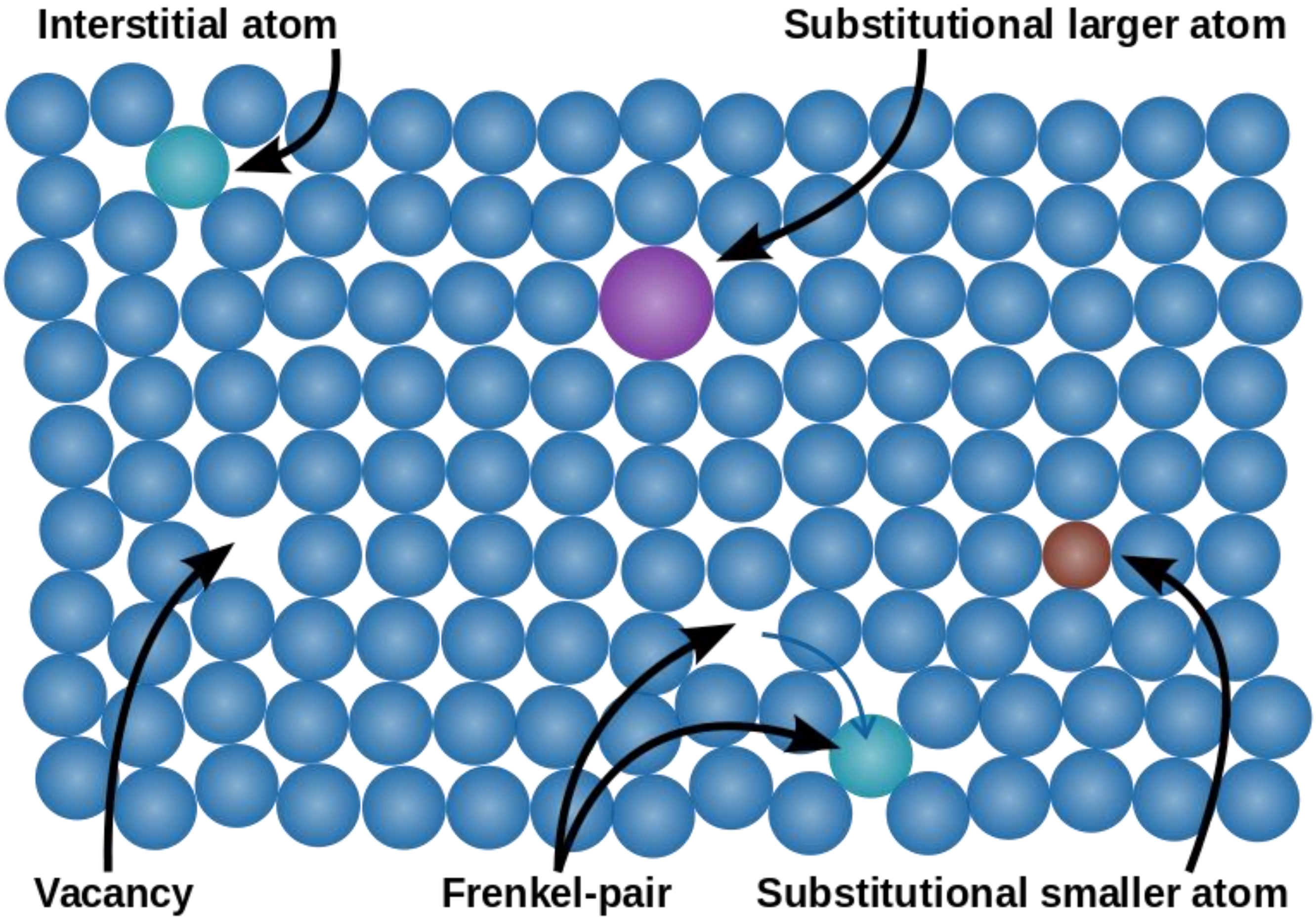
Continued…



Defects in crystalline solid materials

Ref-http://www.minaprem.com/materials-science/defects/point-defect-imperfections-in-solids-materials-science/

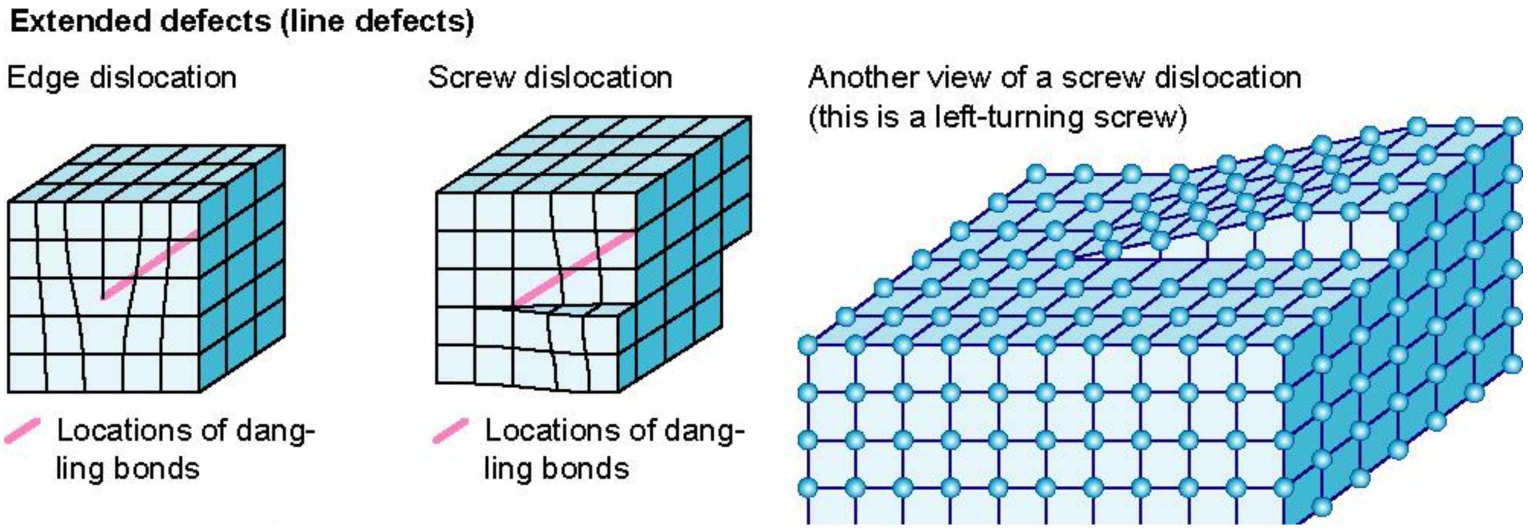
Continued…



Points defects in crystalline solid material

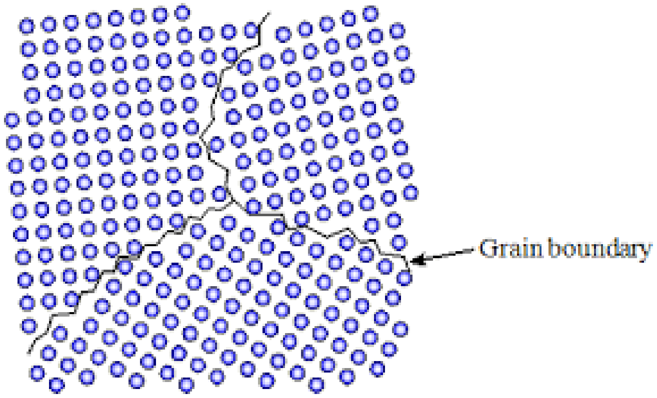
Ref- https://www.differencebetween.com/difference-between-point-defect-and-line-defect/

Continued…



Line defects in crystalline solid material

Ref-http://1.bp.blogspot.com/-UliOEYWbW5s/UHgkWQex3gI/AAAAAAAAACY/48_X38HeXl0/s1600/Materials-Types-of-point-and-extended-defects.jpg



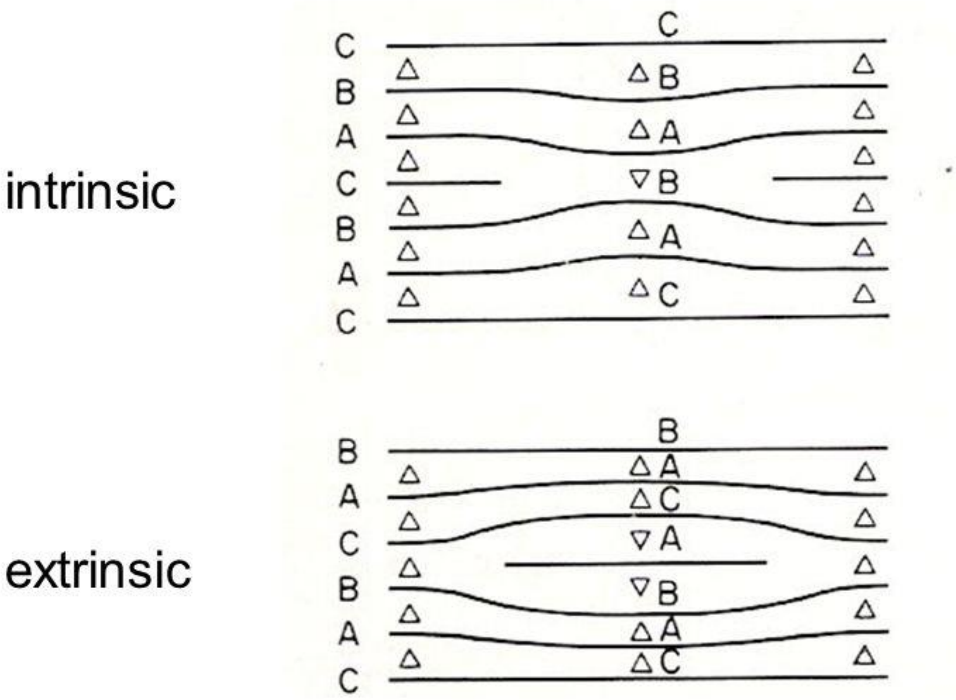
GB in crystalline solid material

Ref-

http://www.engineeringarchives.com/les_matsci_surfacedefects.html

Continued…

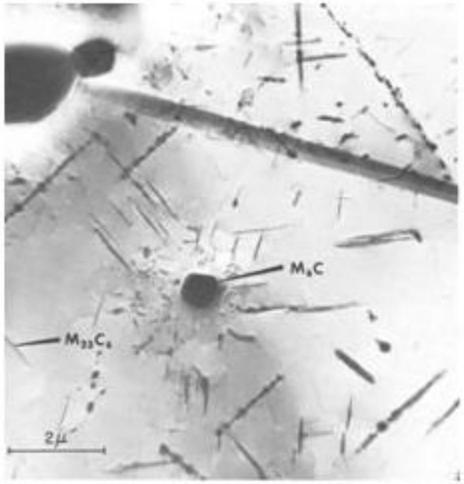
stacking faults of (111) planes in fcc lattice



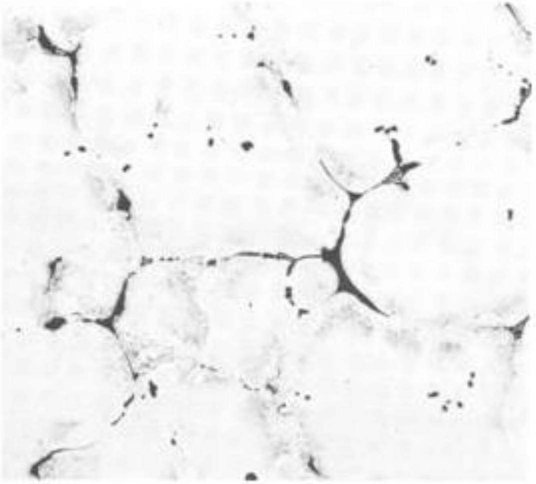
Ref-https://slideplayer.com/slide/8125889/

Continued…

Volume Defects



Inclusion



Voids/Pores

Ref- https://slideplayer.com/slide/10119709/

Continued…

At constant pressure U can be expressed in differential form as

$$\mathrm{dU} = \left(\frac{\partial \mathrm{U}}{\partial \mathrm{V}}\right)_{\mathrm{T}} \mathrm{dV} + \left(\frac{\partial \mathrm{U}}{\partial \mathrm{T}}\right)_{\mathrm{V}} \mathrm{dT} \qquad (147)$$

Put equation (147) in equation (146) we have

$$\delta \mathrm{q} = \left(\frac{\partial \mathrm{U}}{\partial \mathrm{V}}\right)_{\mathrm{T}} \mathrm{dV} + \left(\frac{\partial \mathrm{U}}{\partial \mathrm{T}}\right)_{\mathrm{V}} \mathrm{dT} + \mathrm{PdV} \qquad (148)$$

Taking derivative of equation (148) w.r.t. T, we got

$$\frac{\delta \mathrm{q}}{\mathrm{dT}} = \left(\frac{\partial \mathrm{U}}{\partial \mathrm{V}}\right)_{\mathrm{T}} \frac{\mathrm{dV}}{\mathrm{dT}} + \left(\frac{\partial \mathrm{U}}{\partial \mathrm{T}}\right)_{\mathrm{V}} + \frac{\mathrm{PdV}}{\mathrm{dT}} \qquad (149)$$

At constant pressure equation (149) becomes

$$\left(\frac{\delta \mathrm{q}}{\mathrm{dT}}\right)_{\mathrm{P}} = \mathrm{C_P} = \left(\frac{\mathrm{dU}}{\mathrm{dV}}\right)_{\mathrm{T}} \frac{\mathrm{dV}}{\mathrm{dT}} + \mathrm{C_V} + \frac{\mathrm{PdV}}{\mathrm{dT}} \qquad (150)$$

Continued…

$$\Rightarrow C_P - C_V = \left(\frac{dU}{dV}\right)_T \frac{dV}{dT} + \frac{PdV}{dT} \quad (151)$$

For ideal gas derivative of U w.r.t. V is zero. So equation (151) becomes

$$C_P - C_V = \frac{PdV}{dT} = R \quad (152)$$

ELLINGHAM – RICHARDSON DIAGRAM: R-E diagram is the simplest method of representing free energy vs Temperature for compounds such as oxides and sulphides. Temperature change in ΔH^0 and ΔS^0 tends to counterbalance each other. Therefore it is possible to express ΔG^0 in the form of a simple equation

$$\Delta G^0 = a - bT \quad (153)$$

[Where a and b are mean values of ΔH^0 and ΔS^0 for temperature range under consideration]

Continued…

- ☐ In this diagram, highly stable oxides are found at the bottom and less stable oxides occupy higher positions.
- ☐ Therefore, an element present at the lower position will always reduce the oxides of another metal lying above it, when all the reactants and products are in their standard states. In the regions, since no phase transformation occur. So plots are almost straight lines.
- ☐ Since ${d\Delta G^0}/_{dT} = -\Delta S^0$, slope of the line gives $-\Delta S^0$ and extrapolated the plot to absolute zero gives intercept of line ΔH^0 on free energy axis.
- ☐ Again since free energy is an extensive property. Hence the value of ΔG of a reaction would depend on number of moles involved.

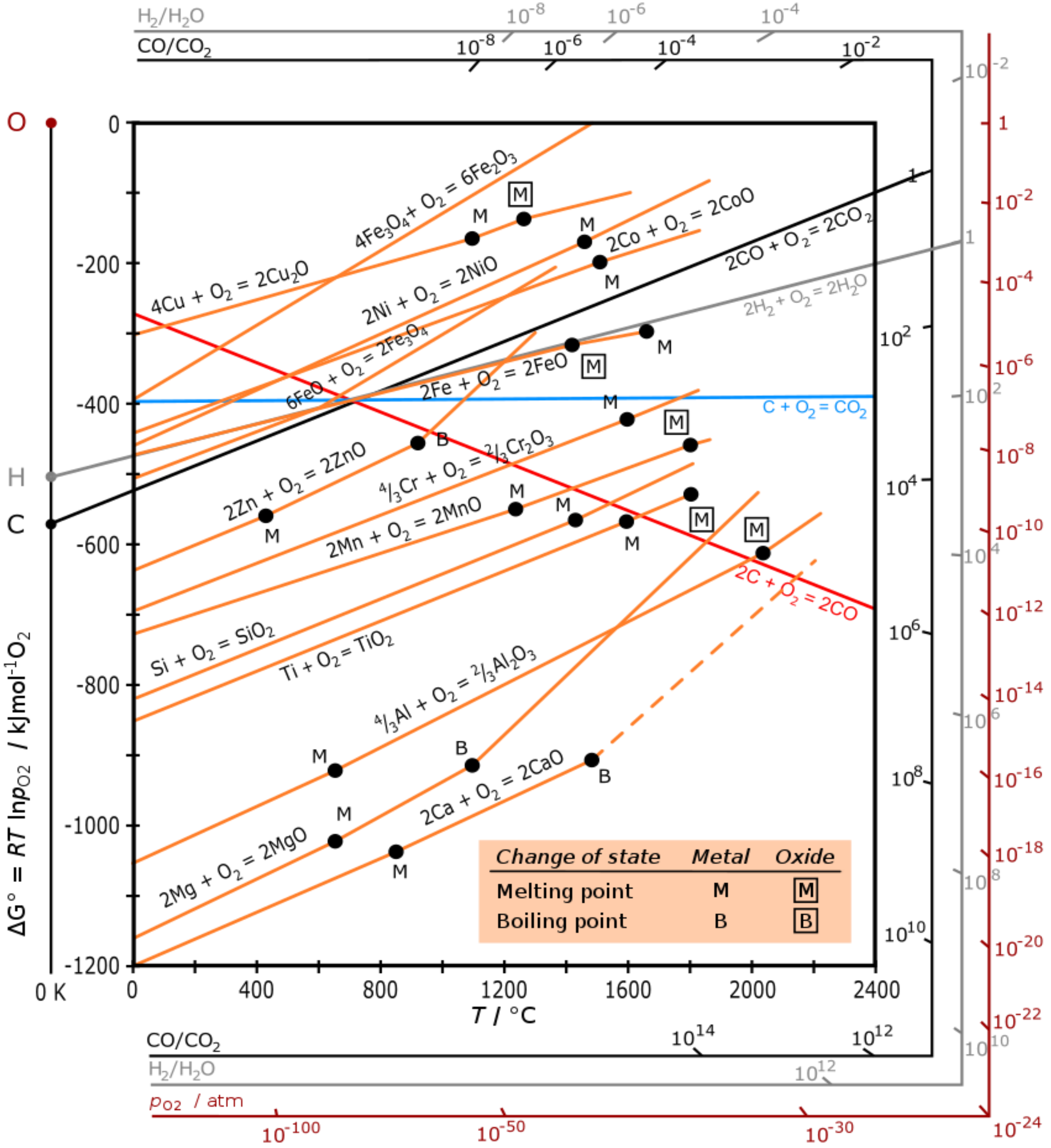
LECTURE-18

Characteristics of R-E Diagram:

- Different metals & its oxides of metallurgical processes are available in R-E diagram.
- The zero free energy is at the top of the diagram & towards down in the Y-axis is negative value is represented.
- This is a standard diagram because the reactant which are metal and products which are oxides in general are in their standard state i.e. unity activity.
- Oxides or compounds which are placed at bottom of the graph indicate more negative free energy i.e. is more stable & they reduce the less stable oxides that placed above it.
- Almost all oxides have negative free energy. However for noble metal case there is some exception.

Continued…

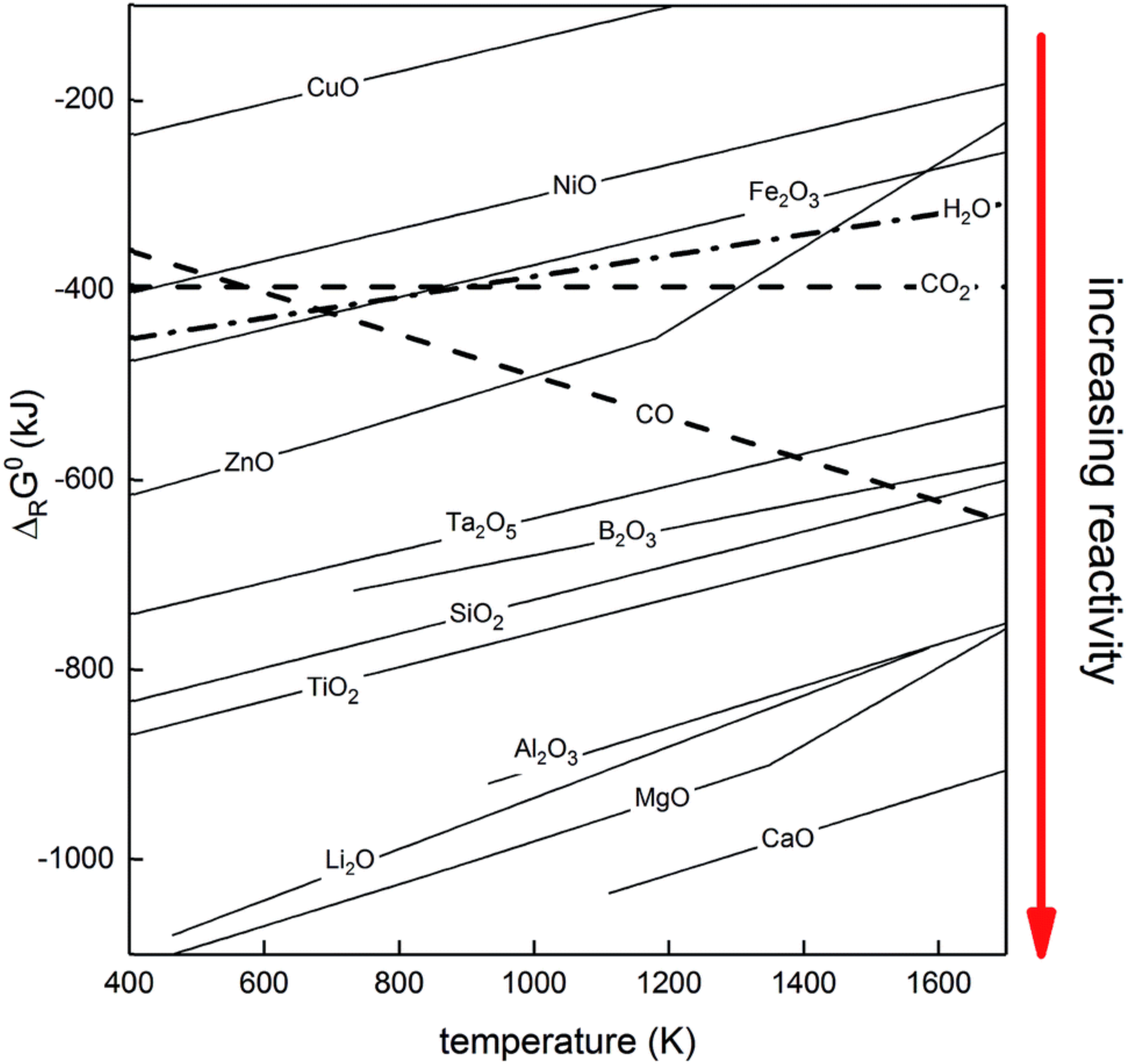
- The line for CO2 would almost parallel to the temperature axis indicates the value.
- Upward slope of most of lines indicates that the oxides become less stable as the temperature increases.



Ellingham Diagram of Selected Oxides

Ref- https://www.wikiwand.com/en/Ellingham_diagram

Continued…



- Increase in reactivity towards downward direction
- **CO is better reducing agent than H2O because** Increase in stability with increase in temperature and cuts maximum number of metal oxide lines.

Ref- Julien, P., & Bergthorson, J. M. (2017). Enabling the metal fuel economy: green recycling of metal fuels. *Sustainable Energy & Fuels*, *1*(3), 615-625.

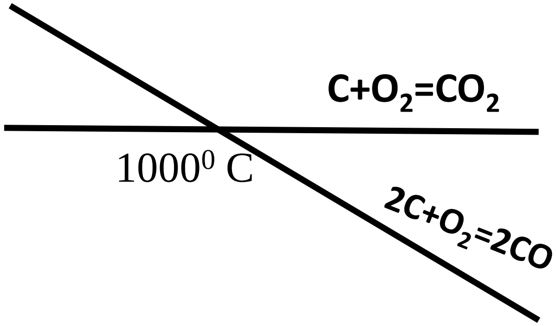
Continued…

- Change in slope indicates phase transformation from one phase to another phase.
  a. Increase in slope indicates reactant undergoing phase transformation.
  b. Decrease in slope indicates product undergoing phase transformation.
  c. Large slope change indicates transformation from condensed phase to gaseous phase.
  d. Small slope phase change indicates melting or change of solid to other phase.
  e. No change in slope indicates no phase transformation.

  - **Carbothermic reactions** involve the reduction of mostly metal oxides in the presence of carbon as the reducing agent. These reactions are usually conducted at temperatures of several hundred degrees Celsius.

Continued…

- Carbothermic based processes are used for production of the elemental forms of many elements. Carbothermic reactions are not useful for few metal oxides like sodium and potassium oxides. The ability of metals to takes part in Carbothermic reactions is predicted mainly from R-E diagram.
- The reaction $2C_{(S)} + O_{2(g)} = 2CO_{(g)}$ extremely important since in this case it has downward slope cutting across the free energy diagram. This indicates, why that all metal oxides can be reduced by CO above 1000^0 C.



- Below 1000^0 C, $2CO_{(g)} = 2CO_{2(g)} + C_{(s)}$ occur. So below 1000^0 C carbon monoxide is unstable.

Continued…

Limitations:

- Both products and reactants are in the standard state (i. e. pure substance at 1 atm).
- No Ellingham diagram for solution because thermodynamic activity data are required.
- No reaction then difficult to predict the rate of reaction.

Continued…

Applications of R-E Diagram

Major applications in metallurgical processes such as

- Selection of efficient reducing agents

Example: Reducing agent for the reduction of Hematite and magnetite ore.

- Metal refining and purification.

Example: Various electro refining and purification of common metals Au, Cu, Fe etc. and their oxides.

- Phase transformation and high temperature stability study

Example: phase transformation and temperature stability of metals oxides like CaO, Al2O3 etc. can be predicted and compared.

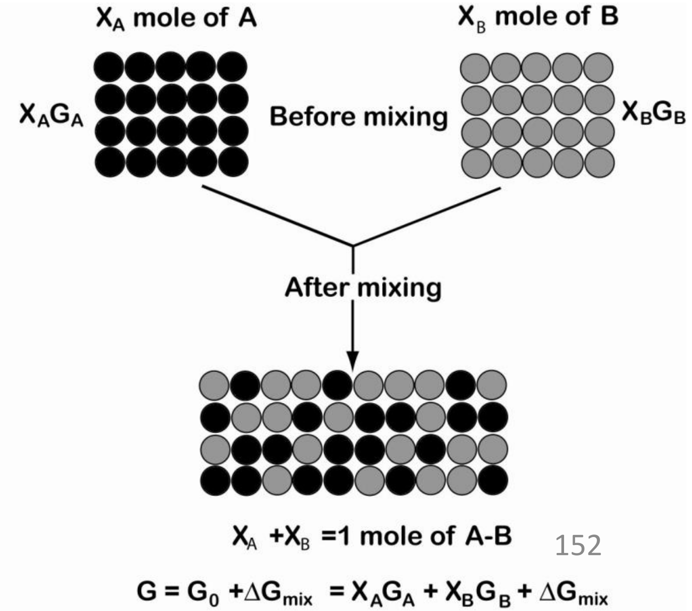
https://www.doitpoms.ac.uk/tlplib/ellingham_diagrams/printall.php

Thermodynamic parameters in a binary system

- Previously we are considered one element only. Now we consider interaction between two elements. This is not straightforward since elements can interact differently and thermodynamic parameters may change accordingly.
- Let us consider a Binary system with elements A and B. For our analysis, we consider X_A mole of A and X_B mole of B so that $\boldsymbol{X_A + X_B = 1}$
- That means we consider total one mole of the system That further means we consider total number of atoms equal to the Avogadro number, N_0 $(= 6.023 \times 10^{23})$,

Where $X_i = \dfrac{N_i}{N_0}$ *is the number of atoms of element i.*

- Unlike single component system, where we determine the change in free energy with temperature, in the binary case we shall find the change in free energy with the change in composition at different constant temperature at a time.
- Let us consider the free energy for one mole of element A is G_A and one mole of B is G_B.



$$G = G_0 + \Delta G_{mix} = X_AG_A + X_BG_B + \Delta G_{mix}$$

Thermodynamic parameters in a binary system

- So before mixing when kept separately, X_A mole of A and X_B mole of B will have the free energy of $X_A G_A$ *and* $X_B G_B$ respectively

Total free energy before mixing $G_0 = X_A G_A + X_B G_B$

- After mixing there will be change in free energy
- Total free energy after mixing $G = G_0 + \Delta G_{mix}$
- ΔG_{mix} is the free energy change of the alloy because of mixing

$$\Delta G_{mix} = G - G_0 = H - TS - (H_0 - TS_0) = (H - H_0) - T(S - S_0)$$

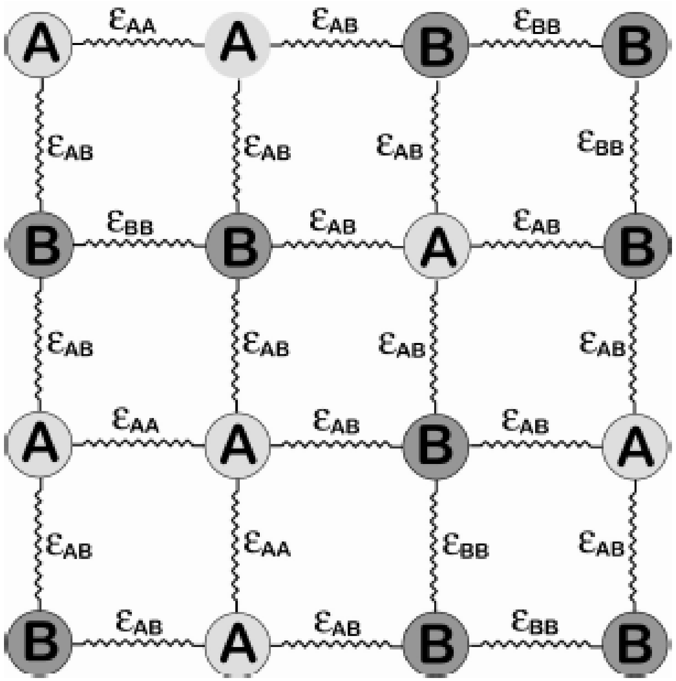
$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

- So, once we determine the change in free energy because of mixing, we can determine the total free energy after mixing.
- Let us first determine, the enthalpy change because of mixing (ΔH_{mix}) and the change in entropy because of mixing (ΔS_{mix})
- Note that system always tries to decrease enthalpy and increase entropy for stability.

The change in enthalpy because of mixing, ΔH_{mix}

- We take the following assumptions:
  - ✓ The molar volume does not change because of mixing
  - ✓ Bond energies between the pure elements do not change with the change in composition
  - ✓ We neglect the role of other energies.
- After mixing, the system can have three different types of bonding, A-A, B-B and A-B
- Enthalpy of mixing can be expressed as $\Delta H_{mix} = N_0 Z X_A X_B \Delta\varepsilon$

  N_0 - Avogrado number, Z = coordination number



- The change in internal energy

$$\Delta\varepsilon = \varepsilon_{AB} - \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})$$

ε_{AB} is the bond energy between A and B

ε_{AA} *is the bond energy between A and A*

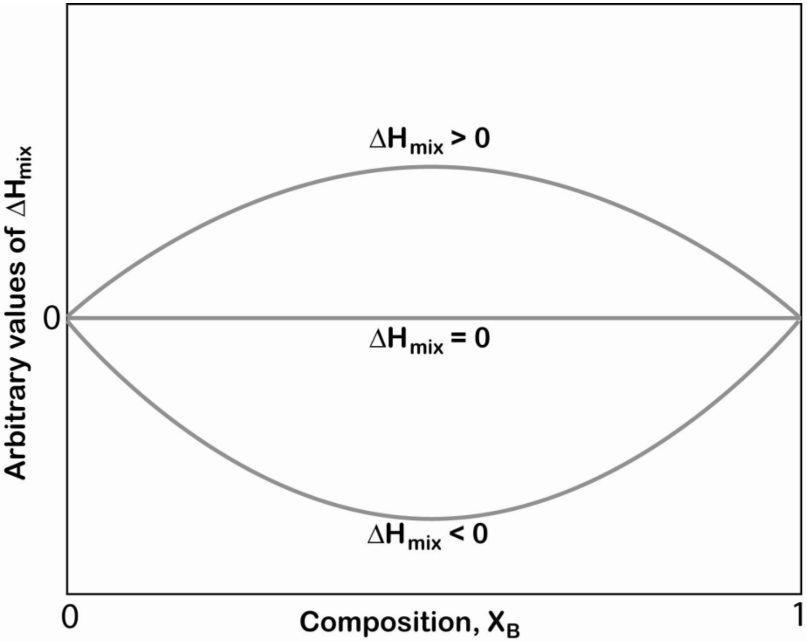
ε_{BB} *is the bond energy between B and B*

- It can be written as

$$\boxed{\Delta H_{mix} = \Omega X_A X_B}$$

Where $\Omega = N_0 Z \Delta\varepsilon$

The change in enthalpy because of mixing, ΔH_{mix}



Situation 1: Enthalpy of mixing is zero

$$\Delta H_{mix} = \Omega X_A X_B = 0$$

That means $\varepsilon_{AB} = \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})$

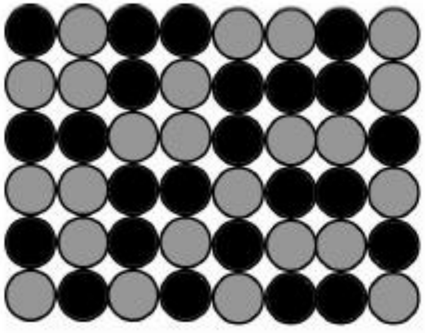
Because of transformation internal energy will increase. That means transformation is to be endothermic. Atoms will try to maximize A-A and B-B bonds.

Situation 2: Enthalpy of mixing is less than zero

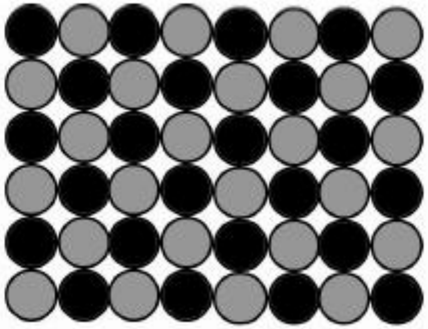
$$\Delta H_{mix} = \Omega X_A X_B < 0$$

That means $\varepsilon_{AB} < \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})$

Because of transformation internal energy will decrease. That means transformation is exothermic. Atoms will try to maximize A-B bonds.



$\Delta H_{mix} = 0$



$\Delta H_{mix} < 0$

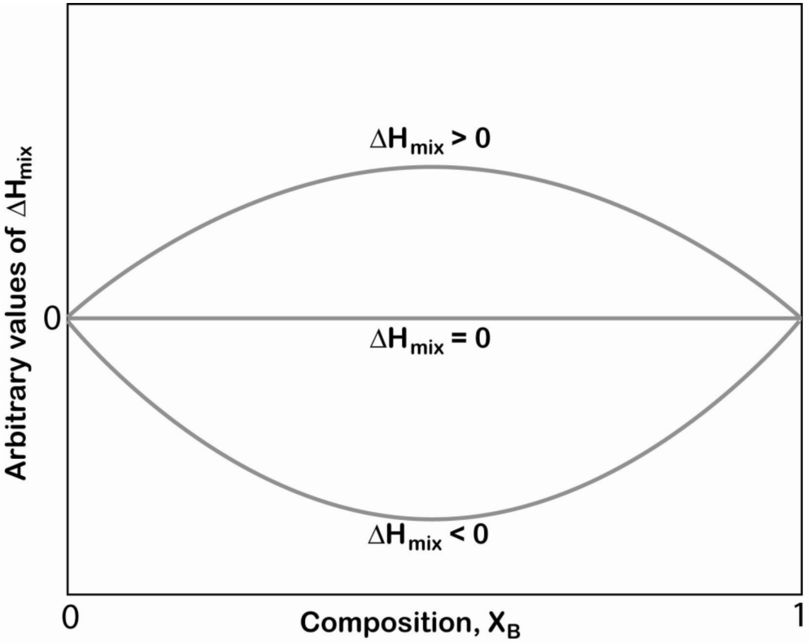
The change in enthalpy because of mixing, ΔH_{mix}

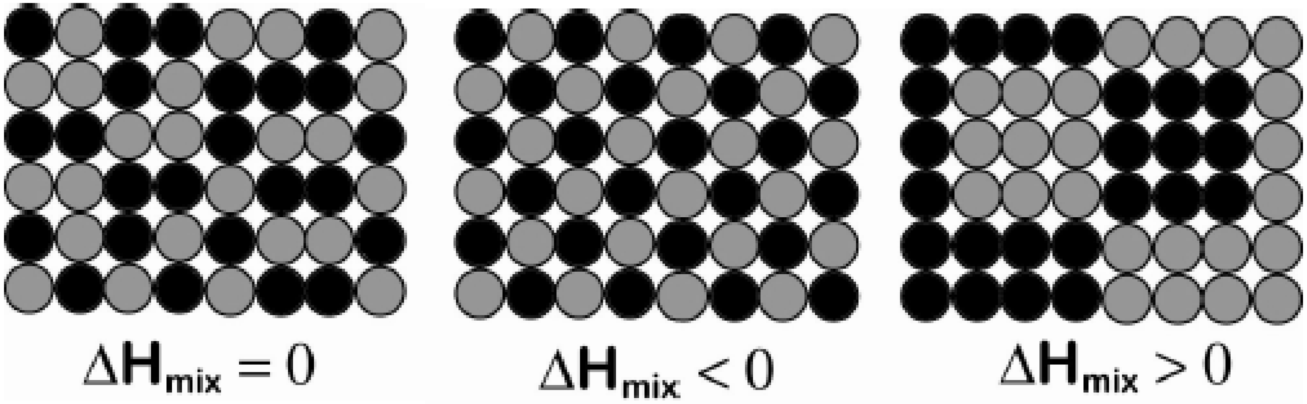
Situation 3: Enthalpy of mixing is greater than zero

$$\Delta H_{mix} = \Omega X_A X_B > 0$$

That means $\varepsilon_{AB} > \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})$

Because of transformation internal energy will increase. That means transformation is to be endothermic. Atoms will try to maximize A-A and B-B bonds.





Effect of Interaction Energy

- If the interaction energy is negative, unlike bonds (A-B bonds) are energetically favored. If it has a ***large negative value, compound formation*** is favored, where every A atom is surrounded by B neighbors and vice versa. E.g., SiO_2, Fe_3C

- If the interaction energy is positive, like bonds (A-A & B-B bonds) are energetically favored. If it is a **large positive value**, the two component atoms do not mix with each other and **immiscibility results**.

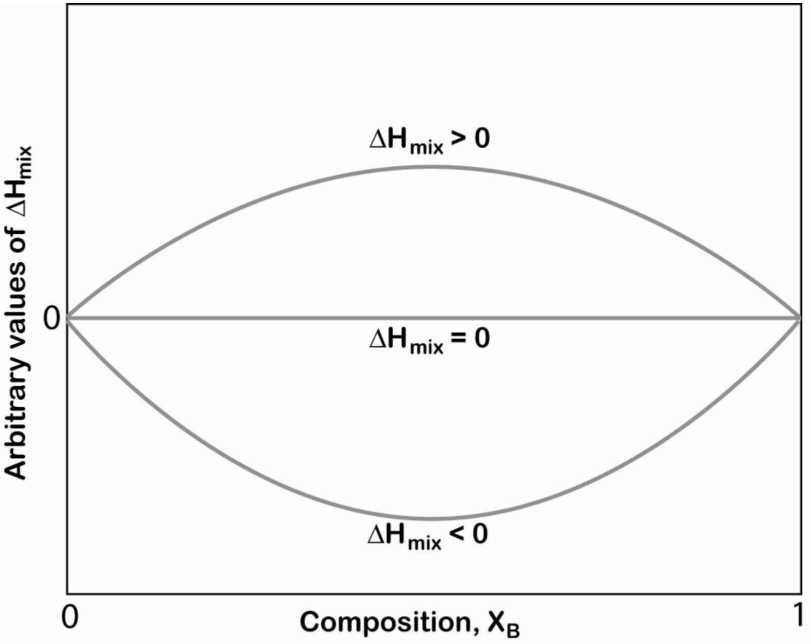
- In solid solutions, the interaction energy is either zero or has a small positive or negative value.

- If interaction energy is **zero**, we have a perfectly **random ideal solution**.

- If it is **negative**, the tendency will be for **short range ordering** in the solid solution. Short range ordering refers to formation of small regions in the solution, where A-B bonds are present preferentially.

- If it is **positive**, the tendency will be for **clustering** of like atoms in the solid solution. Clustering refers to the formation of small regions in the solid solution, where A-A and B-B bonds are preferentially present.

Slope/maximum/minimum of the enthalpy of mixing curve



$$\Delta H_{mix} = \Omega X_A X_B = \Omega (X_B - X_B^2)$$

$$\frac{d(\Delta H_{mix})}{dX_B} = \Omega(1 - 2X_B)$$

At maximum/minimum $\frac{d(\Delta H_{mix})}{dX_B} = 0$ *This implies X_B = 0.5. That means maximum or minimum will be at X_B =0.5*

Further $\frac{d(\Delta H_{mix})}{dX_B} at X_B \xrightarrow{\lim} 0 = \Omega$ *That means the slope at the beginning has a finite value of x*

The change in entropy because of mixing, ΔS_{mix}

- Since we are considering transformation at a particular temperature, the change in entropy because of the change in temperature can be neglected.
- We need to consider only the configurational entropy change. Configurational entropy change comes from the possibilities of different ways of arrangement of atoms.
- Following statistical thermodynamics the configurational entropy can be expressed as

$$S = l \ln \omega$$

k is the Boltzmann constant
w is the measure of randomness

$$\Delta S_{mix} = S - S_0 = k \ln \omega - k \ln 1 = k \ln \omega$$

since atoms at their pure state before mixing can be arranged in only one way

- If we consider the random solid solution, then

$$\omega = \frac{(n_A + n_B)!}{n_A! n_B!}$$

n_A and n_B are the number of atoms of A and B

- *Following Stirling's approximation* $\ln N! = N \ln N - N$

The change in entropy because of mixing, ΔS_{mix}

- ***So, ΔS_{mix} can be written as***

$$\Delta S_{mix} = k \ln \omega = k\{[(n_A + n_B)\ln(n_A + n_B) - (n_A + n_B)] - [n_A \ln n_A - n_A] - [n_B \ln n_B - n_{\mathbf{B}}]\}$$

$$\Delta S_{mix} = -k\left[n_A \ln \frac{n_A}{n_A + n_B} + n_B \ln \frac{n_A}{n_A + n_B} \right]$$

Number of atoms can be related to the mole fraction, X and the Avogadro number N_0 following

$$n_A = X_A N_0 \qquad n_B = X_B N_0$$

$$X_A + X_B = 1 \qquad n_A + n_B = N_0$$

$$\Delta S_{mix} = -kN_0[X_A \ln X_A + X_B \ln X_B]$$

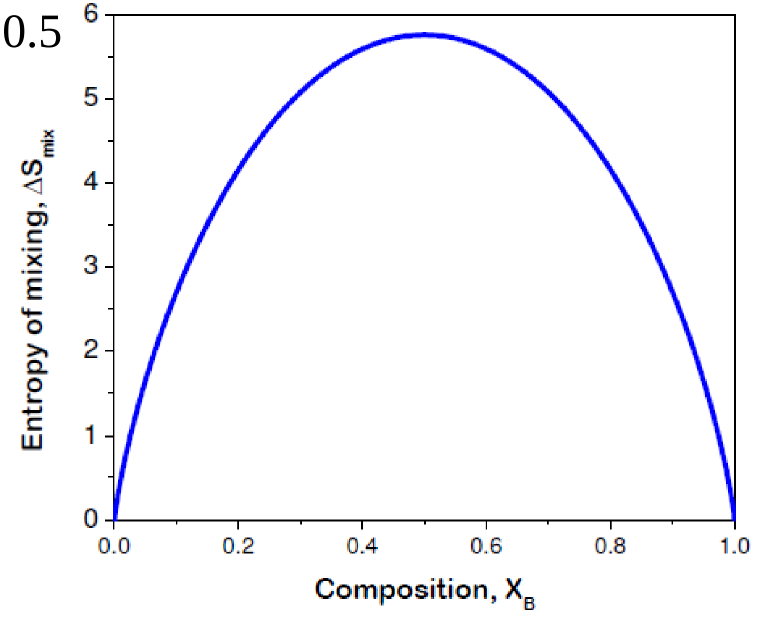
$$= R[X_A \ln X_A + X_B \ln X_B]$$

where, R is the gas constant

Slope/maximum of the entropy of mixing curve

$$\frac{d(\Delta S_{mix})}{dX_B} = -R\left[-\ln(1-X_B)-(1-X_B)\frac{1}{(1-X_B)}+\ln X_B + X_B\frac{1}{X_B}\right] = -R\ln\frac{X_B}{1-X_B}$$

$$\frac{d(\Delta S_{mix})}{dX_B} = 0$$ at maximum, this corresponds to $X_B = 0.5$



Further, the slope at $X_B \rightarrow 0$ is infinite. That means the entropy change is very high in a dilute solution

As mentioned earlier the total free energy after mixing can be written as $G = G_0 + \Delta G_{mix}$

where

$$G_0 = X_A G_A + X_B G_B$$

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

$$\Delta H_{mix} = \Omega X_A X_B$$

$$\Delta S_{mix} = -R[X_A \ln X_A + X_B \ln X_B]$$

So ΔG_{mix} can be written as $\Delta G_{mix} = \Omega X_A X_B + RT[X_A \ln X_A + X_B \ln X_B]$

Following, total free energy of the system after mixing can be written as

$$\boxed{G = X_A G_A + X_B G_B + \Omega X_A X_B + RT[X_A \ln X_A + X_B \ln X_B]}$$

Free energy of mixing

We need to consider three situations for different kinds of enthalpy of mixing

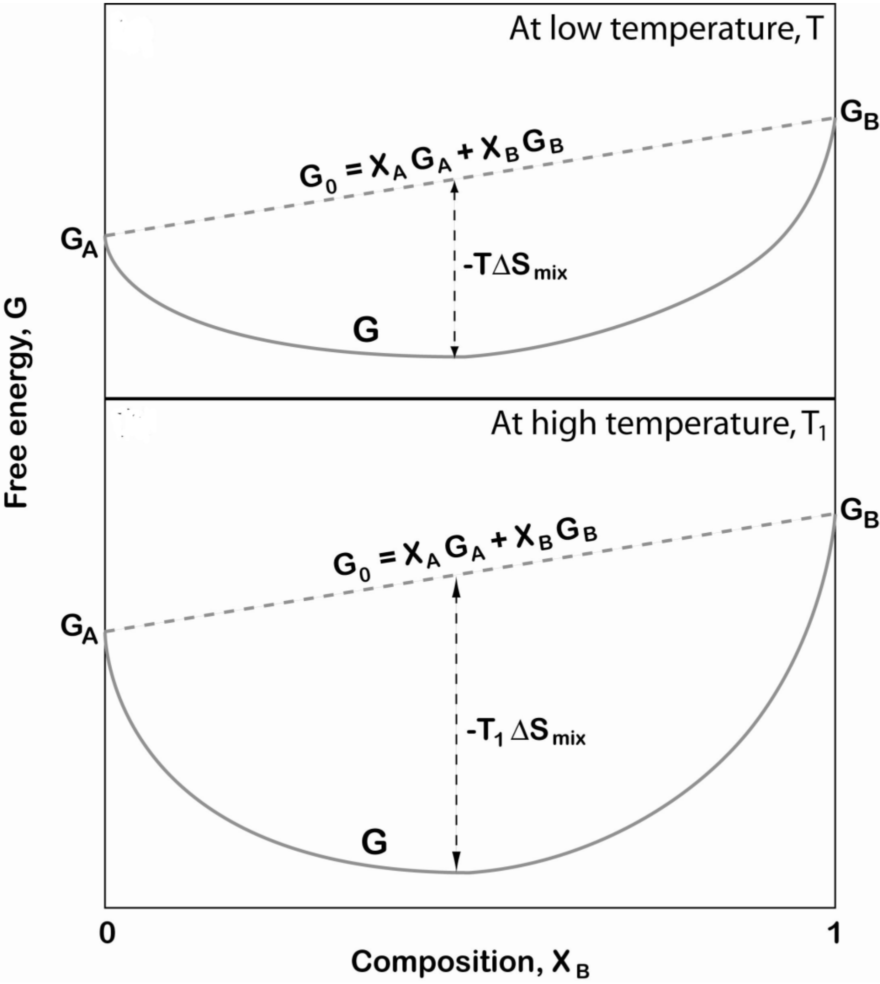
Situation 1: Enthalpy of mixing is zero

$$G = G_0 + \Delta G_{mix}$$

$$= G_0 - T\Delta S_{mix}$$

$$= X_A G_A + X_B G_B + RT[X_A \ln X_A + X_B \ln X_B]$$

- With the increase in temperature, -T∆S_{mix} will become even more negative.
- The values of G_A and G_B also will decrease.
- Following the slope G_o *might change since* G_A *and* G_B will change differently with temperature.

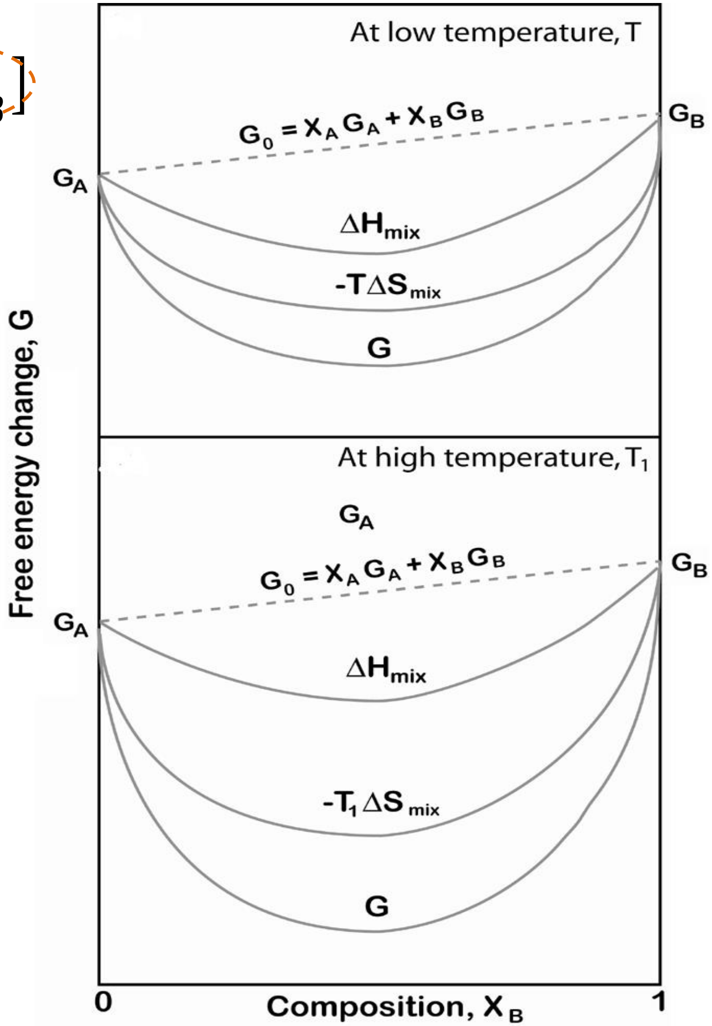


Free energy of mixing

Situation 2: Enthalpy of mixing is negative

$$G = \underbrace{X_A G_A + X_B G_B}_{G_0} + \underbrace{\Omega X_A X_B}_{\text{Negative } \Delta H_{mix}} + \underbrace{RT[X_A \ln X_A + X_B \ln X_B]}_{-T\Delta S_{mix}}$$

- ❑ Here both ΔH_{mix} and $-T\Delta S_{mix}$ are negative
- ❑ With increasing temperature G will become even more negative.
- ❑ Note that here also G_0 may change the slope because of change of G_A and G_B differently with temperature.

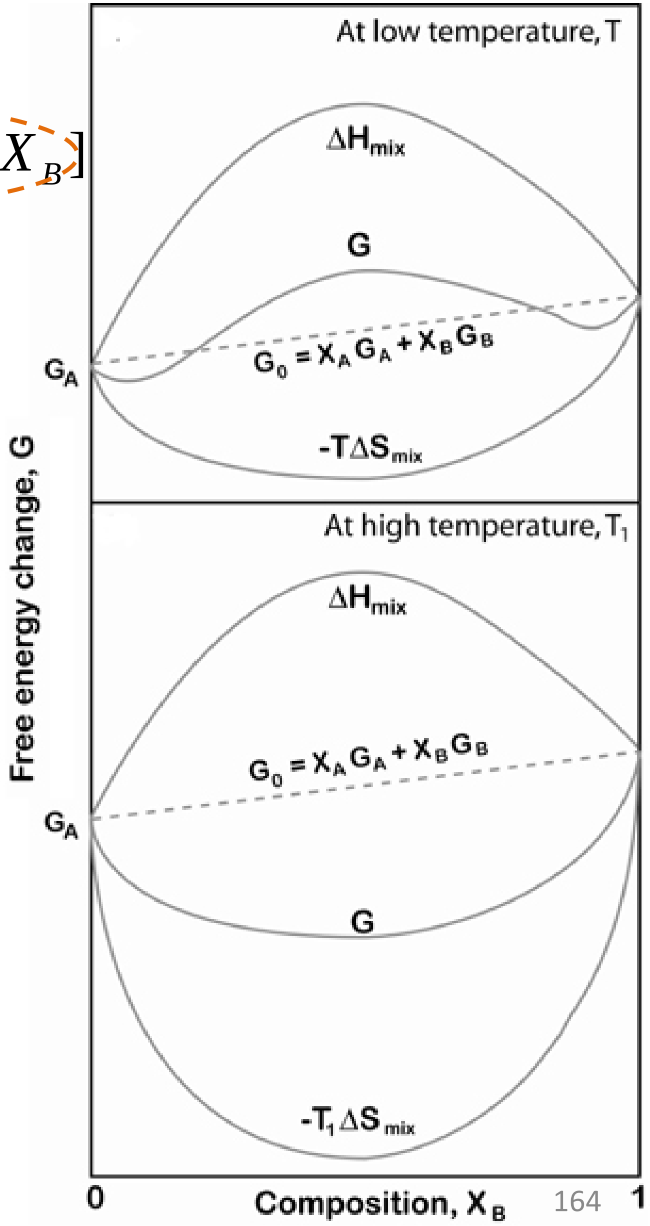


Free energy of mixing

Situation 3: Enthalpy of mixing is positive

$$G = \underbrace{X_A G_A + X_B G_B}_{G_0} + \underbrace{\Omega X_A X_B}_{\text{Positive } \Delta H_{mix}} + \underbrace{RT[X_A \ln X_A + X_B \ln X_B]}_{-T\Delta S_{mix}}$$

- ΔH_{mix} is positive but $-T\Delta S_{mix}$ is negative. At lower temperature, in a certain mole fraction range the absolute value of ΔH_{mix} could be higher than $T\Delta S_{mix}$ so that G goes above the G_0 line.
- However to G_A and G_B, G will always be lower than G_0, since ΔH_{mix} has a finite slope, where as ΔS_{mix} has infinite slope. The composition range, where G is higher than G_0 will depend on the temperature i.e., $-T\Delta S_{mix}$
- Because of this shape of the G, we see miscibility gap in certain phase diagrams.
- At higher temperature, when the absolute value of $-T\Delta S_{mix}$ will be higher than ΔH_{mix} at all compositions, G will be always lower than G_0



Concept of the chemical potential and the activity of elements

- Gibb’s free energy, G is function of temperature, T, pressure, P and amount of elements, n_A, n_B.

  $$G = G(T, P, n_A, n_B \ldots\ldots)$$

- At particular temperature and pressure, partial derivative gives

$$dG = \frac{\partial G}{\partial n_A} dn_A + \frac{\partial G}{\partial n_B} dn_B$$

$$= \mu_A dn_A + \mu_B dn_B$$

$\frac{\partial G}{\partial n_A} = \mu_A$ is the chemical potential of element A. It measures the change in free energy because of very minute change of element A.

$\frac{\partial G}{\partial n_B} = \mu_B$ is the chemical potential of element B. It measures the change in free energy because of very minute change of element B.

- It should be noted here that the change should be so minute that there should not be any change in concentration because the chemical potential is a concentration dependent parameter.

Concept of the chemical potential and the activity of elements

- Let us consider an alloy of total X moles where it has X_A mole of A and X_B mole of B. Note that x is much higher than 1 mole.
- Now suppose we add small amounts of A and B in the system, keeping the ratio of $X_A : X_B$ the same, so that there is no change in overall composition.
- So if we add four atoms of A, then we need to add six atoms of B to keep the overall composition fixed. Following this manner, we can keep on adding A and B and will reach to the situation when X_A mole of A and X_B mole of B are added and total added amount is $X_A + X_B = 1$
- Since previously we have considered that the total free energy of 1 mole of alloy after mixing is G, then we can write

$$G = \mu_A X_A + \mu_A X_B$$

- ***Previously, we derived***

$$G = X_A G_A + X_B G_B + \Omega X_A X_B + RT[X_A \ln X_A + X_B \ln X_B]$$

- ***Further, we can write*** $X_A X_B = X_A^2 X_B + X_A X_B^2$

$$G = X_A(G_A + \Omega X_B^2 + RT \ln X_B) + X_B(G_B + \Omega X_A^2 + RT \ln X_B)$$

Concept of the chemical potential and the activity of elements

Further, comparing the expressions for free energy, we can write

$$\mu_A = G_A + \Omega X_B^2 + RT\ln X_A$$

$$\mu_A = G_A + \Omega(1 - X_A)^2 + RT\ln X_A$$

$$\mu_B = G_B + \Omega(1 - X_B)^2 + RT\ln X_B$$

In terms of activity

$$\mu_A = G_A + RT\ln a_A$$

$$\mu_B = G_B + RT\ln a_B$$

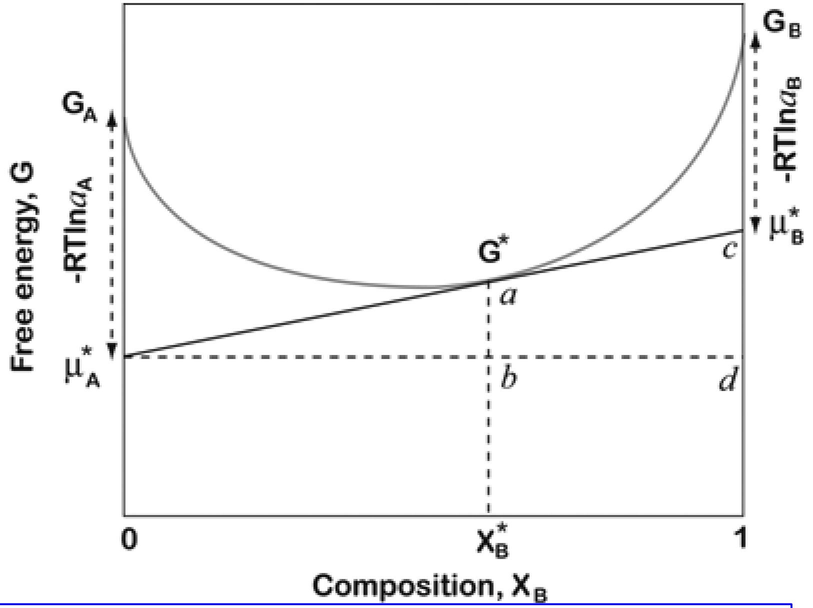
So the relations between the chemical potential and activity are

$$RT\ln a_A = \Omega(1 - X_A)^2 + RT\ln X_A$$

$$RT\ln a_B = \Omega(1 - X_B)^2 + RT\ln X_B$$

Concept of the chemical potential and the activity of elements

- Activities and chemical potentials are determined from a free energy curve after taking a slope, as explained in the figure.
- If we are interested to determine the activities or chemical potentials in a binary system A-B, let say at X_B^*, we need to take a slope on the free energy curve at the free energy, G^* and extended it to pure element, A ($X_B = 0$) and pure element B ($X_B = 1$).



- The point at which it hits $N_B = 0$, the value corresponds to the chemical potential of element A (μ_A^*).
- From previous slide, we can write $-RT\ln a_A = G_A - \mu_A^*$
- So, once the chemical potential is known, the activity of the element can be calculated using the above equation, as explained in the graph.
- It can be proved that, by taking slope and then extending to $X_B = 0$ and $X_B = 1$, we can find the chemical potentials. We can write $G^* = \mu_A^* + ab$
- Further we can write $\frac{ab}{X_B^*} = \frac{cd}{1}$ $\Rightarrow ab = X_B^* cd = X_B^*(\mu_B^* - \mu_A^*)$ $\boxed{\Rightarrow G^* = \mu_A^* X_A^* + \mu_B^* X_B^*}$

Concept of the chemical potential and the activity of elements

Further, we can write

$$\ln\left(\frac{a_A}{X_A}\right) = \frac{\Omega}{RT}(1 - X_A)^2$$

$$a_A = X_A \exp\left[\frac{\Omega}{RT}(1 - X_A)^2\right] = \gamma_A X_A$$

$$\gamma_A = \exp\left[\frac{\Omega}{RT}(1 - X_A)^2\right]$$

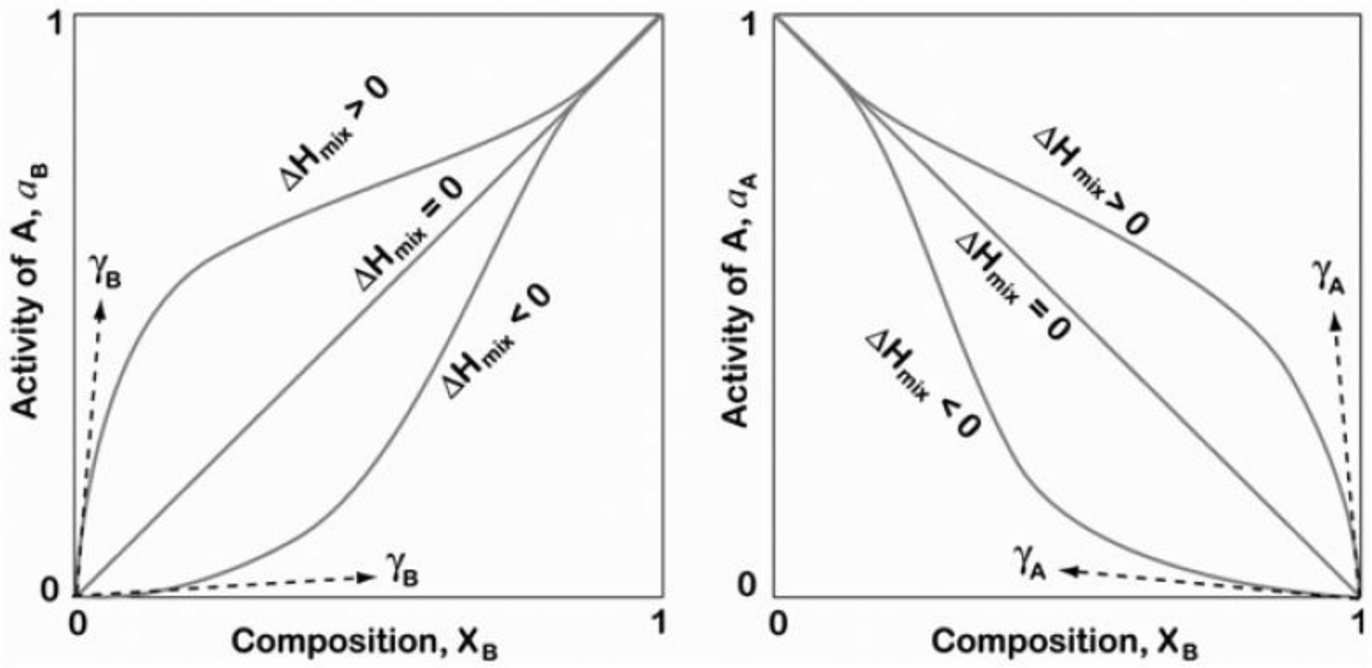
$$\ln\left(\frac{a_B}{X_B}\right) = \frac{\Omega}{RT}(1 - X_B)^2$$

$$a_B = X_B \exp\left[\frac{\Omega}{RT}(1 - X_B)^2\right] = \gamma_B X_B$$

$$\gamma_B = \exp\left[\frac{\Omega}{RT}(1 - X_B)^2\right]$$

- ☐ γ_i are the activity coefficient of element i.
- ☐ In an ideal solution, $\Omega = 0$, and $A_i = X_i$.
- ☐ In a non ideal solution, activity coefficient indicates the deviation from the ideal line.

Concept of the chemical potential and the activity of elements



$$\gamma_A = \exp\left[\frac{\Omega}{RT}(1 - X_A)^2\right]$$

$$\gamma_B = \exp\left[\frac{\Omega}{RT}(1 - X_B)^2\right]$$

In the case of positive enthalpy of mixing, activity deviates positively and in the case of negative enthalpy of mixing activity deviates negatively from the ideal mixing line.

$$X_A \to 0, \gamma_A \to \exp\left(\frac{\Omega}{RT}\right)$$

$$X_B \to 0, \gamma_B \to \exp\left(\frac{\Omega}{RT}\right)$$

$$X_A \to 1, \gamma_A \to 1$$

$$X_B \to 1, \gamma_B \to 1$$

Henry’s law: activity of elements is more or less the constant in a very dilute solution.

Rault’s law: activity is equal to the mole fraction near the mole fraction of 1.

Equilibrium conditions between different phases

- As explained previously, while discussing the phase diagrams, we have shown that at certain conditions two phases, such as solid and liquid or two solid phases α and β can stay together.
- This can be explained with respect to chemical potential of elements. For the sake of explanation let us consider that there are two phases α and β which are staying together.
- If you remove dn_B of element B from the β phase and add them to α phase, then the change in free energy of the α and β phases will be

$$dG^{\alpha} = \mu_B^{\alpha} dn_B$$

$$dG^{\beta} = -\mu_B^{\beta} dn_B$$

- So the total free energy change of the system will be

$$dG = \mu_B^{\alpha} dn_B - \mu_B^{\beta} dn_B = (\mu_B^{\alpha} - \mu_B^{\beta}) dn_B$$

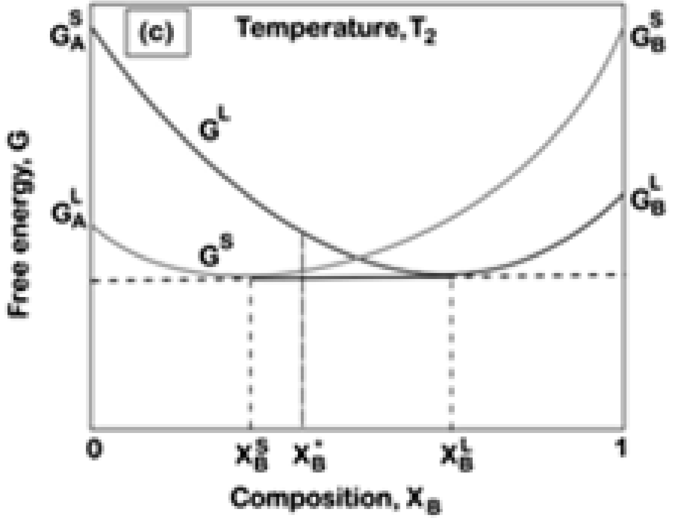
- However we know that in equilibrium condition dG = 0. That means the chemical potential of element B in both the phases should be the same.
- That further means that even if a small amount of material is transferred from the β to the α phase, there will be no difference in equilibrium as long as the chemical potential of elements are the same in both the phases.

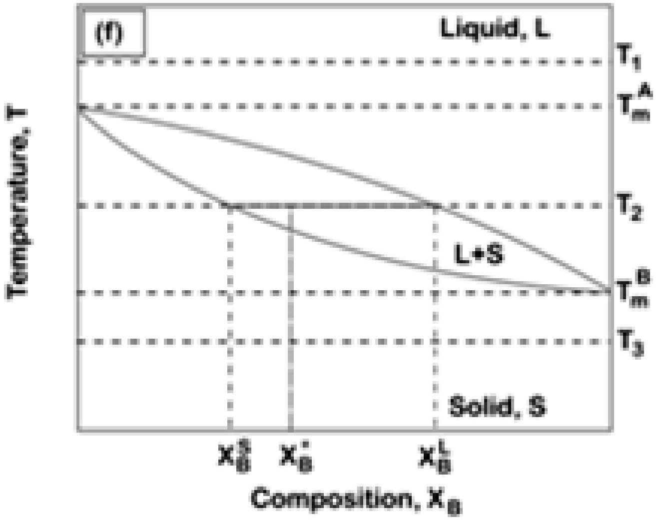
Equilibrium conditions between different phases

- Previously, we have shown that the system will not be in equilibrium that is it will go through irreversible transformation if $dG < 0$. *That means*

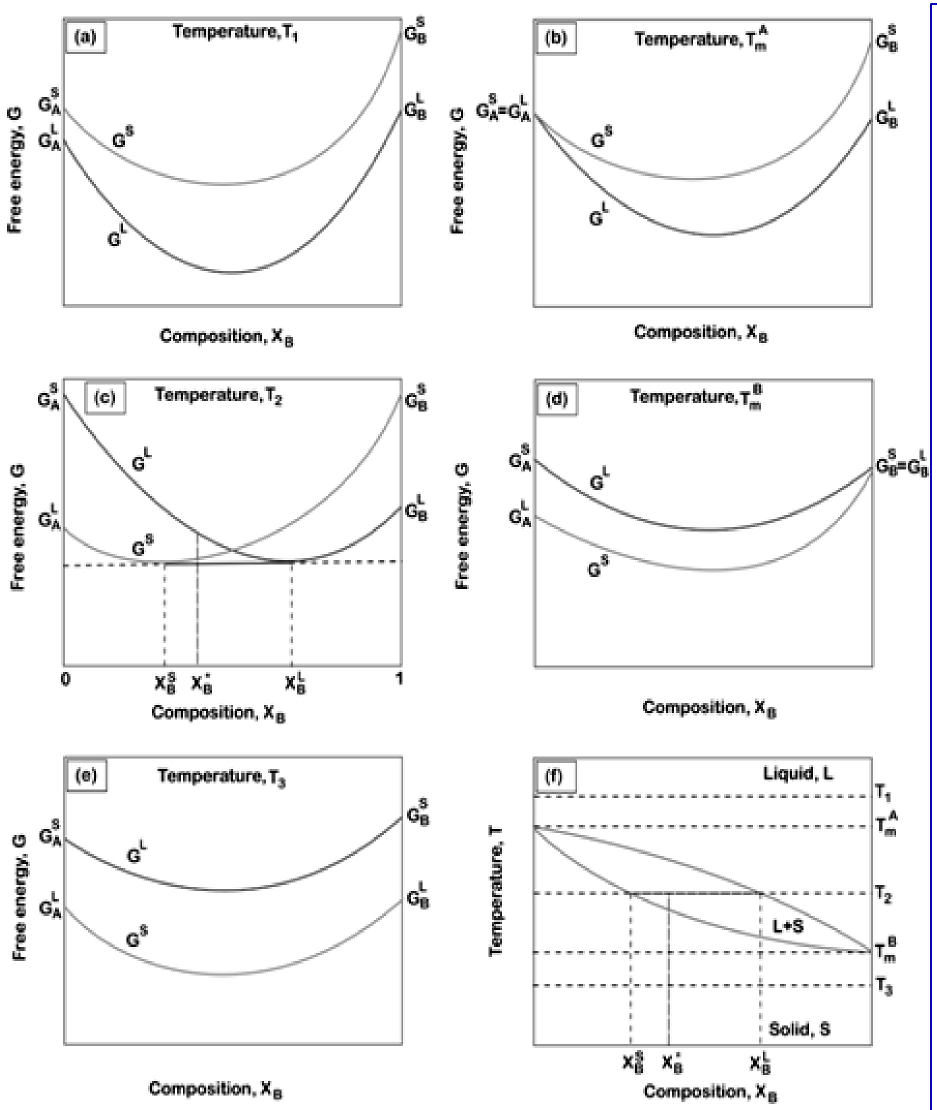
$$(\mu_B^\alpha - \mu_B^\beta)dn_B < 0$$

- This indicates that the chemical potential of B in the α phase is less then the chemical potential of the same element in the β phase.
- So to reach to the equilibrium system will transfer B from the β phase to the α phase.
- Now we understand, why both solid and liquid phases can stay together in certain composition range. It can be understood from the common tangent between X_B^S and X_B^L chemical potential of any of the elements are the same in both the phases .





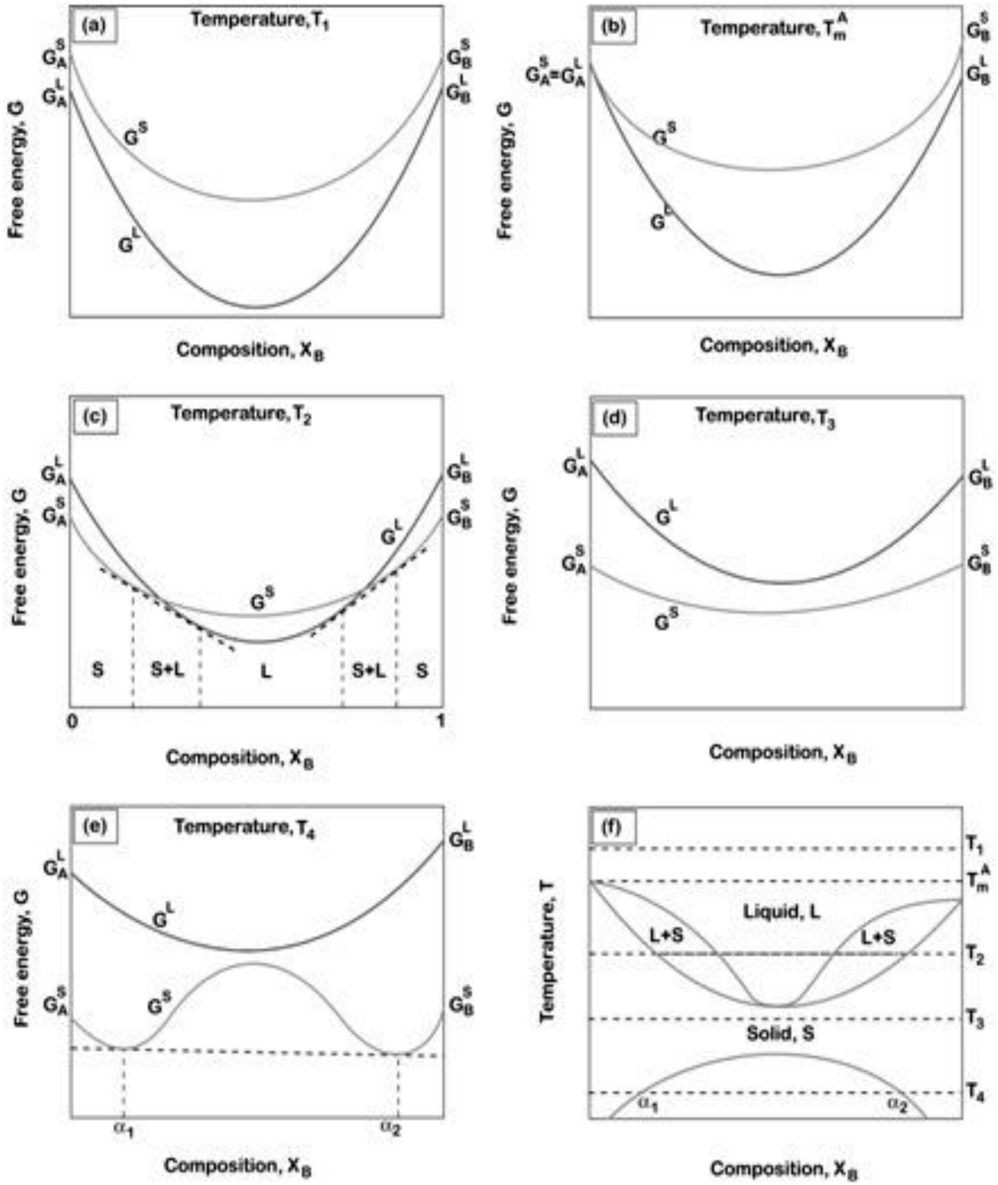
Free energy Vs Composition Phase Diagrams



Both the liquid and solid phases can stay together because overall free energy will be less than the free energy when considered separately.

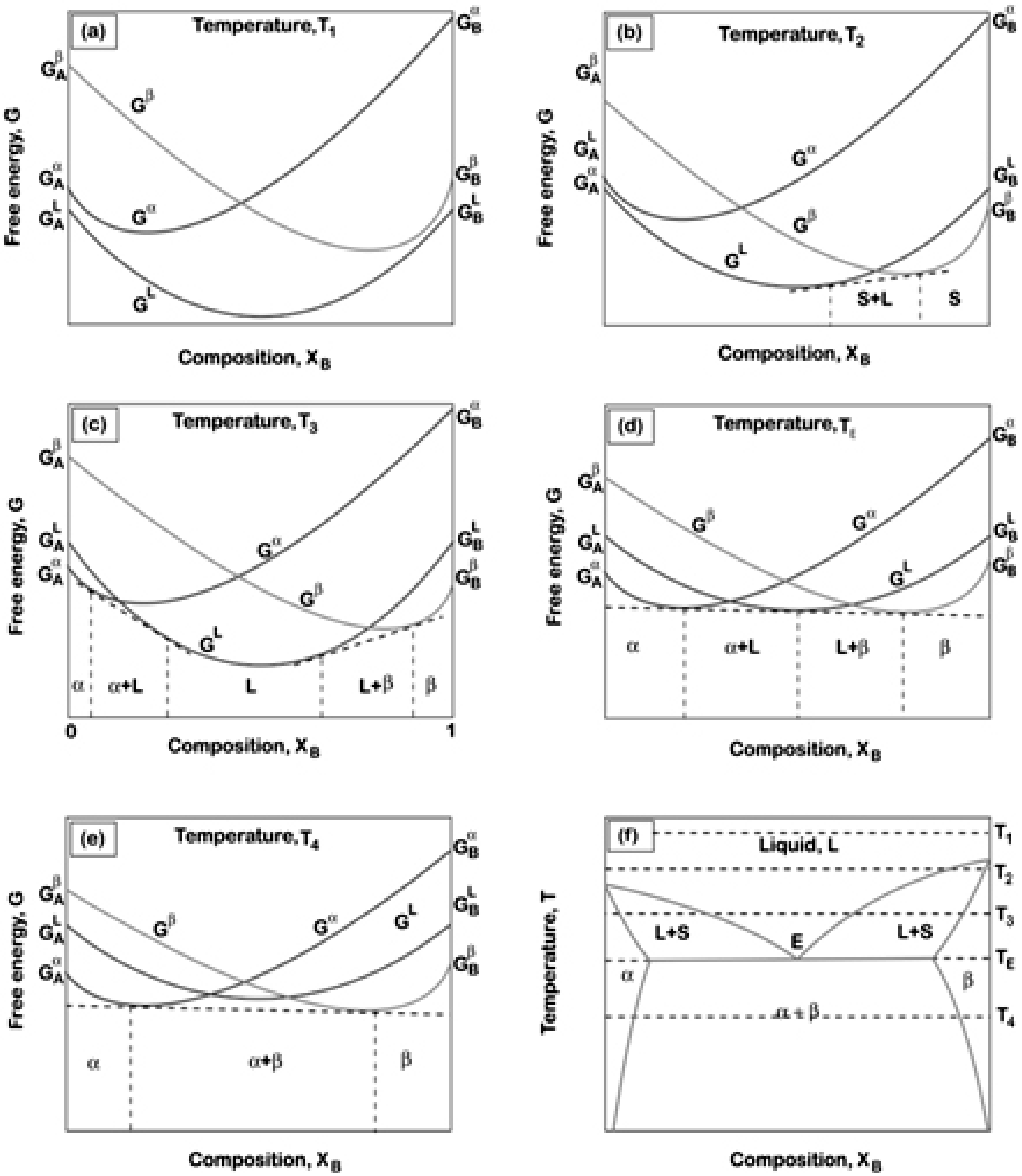
- With decreasing temperature, free energy for the solid, G_S and liquid phase G_L will change differently with different rates of change of G_A and G_B.
- At higher temperature, $G_L < G_S$ (fig a), so that the liquid phase is stable. At lower temperature $G_S < G_L$ (fig e) so that the solid phase is stable.
- In between, G_S and G_L intersects to find the situation as explained in Fig. c.
- Common tangent drawn gives the composition range where both solid and liquid phases can be found together.
- That means, if average composition is X_B* as shown in the phase diagram, it will have the solid phase with composition of X_B^S and the liquid phase with composition of X_B^L Phase fractions can be found with the help of lever rule.

Free energy Vs Composition Phase Diagrams



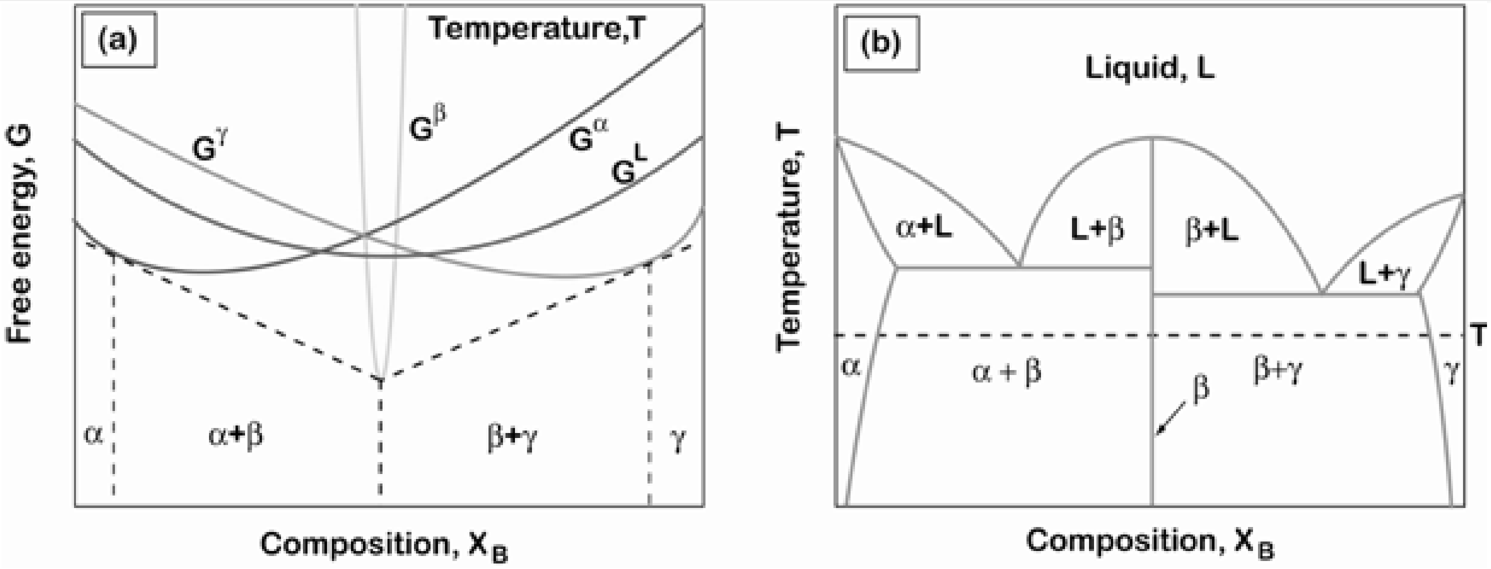
- This kind of phase diagram is found when the system has positive enthalpy of mixing, especially for the solid phase.
- Because of the shape of the G_S at low temperature as as shown in Fig. e, it is possible to draw a common tangent, which indicates that the solid phase with the average composition between α_1 and α_2 will have a phase separation . This corresponds to the miscibility gap in the phase diagram.
- It may also come to the situation, as it is shown in Fig. c, G_L and G_S intersects twice. In that case these will be two separate regions where both the solid and liquid phases coexist.

Free energy Vs Composition Phase Diagrams

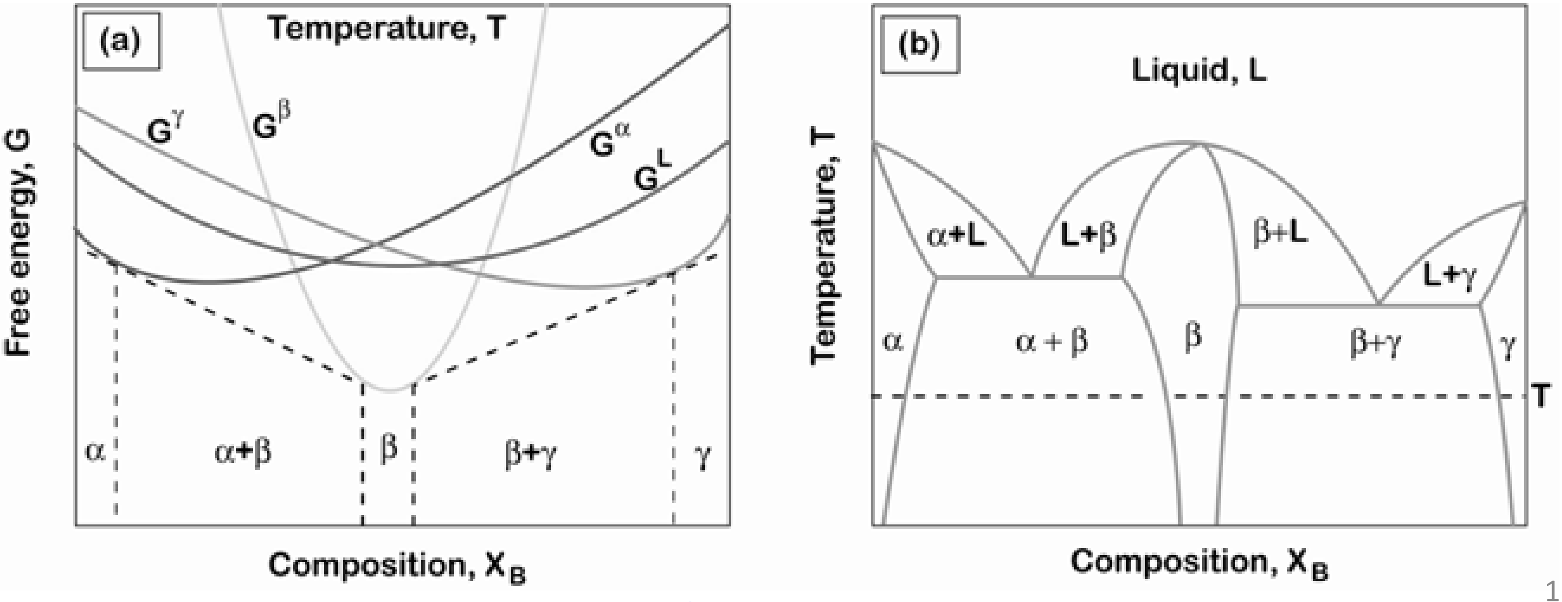


- ❑ In this system, there are two solid state phases and one liquid phase. So three free energy curves should be considered.
- ❑ At certain temperature, T_E, one common tangent can be drawn, which will touch all the free energy curves.
- ❑ This indicates that all the three phases at a particular composition E, as shown in Fig. d and f can coexist. This is called eutectic point.

Free energy Vs Composition Phase Diagrams



β phase is an intermetallic compound that is an ordered phase with very narrow homogeneity range.



Sometimes β phase can be found with wider homogeneity range.