METALLURGICAL THERMODYNAMICS AND KINETICS

B.TECH, 3RD SEMESTER

LECTURES NOTE

BY

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BPUT SYLLABUS

Metallurgical thermodynamics and Kinetics

Importance of Thermodynamics, definition of thermodynamic terms (phase, component, equilibrium, processes); concept of states, simple equilibrium. Equation of states, extensive and intensive properties, homogeneous and heterogeneous systems. Phase diagram of a single component system. Internal energy, heat capacity, enthalpy, isothermal, and adiabatic processes.

Second law of thermodynamics, entropy, degree of reversibility and irreversibility, criteria of equilibrium, auxiliary functions, combined statements, Maxwell's relations, transformation formula, Gibbs-Helmoltz equation.

Importance of Thermodynamics

In materials science, rather than randomly looking for and discovering materials and exploiting their properties, the actual aim is to understand materials so that new materials with the **desired properties** can be created.

The basis of materials science involves relating the desired properties and relative performance of a material in a certain application to the structure of the atoms and phases in that material through characterization. The major determinants of the structure of a material and thus of its properties are its constituent chemical elements and the way in which it has been processed into its final form. These characteristics, taken together and related through the laws of thermodynamics, govern a material's microstructure, and thus its properties.

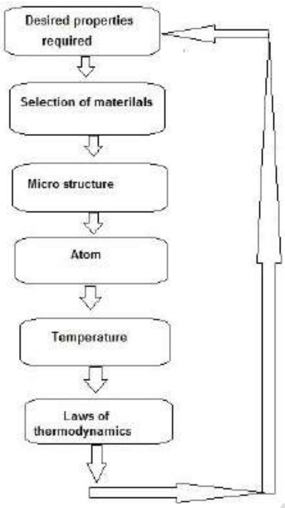
The manufacture of a perfect crystal of a material is currently physically impossible. Instead materials scientists manipulate the defects in crystalline materials such as precipitates, grain boundaries (Hall-Petch relationship), interstitial atoms, vacancies or substitutional atoms, to create materials with the desired properties.

All materials depend upon thermodynamics in one way or other.

Since most (all) of modern technology relies on electricity, and the flow of electricity generates heat, all technology is dependant on the laws of thermodynamics to function properly.

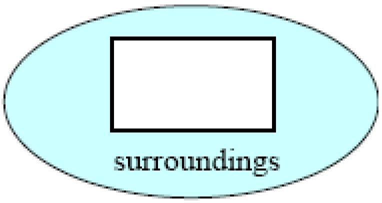
Of course, even non-modern technology is dependant on thermodynamics: anything requiring movement (screws, levers, planes, wheels, pulleys and other simple machines) all have to first over come the force of friction, which again relies on thermodynamics (as friction generates heat).

The main use of thermodynamics in physical metallurgy is to allow the prediction of whether an alloy is in equilibrium. In considering phase transformations, we are always concerned with changes towards equilibrium. And thermodynamics is therefore a very powerful tool.



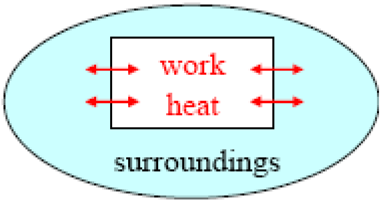
Definitions of thermodynamic terms

Types of thermodynamic systems



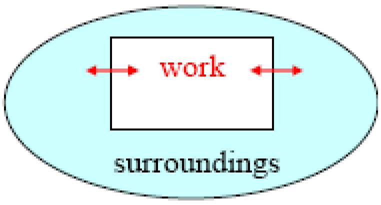
Isolated system No energy and no matter can pass through the boundaries of the system.

Closed system



Energy can pass through the boundaries (as heat and/or work), but matter cannot.

Adiabatic system



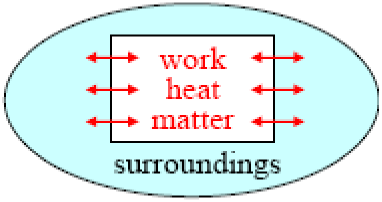
No heat can pass through the boundary (Neither can matter that can carry heat) –ideal thermos.

Work can be performed on or by the system.

An alternative formulation of the 1st law of thermodynamics:

The work done on a system during an adiabatic process is a state function and numerically equal to the change in internal energy of the system.

Open system



Both energy and matter may pass through the boundaries.

Phase:

Materials consist of phases or mixtures of phases. A **phase** is a portion of a system that has uniform properties, physically distinct, chemically homogeneous and mechanically separable.

Ex-Water (Single phase), liquid water and ice (Double phase)

The phase may or may not be in an equilibrium state.

Homogeneous and Heterogeneous:

A single-phase system is called **homogeneous** (e.g. ice, α-ferrite, Fe_3C)**.** Systems with two or more phases are **mixtures** or **heterogeneous (e.g.** mixture of ice+water, peartite etc) .systems. Two distinct phases in a system have distinct chemical **or** physical characteristics (e.g. liquid water and ice) and are separated from each other by definite **phase boundaries**. A phase may contain one or more components.

Component:

The **components** of a given system are the different elements or chemical compounds which make up the system, and the composition of a phase or the system can be described by giving the relative amounts of each component. Chemically recognizable species (Fe and C in carbon steel, H_2O and Sucrose in sugar solution in water) are examples of components.

Single component (Unary) Ex-water,

A **binary** alloy contains two components, a **ternar**y alloy - three, etc.
Two component (Binary) Ex-Fe-C,steel, Three component (Ternary)

Equilibrium –

Equilibrium is the state in which the system parameters no longer change with time (there are no exchange of matter or energy, small disturbances decay, …). The state along the path to the equilibrium may appear to be stable . this is called a metastable state.

There are three types of equilibrium.

(1) Mechanical equilibrium (pressure constant)
(2) Chemical equilibrium (composition is same)
(3) Thermal equilibrium (temp constant)

Above three type of equilibriums together is called thermodynamic equilibrium. The phases that are **not in equilibrium** can undergo a **spontaneous** phase transformation to an equilibrium phase or mixture of phases.

Equilibrium is the state that is achieved given ***sufficient*** time. But the time to achieve equilibrium may be very long (the kinetics can be slow) and a state along the path to the equilibrium may ***appear*** **to be stable**. This is called a **metastable state**.

What are thermodynamics variables?

There are two approaches to describe properties and behavior of a material:

1. *Microscopic approach* - to describe the material in terms of microscopic variables (positions, velocities, charges, etc. of all particles in the system). But there are too many particles ($N_A = 6.022\times10^{23}$ mol^{-1}) and this approach in unpractical in most cases.

2. *Classical (continuum) thermodynamics* – to describe the material in terms of average quantities, or **thermodynamic variables**, such as temperature, internal energy, pressure, etc.

Statistical thermodynamics provides the connection between the classical thermodynamics and the behavior of the microscopic constituents of matter (atoms and molecules). Although in this course we will focus on classical thermodynamics, we will also consider a few elements of statistical thermodynamics, in particular in our discussion of heat capacity and entropy.

What are state, state variables, state functions and equation of state?

State:

It is the set of independent variables that can define the system at equilibrium that is called state. And the variables are called state variable.

System can be described by a number of thermodynamic variables that are *independent of the history of the system*. Such variables are called **state variables** or **state functions** depending on the context.

We can describe a system by a set of *independent state variables* and we can express other variables (*state functions*) through this set of independent variables. e.g. V=V(P,T), U = U(P,T). They are connected by **equation of state**,

Relationships between independent state variables are called <u>state function or eq^n of state.</u>

Ex-PV=nRT, V=V(P,T), U=U(P,T)

For example, we can describe ideal gas by P and T, and use V = RT/P to define V. For different applications we can choose different sets of independent variables that are the most convenient.

Intensive and extensive variables

Intensive properties – independent of the size of the system, e.g. T, P. Ex-Temperature(T), Pressure(P), Density(ρ), Mole fraction(x), Dielectric Constant(ε), Molar Mass(M), Expansion Coefficient(α).

Extensive properties – proportional to the quantity of material, e.g. Mass(m), Number of moles(n), Volumes(V), Internal Energy(U), Enthalpy(H), Specific heat (C), Entropy(S), Gibbs free energy (G)

Example: if V1 = V2, T1 = T2, P1 = P2 then

$\boxed{1} + \boxed{2} = \boxed{1+2}$

V12 = V1 + V2 (extensive)

But T12 = T1 = T2 (intensive)

We can also consider "*derived intensive variables*," e.g. Mass/Volume or Energy/Volume, that do not depend on the size of the system.

A numbers of rules apply when we consider whether physical quantities are intensive or extensive.

1. Thermodynamics variables or properties are either extensive or intensive.
2. Two quantities can only be added to equated to or substracted from one another if they are both extensive or both intensive.
3. The ratio of two extensive quantities is an intensive quantity. E g. m/V=ρ
4. The product of intensive quantity by an extensive quantity is an extensive quantity.
5. Extensive/Intensive=Extensive

Process:

When one or more of the parameters of a system is changed the state of the system changes and it is said that a system undergoes a process. i.e. changing from one state to other is called process.

- Work done by the system on the surrounding is +ve, Work done on the system by the surrounding is –ve.
- Heat given into the system is +ve (endothermic reaction). Heat out of the system is –ve (exothermic reaction).

Process can also divided in to five types they are

1. Cyclic process

2. Isothermal process
3. Adiabatic process
4. Isochoric process
5. Isobaric process

Laws of conservation of energy:

Energy cannot be created nor be destroyed but it can be converted and transferred from one body to other.When potential energy is converted in to any of the six forms of a kinetic energy the total energy in the system before the conversion equals to the total energy after the conversion.

.i.e.PE+KE=PE+KE.

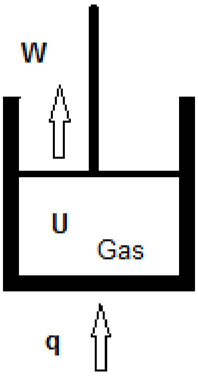
This is the law of conservation of energy.

Internal Energy(U)

Internal energy is the total energy contended by the thermodynamic system.It is the sum of kinetic and potential energy and all the form of energy.

- It is denoted as “U”.

The absolute value of internal energy for a system cannot be determine we can only determine the change in internal energy(ΔU).



q=U+W

q=ΔU+W

First law of thermodynaics:

The first law of thermodynamics states that energy can’t be created nor be destroyed.

i.e. Incresses in interna energy of a system =heat supplied to the system+work done on the system.

$\delta q = du + \delta W$

- Internal energy of a system dependes on its mass,chemical composition,structure as well as temperature.
- For a materail of fix mass,composition,structure then internal energy become function of only temperature.

Internal energy for isochoric process:(V=Const.)

$dU = \delta q - \delta W$

$= \delta q - \int PdV \qquad dV=0$

$dU = \delta q$

Internal energy for Isobaric process:(P=Const.)

$dU = \delta q - \delta w$

$= \delta q - \int_{V1}^{V2} PdV$

$= \delta q - P(V_2 - V_1)$

$\Delta U = \delta q - P(V_2 - V_1)$

$(U_2 - U_1) = \delta q - P(V_2 - V_1)$

$(U_2 - U_1) + P(V_2 - V_1) = \delta q$

$(U_2 + PV_2) - (U_1 + PV_1) = \delta q$

$H_2 - H_1 = \delta q$

$dH = \delta q$

$H = U + PV$

Heat Capacity:

Heat capacity is defined as amount of heat required to raised as amount of heat required to raised the temp of a system of one degree.

- It is denoted as “C”.

  $C = \left(\frac{\delta q}{dT}\right)$

Heat Capacity in isobaric process:

Heat capacity in isobaric process is denoted as C_p.

$C_p = \left(\frac{\delta q}{dT}\right)_p$

$= \left(\frac{dH}{dT}\right)_p$

$dH = C_p dT$

Heat capacity in isochoric process:

Heat capacity in isochoric process is denoted as C_V.

$C_p = \left(\frac{\delta q}{dT}\right)_V$

$= \left(\frac{dU}{dT}\right)_V$

$dU = C_V dT$

Relation between C_P and C_V:

The difference between the heat capacity is

$C_P - C_V = \frac{dH}{dT} - \frac{dU}{dT}$ ……(1)

We know $H = U + PV$………(2)

For one mole of ideal gas the gas equation is $PV = RT$……….(3)

Putting the value of ideal gas eq^n in 2nd eq^n we have

$H=U+RT$……….(4)

Differencing the eq^n (4) w.r.t T

$\frac{dH}{dT}=\frac{dU}{dT}+R\frac{dT}{dT}$

$\frac{dH}{dT}=\frac{dU}{dT}+R$

$\frac{dH}{dT}-\frac{dU}{dT}=R$

$C_P-C_V=R$

Thermodynamics can be used to predict weather the system is in equilibrium and to analyze the **phase stability and phase transformations**.

Questions thermodynamics can answer:

Is a particular process possible? Is a spontaneous evolution in a particular direction possible? What is the final/equilibrium state of the system?

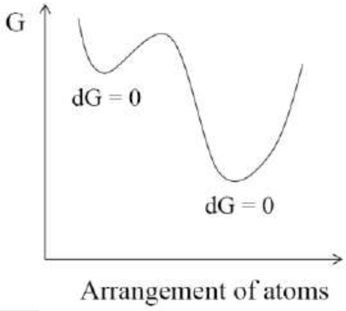
For example, for transformation occurring at constant T and P the relative stability of the phases in a system is determined by their Gibbs free energies,

$\Delta G = G_{final} - G_{initial} = \Delta H - T \Delta S$

$\Delta G < 0$ => process is allowed, spontaneous, feasible, natural

$\Delta G > 0$ => process is forbidden

$\Delta G = 0$ => equilibrium

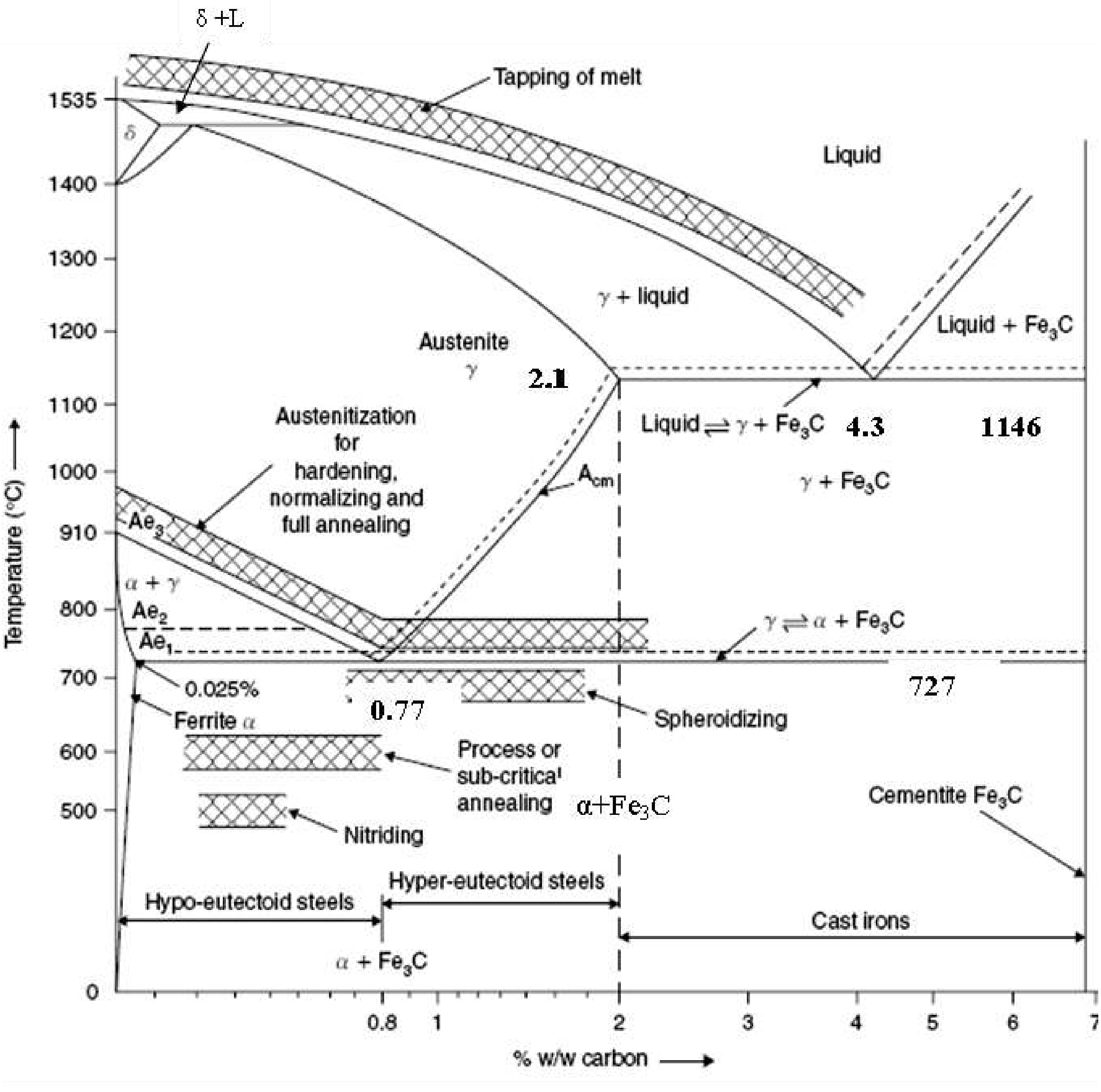


Understanding of phase stability is very important in material science – all properties of a material - optical, electronic, magnetic, thermal, mechanical depend on its phase composition.

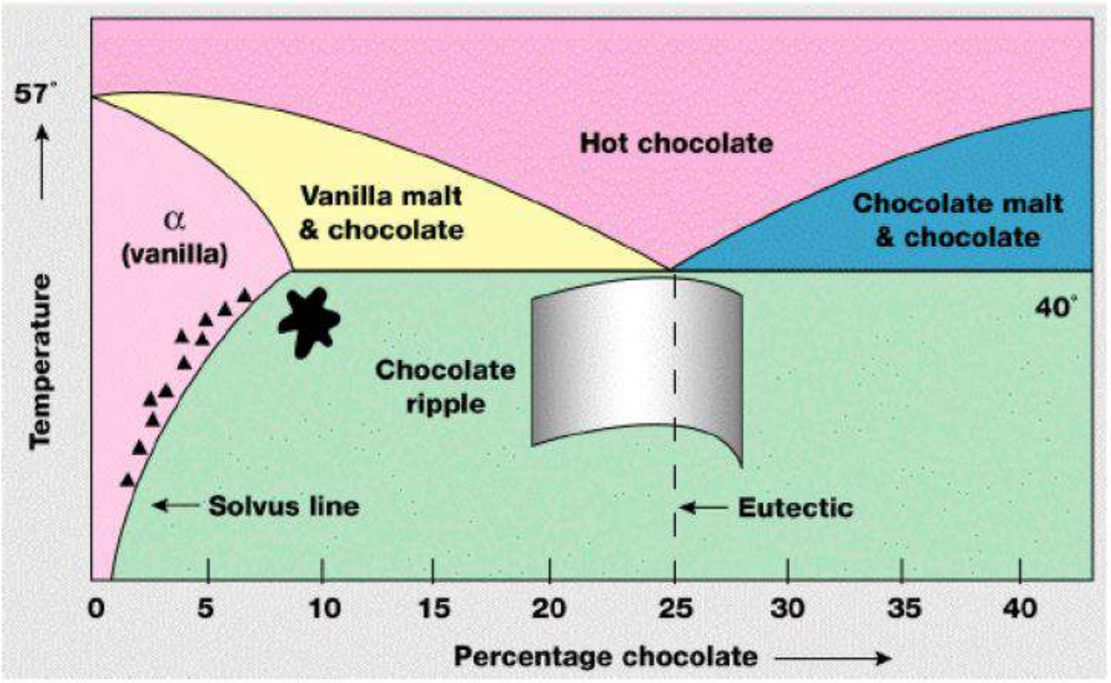
A phase diagram is a graphical representation of all the **equilibrium** phases as a function of temperature, pressure, and composition.

Phase diagrams arise from minimizing free energies for each phase. They can be used to describe gas - liquid – solid transitions, polymorphic solid-to-solid transitions, stable phases in alloys of different composition, etc.

Example of a binary phase diagram: iron–iron carbide (Fe–Fe_3C)



Another example: phase diagram for chocolate and vanilla



Review of classical thermodynamics Fundamental Laws, Properties and Processes

First Law - Energy Balance

Thermodynamic functions of state

Internal energy, heat and work

Types of paths (isobaric, isochoric, isothermal, adiabatic, cyclic)

Enthalpy, heat capacity, heat of formation, phase transformations

Calculation of enthalpy as a function of temperature

Heats of reactions and the Hess's law

Reading: Chapters 2, 6.1, 6.4 of Gaskell or the same material in any other textbook on thermodynamics

Internal energy, heat, and work: not very rigorous definitions:

It is impossible to give a rigorous definition of energy. ("...in physics today, we have no knowledge of what energy is." - *the Feynman Lectures on Physics*). Thermodynamics laws do not define energy,

Thermodynamics is dealing with transfer of energy.

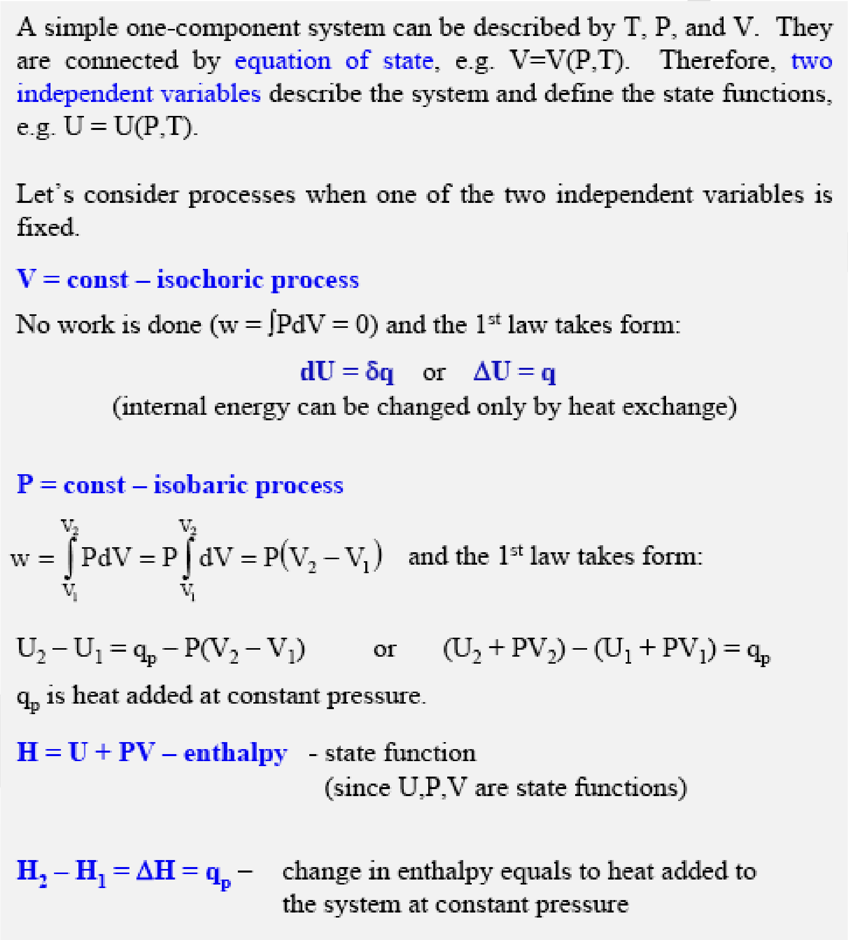
In particular, the 1st law of thermodynamics postulates the energy conservation. In thermodynamics of materials we usually do not consider the kinetic energy of the center-of-mass motion of the system or gravitational energy (mgh), only *internal energy*, intrinsic to the body is considered.

Internal energy U is a sum of all potential and kinetic energies in the system (not only of mechanical origin). Thermodynamics is only dealing with change of U. The absolute value of U is not defined by the laws of thermodynamics, but an arbitrary zero point is often chosen for convenience.

Heat is the energy being transferred to a system as a result of temperature difference (work-less transfer of internal energy).

Work can be defined as the energy being transferred to a system as a result of (generalized) force acting over a (generalized) distance.

Work and heat are both **functions of the path** of the process – they are **not state functions. Systems never possess heat and work!** Heat and work are transient phenomena – describe energy *being transferred* to/from the system.



A simple one-component system can be described by T, P, and V. They are connected by equation of state, e.g. V=V(P,T). Therefore, two independent variables describe the system and define the state functions, e.g. U = U(P,T).

Let's consider processes when one of the two independent variables is fixed.

V = const – isochoric process

No work is done ($w = \int PdV = 0$) and the 1st law takes form:

$$dU = \delta q \quad \text{or} \quad \Delta U = q$$

(internal energy can be changed only by heat exchange)

P = const – isobaric process

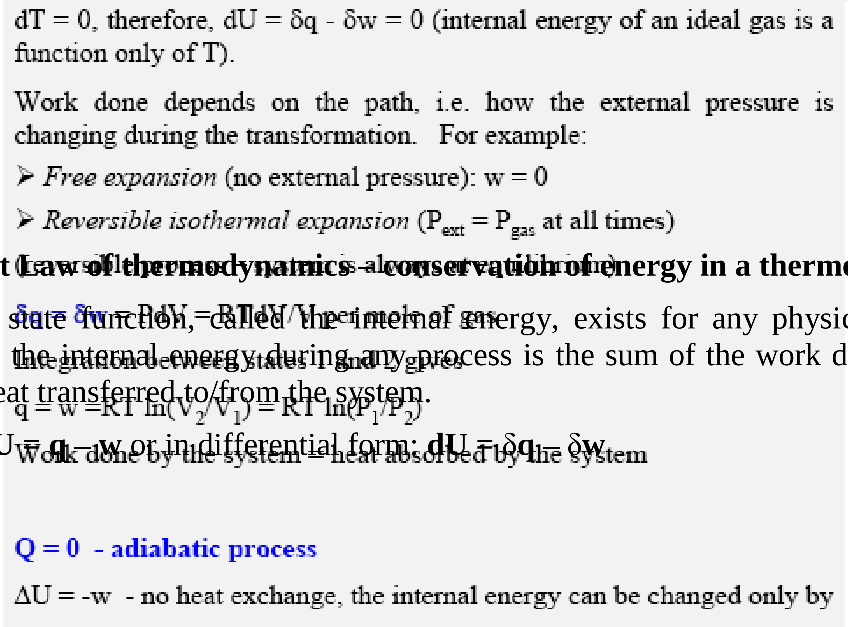
$$w = \int_{V_1}^{V_2} PdV = P\int_{V_1}^{V_2} dV = P(V_2 - V_1)$$ and the 1st law takes form:

$$U_2 - U_1 = q_p - P(V_2 - V_1) \qquad \text{or} \qquad (U_2 + PV_2) - (U_1 + PV_1) = q_p$$

q_p is heat added at constant pressure.

H = U + PV – enthalpy - state function (since U,P,V are state functions)

$H_2 - H_1 = \Delta H = q_p$ – change in enthalpy equals to heat added to the system at constant pressure



dT = 0, therefore, dU = δq - δw = 0 (internal energy of an ideal gas is a function only of T).

Work done depends on the path, i.e. how the external pressure is changing during the transformation. For example:

- *Free expansion* (no external pressure): w = 0
- *Reversible isothermal expansion* ($P_{ext} = P_{gas}$ at all times)

(reversible process: system is always at equilibrium)

$\delta q = \delta w = PdV = RTdV/V$ per mole of gas

Integration between states 1 and 2 gives

$q = w = RT \ln(V_2/V_1) = RT \ln(P_1/P_2)$

Work done by the system = heat absorbed by the system

Q = 0 - adiabatic process

ΔU = -w - no heat exchange, the internal energy can be changed only by

1st Law of thermodynamics – conservation of energy in a thermodynamic process.

A state function, called the internal energy, exists for any physical system – and the change in the internal energy during any process is the sum of the work done on/by the system and the heat transferred to/from the system.

$\Delta\mathbf{U} = \mathbf{q} - \mathbf{w}$ or in differential form: $\mathbf{dU} = \delta\mathbf{q} - \delta\mathbf{w}$

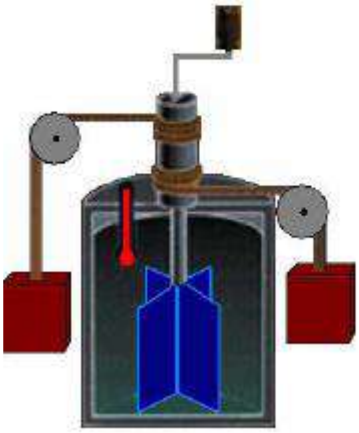
(“d” for exact differential, δ for path dependant)

U – internal energy (all potential and kinetic energies). It is a **state function** – depends only on thermodynamic state of the system (e.g. P, V, & T for a simple system). Doesn’t depend on path.

q – energy added into the system as heat. Positive (+) when the system gains heat from outside (**endothermic** process), negative (-) when heat flows out of the system (**exothermic** process).

w - work done by the system on its surroundings. Positive (+) when work is done by the system, and negative if work done on the system. If body does work, it expends energy and the internal energy of the body must decrease.

Equivalence of heat and work: Joule experiment



In Joule's experiment the mechanical energy can be measured simultaneously with temperature (thermal energy).

Joule found that the loss in mechanical energy is proportional to an increase in temperature of the water and the amount of water used. the constant or proportionality is 4.4J/g ºC (modern data is 4.186 J/g ºC)

Heat and work can independently produce identical changes in the system.

T is not a good measure of heat but heat can be measured through work, and heat capacity can be determined.

Heat Capacity

The heat capacity, C, of a system is the ratio of the heat added to the system, or withdrawn from the system, to the resultant change in the temperature:

$C = q/\Delta T = \delta q/dT$ [J/deg]

This definition is only valid in the absence of phase transitions. Usually C is given as *specific heat capacity,* c, per gram or per mol

New state of the system is not defined by T only, need to specify or constrain second variable:

$C_V = \left(\frac{\delta q}{dT}\right)_V$ - heat capacity at constant volume

$C_P = \left(\frac{\delta q}{dT}\right)_P$ - heat capacity at constant pressure

The fact that δq is not a state function and depends on the path is reflected in the dependence of the heat capacity on the path, $c_p \neq c_v$ (note that small c is used for the derived intensive quantity, per mass, per volume, or per mole, versus capital C for the extensive quantity. For a system containing n moles $C_p = nc_p$ and $C_v = nc_v$ where c_p and c_v are molar values). c_V and c_P can be measured experimentally

Isobaric process: $dH = \delta q = c_P dT$, Isochoric process: $dU = \delta q = c_V dT$

H and U can be calculated from c_P and c_V.

c_v vs. c_p

If material is allowed to expand during heating, how this affects its heat capacity?

$$c_p = \left(\frac{\delta q}{dT}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

$$c_v = \left(\frac{\delta q}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$c_p - c_v = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$$

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

Differentiation with respect to T at constant P gives

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial T}\right)_V \qquad \text{therefore}$$

$$c_p - c_v = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial T}\right)_V + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial V}{\partial T}\right)_P \left(P + \left(\frac{\partial U}{\partial V}\right)_T\right)$$

$\left(\frac{\partial V}{\partial T}\right)_P P$ work of expansion at constant P due to the temperature increase by dT

$\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial U}{\partial V}\right)_T$ work of expansion against internal cohesive forces due to the temperature increase by dT

Calculation of enthalpy from heat capacity

For $P = \text{const}$ $dH = c_p dT$ and integration gives:

$$\int_{H_1}^{H_2} dH = H_2 - H_1 = \int_{T_1}^{T_2} c_p dT \qquad\qquad H_2 = H_1 + \int_{T_1}^{T_2} c_p dT$$

Example:
Let us find enthalpy for copper at 500K.
$c_p \approx 24.4\ \text{Jmol}^{-1}\text{K}^{-1}$ for copper at 1 atm.

From the 1st law can only calculate the difference ΔH - need a reference enthalpy. Enthalpy at 1 atm and 298 K is called **enthalpy of formation**, H_{298}. For pure elements in their equilibrium states $H_{298} = 0$.

$$H_{500} = H_{298} + \int_{298}^{500} c_p dT = 0 + \int_{298}^{500} 24.4 dT = 4.9\text{kJ/mol}$$

Enthalpy of substances other than pure elements can also be calculated. The enthalpy of a compound at 298 K = **standard heat of formation** of the substance from the elements.

In general, heat capacity is a function of temperature. For example, for alumina, Al_2O_3, the temperature dependence can be described by
$c_p° = 117.5 + 10.4\times10^{-3}\ T - 37.1\times10^{5}\ T^{-2}$ in the range 298-2325 K

$$H_{500}^{Al_2O_3} = H_{298}^{Al_2O_3} + \int_{298}^{500} c_p(T)dT = -1675.7\ \text{kJ/mol} +$$
$$+ \int_{298}^{500}\left[117.5 + 10.4\times10^{-3}\ T - 37.1\times10^{5}\ T^{-2}\right]dT$$

The standard heat of formation, $H_{298}^{Al_2O_3}$, and heat capacity, $c_p(T)$, are measured experimentally and can be found in themochemical tables, e.g. at http://webbook.nist.gov/chemistry/ or at the end of Gaskell's textbook

In most cases, thermal treatment of materials is carried out under atmospheric pressure and no work other than that against the atmosphere is produced. Enthalpy change is used to describe such processes.

Enthalpy and phase transformations

If the system undergoes a phase transformation (or a chemical reaction) then the enthalpy change due to the phase change, ΔH, has to be

Heat of formation and phase transformations

If the temperature of interest is higher than the melting temperatures for both the metal and its oxide, the enthalpy change for $M^{liquid} + ½\ O_2^{gas} =$ MO^{liquid} is then

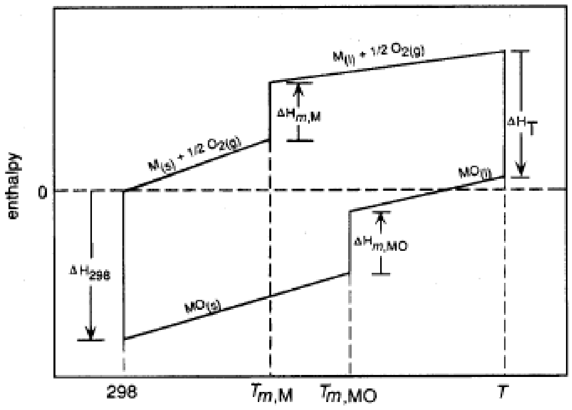
$$\Delta H_T = \Delta H_{298} + \int_{298}^{T_m^M}\left[c_p^{MO,solid} - c_p^{M,solid} - \frac{1}{2}c_p^{O_2,gas}\right]dT -$$
$$- \Delta H_m^M + \int_{T_m^M}^{T_m^{MO}}\left[c_p^{MO,solid} - c_p^{M,liquid} - \frac{1}{2}c_p^{O_2,gas}\right]dT +$$
$$+ \Delta H_m^{MO} + \int_{T_m^{MO}}^{T}\left[c_p^{MO,liquid} - c_p^{M,liquid} - \frac{1}{2}c_p^{O_2,gas}\right]dT$$

$.86\times10^4\ T^{-2}$
la for $c_p(T)$

ratures, we
4 $Jmol^{-1}K^{-1}$

on T)

63kJ mol^{-1}



Heats of Reactions –Hess's Law

Heat absorbed or released in a given chemical reaction is the same weather the process occurs in one or several steps (Hess, 1840).

Example:

C (graphite) + O_2 (gas) = CO_2 (gas) Q = -393.6 kJ mol^{-1}

C (graphite) + ½ O_2 (gas) = CO (gas) Q = - 110.5 kJ mol^{-1}

CO (gas) + ½ O_2 (gas) = CO_2 (gas) Q = -283.1 kJ mol^{-1}

Total: -393.6 kJ mol^{-1}

- Hess's Law allows one to calculate Q for reactions that is hard to measure
- Presence of catalysts change the activation energy of reaction but not the net heat of reaction.

The Hess's law is just a consequence of the 1st law of thermodynamics: for P = const, ΔH = Q. Since H is a state function, total heat is independent of path.

Calculation of heat of transition from heats of reactions

Let's find if an allotropic transition from diamond to graphite under ambient conditions results in the release or absorption of heat.

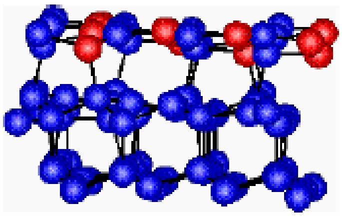
C (graphite) + O_2 (gas) = CO_2 (gas) ΔH_{298} = - 393.6 kJ mol^{-1}

C (diamond) + O_2 (gas) = CO_2 (gas) ΔH_{298} = - 395.5 kJ mol^{-1}

Then for reaction C (diamond) = C (graphite)

ΔH_{298} = 393.6 – 395.5 = -1.9 kJ mol^{-1}

Transition of diamond to graphite is an exothermic reaction



Graphitization of a surface region of diamond at elevated temperature – Figure from a computer simulation

1. What is the analytical expression for the first law of thermodynamics?
2. Which of the following are state functions: heat, work, internal energy?
3. Which of the following are system parameters: temperature, volume, number of molecules, ideal gas constant, pressure, internal energy?
4. What are the dimensions of the molar heat capacity?
5. Work done by an ideal gas under different conditions.

1. Isothermal process
2. Isobaric process
3. Adiabatic process

1 g of ice at T = 0°C and 10 g of water at T = 100°C are mixed in an adiabatic container. What is the temperature within the container when its contents reach equilibrium? Express your answer in K.
For H_2O, the change in enthalpy on melting $\Delta H_{\mathrm{melt}} = 6.01$ kJ/mole and $c_p = 75.3$ J/K mole.

It is obvious that the equilibrium temperature must be between 273.2 K and 373.2 K (initial temperatures of the ice and water, respectively). Since the system is in an adiabatic container, it does not exchange heat with its surrounding, therefore $\Delta H = 0$. The following three processes occur:

(1) the ice melts;
(2) the water produced from the melting ice warms up to the equilibrium temperature T_e;
(3) the 100°C water that was initially part of the system cools down to the equilibrium temperature T_e.

In order to find the equilibrium state, it does not matter in which order these processes proceed. Rather, we simply sum the change in enthalpy for each of the processes and insist that the change in the total enthalpy is zero. In this way, we obtain:

$$0 = \Delta H = \frac{m_{\mathrm{ice}}}{M}\Delta H_{\mathrm{melt}} + \frac{m_{\mathrm{ice}}}{M} c_{\mathrm{p}}\left(T_{\mathrm{e}} - T_{\mathrm{melt}}\right) + \frac{m_{\mathrm{water}}}{M} c_{\mathrm{p}}\left(T_{\mathrm{e}} - T_{\mathrm{boil}}\right),$$

where M is the molecular weight of water, m_{ice} and m_{water} are the initial masses of ice and water, respectively. Solving this equation for the equilibrium temperature yields:

$$T_{\mathrm{e}} = \frac{c_{\mathrm{p}}\left(m_{\mathrm{ice}} T_{\mathrm{melt}} + m_{\mathrm{water}} T_{\mathrm{boil}}\right) - m_{\mathrm{ice}}\Delta H_{\mathrm{melt}}}{c_{\mathrm{p}}\left(m_{\mathrm{ice}} + m_{\mathrm{water}}\right)} = \frac{75.3(1 \cdot 273.2 + 10 \cdot 373.2) - 1 \cdot 6010}{75.3(1 + 10)} = 356.9\ \mathrm{K}.$$

2 g of air was isobarically heated from $T_1 = 0$°C to $T_2 = 1$°C at a pressure $p = 1$ atm. The density of air at $T = 0$°C is $\rho = 0.00129\ \mathrm{g/cm^3}$. What is the work of expansion?

Since the gas is heated at constant pressure, it will expand and, therefore, perform work. Hence, the answer must be positive. The ideal gas law and Eq. (1.20) can then be used to obtain the work performed by the gas:

$$W = nR\Delta T = \frac{p_1 V_1 R \Delta T}{R T_1} = \frac{p_1 m \Delta T}{T_1 \rho_1} = \frac{1.013 \cdot 10^5 \cdot 2 \cdot 1}{273.2 \cdot 0.00129 \cdot 10^6} = 0.575\ \mathrm{J}.$$

2 l of nitrogen, originally at $T = 0$°C and $p_1 = 5$ atm, isothermally expands until the final pressure is $p_2 = 1$ atm. How much heat flows into this system during the expansion?

Since the gas expands, it performs (positive) work. The internal energy of an ideal gas does not change during an isothermal process. Therefore, all of the heat added to the gas is converted into work, that is, $Q = W > 0$. Applying Eq. (1.19) to the present situation yields

$$Q = W = nRT \ln\frac{p_1}{p_2} = p_1 V_1 \ln\frac{p_1}{p_2}$$
$$= 5 \cdot 1.013 \cdot 10^5 \cdot 2 \cdot 10^{-3} \ln\frac{5}{1} = 1630 \text{ J}.$$

10 g of nitrogen, originally at $T_1 = 17°\text{C}$, is adiabatically compressed from 8 to 5 *l*. How much work was done to compress the nitrogen? The isochoric heat capacity of a mole of nitrogen is $2.5R$.

Since the gas contracts, the work performed by the gas must be negative. Application of Eqs (1.23), (1.22), and (1.21) shows:

$$W = -nc_V \Delta T = -\frac{m}{M} c_V \Delta T$$

$$\left.\begin{matrix} pV^\gamma = \text{const} \\ pV = nRT \end{matrix}\right\} \Rightarrow TV^{\gamma-1} = \text{const}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}; \qquad T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$\gamma = \frac{c_P}{c_V} = \frac{c_V + R}{c_V} = \frac{7}{5} = 1.4$$

$$T_2 = 290\left(\frac{8}{5}\right)^{1.4-1} = 350 \text{ K}$$

$$W = -\frac{10}{28.02} 2.5 \cdot 8.314 \cdot (350 - 290) = -445 \text{ J}.$$

4. 1 mole of an ideal gas undergoes the following cycle:

$$\begin{tikzcd}
\boxed{p_1, T_1} \arrow[r, "p=\text{const}"] & \boxed{p_1, T_2} \arrow[r, "T=\text{const}"] & \boxed{p_2, T_2} \arrow[r, "p=\text{const}"] & \boxed{p_2, T_1} \arrow[lll, bend left, "T=\text{const}"]
\end{tikzcd}$$

Derive an expression for the heat added to the gas during this process using only those parameters shown in the figure.

Since the internal energy is a state function, it does not change when we go around a complete circuit. Therefore, the first law of thermodynamics reduces to $Q = W$. Writing expressions for the work associated with each process, we find:

$$Q = W = nR(T_2 - T_1) + nRT_2 \ln\frac{p_1}{p_2} + nR(T_1 - T_2)$$
$$+ nRT_1 \ln\frac{p_2}{p_1} = nR(T_2 - T_1) \ln\frac{p_1}{p_2}.$$

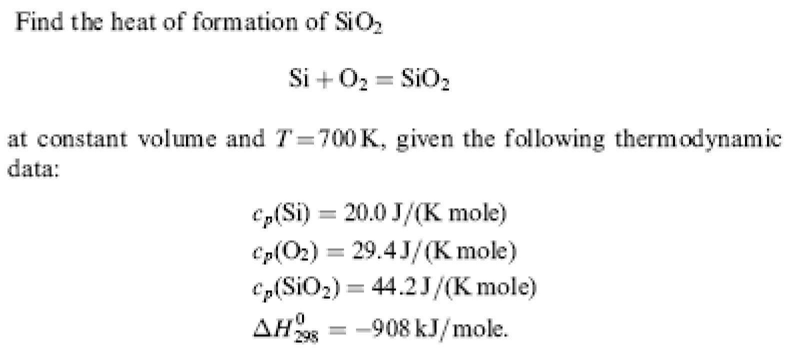
Calculate the heat of reaction for

$$CH_4 + 2CO = 3C_{(gr)} + 2H_2O$$

at 1100 K. The following thermodynamic data are available from standard thermodynamic databases:

Substance	CH_4	CO	C_{gr}	H_2O
$\Delta H^0_{f\,298}$ kJ/mole	– 74.60	– 110.53	0	– 241.81
S^0_{298}, J/(K mole)	186.26	197.55	5.74	188.72
a	42.06	28.41	16.86	30.00
b	31.50	4.10	4.77	10.71
c	– 17.29	– 0.46	– 8.54	0.33

where the temperature dependence of the heat capacities of the reactants



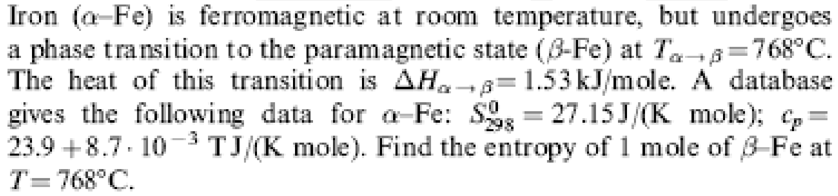
Find the heat of formation of SiO_2

$$Si + O_2 = SiO_2$$

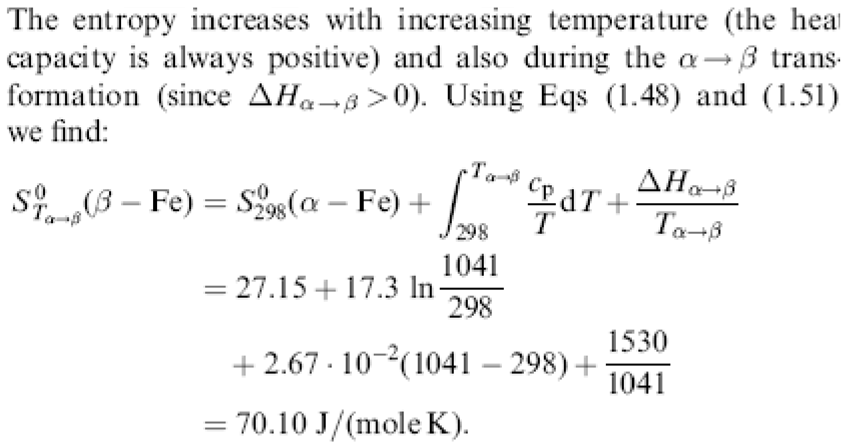
at constant volume and $T = 700\,K$, given the following thermodynamic data:

$$c_p(Si) = 20.0\,J/(K\,mole)$$
$$c_p(O_2) = 29.4\,J/(K\,mole)$$
$$c_p(SiO_2) = 44.2\,J/(K\,mole)$$
$$\Delta H^0_{298} = -908\,kJ/mole.$$

1. On what system parameters does the internal energy of a mole of an ideal gas depend?
2. On what system parameters does the enthalpy of a mole of an ideal gas depend?
3. Which ideal gas system parameter must be held fixed for $Q = RT \ln (V_2/V_1)$ to be valid?
4. Does the change of the entropy depend on the path by which the system goes from one state to another?
5. What are the dimensions of entropy?
6. Does the entropy of the system increase or decrease upon heating a substance at constant volume or at constant pressure?
7. Does the entropy of the system increase or decrease when two ideal gases are mixed?
8. Can entropy be negative?



Iron (α–Fe) is ferromagnetic at room temperature, but undergoes a phase transition to the paramagnetic state (β-Fe) at $T_{\alpha\to\beta} = 768°C$. The heat of this transition is $\Delta H_{\alpha\to\beta} = 1.53\,kJ/mole$. A database gives the following data for α–Fe: $S^0_{298} = 27.15\,J/(K\ mole)$; $c_p = 23.9 + 8.7 \cdot 10^{-3}\,T\,J/(K\ mole)$. Find the entropy of 1 mole of β–Fe at $T = 768°C$.

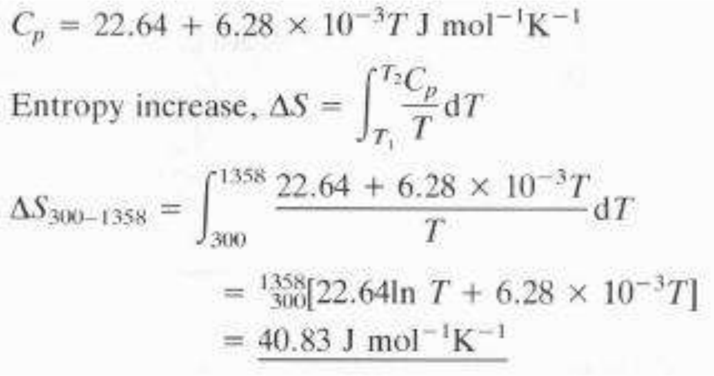


The entropy increases with increasing temperature (the heat capacity is always positive) and also during the $\alpha \to \beta$ transformation (since $\Delta H_{\alpha\to\beta} > 0$). Using Eqs (1.48) and (1.51) we find:

$$\begin{aligned} S^0_{T_{\alpha\to\beta}}(\beta - \mathrm{Fe}) &= S^0_{298}(\alpha - \mathrm{Fe}) + \int_{298}^{T_{\alpha\to\beta}} \frac{c_p}{T}\,dT + \frac{\Delta H_{\alpha\to\beta}}{T_{\alpha\to\beta}} \\ &= 27.15 + 17.3 \ln\frac{1041}{298} \\ &\quad + 2.67 \cdot 10^{-2}(1041 - 298) + \frac{1530}{1041} \\ &= 70.10\ J/(\mathrm{mole\,K}). \end{aligned}$$

1. Does the Gibbs free energy increase or decrease when a substance is heated at constant pressure?
2. Does the Helmholtz free energy increase or decrease when a substance expands at constant temperature?
3. If you know the Gibbs free energy of a substance at some temperature and pressure and you know its enthalpy as function of temperature and pressure, how would you calculate the Gibbs free energy at a different temperature and the same pressure?

The specific heat of solid copper ahove 300 K 15 given by ***C,,*** = 22.64 + 6.78 x 10^{-3} T J mol^{-1} K^{-1}
By how much does the entropy of copper increase **on** heating from 300 to 1358 K?



$$C_p = 22.64 + 6.28 \times 10^{-3}T \text{ J mol}^{-1}\text{K}^{-1}$$

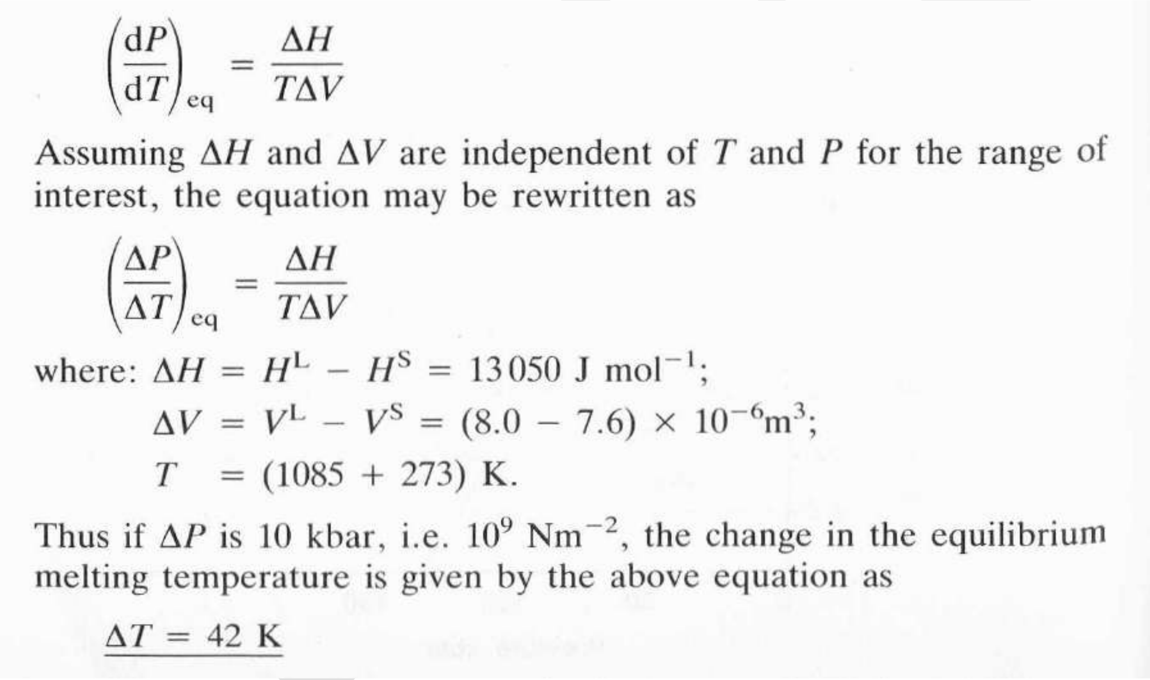
Entropy increase, $\Delta S = \int_{T_1}^{T_2} \frac{C_p}{T} \mathrm{d}T$

$$\Delta S_{300-1358} = \int_{300}^{1358} \frac{22.64 + 6.28 \times 10^{-3}T}{T} \mathrm{d}T$$

$$= {}^{1358}_{300}[22.64 \ln T + 6.28 \times 10^{-3}T]$$

$$= \underline{40.83 \text{ J mol}^{-1}\text{K}^{-1}}$$

Estimrtte the change in the equilibrium melting point of copper caused by a change of pressure of 10 kbar. The molar volume nf cupper is 8.0 x 10 $^{-6}$ m' for the liquid. and 7.6 x 10^{-6} fur the solid phase. The latent heat of fusion of copper is 13.05 kJ mol' . The melting point is 1085 "C.



$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{\mathrm{eq}} = \frac{\Delta H}{T\Delta V}$$

Assuming ΔH and ΔV are independent of T and P for the range of interest, the equation may be rewritten as

$$\left(\frac{\Delta P}{\Delta T}\right)_{\mathrm{eq}} = \frac{\Delta H}{T\Delta V}$$

where: $\Delta H = H^{\mathrm{L}} - H^{\mathrm{S}} = 13050 \text{ J mol}^{-1}$;

$\Delta V = V^{\mathrm{L}} - V^{\mathrm{S}} = (8.0 - 7.6) \times 10^{-6}\text{m}^3$;

$T = (1085 + 273)$ K.

Thus if ΔP is 10 kbar, i.e. 10^9 Nm^{-2}, the change in the equilibrium melting temperature is given by the above equation as

$$\underline{\Delta T = 42 \text{ K}}$$

15 g 3g gold and 25 g of silver are mixed to form a single-phase ideal solid solution.

(a) How many moles of solution are there?

(b) What are the mole fractions of gold and silver?

(c) What is the molar entropy of mixing?

(d) What is the total entropy of mixing?

(e) What is the molar free energy change at 500 "C?

(f) What are the chemical potentials of Au and Ag at 500 "C taking the free energies of pure Au and Ag as zero?

g) By how much will the free energy of the solution change at 500 O C if one Au atom is added? Express your answer in eV/atom.

(a) Atomic weight of Au = 197
Atomic weight of Ag = 108

$$\text{No. of moles of Au} = \frac{15}{197} = 0.076$$

$$\text{No. of moles of Ag} = \frac{25}{108} = 0.231$$

$\therefore$ no. of moles of solution = $\underline{0.307}$

(b) $$\text{Mole fraction of Au} = \frac{0.076}{0.307} = \underline{0.248}$$

$$\text{Mole fraction of Ag} = \frac{0.231}{0.307} = \underline{0.752}$$

(c) Molar entropy of mixing, $\Delta S_{\text{mix}} = -R(X_A \ln X_A + X_B \ln X_B)$

$$\therefore \quad \Delta S_{\text{mix}} = -8.314(0.248 \cdot \ln 0.248 + 0.752 \cdot \ln 0.752)$$
$$= \underline{4.66\ \text{J K}^{-1}\ \text{mol}^{-1}}$$

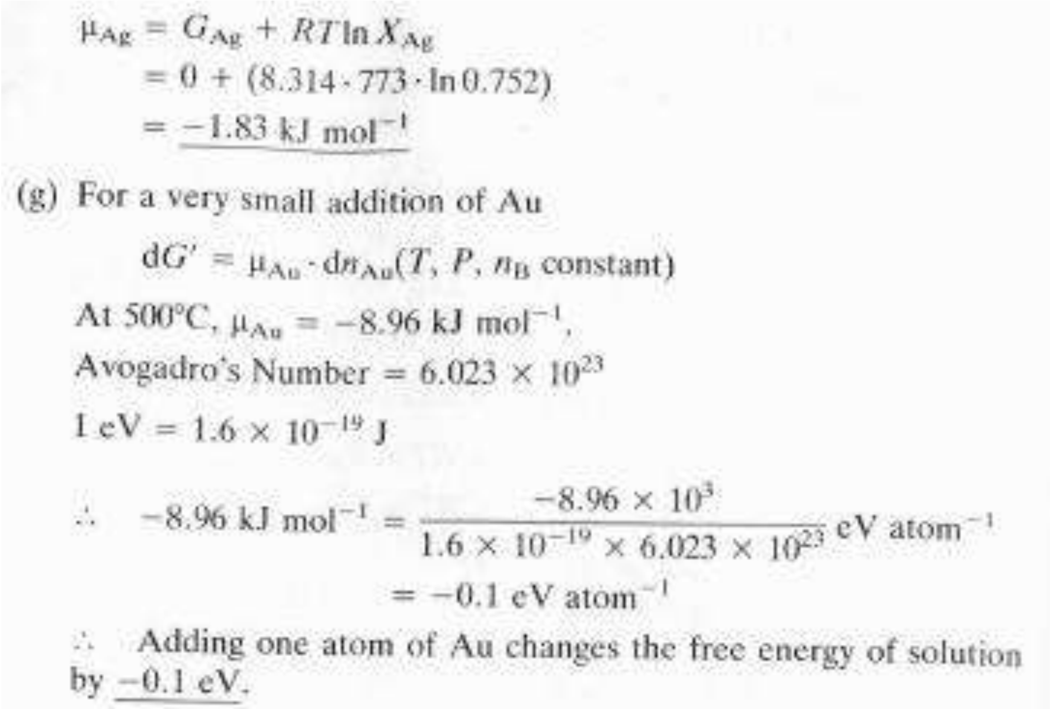
(d) Total entropy of mixing = Molar entropy of mixing × no. of moles of solution

$$= 4.66 \times 0.307$$
$$= \underline{1.43\ \text{J K}^{-1}}$$

(e) Molar free energy change at 500°C = ΔG_{mix}
$= RT(X_A \ln X_A + X_B \ln X_B)$

$$\therefore \quad \Delta G_{\text{mix}} = -T\Delta S_{\text{mix}} = -773 \times 4.66 = \underline{-3.60\ \text{kJ mol}^{-1}}$$

(f) $$\mu_{\text{Au}} = G_{\text{Au}} + RT \ln X_{\text{Au}}$$
$$= 0 + (8.314 \cdot 773 \cdot \ln 0.248)$$
$$= \underline{-8.96\,\text{kJ mol}^{-1}}$$



$$\mu_{Ag} = G_{Ag} + RT \ln X_{Ag}$$
$$= 0 + (8.314 \cdot 773 \cdot \ln 0.752)$$
$$= \underline{-1.83\ \text{kJ mol}^{-1}}$$

(g) For a very small addition of Au

$$dG' = \mu_{Au} \cdot dn_{Au} (T,\ P,\ n_B \text{ constant})$$

At 500°C, $\mu_{Au} = -8.96$ kJ mol^{-1},

Avogadro's Number = 6.023×10^{23}

1 eV = 1.6×10^{-19} J

$$\therefore \quad -8.96\ \text{kJ mol}^{-1} = \frac{-8.96 \times 10^3}{1.6 \times 10^{-19} \times 6.023 \times 10^{23}}\ \text{eV atom}^{-1}$$
$$= -0.1\ \text{eV atom}^{-1}$$

$\therefore$ Adding one atom of Au changes the free energy of solution by $\underline{-0.1\ \text{eV}}$.

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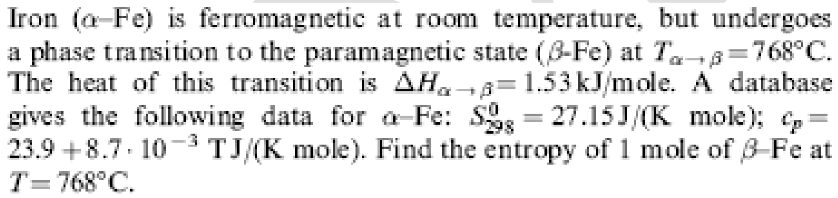

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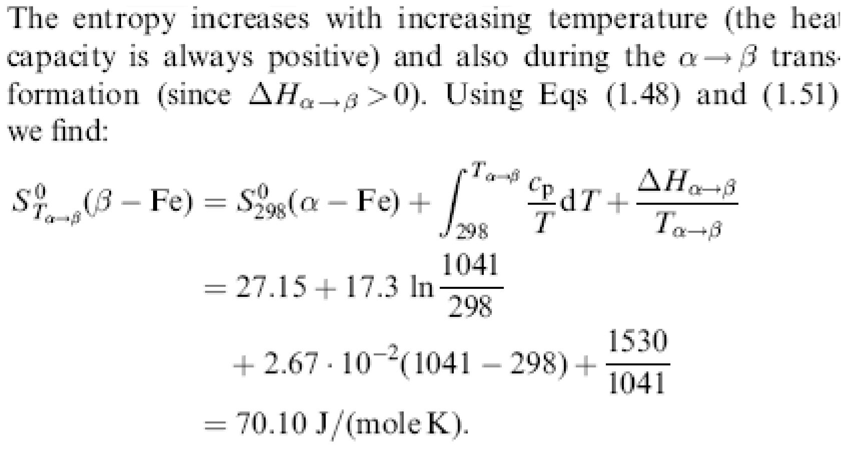

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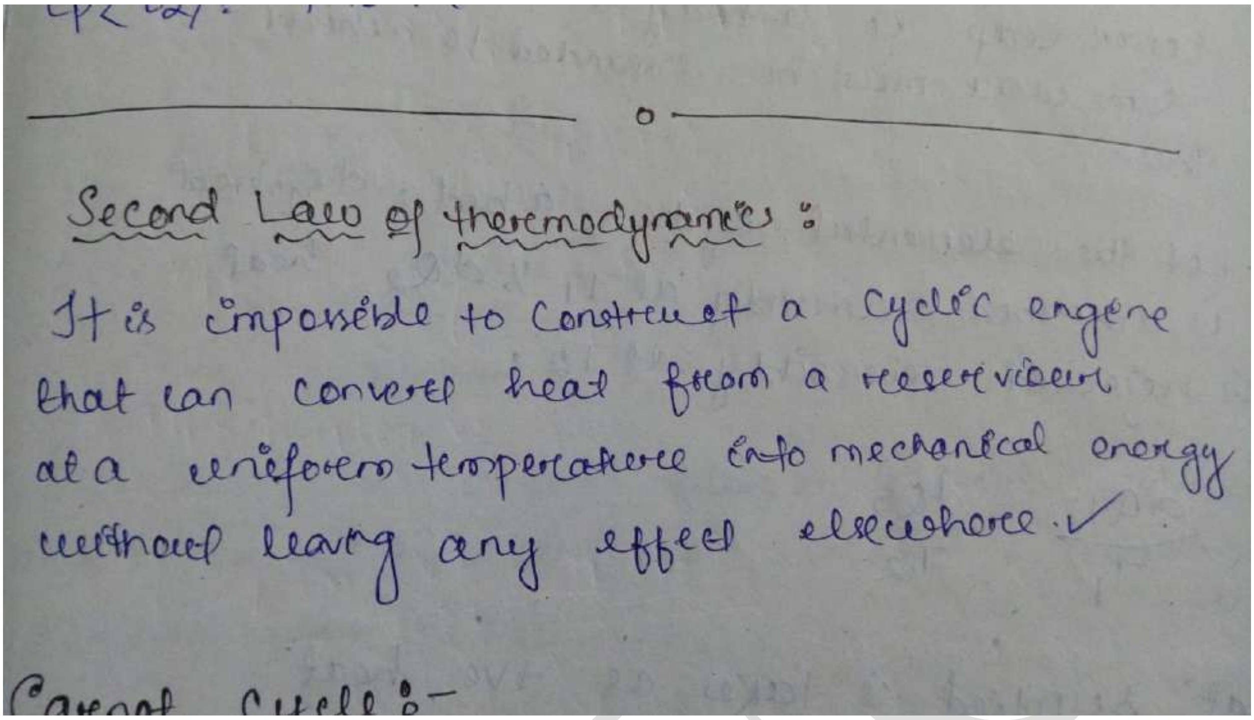


Second Law of thermodynamics :

It is impossible to construct a cyclic engine that can convert heat from a reservoir at a uniform temperature into mechanical energy without leaving any effect elsewhere. ✓

Carnot cycle :-

Dt: 30/8/16

Clausius - statement of 2nd Law :

It is impossible to construct a device which operates in a cycle, will produce no effect other than the transfer of heat from a cooler to the hotter body.

Heat can't flow of itself from a body at lower temp to a body at high temp. Some work need be expanded to achieve this.

Let the elemental cycle abcd, dQ_1 heat is absorbed reversibly at T_1 & dQ_2 heat is rejected reversibly at T_2,

$$\frac{dQ_1}{T_1} = \frac{dQ_2}{T_2}$$

Heat supplied is taken as +ve heat rejected is taken as negative.

$$\frac{dQ_1}{T_1} + \frac{dQ_2}{T_2} = 0$$

also, $\frac{dQ_3}{T_3} + \frac{dQ_4}{T_4} = 0$

Then, for the whole original cyclic,

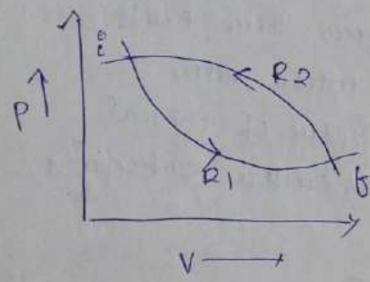
$$\boxed{\oint_R \frac{dQ}{T} = 0}$$

This is known as clausius theorem.

R = denotes eq^n is valid only for reversible process.

Entropy :-

It is defined as a major of degree of randomness or disorderness of the system



Let a system be taken from an initial equilibrium state to final equilibrium state 'f' by following reversible path R1 & R2.

from clausius theorem

$$\oint_{R_1R_2} \frac{dQ}{T} = 0 \quad \text{— (i)}$$

$$\int_{i\,R_1}^{f} \frac{dQ}{T} + \int_{i\,R_2}^{f} \frac{dQ}{T} = 0$$

$$\Rightarrow \int_{i\,R_1}^{f} \frac{dQ}{T} = -\int_{i\,R_2}^{f} \frac{dQ}{T}$$

Since R_2 is reversible path,

So, $\int_{R_1\, i}^{f} \frac{dQ}{T} = \int_{R_2\, i}^{f} \frac{dQ}{T}$

Since R_1 and R_2 represents any two reversible path,

$\int_{R\, i}^{f} \frac{dQ}{T}$ is independent of reversible path connecting i and f. Therefore there exists a property of the system whose value at the final state minus its value of initial state. This property is called entropy(S).

$$\int_{R\, i}^{f} \frac{dQ}{T} = S_f - S_i \quad \text{— ②}$$

when two equation states are infinitesimaly near, $\frac{dQ_R}{T} = ds$ — ③

ds is an exact differential. It is an extensive property and unit is J/K

Temp dependence of entrop

Variation of entropy of a system at constant pressure and const volume :-

Costant volume

we know,

$$ds = \frac{dq}{T}$$

$\Rightarrow dq = Tds$

$dq = du + dw$

$\Rightarrow Tds = du + pdv$

$\Rightarrow du = Tds - pdv$ —— (1)

At const. volume, $dv = 0$

eq(1) becomes -

$$du = Tds$$

$$\Rightarrow ds = \frac{du}{T} = \frac{C_v dT}{T} \quad \text{—— (2)}$$

Integrating eq(2),

$$\int_{S_{T_1}}^{S_{T_2}} ds = \int_{T_1}^{T_2} \frac{C_v dT}{T}$$

$$= \int_{T_1}^{T_2} C_v \, d \ln T$$

$$\Rightarrow S_{T_2} - S_{T_1} = \int_{T_1}^{T_2} C_v d \ln T$$

So, at any temp, $\boxed{S_T = \int_0^T C_v d \ln T}$ — (3)

At const. pressure :—

we know,

$$H = U + PV$$

$$\Rightarrow dH = du + pdv + vdp \quad \text{— (4)}$$

putting eq(1) in eq(4)

$$dH = Tds - \cancel{p}dv + \cancel{p}dv + vdp$$

$$dH = Tds + vdp$$

$$\Rightarrow dH = Tds + vdp$$

At const. pressure, $Vdp = 0$

So, $dH = Tds$ —— (5)

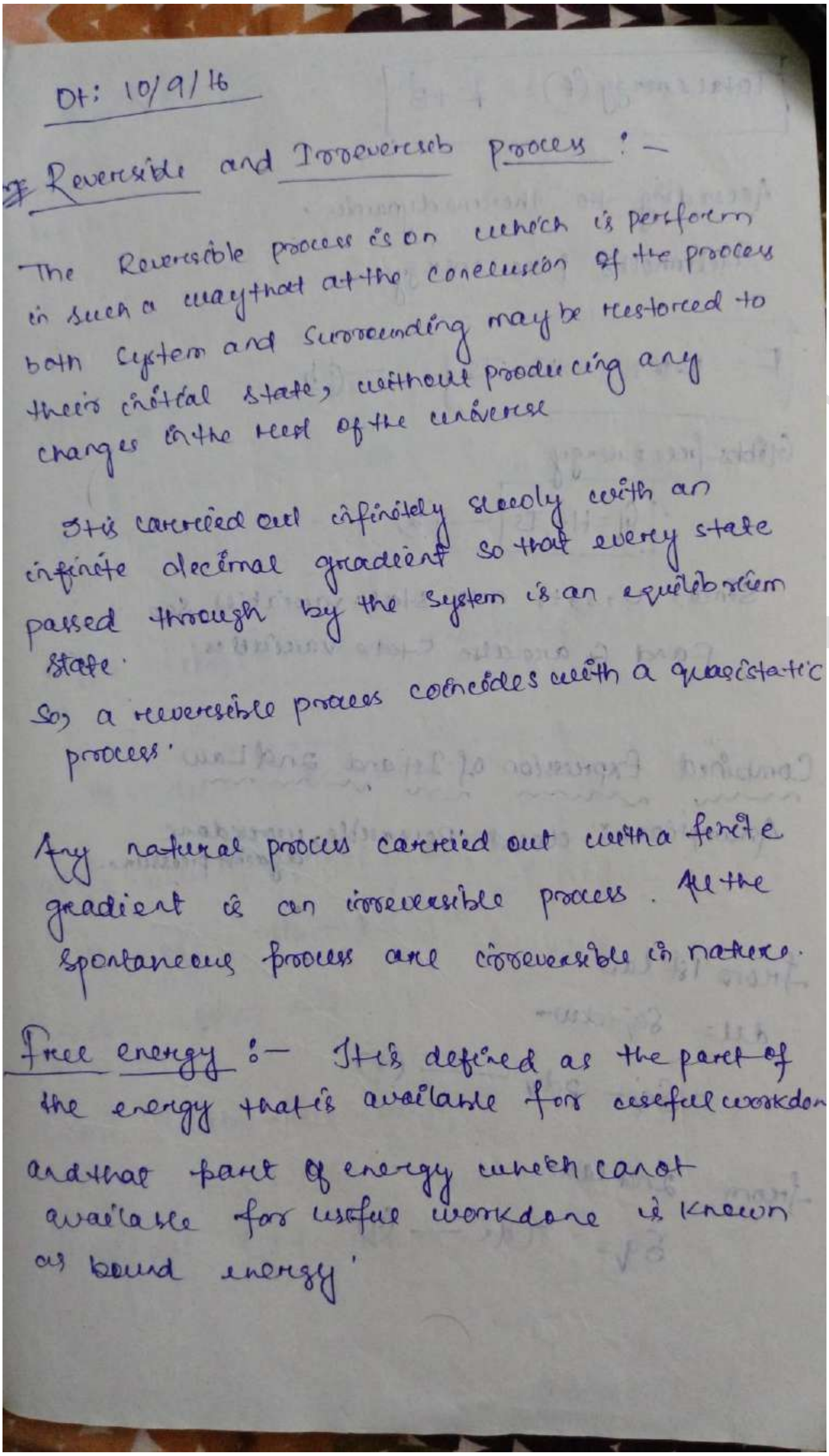
$$ds = \frac{dq}{T} = \frac{dH}{T} = \frac{C_p dT}{T}$$

$$\Rightarrow ds = \frac{C_p dT}{T} \quad \text{—— (6)}$$

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

$$\Rightarrow S_{T_2} - S_{T_1} = C_p \int_{T_1}^{T_2} d\ln T$$

At any temp, $\boxed{S_T = \int_0^T C_p \, d\ln T}$ — ⑦



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Reversible and Irreversib process :-

The Reversible process is one which is perform in such a way that at the conclusion of the process both system and surrounding may be restored to their initial state, without producing any changes in the rest of the universe

It is carried out infinitely slowly with an infinite decimal gradient so that every state passed through by the system is an equilibrium state.

So, a reversible process coincides with a quasistatic process.

Any natural process carried out with a finite gradient is an irreversible process. All the spontaneous process are irreversible in nature.

Free energy :- It is defined as the part of the energy that is available for useful workdone and that part of energy which canot available for useful workdone is known as bound energy.

$\boxed{\text{Total energy } (E): \; F + B}$

According to thermodynamics,

Helmholtz free energy

$$\boxed{F = U - TS'} \; \text{—} (1)$$

Gibbs free energy

$$\boxed{G = H - TS} \; \text{—} (2)$$

Since, U, S, H are state variables, So, F and G are also state variables.

Combined Expression of Ist and 2nd Law

Assumptions: closed, Reversible, workdone against pressure.

from Ist Law

$$du = \delta q - dw$$

$$= \delta q - p\,dv \; \text{—} (3)$$

from 2nd law

$$\delta q = T\,ds \; \text{—} (4)$$

Combining eqⁿ (3) and (4)

$du = Tds - pdv$ —(5).

we know,

$H = U + PV$

$\Rightarrow dH = du + pdv + vdp$ —(6)

Replacing the term du from eqⁿ (5) in eqⁿ (6)

$dH = Tds - \cancel{pdv} + \cancel{pdv} + vdp$

$\boxed{dH = Tds + VdP}$ —(7)

from helmholtz free energy eqⁿ

$\boxed{F = U - TS}$

$\Rightarrow df = du - (Tds + sdT)$ —(8)

put the value of eqⁿ(5) in eqⁿ(8)

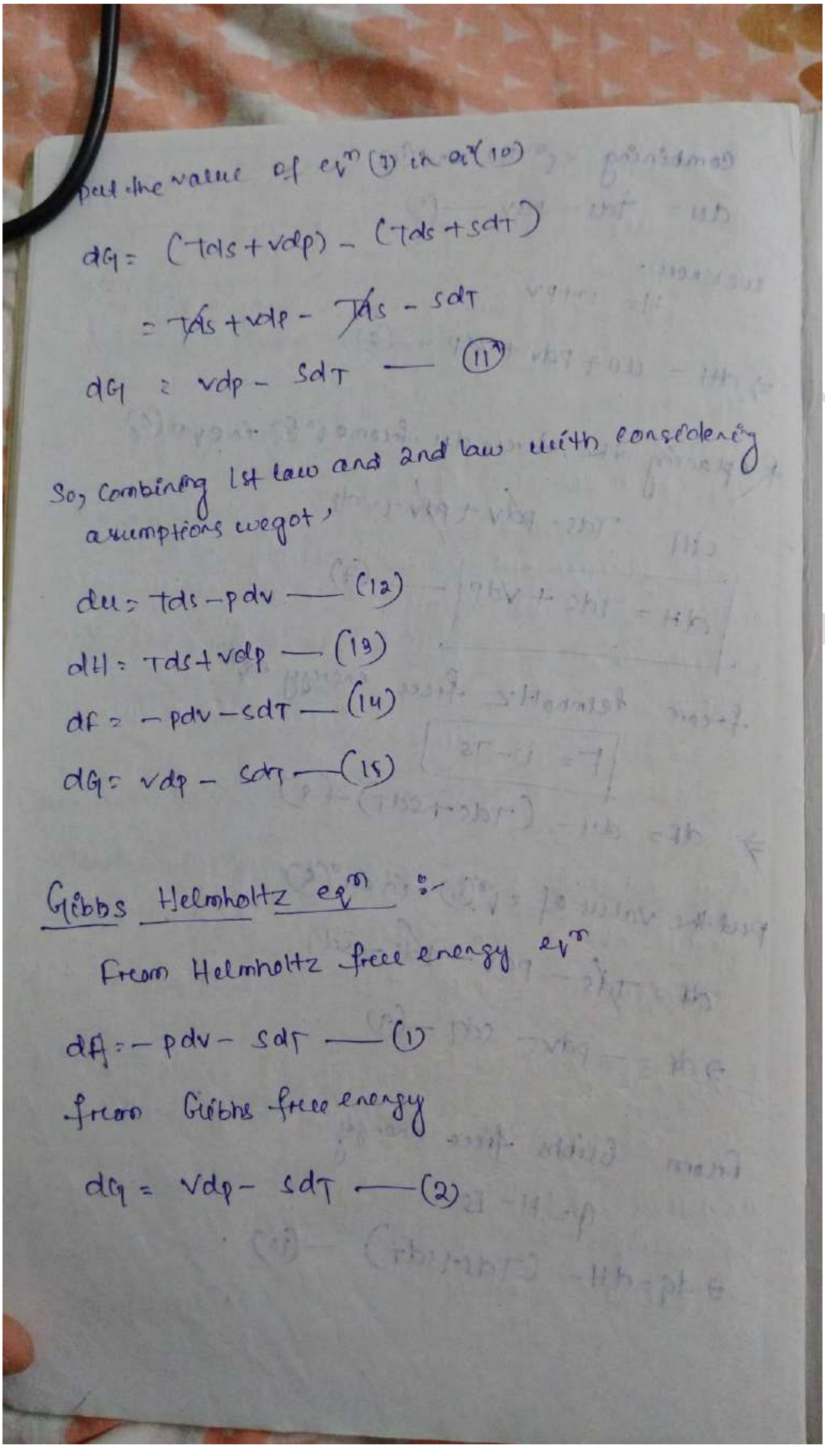
$df = \cancel{Tds} - pdv - \cancel{Tds} - sdT$

$\Rightarrow df = -pdv - sdT$ —(9)

From Gibbs free energy

$G = H - TS$

$\Rightarrow dG = dH - (Tds + sdT)$ —(10).



put the value of eq^n (7) in eq^n(10)

$$dG = (Tds + vdp) - (Tds + sdT)$$

$$= \cancel{T}ds + vdp - \cancel{T}ds - sdT$$

$$dG = vdp - sdT \quad — ⑪$$

So, combining 1st law and 2nd law with considering assumptions we got,

$$du = Tds - pdv \quad — (12)$$

$$dH = Tds + vdp \quad — (13)$$

$$dF = -pdv - sdT \quad — (14)$$

$$dG = vdp - sdT \quad — (15)$$

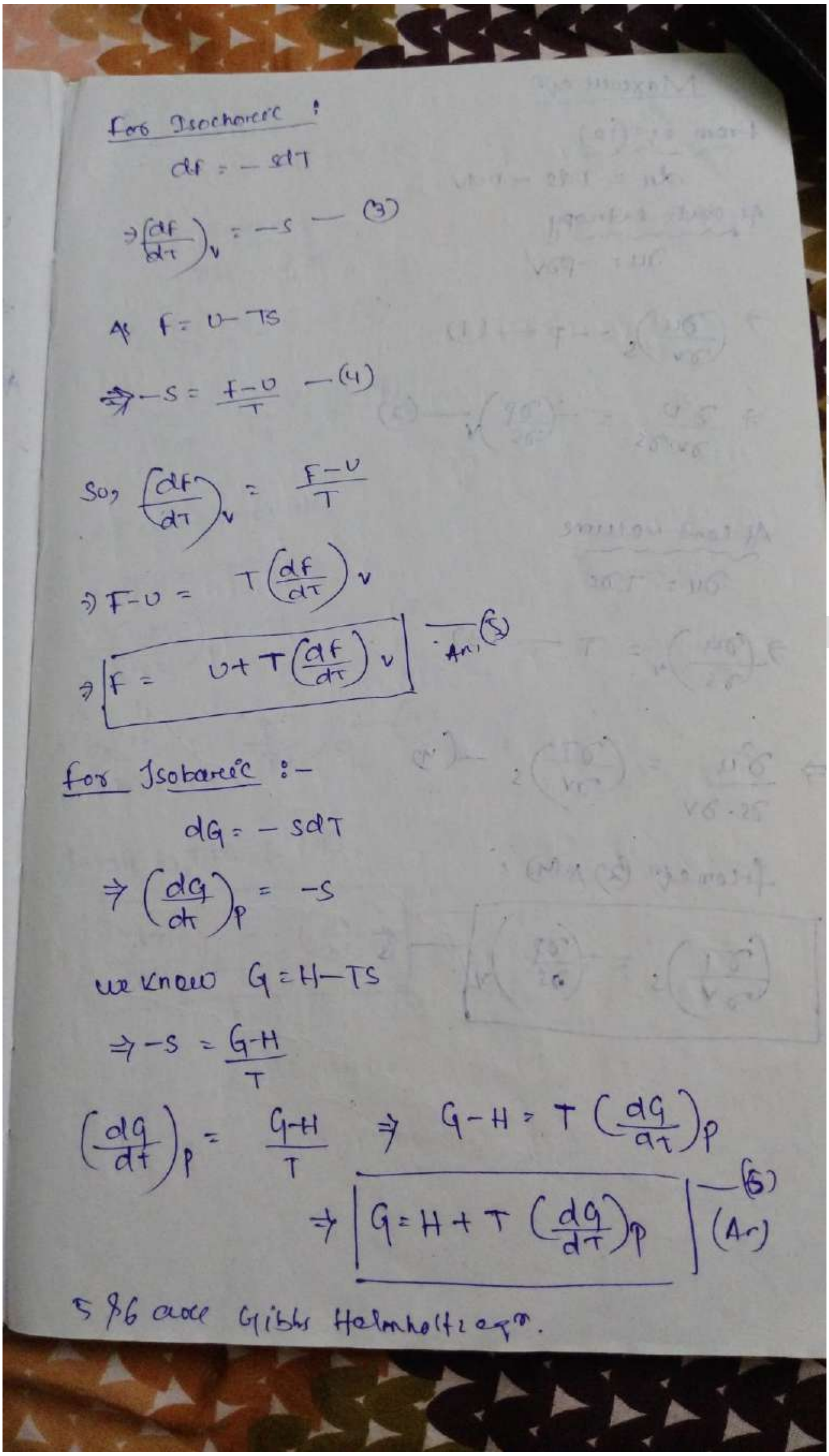
Gibbs Helmholtz eq^n :-

From Helmholtz free energy eq^n.

$$dA = -pdv - sdT \quad — (1)$$

from Gibbs free energy

$$dG = vdp - sdT \quad — (2)$$



For Isochoric :

$$dF = -SdT$$

$$\Rightarrow \left(\frac{dF}{dT}\right)_V = -S \quad \text{— (3)}$$

As $F = U - TS$

$$\Rightarrow -S = \frac{F-U}{T} \quad \text{— (4)}$$

So, $\left(\frac{dF}{dT}\right)_V = \frac{F-U}{T}$

$$\Rightarrow F - U = T\left(\frac{dF}{dT}\right)_V$$

$$\Rightarrow \boxed{F = U + T\left(\frac{dF}{dT}\right)_V} \quad \text{— (5) Ans}$$

For Isobaric :-

$$dG = -SdT$$

$$\Rightarrow \left(\frac{dG}{dT}\right)_P = -S$$

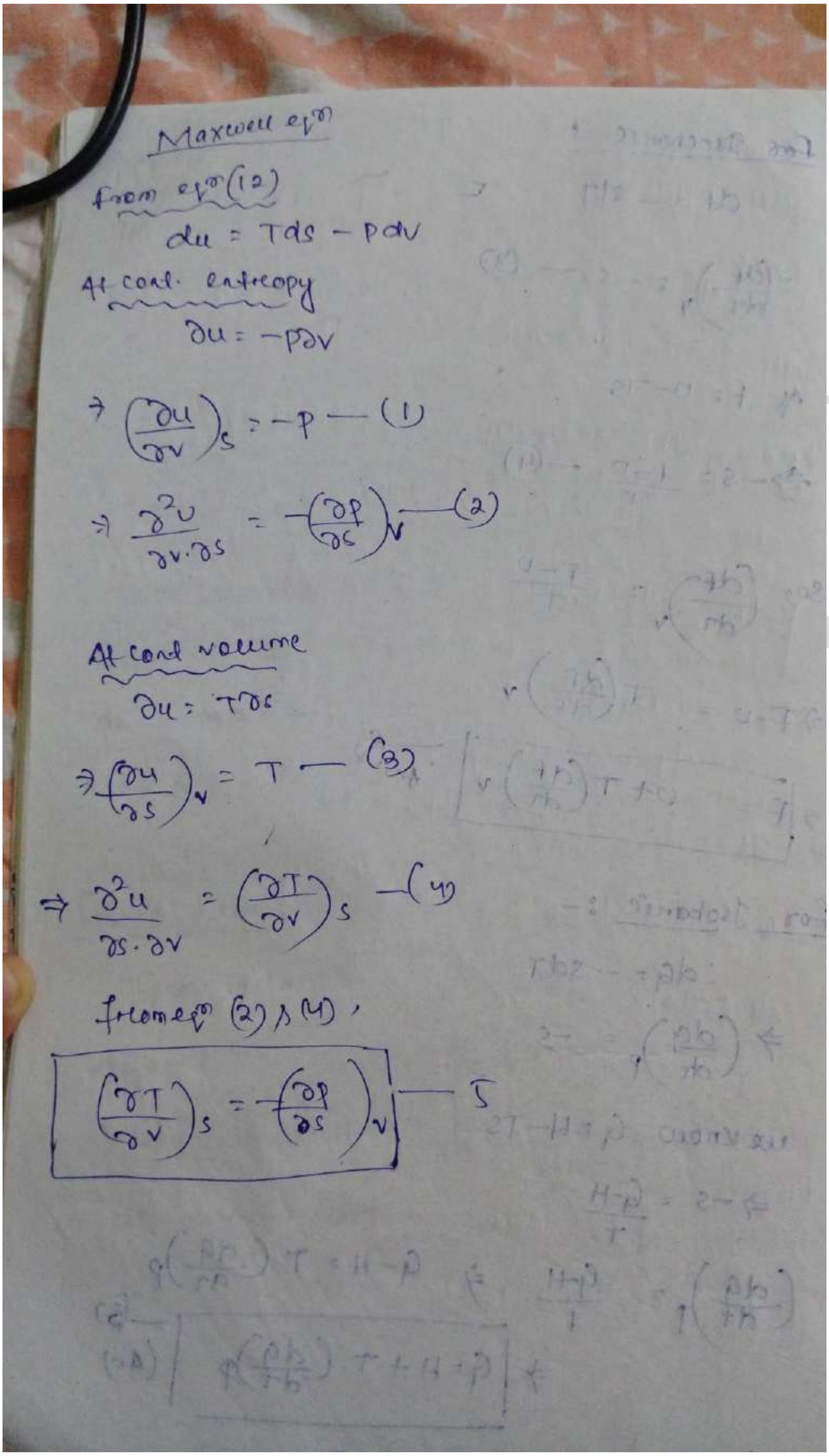
we know $G = H - TS$

$$\Rightarrow -S = \frac{G-H}{T}$$

$$\left(\frac{dG}{dT}\right)_P = \frac{G-H}{T} \Rightarrow G - H = T\left(\frac{dG}{dT}\right)_P$$

$$\Rightarrow \boxed{G = H + T\left(\frac{dG}{dT}\right)_P} \quad \text{— (6) (Ans)}$$

5 & 6 are Gibbs Helmholtz eqn.



Maxwell eqn

from eqn (12)

$$du = Tds - pdv$$

At const. entropy

$$\partial u = -p\partial v$$

$$\Rightarrow \left(\frac{\partial u}{\partial v}\right)_s = -p \text{ — (1)}$$

$$\Rightarrow \frac{\partial^2 u}{\partial v \cdot \partial s} = -\left(\frac{\partial p}{\partial s}\right)_v \text{ — (2)}$$

At const volume

$$\partial u = T\partial s$$

$$\Rightarrow \left(\frac{\partial u}{\partial s}\right)_v = T \text{ — (3)}$$

$$\Rightarrow \frac{\partial^2 u}{\partial s \cdot \partial v} = \left(\frac{\partial T}{\partial v}\right)_s \text{ — (4)}$$

from eqn (2) & (4),

$$\boxed{\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v} \text{ — 5}$$

from eqⁿ 13

$$dH = Tds + Vdp$$

At const entropy

$$\partial H = V\partial P$$

$$\Rightarrow \left(\frac{\partial H}{\partial P}\right)_S = V \text{ --- } (6)$$

$$\Rightarrow \frac{\partial^2 H}{\partial S \partial P} = \left(\frac{\partial V}{\partial S}\right)_P \text{ --- } (7)$$

At const. pressure

$$\partial H = T\partial S$$

$$\Rightarrow \left(\frac{\partial H}{\partial S}\right)_P = T \text{ --- } (8)$$

$$\Rightarrow \frac{\partial^2 H}{\partial S . \partial P} = \left(\frac{\partial T}{\partial P}\right)_S \text{ --- } (9)$$

from eqⁿ (7) & (9)

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P} \text{ --- } 10.$$

from eqn (14)

$df = -pdV - SdT$

At cont. temp

$\partial f = -p\partial V$

$\Rightarrow \left(\frac{\partial f}{\partial V}\right)_T = -p$ — ⑪

$\Rightarrow \left(\frac{\partial^2 f}{\partial V \partial T}\right) = \left(\frac{-\partial P}{\partial T}\right)_V$ — (12)

At cont. vol

$\partial f = -S\partial T$

$\Rightarrow \left(\frac{\partial f}{\partial T}\right)_V = -S$ — (13)

$\Rightarrow \frac{\partial^2 f}{\partial T \partial V} = -\left(\frac{\partial S}{\partial V}\right)_T$ — (14)

from (12) & (14)

$$\boxed{\left(\frac{-\partial P}{\partial T}\right)_V = \left(\frac{-\partial S}{\partial V}\right)_T} \text{ — } 15$$

from 15

$$dG = vdp - SdT$$

At const press.

$$\partial G = -S\,dT$$

$$\Rightarrow \left(\frac{\partial G}{\partial T}\right)_P = -S \quad \text{—(16)}$$

$$\Rightarrow \frac{\partial^2 G}{\partial T\,\partial P} = -\left(\frac{\partial S}{\partial P}\right)_T \quad \text{—(17)}$$

At const temp,

$$\partial G = vdp$$

$$\Rightarrow \left(\frac{\partial G}{\partial P}\right)_T = v \quad \text{—(18)}$$

$$\Rightarrow \frac{\partial^2 G}{\partial P\,\partial T} = \left(\frac{\partial v}{\partial T}\right)_P \quad \text{—(19)}$$

$$\boxed{\left(\frac{\partial v}{\partial T}\right)_P = \left(\frac{-\partial S}{\partial P}\right)_T \quad \text{— 20}}$$

Dt: 17/9/16

Third Law of thermodynamics :-

It states that the entropy of any substance (which is at complete equilibrium) may be taken as zero.

Consequences of third law :-

→ when disorder in a substance completely vanished it becomes perfectly ordered and has only one possible arrangement of atoms.

→ Then, in this case complete internal equilibrium is established

→ The causes for deviation from perfect order are

(i) The thermal energy and resulting motion of atoms and molecules

(ii) Non- crystallinity as in amorphous solids or liquids.

(iii) Crystal defects i.e vacancies, interstitial atoms, dislocations etc.

PTO →.

iv) disordered compound structure.

v) disorder solid solution

Relationship betⁿ ~~stasl~~ statistical interpretation of entropy:

→ entropy is additive in nature
for eg: if we take 2 particles of 'A' & 'B' which have entropy S_A and S_B
then, net entropy

$$S = S_A + S_B \quad \text{——} (1)$$

probability function is multiplicative in nature.

$$f(\omega) = f(\omega_A \cdot \omega_B) \quad \text{——} (2)$$

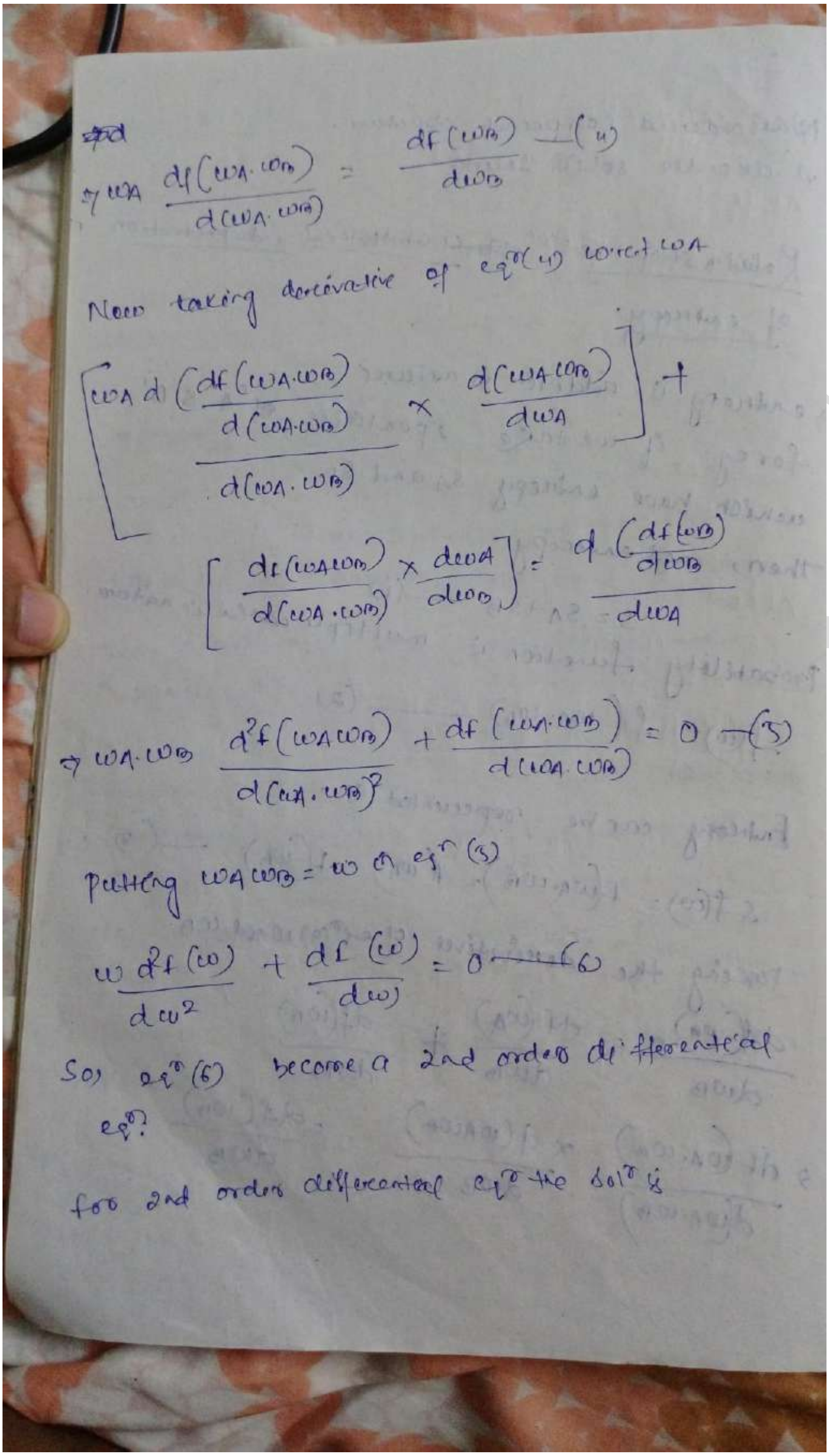
Entropy can be represented as :

$$S\, f(\omega) = f(\omega_A \cdot \omega_B) = f(\omega_A) \;\; f(\omega_B) \quad \text{——} (3).$$

Taking the derivatives of eqⁿ (3) w.r.t ω_B

$$\frac{df(\omega_B)}{d\omega_B} = \frac{df(\omega_A)}{d\omega_B} + \frac{df(\omega_B)}{d\omega_B}$$

$$\Rightarrow \frac{df(\omega_A \cdot \omega_B)}{d(\omega_A \cdot \omega_B)} \times \frac{d(\omega_A \omega_B)}{d\omega_B} = \frac{df(\omega_B)}{d\omega_B}$$



~~and~~

$$\Rightarrow \omega_A \frac{df(\omega_A \cdot \omega_B)}{d(\omega_A \cdot \omega_B)} = \frac{df(\omega_B)}{d\omega_B} \quad \text{—(4)}$$

Now taking derivative of eqⁿ(4) w.r.t. ωA

$$\left[\omega_A \frac{d\left(\frac{df(\omega_A \cdot \omega_B)}{d(\omega_A \cdot \omega_B)}\right)}{d(\omega_A \cdot \omega_B)} \times \frac{d(\omega_A \omega_B)}{d\omega_A}\right] +$$

$$\left[\frac{df(\omega_A \omega_B)}{d(\omega_A \cdot \omega_B)} \times \frac{d\omega_A}{d\omega_B}\right] = \frac{d\left(\frac{df(\omega_B)}{d\omega_B}\right)}{d\omega_A}$$

$$\Rightarrow \omega_A \cdot \omega_B \frac{d^2 f(\omega_A \omega_B)}{d(\omega_A \cdot \omega_B)^2} + \frac{df(\omega_A \cdot \omega_B)}{d(\omega_A \cdot \omega_B)} = 0 \quad \text{—(5)}$$

putting $\omega_A \omega_B = \omega$ in eqⁿ (5)

$$\omega \frac{d^2 f(\omega)}{d\omega^2} + \frac{df(\omega)}{d\omega} = 0 \quad \text{—(6)}$$

So, eqⁿ (6) become a 2nd order differential eqⁿ.

for 2nd order differential eqⁿ the solⁿ is

$f(w) = c_1 \ln w + c_2$ ∴

$\Rightarrow S = c_1 \ln w + c_2$ —— ⑦

for no disorderess $S=0$,

∴ $c_1 \ln w + c_2 = 0$ — ⑧

Again as $S=0$, there is only one microstate possible

$w \simeq 1$

$\Rightarrow \ln w = 0$ —— (9)

So, eq ① becomes. $c_2 = 0$

Now taking $c_1 = \frac{R}{N_0} = K$ —— (10)

R = universal gas const.

N_0 = Avogadro's No.

K = Boltzman cont.

Now using eq (9) & (10) in eq (7) we got.

$$\boxed{S = K \ln w} \quad \text{—— (11)}$$

Heat capacity of Ideal gases :-

Types of gases	Examples	Cv	Cp
Monoatomic	He, Ne, Ar	$\frac{3}{2}R$	$\frac{5}{2}R$
Diatomic	O_2, H_2, N_2	$\frac{5}{2}R$	$\frac{7}{2}R$
Triatomic	O_3	$\frac{7}{2}R$	$\frac{9}{2}R$

Einstein theory of heat capacity of solids :-

Einstein treated the atom in a crystal as 'N' simple harmonic oscillator all of having the same frequency ν_E

The frequency ν_E depends on the strength of the restoring force acting on the atom i.e the strength of the chemical bonds.

Since, the eqn of motion for each atom decomposes into 3 independent eqns for x, y, z component of displacements and n atom is equivalent to 3N harmonic oscillator each vibrate independently of frequency ν_E so, the energy level of the harmonic oscillator

$$E_v = h\nu_E\left(v+\frac{1}{2}\right) \text{ —— (i)}$$

Assuming the oscillator are in thermal equilibrium at temp T.

For a single oscillator,

exp → exponential

$$q = \sum_{v=0}^{\infty} \exp\left[-\beta E_v\right]$$

$$= \sum_{v=0}^{\infty} \exp\left[-\beta h\nu_E\left(v+\frac{1}{2}\right)\right]$$

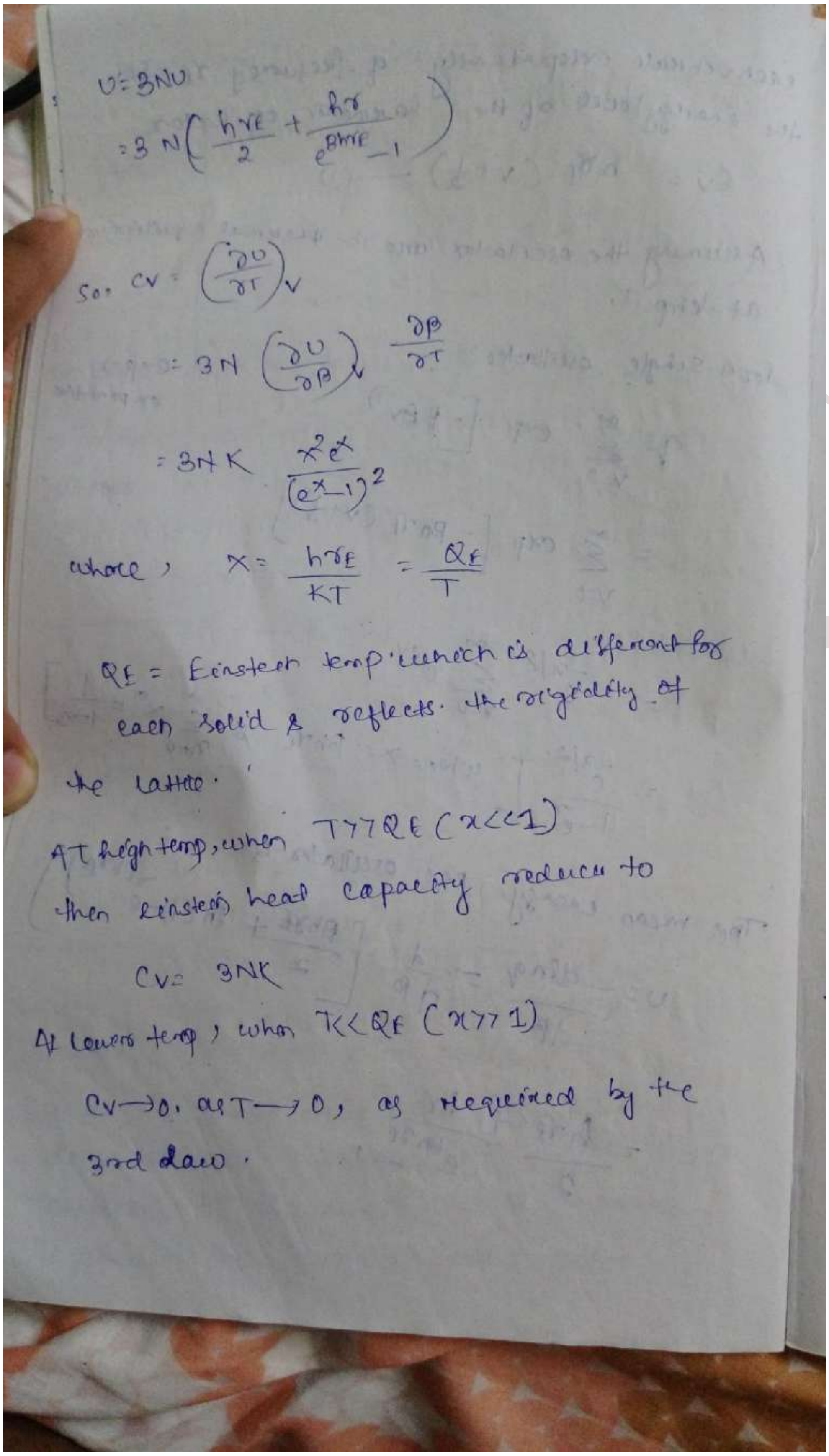
$$= e^{-x/2} \sum_{v=0}^{\infty} e^{-xv}$$

$$= \frac{e^{-x/2}}{1-e^{-x}} \left[\text{where } x = \beta h\nu_E \text{ \& } \sum_{n=0}^{\infty} x^n = \frac{1}{1-x}\right]$$

The mean energy per oscillator is

$$U = -\frac{d\ln q}{d\beta} = -\frac{d}{d\beta}\left[\frac{\beta h\nu_E}{2} + \ln\left(1-e^{-\beta h\nu_E}\right)\right]$$

$$= \frac{h\nu_E}{2} + \frac{h\nu}{e^{\beta h\nu_E}-1}$$



$$U = 3NU$$

$$= 3N\left(\frac{h\nu_E}{2} + \frac{h\nu}{e^{\beta h\nu_E} - 1}\right)$$

So, $$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$= 3N\left(\frac{\partial U}{\partial \beta}\right)_V \frac{\partial \beta}{\partial T}$$

$$= 3NK\,\frac{x^2 e^x}{(e^x - 1)^2}$$

where, $x = \frac{h\nu_E}{KT} = \frac{Q_E}{T}$

Q_E = Einstein temp which is different for each solid & reflects the rigidity of the lattice.

At high temp, when $T \gg Q_E$ $(x \ll 1)$ then Einstein heat capacity reduces to

$$C_V = 3NK$$

At lower temp, when $T \ll Q_E$ $(x \gg 1)$

$C_V \to 0$, as $T \to 0$, as required by the 3rd law.

Fugacity, activity, equilibrium constant, use of S-functions, controlled atmospheres, homogeneous and heterogeneous equilibria.

Ellingham – Richardson diagrams, phase stability diagrams.

Solutions: partial molal quantities, ideal and non-ideal solutions, Henry’s law, Gibbs – Duhem equation, regular solution, quasi-chemical approach to solution, statistical treatment. One weight percentage standard state, chemical potential, phase relations and phase rule – its applications.

Dt: 20/9/16 II - Module .

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 ~~consist of~~ liquid phase and gaseous phase of water.

To express the escaping tendency or migration of molecules from one phase to another, thermodynamic parameter i.e thermodynamic potential is used.

So, here 3 cases arises :-

case I : when the system is in equilibrium i.e no migration of molecules from one phase to another

$$\boxed{G_{vapour} = G_{liquid}}$$

$\therefore \overline{\Delta G} = 0$ —— (i)

case II :- when temp is slightly increases as a result the liquid molecules start vapourising

$G_{vapour} < G_{liquid}$ —— (ii)

$\therefore \overline{\Delta G} = +ve$

retorts are heated

case III :- when the temp is lowered, then condensation of gas molecules starts i.e

$G_{vapour} > G_{liq}$

$\Rightarrow \Delta G = -ve$ —— (iii)

Fugacity :-

It is a measure of chemical potential in the form of adjusted pressure. It directly relates to the tendency of the substance to prefer one phase over another (solid-liq & gas)

At a fixed temp and pressure water will have different fugacity for each phase.

The phase with lowest fugacity will be most favourable i.e the substance minimizes the free energy.

It is not a physical property of a substance rather it is a calculated property. when a system approaches the ideal gas state (very low pressure) then the chemical potential approaches -ve infinity, which for the purpose of mathematical modeling is undesirable.

$dG = vdp - SdT$ ——— (i)

At const. temp

$dG = vdp$

$\because PV = RT$

$\Rightarrow V = \frac{RT}{P}$

$\Rightarrow dG = \frac{RT}{P} dp$

$\Rightarrow dG = RT d \ln P$ —— (ii)

If press changes $P_1 \rightarrow P_2$

$\Delta G = RT d \ln \frac{P_2}{P_1}$

$\Rightarrow \boxed{\Delta G = RT d \ln f}$ —— (3)

fugacity, it is related with pressure.

Relationship of fugacity for non-ideal gas :-

$V = \frac{RT}{P} - \alpha$ —— (4)

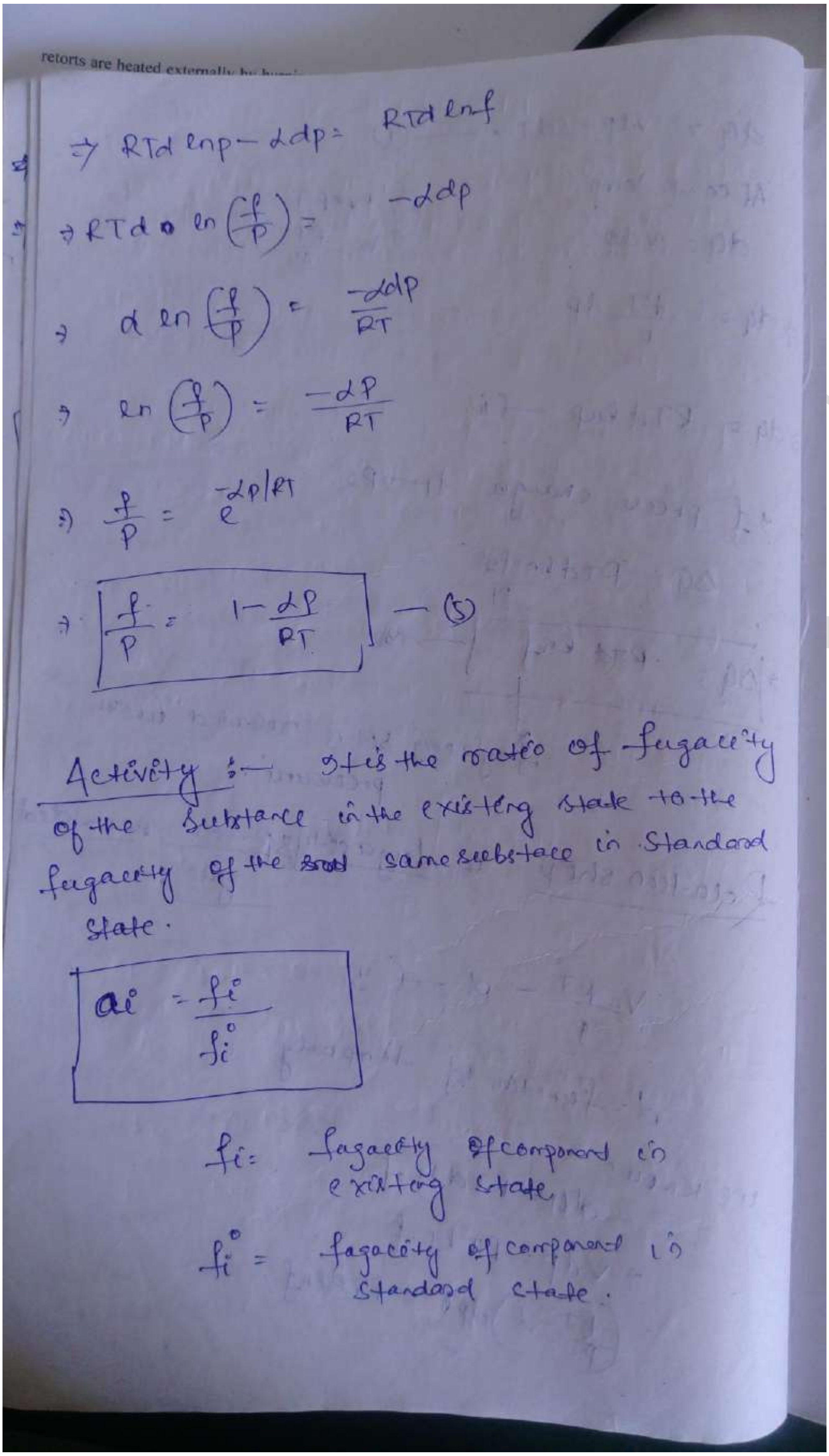
α = function of temp only

we know

$dG = RT d \ln f$

$\Rightarrow Vdp = RT \ln f$

$= \left(\frac{RT}{P} - \alpha\right) dp = RT d \ln f$.



retorts are heated externally by

$$\Rightarrow RTd\ln p - \alpha dp = RTd\ln f$$

$$\Rightarrow RTd\ln\left(\frac{f}{p}\right) = -\alpha dp$$

$$\Rightarrow d\ln\left(\frac{f}{p}\right) = \frac{-\alpha dp}{RT}$$

$$\Rightarrow \ln\left(\frac{f}{p}\right) = \frac{-\alpha P}{RT}$$

$$\Rightarrow \frac{f}{p} = e^{-\alpha P/RT}$$

$$\Rightarrow \boxed{\frac{f}{p} = 1 - \frac{\alpha P}{RT}} \quad \text{— (5)}$$

Activity :— It is the ratio of fugacity of the substance in the existing state to the fugacity of the ~~std~~ same substance in Standard state.

$$\boxed{a_i = \frac{f_i}{f_i^0}}$$

f_i = fugacity of component in existing state.

f_i^0 = fugacity of component in Standard state.

for real gas,

$$\int_{G_i^0}^{G_i} dG_{real} = RT \int_{f_i^0}^{f_i} d\ln f \text{ —— (ii)}$$

$$\Rightarrow G_i - G_i^0 = RT \ln\left(\frac{f_i}{f_i^0}\right) \text{ — (iii)}$$

Since, $a_i^0 = \frac{f_i^0}{f_i^0}$. So, eq^n (iii)

$$\boxed{G_i - G_i^0 = RT \ln a_i} \text{ —— (iv)}$$

In an ideal gas mixture, $P_i = f_i$

Hence,

$$G_i - G_i^0 = RT \ln (P_i - P_i^0)$$

$$= RT \ln\left(\frac{P_i}{P_i^0}\right) \text{ — (v)}$$

Since $P_i^0 = 1$ atm, so eq^n(5) becomes

$$G_i - G_i^0 = RT \ln P_i \left(\because \ln P_i^0 = \ln 1 = 0 \right) \text{ — (6)}$$

from eq^n (4) & (6)

$$RT \ln a_i^0 = RT \ln P_i^0$$

$$\Rightarrow \boxed{a_i = P_i^0} \text{ — (7)}$$

Note:-

(i) a_i is dimensionless quantity

(ii) value of a_i is numerically equal to the value of P_i (in atm)

Arrhenius eqn :

The arrhenius eqn is a simple but remarkable accurate formula for the temp dependence of the reaction rates.

It gives the dependence of the rate constant 'K' of a chemical reaction on the absolute temp 'T' in Kelvin:

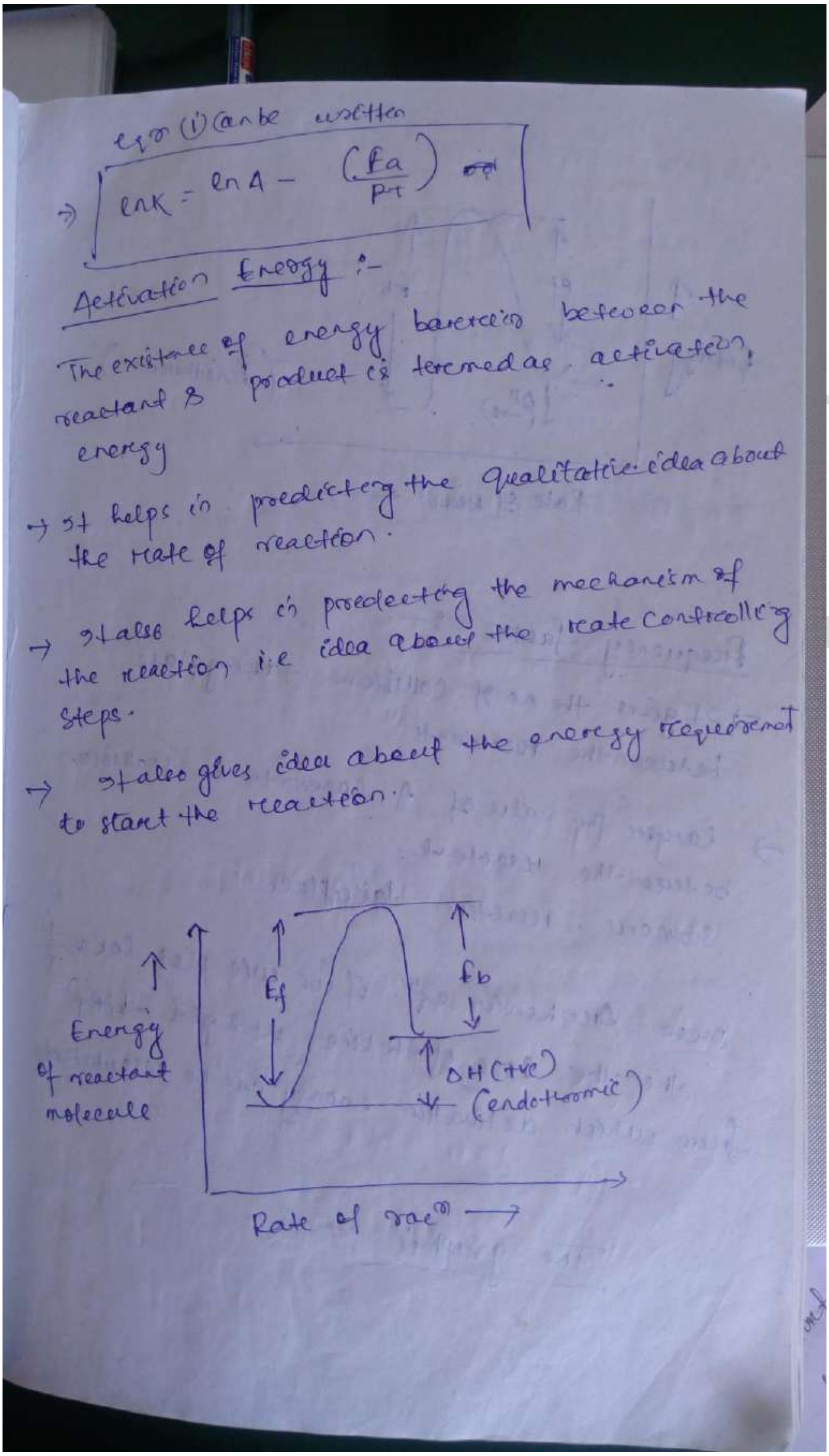
$$\boxed{K = A e^{-(Ea/RT)}}$$

K = Rate constant

A = pre exponential / frequency factor

Ea = Activation energy

R = universal gas constant.



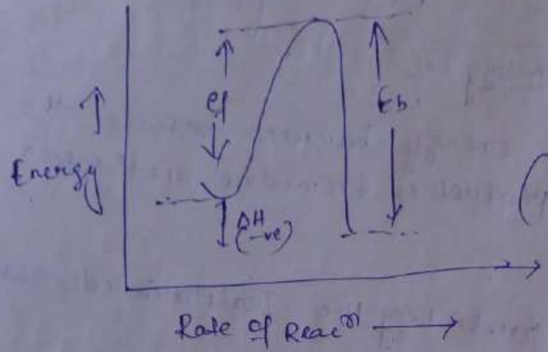
eqn (i) can be written

$$\Rightarrow \boxed{\ln K = \ln A - \left(\frac{E_a}{RT}\right)}$$

Activation Energy :-

The existence of energy barrier between the reactant & product is termed as activation energy

- → It helps in predicting the qualitative idea about the rate of reaction.
- → It also helps in predicting the mechanism of the reaction i.e idea about the rate controlling steps.
- → It also gives idea about the energy requirement to start the reaction.



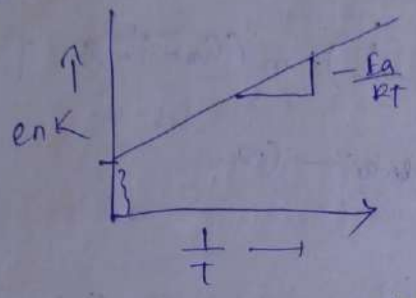
Frequency factor :-

→ It gives the no of collisions taking place between the reactants

→ Larger the value of A larger the no of collision between the reactant.
So, more reaction takes place.

From Arrhenius eqⁿ if we will plot $\ln K$ vs $\frac{1}{T}$ then the slope of the line will give $\left(-E_a/RT\right)$ from which activation energy can be calculated.

The graph is :-



Relationship of $\overset{\text{eq. constant}}{K}$ with std free energy of reac^n:

consider the following reac^n at cont temp & pressure.

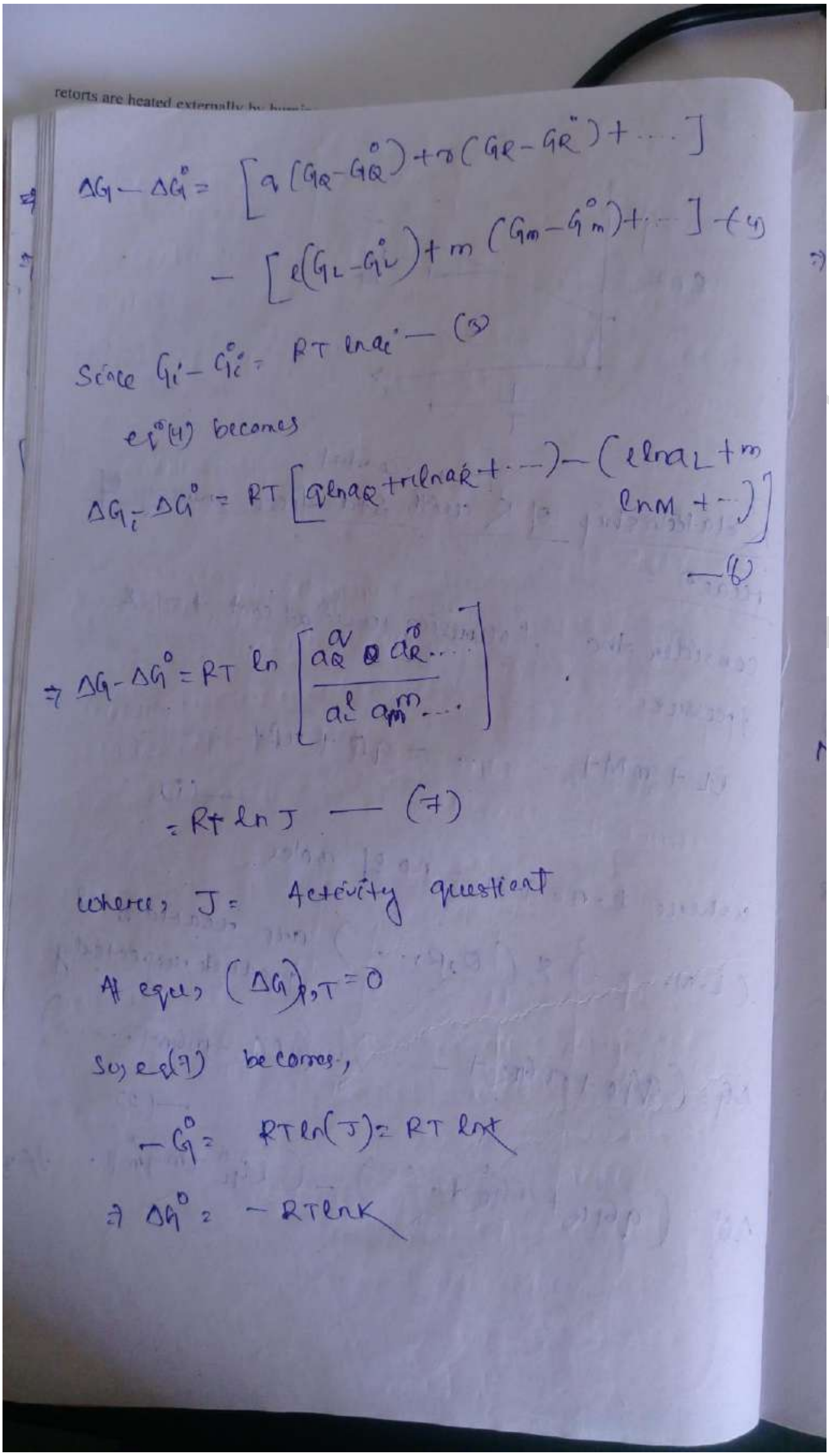
$$lL + mM + \ldots\ldots = qQ + rR + \ldots\ldots \quad \text{—(i)}$$

where l, m, q, r = no of moles

(L, M, ----) & (Q, R, ...) are reactants & products respectively

$$\Delta G = (qG_Q + rG_R + \text{-----}) - (lG_L + mG_M + \ldots\ldots) \quad \text{—(2)}$$

$$\Delta G^0 = (qG^0_Q + rG^0_R + \ldots\ldots) - (lG^0_L + mG^0_m + \ldots) \text{—(3)}$$



retorts are heated externally by

$$\Delta G - \Delta G^\circ = \left[q(G_Q - G_Q^\circ) + r(G_R - G_R^\circ) + \ldots\right] - \left[l(G_L - G_L^\circ) + m(G_M - G_M^\circ) + \ldots\right] \quad (4)$$

Since $G_i - G_i^\circ = RT \ln a_i$ — (5)

eq(4) becomes

$$\Delta G - \Delta G^\circ = RT\left[(q \ln a_Q + r \ln a_R + \ldots) - (l \ln a_L + m \ln M + \ldots)\right] \quad (6)$$

$$\Rightarrow \Delta G - \Delta G^\circ = RT \ln\left[\frac{a_Q^q \, a_R^r \ldots}{a_L^l \, a_M^m \ldots}\right]$$

$$= RT \ln J \quad (7)$$

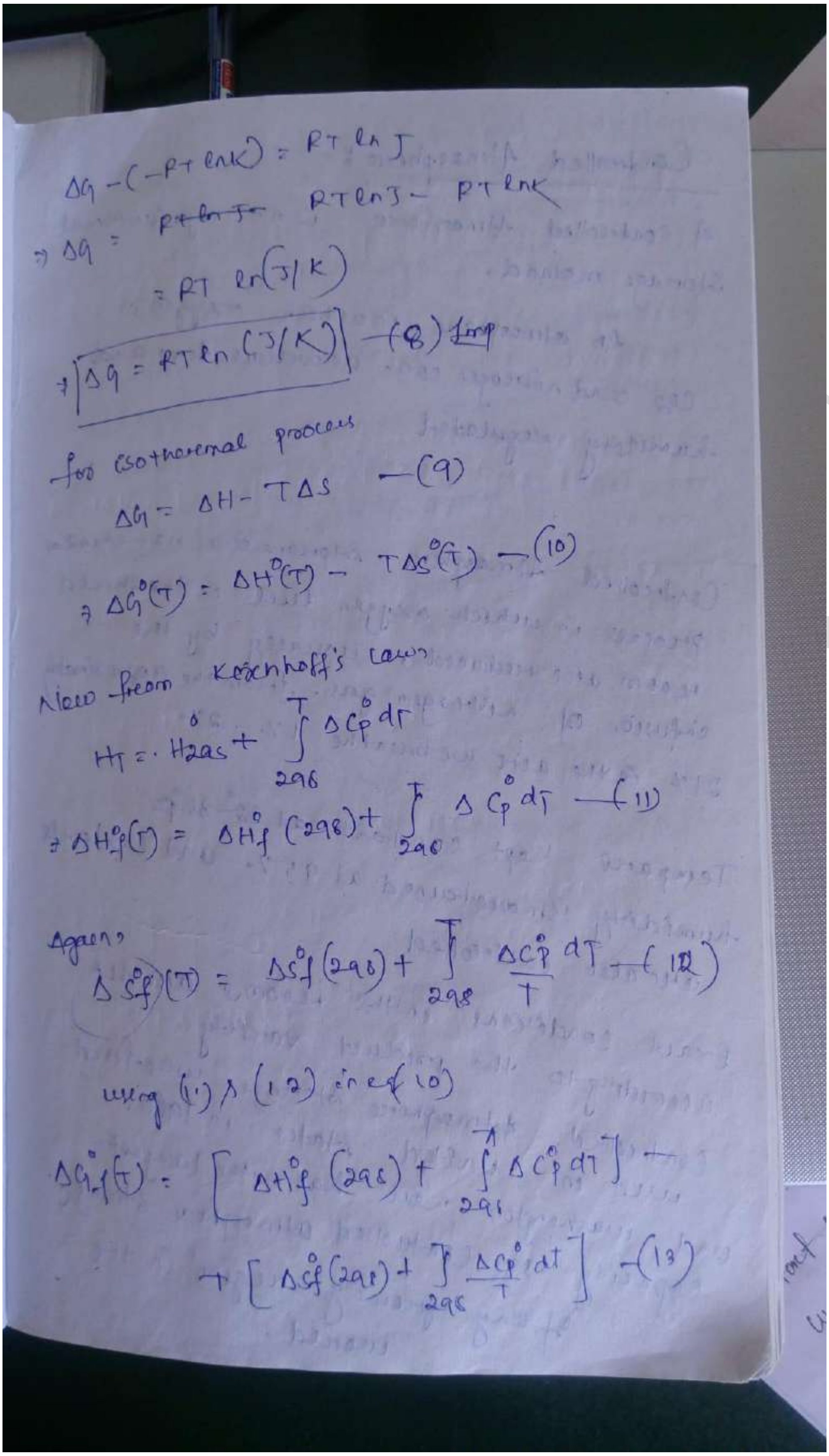
where, J = Activity quotient

At equ, $(\Delta G)_{P,T} = 0$

So, eq(7) becomes,

$$-G^\circ = RT \ln(J) = RT \ln K$$

$$\Rightarrow \Delta G^\circ = -RT \ln K$$



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

$\Rightarrow \Delta G = ~~RT\ln J~~ \; RT\ln J - RT\ln K$

$= RT\ln(J/K)$

$\Rightarrow \boxed{\Delta G = RT\ln(J/K)}$ —(8) Imp

for isothermal process

$\Delta G = \Delta H - T\Delta S$ —(9)

$\Rightarrow \Delta G^0(T) = \Delta H^0(T) - T\Delta S^0(T)$ —(10)

Now from Kirchhoff's law

$H_T = H^0_{298} + \int_{298}^{T} \Delta C_p^0 \, dT$

$\Rightarrow \Delta H_f^0(T) = \Delta H_f^0(298) + \int_{298}^{T} \Delta C_p^0 \, dT$ —(11)

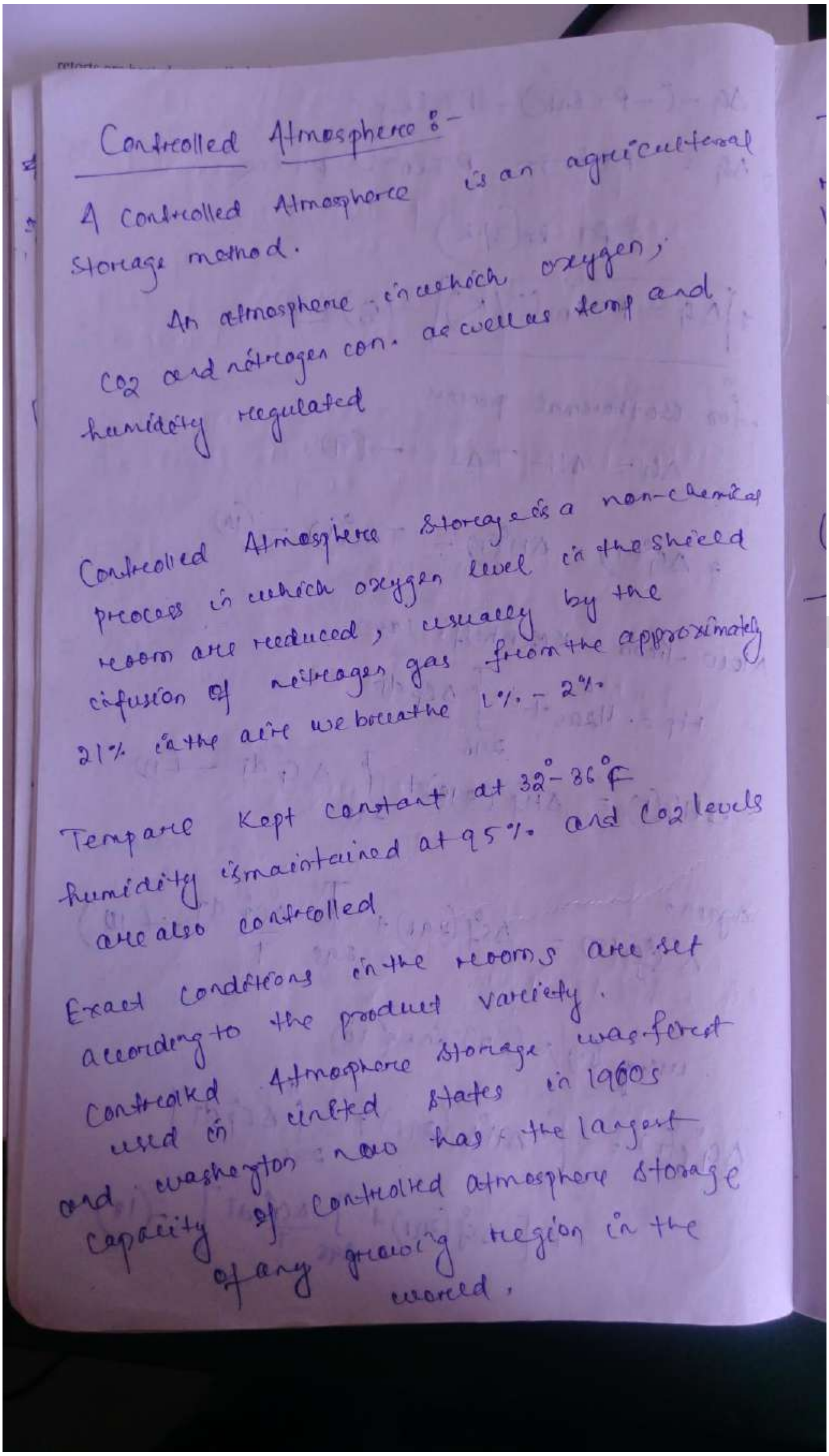
Again,

$\Delta S_f^0(T) = \Delta S_f^0(298) + \int_{298}^{T} \frac{\Delta C_p^0}{T} \, dT$ —(12)

using (11) & (12) in eq (10)

$\Delta G_f^0(T) = \left[\Delta H_f^0(298) + \int_{298}^{T} \Delta C_p^0 \, dT\right] -$

$+ \left[\Delta S_f^0(298) + \int_{298}^{T} \frac{\Delta C_p^0}{T} \, dT\right]$ —(13)



Controlled Atmosphere :-

A Controlled Atmosphere is an agricultural storage method.

An atmosphere in which oxygen, CO2 and nitrogen con. as well as temp and humidity regulated

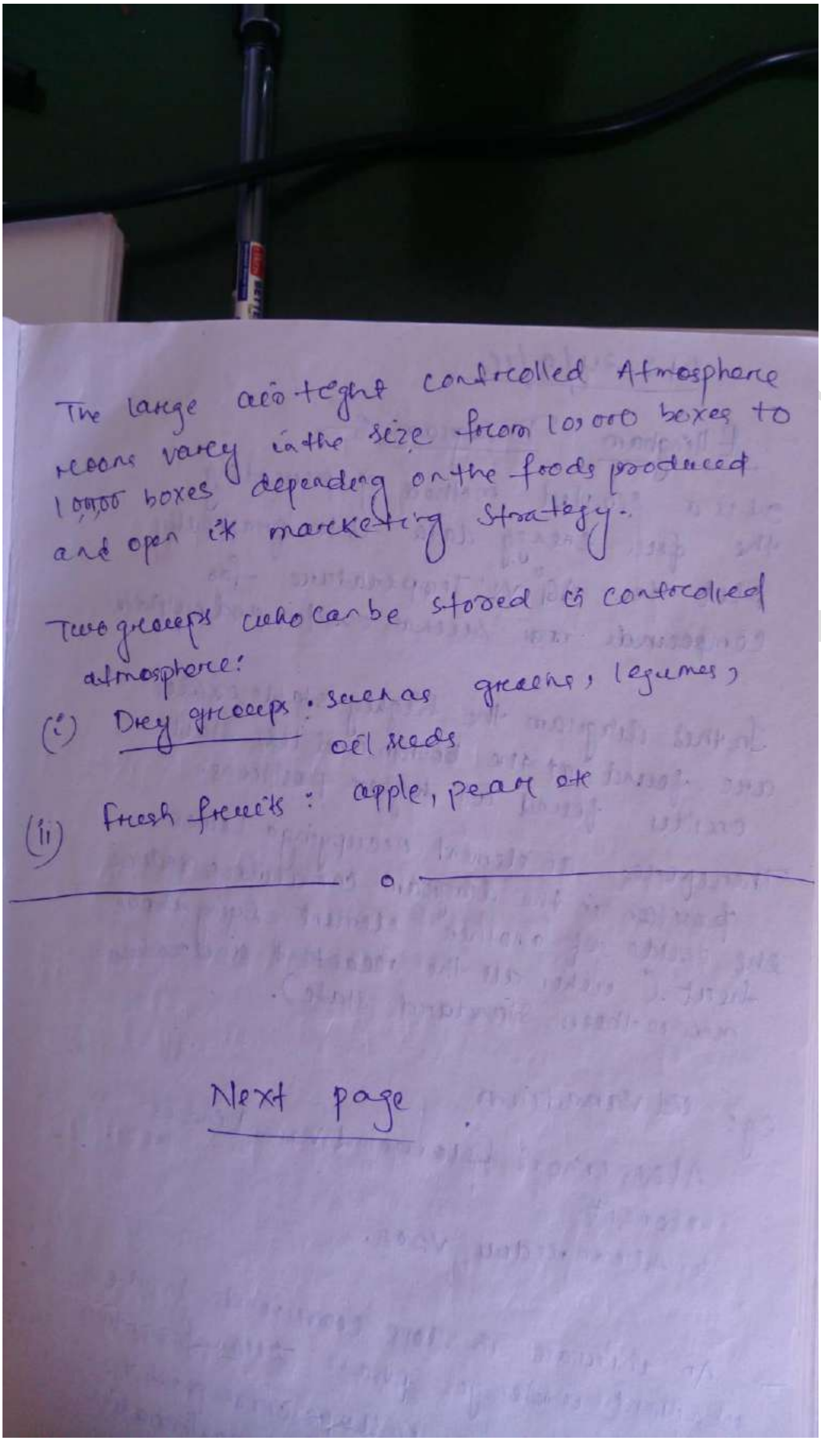
Controlled Atmosphere Storage is a non-chemical process in which oxygen level in the sealed room are reduced, usually by the infusion of nitrogen gas from the approximately 21% in the air we breathe 1% - 2%.

Tempare kept constant at 32°-36°F

humidity is maintained at 95% and CO2 levels are also controlled

Exact conditions in the rooms are set according to the product variety.

Controlled Atmosphere storage was first used in united states in 1960s and washington now has the largest capacity of controlled atmosphere storage of any growing region in the world.



The large air-tight controlled Atmosphere rooms vary in the size from 10,000 boxes to 1,00,00 boxes depending on the foods produced and open it marketing Strategy.

Two groups who can be stored in controlled atmosphere:

(i) Dry groups : such as grains, legumes, oil seeds

(ii) Fresh fruits : apple, pear etc

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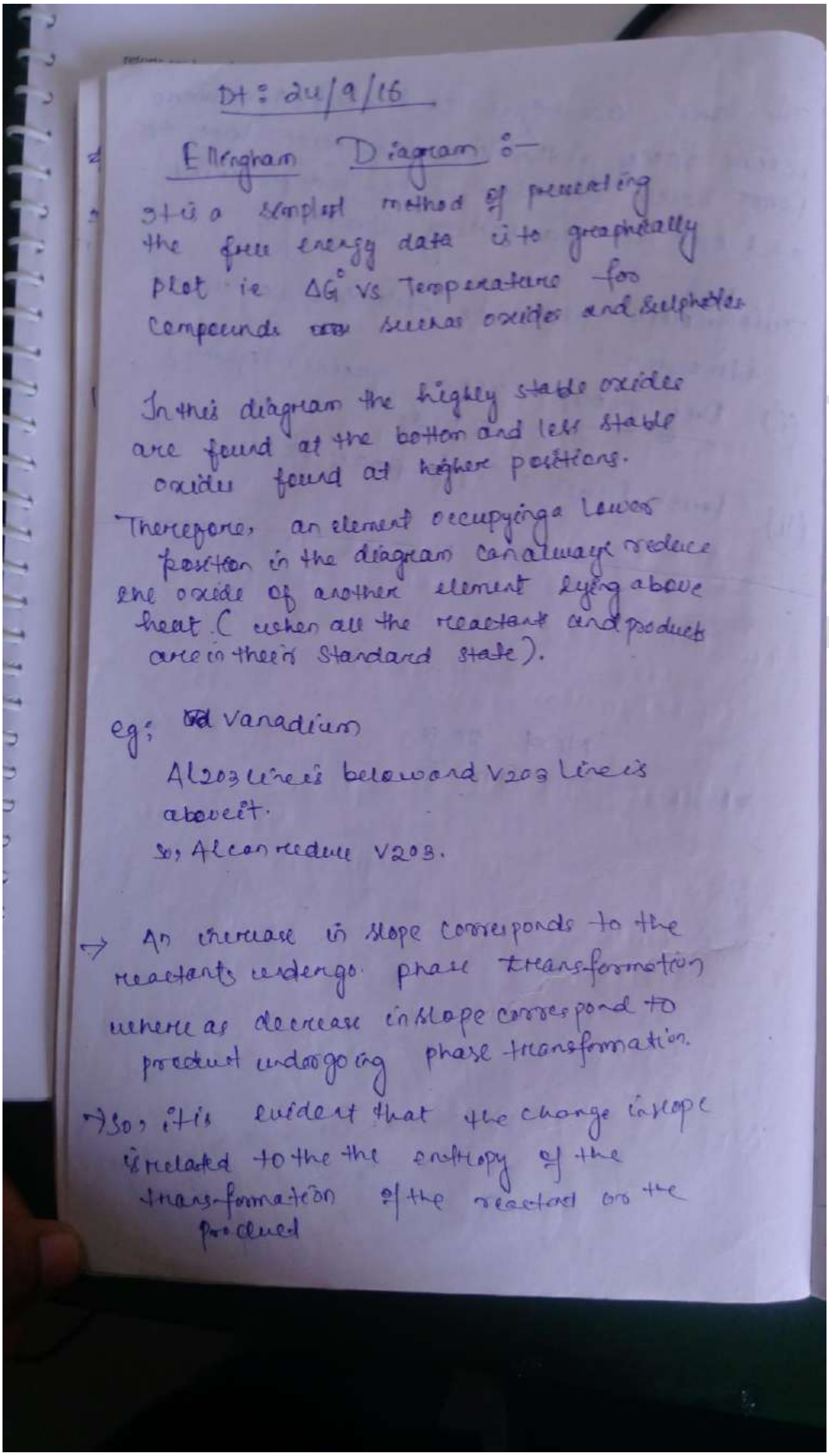

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Ellingham Diagram :-

It is a simplest method of presenting the free energy data i.e to graphically plot ie ΔG° vs Temperature for compounds such as oxides and sulphides

In this diagram the highly stable oxides are found at the bottom and less stable oxides found at higher positions.

Therefore, an element occupying a lower position in the diagram can always reduce the oxide of another element lying above heat (when all the reactants and products are in their standard state).

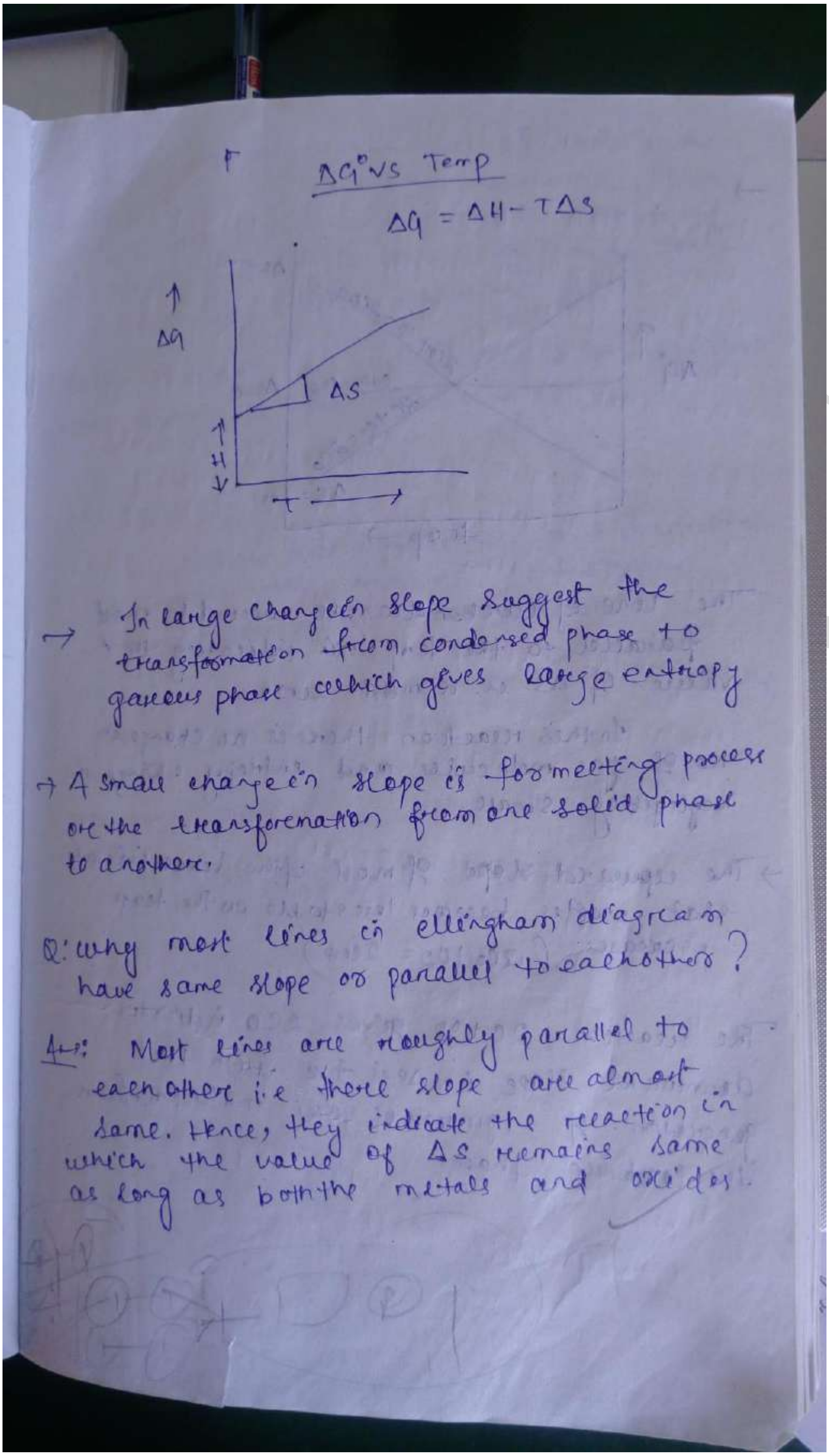
eg: Vanadium

Al2O3 line is below and V2O3 line is above it.

So, Al can reduce V2O3.

→ An increase in slope corresponds to the reactants undergo phase transformation whereas decrease in slope correspond to product undergoing phase transformation.

→ So, it is evident that the change in slope is related to the the entropy of the transformation of the reactant or the product



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ΔG° vs Temp

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

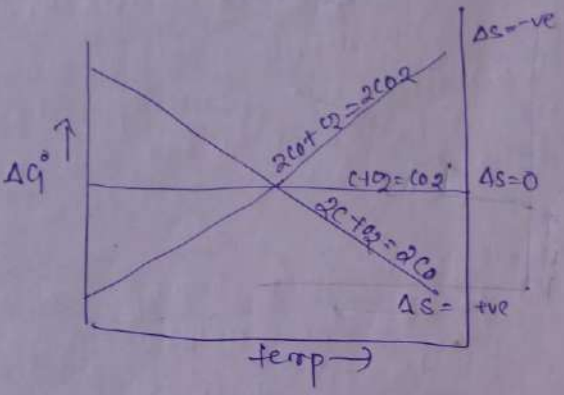
→ In large change in slope suggest the transformation from condensed phase to gaseous phase which gives large entropy

→ A small change in slope is for melting process or the transformation from one solid phase to another.

Q: why most lines in ellingham diagram have same slope or parallel to each other?

Ans: Most lines are roughly parallel to each other i.e there slope are almost same. Hence, they indicate the reaction in which the value of ΔS remains same as long as both the metals and oxides.

→

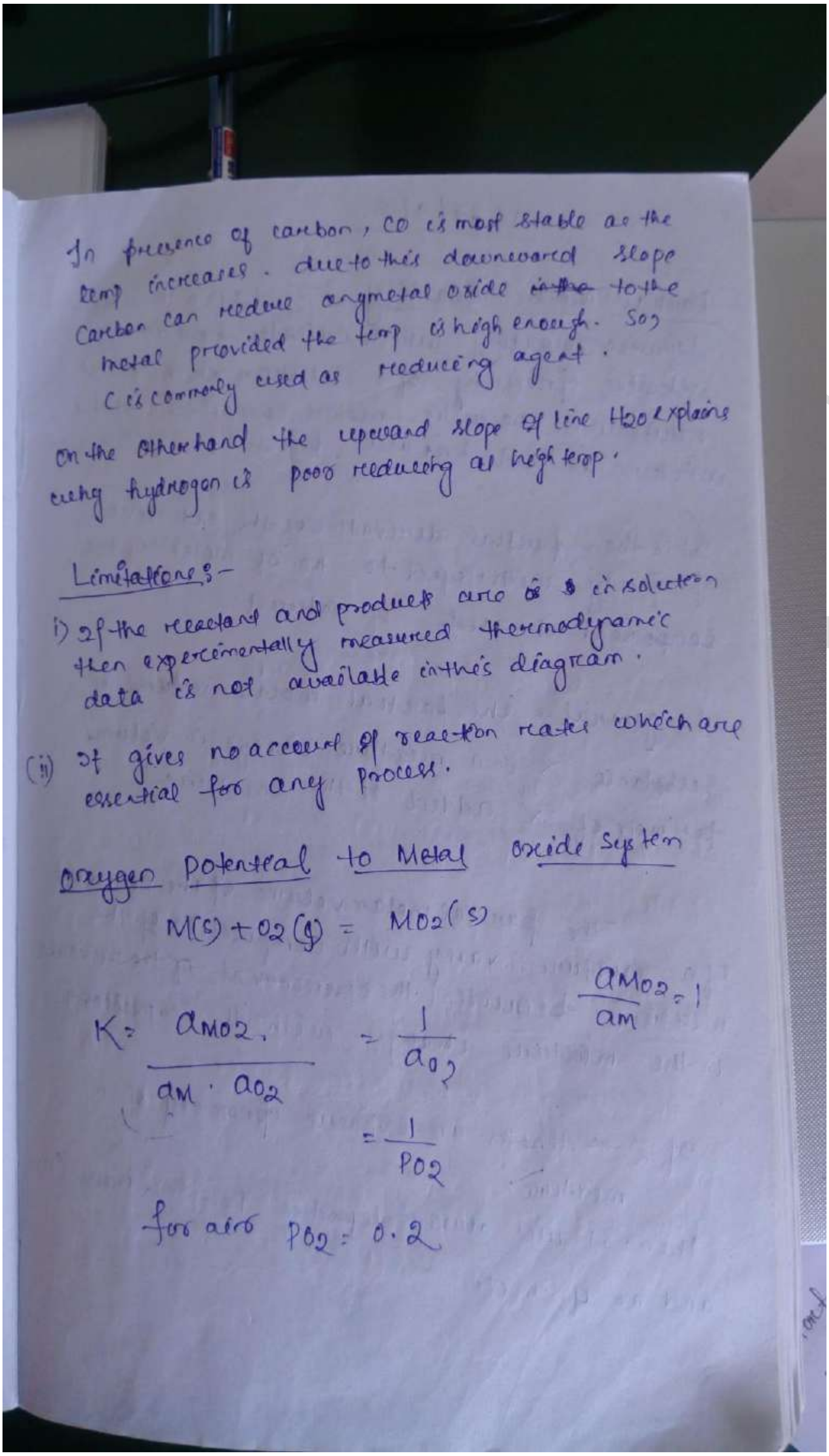


The line of carbon dioxide would be most parallel to the temp axis indicating the value of ΔS is almost zero

In this reaction there is no change in no of gas molecules and entropy change is negligibley small

→ The upward slope of most of the lines indicate that oxides becomes less stable as the temp increases. ($2CO + O_2 = 2CO_2$)

The reaction $2C + O_2$ gives $2CO$ indicates downward slope i.e ΔS is +ve with the generation of 1 gm mole of gas material from the condensed phase.



In presence of carbon, CO is most stable as the temp increases. due to this downward slope carbon can reduce any metal oxide ~~in the~~ to the metal provided the temp is high enough. So, C is commonly used as reducing agent.

On the other hand the upward slope of line H_2O explains using hydrogen is poor reducing at high temp.

Limitations:-

i) If the reactant and products are in solution then experimentally measured thermodynamic data is not available in this diagram.

(ii) It gives no account of reaction rates which are essential for any process.

Oxygen Potential to Metal oxide System

$$M(s) + O_2(g) = MO_2(s)$$

$$\frac{a_{MO_2}}{a_M} = 1$$

$$K = \frac{a_{MO_2}}{a_M \cdot a_{O_2}} = \frac{1}{a_{O_2}} = \frac{1}{P_{O_2}}$$

for air $P_{O_2} = 0.2$

partial molal quantities

The properties of a solution are characterized by thermodynamic functions such as V, S, U, H, A, and G. These values are extensive and refer to the entire solution. It is convenient to use intensive values (e.g. pressure, temperature, and concentrations) as parameters since these values do not depend on the quantity of the solution. In order to estimate the contribution to the extensive property (F) made by each of the i-components in the solution, Lewis defined the partial molar values of a property as

$$\overline{F}_i = \left(\frac{\partial F}{\partial n_i}\right)_{p,\, T,\, n_{j\neq i}}.$$

The chemical potential is an example of a partial molar value; it is the partial molar Gibbs free energy.

Gibbs free energy of a binary solution

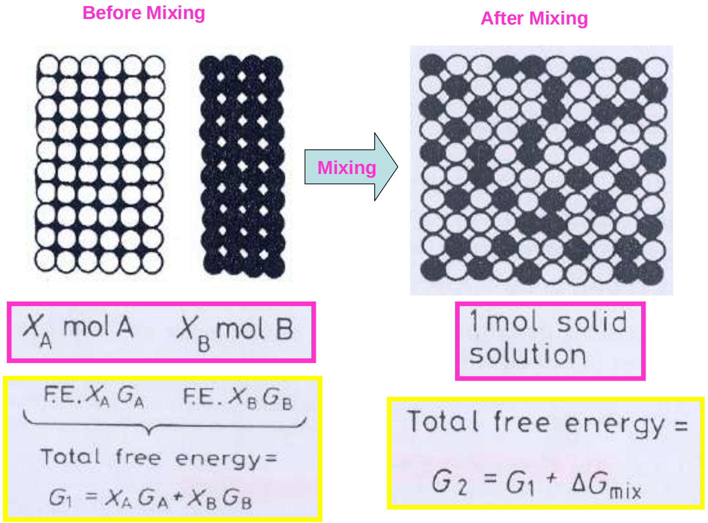
Let’s consider a binary solution of A and B atoms that have the same crystal structures in their pure states and can be mixed in any proportions - form a solid solution with the same crystal structure (satisfy hume ruthery rules of unlimited solid solubility). Example: Cu and Ni.

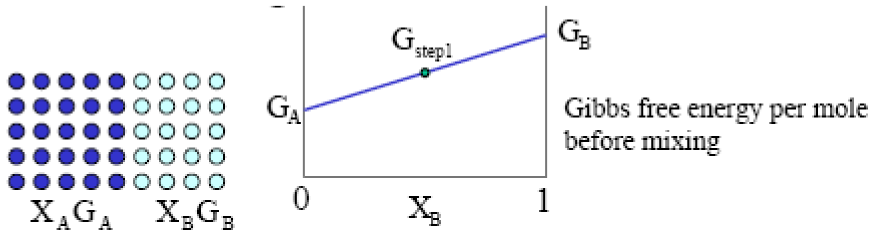
1 mol of homogeneous solid solution contains X_A mol of A and X_B mol of B.

X_A and X_B are the mole fractions of A and B in the alloy. $X_A + X_B = 1$

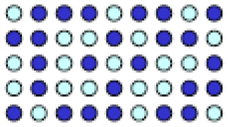
Let’s consider two steps of mixing:

1. Bring together X_A mol of pure A and X_B mol of pure B
2. Mix A and B to make a homogeneous solution





After step 1 the free energy of the system is $G_{step1} = X_A G_A + X_B G_B$



After step 2 the free energy of the system is $G_{step2} = G_{step1} + \Delta G_{mix}$

Where ΔG_{mix} is the change of the Gibbs free energy caused by the mixing.

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

$\Delta H_{mix} = H_{step2} - H_{step1}$ - heat of mixing of the components

(heat of formation of a solution)

$\Delta S_{mix} = S_{step2} - S_{step1}$ - difference in entropy between mixed and unmixed states

(entropy of formation of a solution)

Ideal solution

Let's first consider an **ideal solution** – interactions between atoms A-A, B-B and A-B are identical, and $\Delta Hmix = 0$, $\Delta Vmix = 0$

ΔG id mix $= \Delta Hmix - T\,\Delta Smix = -T\Delta\, Smix$ (because $\Delta Hmix = 0$)

Δ S mix = S step2 $-$S step1

S, the entropy (disorder ness) consists of two parts i.e. thermal and configurational entropy

In statistical thermodynamics, $S = k \ln w$

- In case of thermal entropy, w is the number of ways in which the thermal energy of the solid can be divided among the atoms or The total numbers of ways in which vibrations can be set up in the solid
- In solutions, additional randomness exist due to the different ways in which the atoms can be arranged leading to the configurational entropy
- If there is **no volume change or heat exchange during mixing** then the only contribution to $\Delta Smix$ is the change in configurational entropy

So the free energy change upon mixing is only due to the change in configurational entropy:

S step1 = k ln1 = 0 because there is only one way the atoms can be arranged before mixing.

Therefore, Δ S mix = S step2

$S = k \ln w$

For mixing of N_A particles of type A with N_B atoms of type B:

$$\Omega = \frac{(\mathrm{N_A} + N_B)!}{\mathrm{N_B}!\,\mathrm{N_A}!} \qquad \Delta \mathrm{S_{mix}} = \mathrm{k_B} \ln \Omega = \mathrm{k_B} \ln \frac{(\mathrm{N_A} + N_B)!}{\mathrm{N_B}!\,\mathrm{N_A}!}$$

Using Stirling formula for big numbers: $\ln \mathrm{N}! \approx \mathrm{N} \ln \mathrm{N} - \mathrm{N}$

$$\Delta \mathrm{S_{mix}} = \mathrm{k_B}\left[\ln(\mathrm{N_A} + \mathrm{N_B})! - \ln \mathrm{N_A}! - \ln \mathrm{N_B}!\right] =$$

$$= \mathrm{k_B}\left[(\mathrm{N_A} + \mathrm{N_B})\ln(\mathrm{N_A} + \mathrm{N_B}) - (\mathrm{N_A} + \mathrm{N_B}) - \mathrm{N_A}\ln \mathrm{N_A} + \mathrm{N_A} - \mathrm{N_B}\ln \mathrm{N_B} + \mathrm{N_B}\right] =$$

$$= -\mathrm{k_B}\left[\mathrm{N_A}\ln\left(\frac{\mathrm{N_A}}{\mathrm{N_A} + \mathrm{N_B}}\right) + \mathrm{N_B}\ln\left(\frac{\mathrm{N_B}}{\mathrm{N_A} + \mathrm{N_B}}\right)\right]$$

$$X_A = \frac{N_A}{N_A + N_B} \qquad X_B = \frac{N_B}{N_A + N_B}$$

If the total amount of material is 1 mol, $N_A + N_B$ = Avogadro's number (N_a), and $N_A = X_A N_a$, $N_B = X_B N_a$, $N_a k_B = R$. Therefore

$$\Delta S_{mix} = -k_B \left[N_A \ln\left(\frac{N_A}{N_A + N_B} \right) + N_B \ln\left(\frac{N_B}{N_A + N_B} \right) \right] =$$

$$= -R\left[X_A \ln X_A + X_B \ln X_B\right]$$

$$\Delta G^{id}_{mix} = -T\Delta S_{mix} = RT\left[X_A \ln X_A + X_B \ln X_B\right]$$

For the total Gibbs free energy of an ideal solution:

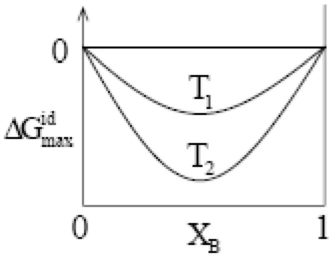
$$G^{id} = G_{step2} = G_{step1} + \Delta G^{id}_{mix} \qquad G_{step1} = X_A G_A + X_B G_B$$

$$\boxed{G^{id} = X_A G_A + X_B G_B + RT\left[X_A \ln X_A + X_B \ln X_B\right]}$$

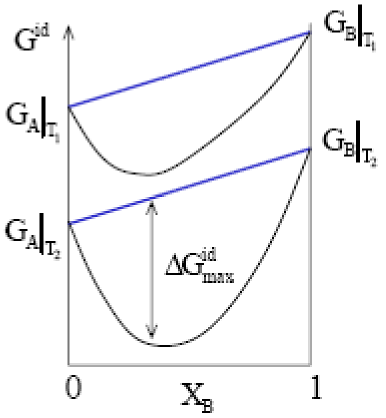
For a nonideal solution we have to take into account heat of formation ΔH_{mix}: $\quad \Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$

$$\Delta G^{id}_{mix} = -T\Delta S_{mix} = RT\left[X_A \ln X_A + X_B \ln X_B\right]$$

$$G^{id} = X_A G_A + X_B G_B + RT\left[X_A \ln X_A + X_B \ln X_B\right]$$



$T_2 > T_1$



Decrease of G_A and G_B with T is due to the temperature dependence of the thermal entropy:

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

Chemical potential of an ideal solution

Remember definition of the chemical potential of the species i :

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j},\ldots} \qquad dG = -SdT + VdP + \sum_{i=1}^{i=k}\left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j},\ldots} dn_i$$

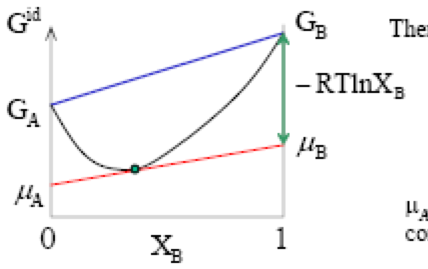
For a binary solution at constant P and T: $dG = \mu_A dn_A + \mu_B dn_B$

Addition of X_A mol of atoms A and X_B mol of atoms B (i. e. $dn_A/dn_B = X_A/X_B$) will increase the size of the system by 1 mol without changing composition and, therefore without changing μ_A and μ_B. The Gibbs free energy of an ideal solution will increase in this case by the molar Gibbs free energy G:

$$G = \mu_A X_A + \mu_B X_B \quad \text{[J/mol]}$$

Since $X_A + X_B = 1 \quad G = \mu_A + (\mu_B - \mu_A)X_B \qquad \frac{\partial G}{\partial X_B} = \mu_B - \mu_A$

Also, $G^{id} = X_A G_A + X_B G_B + RT[X_A \ln X_A + X_B \ln X_B]$



Therefore, **for an ideal solution**:

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

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

μ_A and μ_B depend on the composition of the phase.

Regular solutions: Heat of formation of a solution

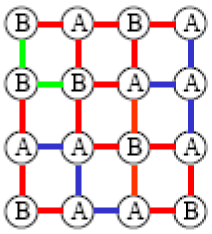
For a nonideal solution we have to take into account heat of formation $\Delta H_{mix} \neq 0$:

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

$\Delta H_{mix} > 0$ - mixing is endothermic (heat absorbed)

$\Delta H_{mix} < 0$ - mixing is exothermic (heat released)

Let's account for the heat of formation $\Delta H_{mix} \neq 0$ using a simple model called statistical or quasi-chemical model. In this model the heat of mixing is only related to the bond energies between adjacent atoms. The assumption is that the interatomic distances and bond energies are independent of composition.



3 types of bonds:

A – A bond (energy E_{AA})

A – B bond (energy E_{AB})

B – B bond (energy E_{BB})

If there are P_{AA}, P_{BB}, P_{AB} bonds of each type, the internal energy of the solution is

$$E = P_{AA}E_{AA} + P_{BB}E_{BB} + P_{AB}E_{AB}$$

Let's calculate the internal energy of the solution:

$$E = P_{AA}E_{AA} + P_{BB}E_{BB} + P_{AB}E_{AB}$$

If z is the coordination number of an atom in a crystal, then the number of atoms N_A and N_B are related to the number of bonds as

$$N_A z = 2P_{AA} + P_{AB} \qquad N_B z = 2P_{BB} + P_{AB}$$

$$P_{AA} = \frac{N_A z}{2} - \frac{P_{AB}}{2} \qquad P_{BB} = \frac{N_B z}{2} - \frac{P_{AB}}{2}$$

Using these expressions for P_{AA} and P_{BB} in the expression for energy, we have

$$E = \left(\frac{N_A z}{2} - \frac{P_{AB}}{2}\right)E_{AA} + \left(\frac{N_B z}{2} - \frac{P_{AB}}{2}\right)E_{BB} + P_{AB}E_{AB} =$$

$$= \underbrace{\frac{N_A z}{2}E_{AA} + \frac{N_B z}{2}E_{BB}}_{\text{energy of unmixed components}} + P_{AB}\left(E_{AB} - \frac{E_{AA}+E_{BB}}{2}\right)$$

Therefore, the energy of mixing (heat of formation ΔH_{mix}) is

$$\Delta H_{mix} = H_{step2} - H_{step1} \approx \Delta E_{mix} = P_{AB}\left(E_{AB} - \frac{E_{AA}+E_{BB}}{2}\right)$$

The energy of mixing (heat of formation ΔH_{mix}) calculated within statistical or quasi-chemical model is

$$\Delta H_{mix} = P_{AB}\left(E_{AB} - \frac{E_{AA}+E_{BB}}{2}\right)$$

If $E_{AB} = \frac{E_{AA}+E_{BB}}{2}$ the solution is ideal: $\Delta H_{mix} = 0$

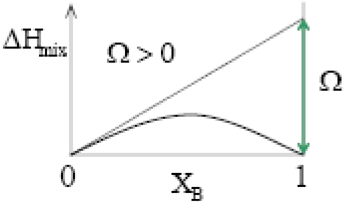
If $E_{AB} > \frac{E_{AA}+E_{BB}}{2}$ $\Delta H_{mix} > 0$ – atoms will tend to be surrounded by atoms of the same type

If $E_{AB} < \frac{E_{AA}+E_{BB}}{2}$ $\Delta H_{mix} < 0$ – atoms will tend to be surrounded by atoms of different type

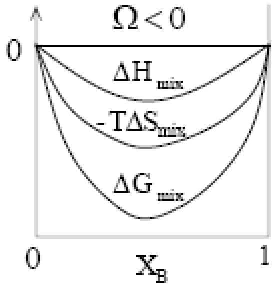
But for small differences between E_{AB} and $(E_{AA}+E_{BB})/2$ (and for high T) we can still consider a random arrangement of atoms in a solution (such solutions are called **regular solutions**). Then

$P_{AB} = zN_{tot}X_A X_B$ and $\Delta H_{mix} = \Omega X_A X_B$ where

$$\Omega = zN_{tot}\left(E_{AB} - \frac{E_{AA}+E_{BB}}{2}\right)$$

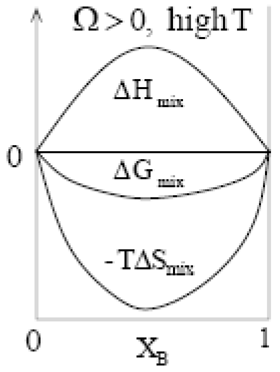


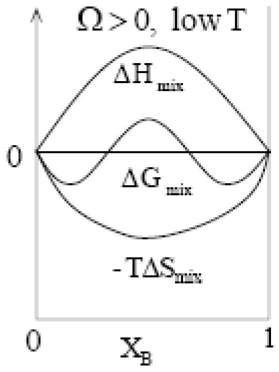
$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} = \Omega X_A X_B + RT(X_A \ln X_A + X_B \ln X_B)$$



For $\Omega < 0$, $\Delta H_{mix} < 0$ – exothermic solution – mixing is favorable at all T

For high $|\Omega|$ and low T $P_{AB} \rightarrow$ max - an ordered alloy could be formed – the assumption of random mixing is not valid, solution is not regular, $\Delta H_{mix} \neq \Omega X_A X_B$

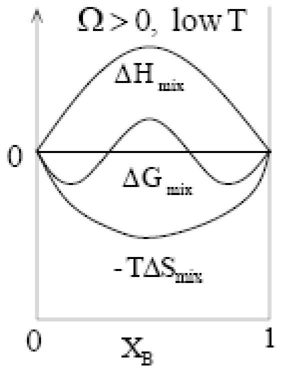




For $\Omega > 0$, $\Delta H_{mix} > 0$ – mixing (formation of A-B pairs is avoided at low T. At high T entropy helps to mix. At low T clustering may occur – solution is not regular.

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} = \Omega X_A X_B + RT(X_A \ln X_A + X_B \ln X_B)$$

Addition of a small amount of solute always leads to the decrease of ΔG_{mix} and G. Why?



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

Or, using definition of chemical potential, $G = \mu_A X_A + \mu_B X_B$

where, for regular solution

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

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

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

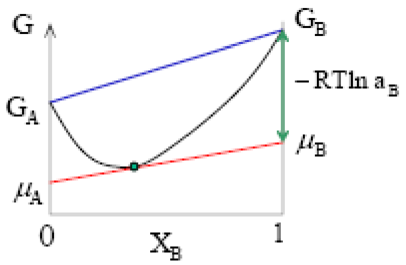
$$G = \mu_A X_A + \mu_B X_B \qquad \mu_A = G_A + \Omega(1-X_A)^2 + RT\ln X_A$$

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

Or we can introduce activities a_A and a_B of components A and B so that expressions for the chemical potentials would have the same form as for ideal solution:

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

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

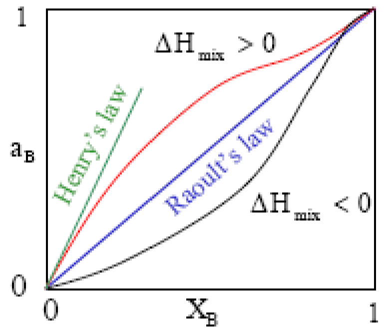


For ideal solutions $a_A = X_A$ and $a_B = X_B$. For regular solutions a_A and a_B are related to X_A and X_B by

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

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

Activity, Henry's law, Raoult's law



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

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

For an ideal solution $a_A = X_A$ and $a_B = X_B$. For a regular solution with $\Delta H_{mix} < 0$ activity of the components is less than in an ideal solution, for $\Delta H_{mix} > 0$ – higher than in an ideal solution.

The ratio a_A/X_A is called the **activity coefficient** γ_A of A.

For a dilute solution of B in A ($X_B \to 0$) we have

$$\gamma_B = \frac{a_B}{X_B} \approx const \ \text{- Henry's law} \qquad \gamma_A = \frac{a_A}{X_A} \approx 1 \ \text{- Raoult's law}$$

Activity and chemical potential are measures of the tendency of an atom to leave a solution. If the activity or chemical potential is low, the atoms are reluctant to leave the solution.

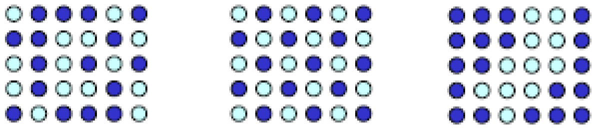
Real solutions

For regular solutions we assumed a random arrangement of atoms in a solution. For many real materials this is not a valid assumption.

If $\Omega < 0$ the internal energy is minimized by increasing the number of A-B bonds – can lead to ordered solution at low T

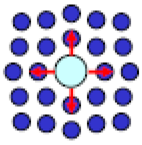
if $\Omega > 0$ the internal energy is minimized by increasing the number of A-A and B-B bonds – can lead to clustering at low T

The arrangement of atoms is a result of compromise between the lowest internal energy and highest entropy. Degree of clustering or ordering decreases with increasing T since the entropy contribution (-TS) to Gibbs free energy becomes more important.

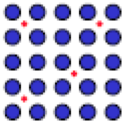


random ordered clustering

If atoms A and B have **different sizes,** the statistical or quasi-chemical model will underestimate ΔH_{mix}. The energy of the elastic strain fields due to the mismatch in atomic sizes should be taken into account. If the size difference is large, the contribution of the strain energy term could as important as the chemical (bonding) term.

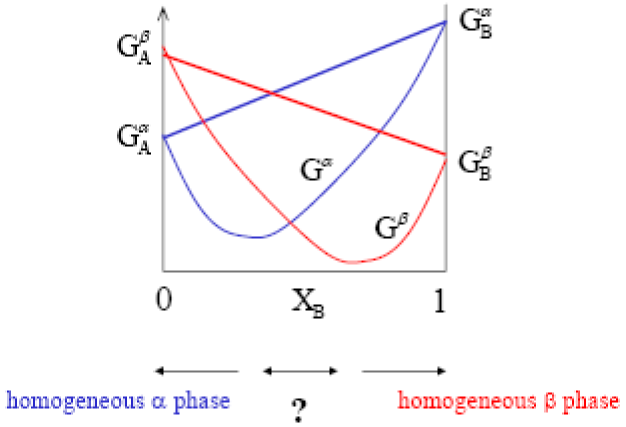


If the size difference between the atoms is very large, then **interstitial solid solutions** are energetically favorable.



In systems with strong chemical bonding between the atoms there is a tendency for formation of **intermediate phases**. The intermediate phases can have a different crystal structure and may be highly ordered.

Systems with two or more phases are heterogeneous systems. If pure components A and B have different equilibrium crystal structures, phase α and phase β, we have to consider two Gibbs free energy curves, one for each phase:



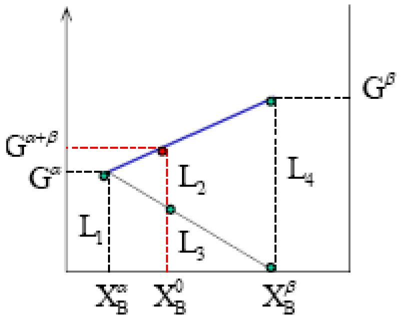
For compositions near cross-over of G_α and G_β, the total Gibbs free energy can be minimized by separation into two phases.

Let's consider a systems with two phases α and β, that have compositions X_B^α and X_B^β and Gibbs free energies G^α and G^β.

If the average composition of the system is X_B^0, the molar free energy $G^{\alpha+\beta}$ is given by the point on a straight line that connects G^α and G^β, and the relative number of moles of phases α and β can be found by **the lever rule**:

$$M^\alpha = (X_B^\beta - X_B^0)/(X_B^\beta - X_B^\alpha)$$

$$M^\beta = (X_B^0 - X_B^\alpha)/(X_B^\beta - X_B^\alpha)$$



$$L_1 = G^\alpha \qquad L_4 = G^\beta$$

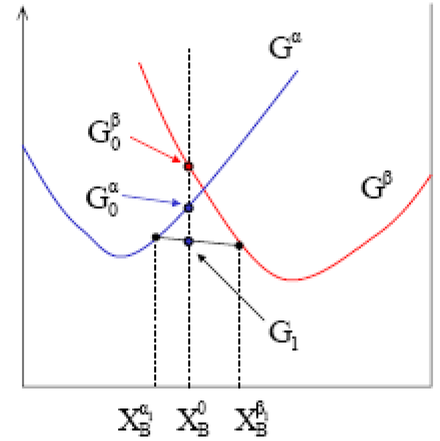
$$\frac{L_3}{L_1} = \frac{X_B^\beta - X_B^0}{X_B^\beta - X_B^\alpha} = M^\alpha$$

$$L_3 = M^\alpha G^\alpha$$

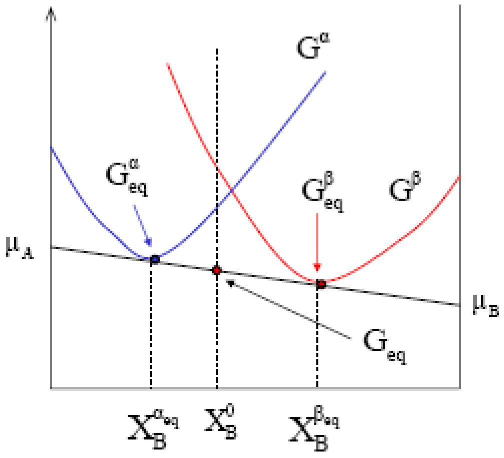
$$\frac{L_2}{L_4} = \frac{X_B^0 - X_B^\alpha}{X_B^\beta - X_B^\alpha} = M^\beta$$

$$L_2 = M^\beta G^\beta$$

Molar free energy of the phase mixture with molar fractions of phases α and β, M^α and M^β → $L_3 + L_2 = M^\alpha G^\alpha + M^\beta G^\beta = G^{\alpha+\beta}$



For composition X_B^0 the lowest Gibbs free energy is G^α_0 for a homogeneous system. The total Gibbs free energy can be additionally decreased by separation into two phases, for example with compositions $X_B^{\alpha_1}$ and $X_B^{\beta_1}$.



The total Gibbs free energy is at minimum if phases α and β have compositions $X_B^{\alpha_{eq}}$ and $X_B^{\beta_{eq}}$

These are the equilibrium compositions of the phases.

In equilibrium tangents to G^α and G^β curves are the same (lie on a common line). Therefore, the condition for heterogeneous equilibrium is equity of the chemical potentials and activities of each component in the two phases.

$$\boxed{\begin{aligned}\mu_A^\alpha &= \mu_A^\beta \\ \mu_B^\alpha &= \mu_B^\beta\end{aligned}} \qquad \boxed{\begin{aligned}a_A^\alpha &= a_A^\beta \\ a_B^\alpha &= a_B^\beta\end{aligned}}$$

$$\mu_B = G_B + RT\ln a_B$$
$$\mu_A = G_A + RT\ln a_A$$

Make sure you understand all the variables, as well as the approximations, basic ideas, and graphical pictures behind these formulas:

$$G^{id} = X_A G_A + X_B G_B + RT[X_A \ln X_A + X_B \ln X_B]$$

$$G^{reg} = X_A G_A + X_B G_B + \Omega X_A X_B + RT[X_A \ln X_A + X_B \ln X_B$$

$$\Omega = zN_{tot}\left(E_{AB} - \frac{E_{AA}+E_{BB}}{2}\right) \qquad G = \mu_A X_A + \mu_B X_B$$

$$\mu_A^\alpha = \mu_A^\beta \qquad a_A^\alpha = a_A^\beta \qquad \mu_A = G_A + RT\ln a_A$$

$$\mu_B^\alpha = \mu_B^\beta \qquad a_B^\alpha = a_B^\beta \qquad \mu_B = G_B + RT\ln a_B$$

Binary phase diagram and Gibbs free energy

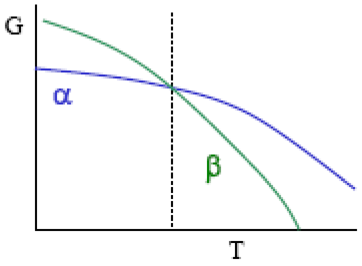
A binary phase diagram is a temperature - composition map which indicates the equilibrium phases present at a given temperature and composition.

The equilibrium state can be found from the **Gibbs free energy dependence on temperature and composition.**

We have discussed the dependence of G of a one-component system on T:

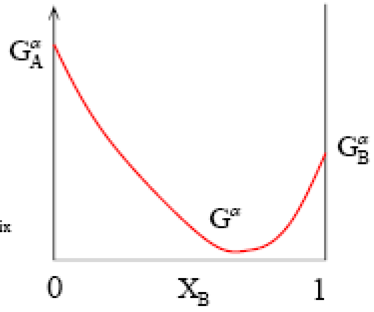
$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_P = -\left(\frac{\partial S}{\partial T}\right)_P = -\frac{c_P}{T}$$



We have also discussed the dependence of the Gibbs free energy from composition at a given T:

$$G = X_A G_A + X_B G_B + \Delta H_{mix} - T\Delta S_{mix}$$

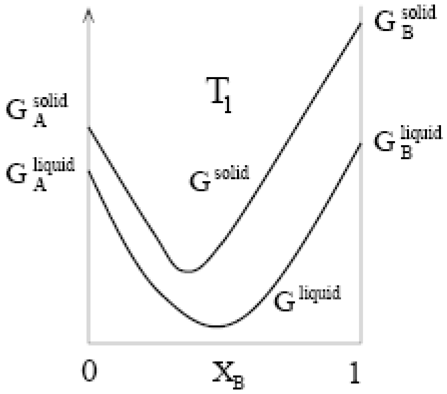


Binary solutions with unlimited solubility

Let's construct a binary phase diagram for the simplest case: A and B components are mutually soluble in any amounts in both solid (**isomorphous system**) and liquid phases, and form *ideal solutions*.

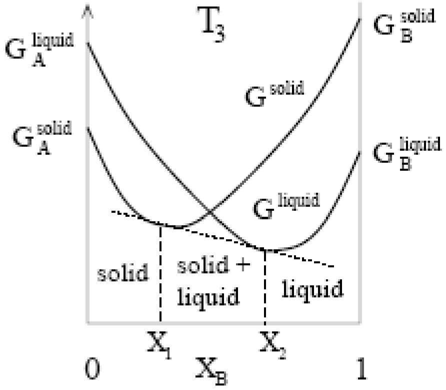
We have 2 phases – liquid and solid. Let's consider Gibbs free energy curves for the two phases at different T

- **T_1** is above the equilibrium melting temperatures of both pure components: $T_1 > T_m(A) > T_m(B)$ → the liquid phase will be the stable phase for any composition.



$$G^{id} = X_A G_A + X_B G_B + RT[X_A \ln X_A + X_B \ln X_B]$$

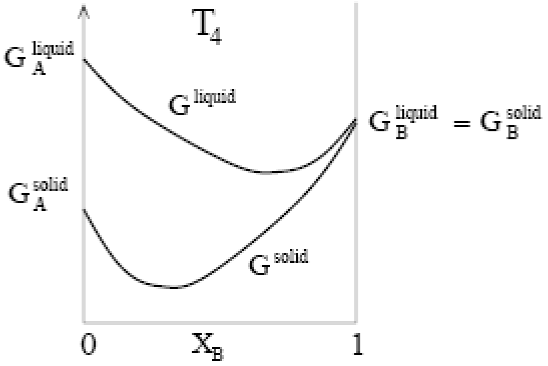
- For even lower temperature $T_3 < T_2 = T_m(A)$ the Gibbs free energy curves for the liquid and solid phases will cross.



As we discussed before, the common tangent construction can be used to show that for compositions near cross-over of G^{solid} and G^{liquid}, the total Gibbs free energy can be minimized by *separation into two phases*.

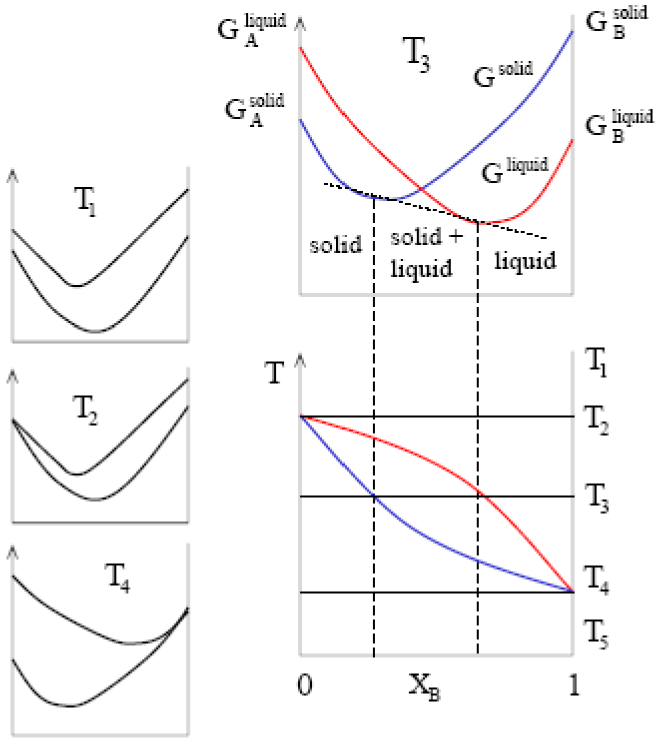
As temperature decreases below T_3 G_A^{liquid} and G_B^{liquid} continue to increase more rapidly than G_A^{solid} and G_B^{solid}

- Therefore, the intersection of the Gibbs free energy curves, as well as points X_1 and X_2 are shifting to the right, until, at T_4 = T_m(B) the curves will intersect at $X_1 = X_2 = 1$



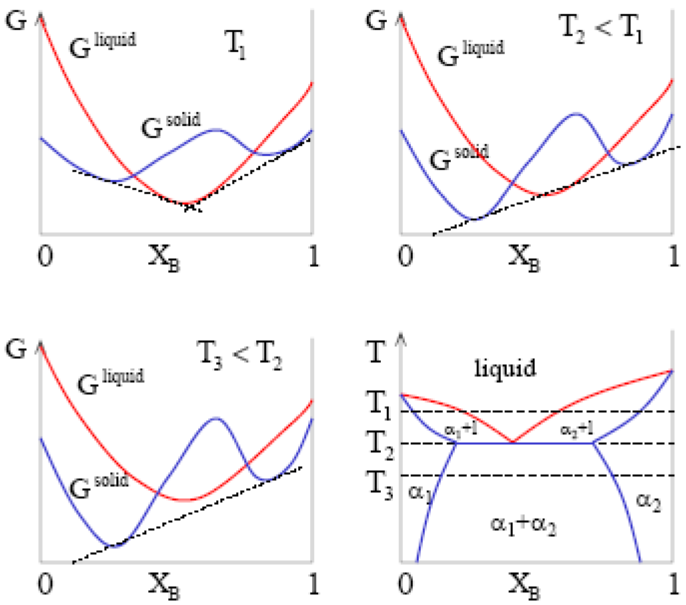
At T_4 and below this temperature the Gibbs free energy of the solid phase is lower than the G of the liquid phase in the whole range of compositions – the solid phase is the only stable phase.

Based on the Gibbs free energy curves we can now construct a phase diagram for a binary isomorphous systems



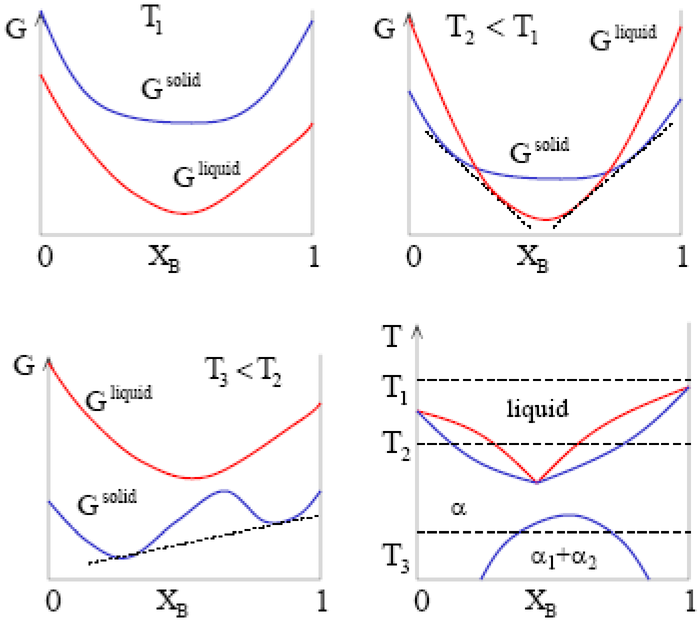
Eutectic phase diagram

For an even larger ΔH_{mix} the miscibility gap can extend into the liquid phase region. In this case we have **eutectic phase diagram**.



Binary solutions with a miscibility gap

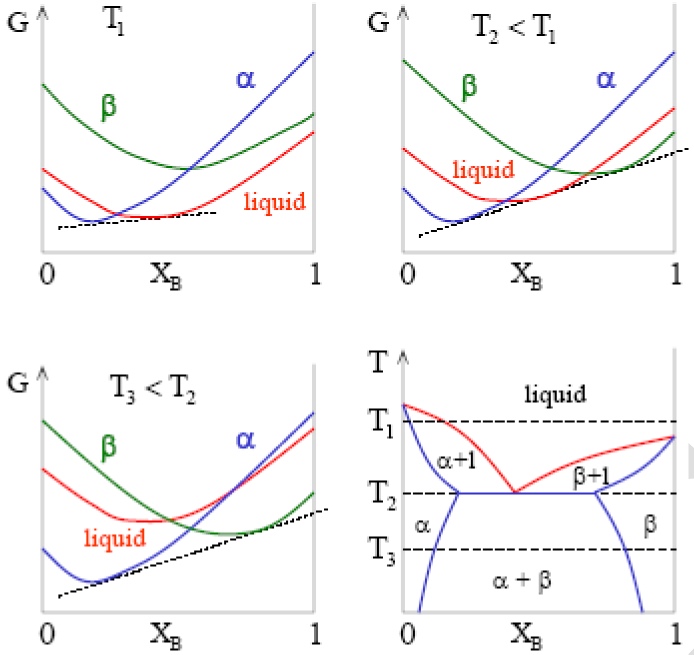
Lets consider a system in which the liquid phase is approximately ideal, but for the solid phase we have $\Delta H_{mix} > 0$



At low temperatures, there is a region where the solid solution is most stable as a mixture of two phases α_1 and α_2 with compositions X_1 and X_2. This region is called a **miscibility gap**.

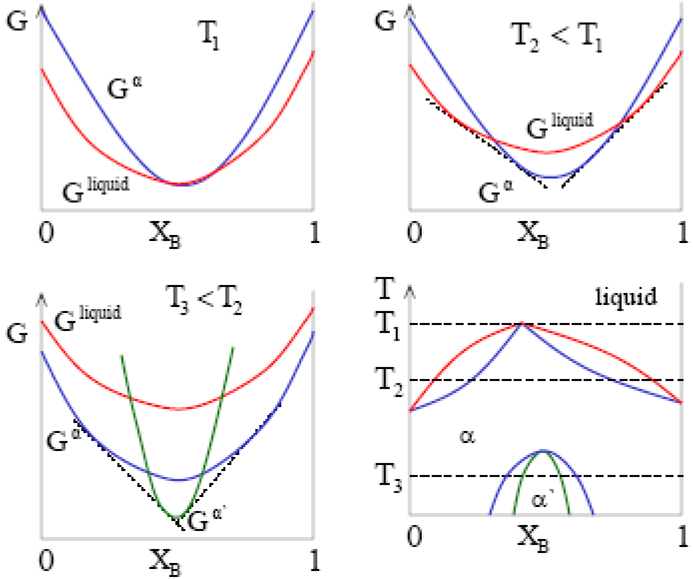
Eutectic phase diagram with different crystal structures of pure phases

A similar eutectic phase diagram can result if pure A and B have different crystal structures.

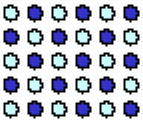


Binary solutions with $\Delta H_{mix} < 0$ - ordering

If $\Delta H_{mix} < 0$ bonding becomes stronger upon mixing → melting point of the mixture will be higher than the ones of the pure components. For the solid phase strong interaction between unlike atoms can lead to (partial) ordering → $|\Delta H_{mix}|$ can become larger than $|\Omega X_A X_B|$ and the Gibbs free energy curve for the solid phase can become steeper than the one for liquid.

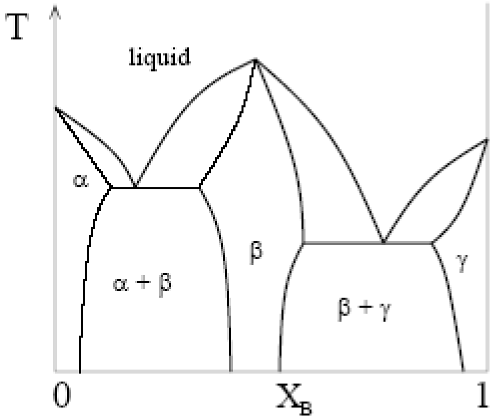


At low temperatures, strong attraction between unlike atoms can lead to the formation of ordered phase α`.



Binary solutions with $\Delta H_{mix} < 0$ - intermediate phases

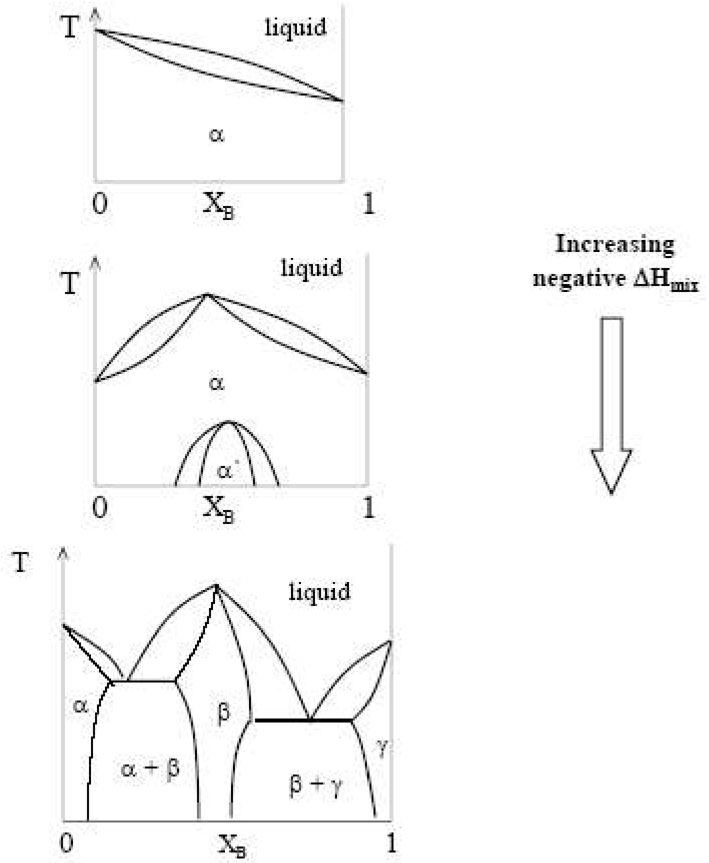
If attraction between unlike atoms is very strong, the ordered phase may extend up to the liquid.



In simple eutectic systems, discussed above, there are only two solid phases (α and β) that exist near the ends of phase diagrams.

Phases that are separated from the composition extremes (0% and 100%)are called **intermediate phases**. They can have crystal structure different from structures of components A and B

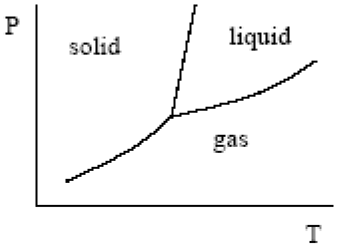
ΔH_{mix}<0 - tendency to form high-melting point intermediate phase



Increasing negative ΔH_{mix}

The Gibbs phase rule (I)

Let's consider a simple one-component system.



In the areas where only one phase is stable both pressure and temperature can be *independently* varied without upsetting the equilibrium → there are 2 **degrees of freedom**.

Along the lines where two phases coexist in equilibrium, only one variable can be *independently* varied without upsetting the two-phase equilibrium (P and T are related by the Clapeyron equation) → there is only one degree of freedom.

At the triple point, where solid liquid and vapor coexist any change in P or T would upset the three-phase equilibrium → there are no degrees of freedom.

In general, the number of degrees of freedom, F, in a system that contains C components and can have Ph phases is given by the **Gibbs phase rule**:

$$\boxed{F = C - Ph + 2}$$

Let's now consider a multi-com ponent system containing C components and having Ph phases.

A thermodynamic state of each phase can be described by pressure P, temperature T, and C - 1 composition variables. The state of the system can be then described by Ph×(C-1+2) variables.

But how many of them are independent?

The condition for Ph phases to be at equilibrium are:

$T_\alpha = T_\beta = T_\gamma = \dots$ - Ph-1 equations

$P_\alpha = P_\beta = P_\gamma = \dots$ - Ph-1 equations

$$\left.\begin{array}{ll} \mu_A^\alpha = \mu_A^\beta = \mu_A^\gamma = \dots & \text{- Ph-1 equations} \\ \mu_B^\alpha = \mu_B^\beta = \mu_B^\gamma = \dots & \text{- Ph-1 equations} \end{array}\right\} \text{C sets of equations}$$

Therefore we have (Ph − 1)×(C + 2) equations that connect the variables in the system.

The number of degrees of freedom is the difference between the total number of variables in the system and the minimum number of equations among these variables that have to be satisfied in order to maintain the equilibrium.

$$F = Ph(C+1) - (Ph-1)(C+2) = C - Ph + 2$$

$F = C - Ph + 2$ **- Gibbs phase rule**

Module III (15 Hours)

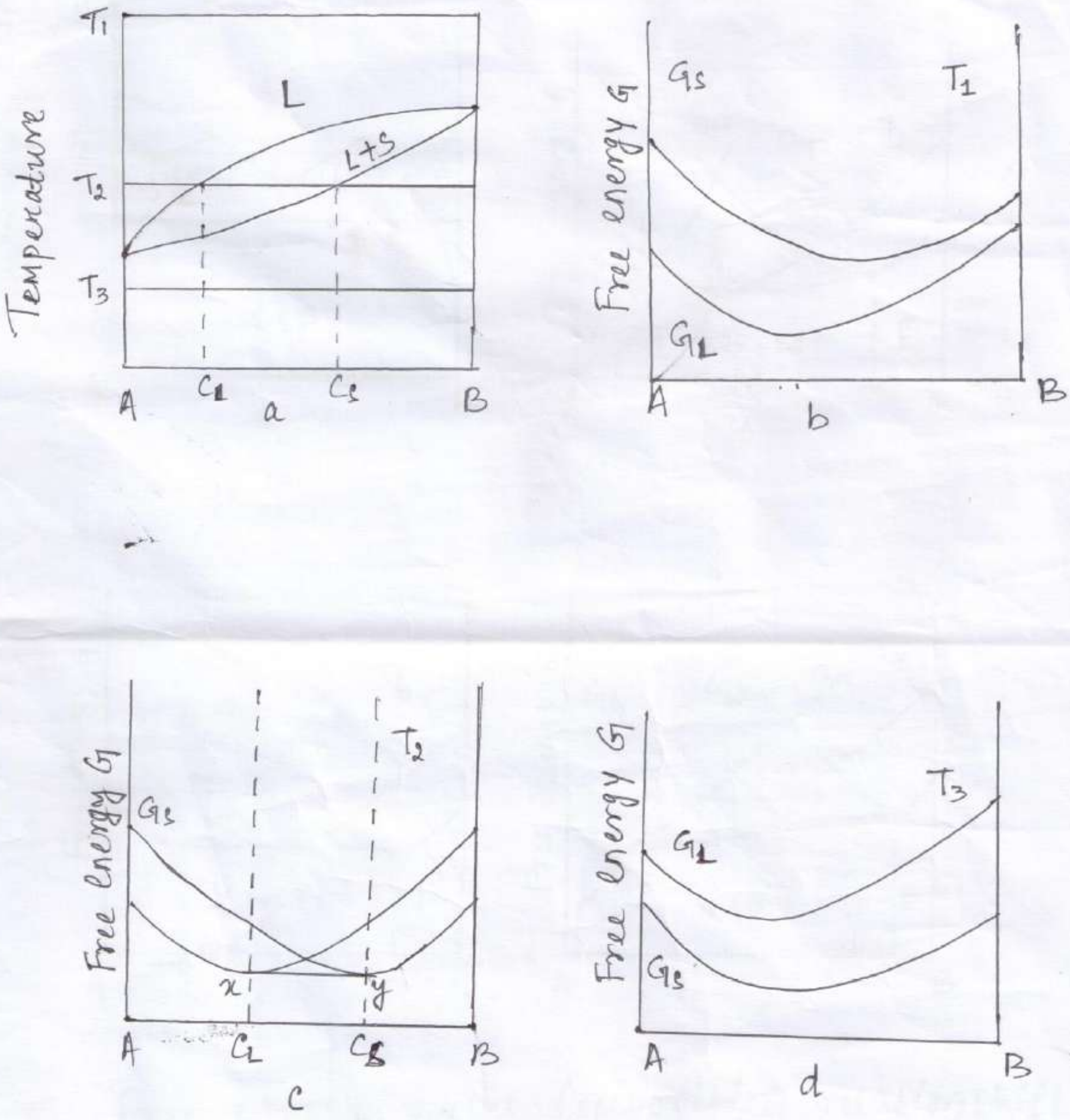
Free energy – composition diagrams for binary alloy systems, determination of liquidus, solidus and solvus lines. Effect of pressure on phase transformation and phase equilibria.

Thermodynamics of electrochemical cells, solid electrolytes. Thermodynamics of point defects in solids.

Introduction to metallurgical kinetics: heterogeneous reaction kinetics: gas-solid, solid – liquid, liquid – liquid and solid-solid systems. Empirical and semi-empirical kinetics, concept of Johnson – Mehl equation, Thermal analysis.

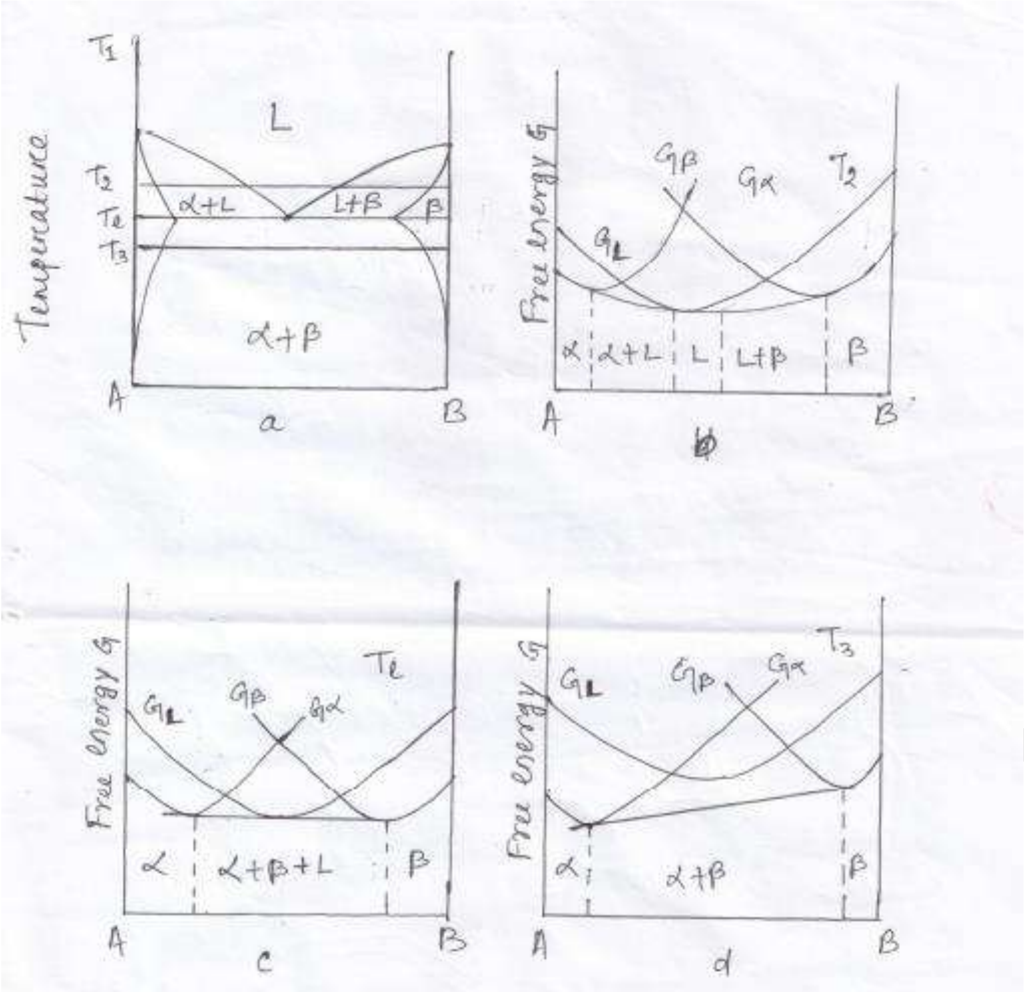
Free energy – composition diagrams for binary alloy systems:

The free energy of each of phases present on a phase diagram can be plotted as a function of composition at a series of temperature. The phases co-exist in equilibrium are those correspond to the lowest free energy of the system. The co-existing phases are determined by the intersection of common tangents with the free energy curves.



Free energy-Composition relationships for an isomorphous system at three temperatures

Fig. Free energy – composition relationships for an isomorphous system at three temperatures.



Free energy versus Composition relationships for a simple eutectic system at different temperatures.

Fig. : Free energy vs. composition relationships for a simple eutectic system at different temperature.

Determination of liquidus, solidus and solvus lines:

These lines refer to the lines of phase diagrams. The liquidus line refers to the line above which all phases are in liquid form. Solidus refers to the line below which all phases are in solid form. Solvus refers to the line separating the single phase solid region and multiphase solid region. For example, the line separating the α and α+β regions of a phase diagram.

A variety of physical techniques are used for the experimental determination these lines, which are subsequently used for construction of phase diagram. Among these the most important techniques are

i. Thermal analysis.
ii. Microscopic examination.
iii. X-ray diffraction.

Thermal analysis

- Thermal analysis is the most important method for determination of the liquid to solid transformations. It is based on the principle of evolution or absorption of heat occurring during a phase change.
- When the temperature of an alloy sample is plotted as a function of time during heating or cooling, abrupt changes in slope of plot occur at points corresponding to the start or finish of a phase change

Cooling Curves:

Curves of single composition for different conditions using thermal analysis explained below and shown in figure below.

(a) Pure metal without super cooling

In this case, evolution of latent heat due to start of solidification is equal to heat loss due to surroundings. So the temperature remains constant for prolonged time. It is shown in Figure (a). Example: Pure metals like Fe, Cu, Ni etc.

(b) Pure metal with super-cooling

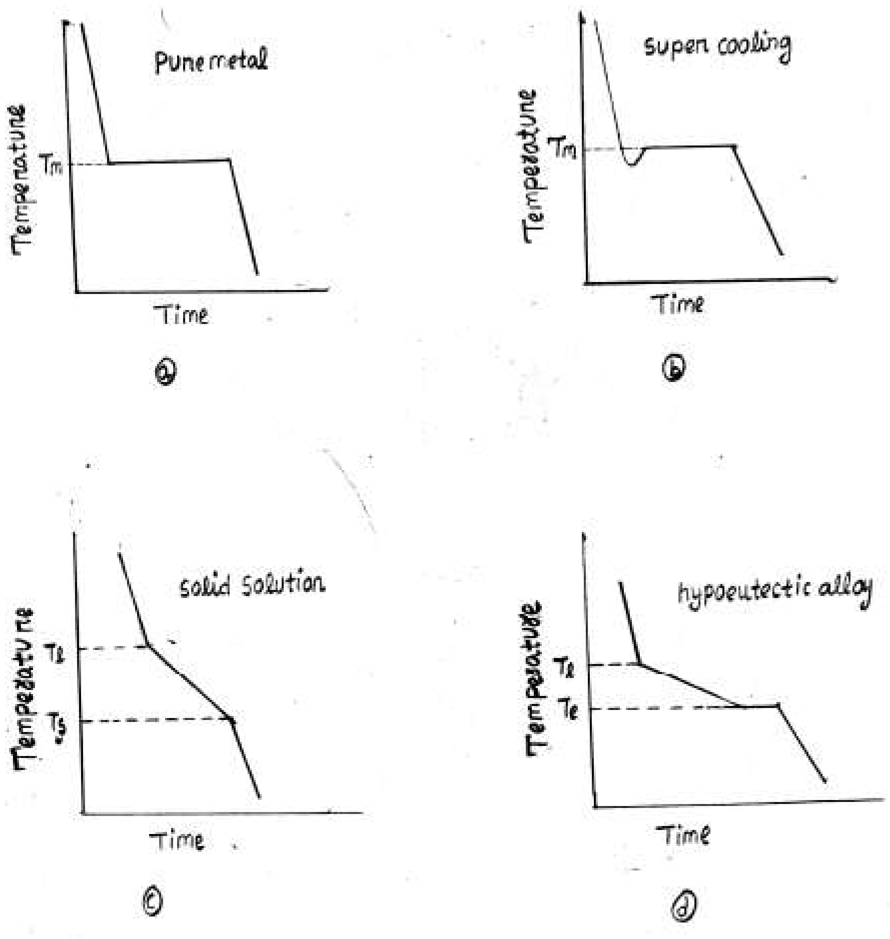
In this case, evolution of latent heat due to the solidification less than heat lost to the surroundings and this process is known as Supercooling. It shown in figure (b). Once Solidification starts heat evolution raise the sample temperature back to freezing point.

(c) Solid solution alloys

As shown in the figure © below, the first arrest of the thermal curve indicates an abrupt decrease in the cooling rate occurs as the liquidus temperature is crossed. Since, over a range of temperature the solidification occurs. So there is no horizontal part. The second arrest is observed at the solidus temperature, when the cooling rate starts to increase again.

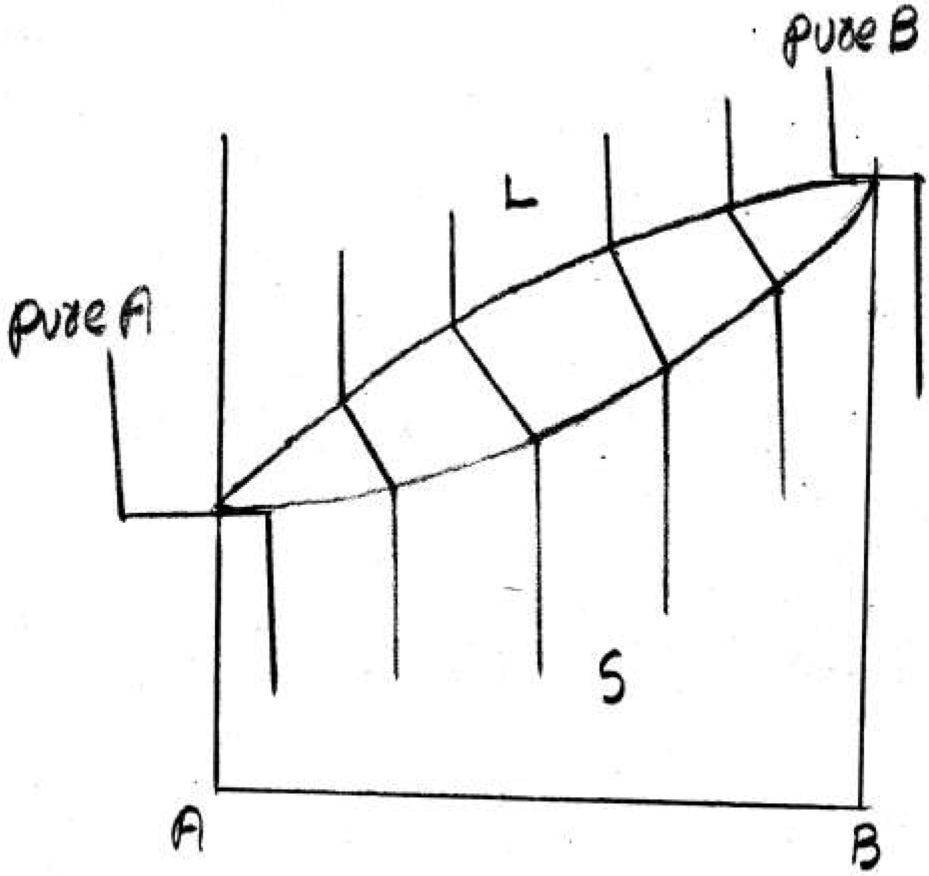
(d) For a hypothetical alloy or pro-eutectic binary alloy

From fig (d) we have, Peritectic alloy also shows the similar behavior as pro-eutectic or hyper-eutectic alloy. The first arrest occurs at the liquidus temperature & the cooling rate decreases. At the eutectic temperature, the cooling curve becomes horizontal as invariant eutectic reaction occurs isothermally. The cooling rate increases again when the eutectic solidification is complete.



Thermal analysis. Cooling curve ⓐ For a pure metal without Supercooling, ⓑ For a pure metal with supercooling, ⓒ For a solid solution alloy, and ⓓ for a hypoeutectic alloy.

Thermal analysis. Cooling curves (a) for a pure metal without supercooling, (b) for a pure metal with supercooling, (c) for a solid solution alloy, (d) for a hypoeutectic alloy.



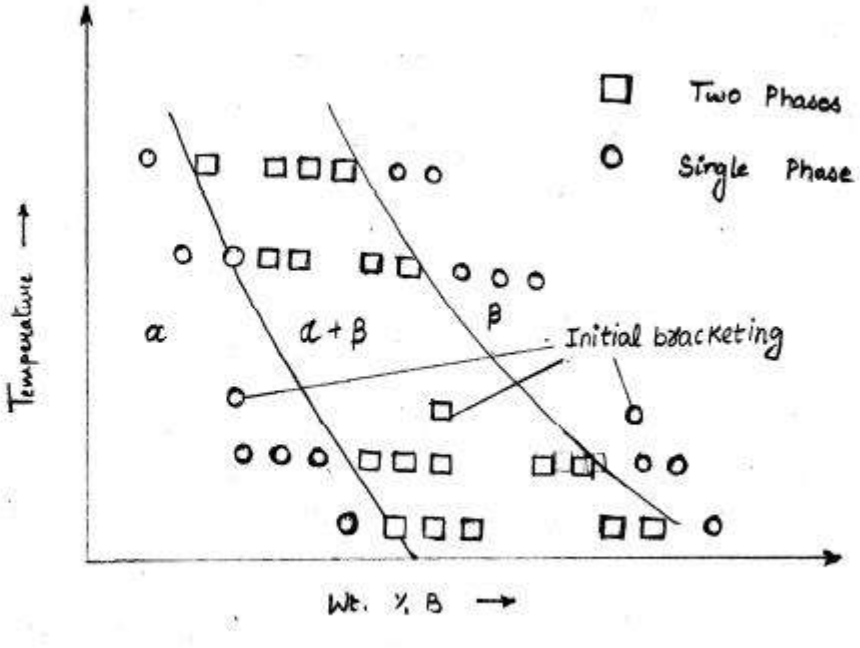
The Construction of liquidus and Solidus phase boundaries from cooling curves Each curve (shown in perspective View) corresponds to a single composition.

The common methods for determining the Solvus are microscopic examination & Xray diffraction. A series of small ingots of alloys of different compositions are prepared and homogenized. They are then annealed at various temperatures for prolonged time (a few days) and quenched.

In such cases, subsequent metallographic and X-ray studies at room temperature disclose the appearance of second phase at some known composition.

In other cases, at high temperature phase may decompose on quenching, If this happens room temperature, X-ray studies are not suitable. So a high temperature X-ray camera used. But even after the decomposition during quenching the metallographic method may be useful, if the transformed phase is in an easily recognizable form.

A phase boundary is first bracketed between two compositions and then exact location of boundary is determined by studying a few more alloys of closely varying composition in the boundary region.

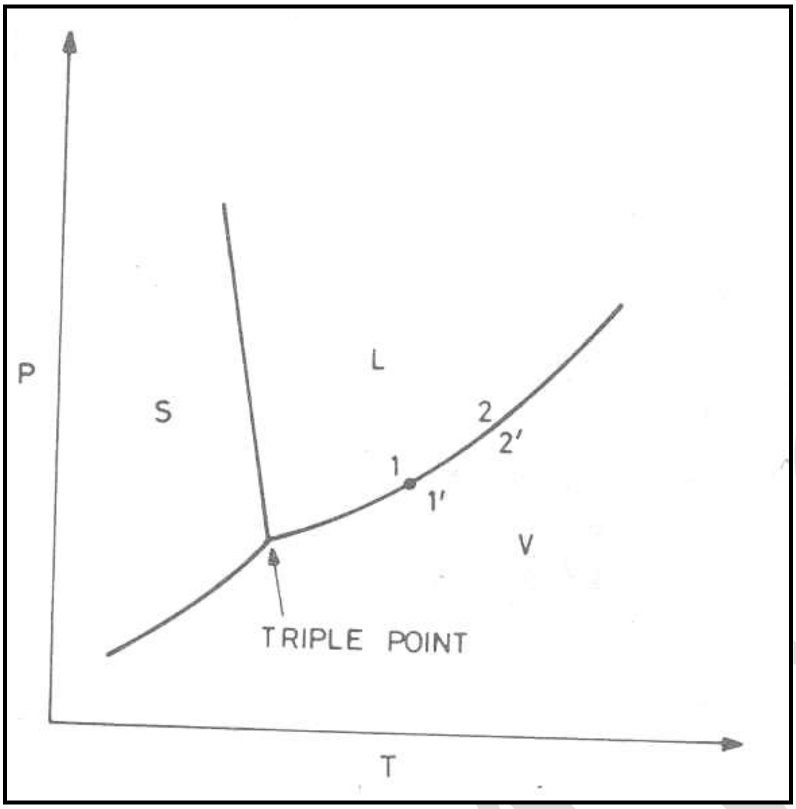


The determination of Solvus boundaries by the metallothermic and X-ray methods

Effect of pressure on phase transformation and phase equilibria:

Clapeyron Equation

To find out the dependence of pressure on equilibrium temperature when two phases coexist. The figure below shows the equlibiriunm co-existing phases at various temperatures. As shownm in figure, along a phase transition line, the pressure and temperature are not independent of each other, since the system is univariant, that is, only one intensive parameter can be varied independently.



When the system is in a state of equilibrium, i.e., thermal, mechanical and chemical equilibrium, the temperature of the two phases has to be identical, the pressure of the two phases has to be equal and the chemical potential also should be the same in both the phases.

Representing in terms of Gibbs free energy, the criterion of equilibrium is:

$$dG = -\hat{s}\,dT + \hat{v}\,dP = 0$$

Consider a system consisting of a liquid phase at state 1 and a vapour phase at state 1’ in a state of equilibrium. Let the temperature of the system is changed from T_1 to T_2 along the vaporization curve.

For the phase transition for 1 to 1’:

$$d\,\hat{G} = -\hat{s}\,dT + \hat{v}\,dP = 0$$

$$\hat{G}_{liquidphase} = G_{vaporphase}$$

$$\hat{G}_1 = \hat{G}_2$$

In reaching state 2 from state 1, the change in the Gibbs free energy of the liquid phase is given by:

$$\hat{G}_2 - \hat{G}_1 = -\hat{s}_f \, dT + \hat{v}_f \, dP$$

Similarly, the change in the Gibbs free energy of the vapour phase in reaching the state 2' from state 1' is given by:

$$G_{2'} - \hat{G}_{1'} = -\hat{s}_g \, dT + \hat{v}_g \, dP$$

Therefore, $-\hat{s}_f \, dT + \hat{v}_f \, dP = -\hat{s}_g \, dT + \hat{v}_g \, dP$

Or $\left(\dfrac{\partial P}{\partial T}\right)_{sat} = \dfrac{\hat{s}_g - \hat{s}_f}{\hat{v}_g - \hat{v}_f}$

Where the subscript *sat* implies that the derivative is along the saturation curve.

The entropy change associated with the phase transition:

$$\hat{s}_g - \hat{s}_f = \frac{\hat{h}_g - \hat{h}_f}{T} = \frac{\hat{h}_{fg}}{T}$$

Hence, $\left(\dfrac{\partial P}{\partial T}\right)_{sat} = \dfrac{\hat{h}_{fg}}{T \hat{v}_{fg}} = \dfrac{\Delta \hat{h}}{T \Delta \hat{v}}$

Which is known as the **Clapeyron equation**

Since $\Delta \hat{h}$ is always positive during the phase transition, $\left(\frac{\partial P}{\partial T}\right)_{\text{sat}}$ will be positive or negative depending upon whether the transition is accompanied by expansion ($\Delta \hat{v} > 0$) or contraction ($\Delta \hat{v} < 0$).

Consider the liquid-vapour phase transition at low pressures. The vapour phase may be approximated as an ideal gas. The volume of the liquid phase is negligible compared to the volume of the vapour phase ($\hat{v}_g >> \hat{v}_f$)and hence $\hat{v}_{fg} = \Delta \hat{v} = \hat{v}_g$ =RT/P.

The Clapeyron equation becomes:

$$\left(\frac{\partial P}{\partial T}\right)_{sat} = \frac{\hat{h}_{fg} P}{RT^2}$$

$$\text{or} \quad \frac{d \ln P}{dT} = \frac{\hat{h}_{fg}}{RT^2}$$

which is known as the **Clausius-Clapeyron equation.**

Assume that $\hat{h}_{fg}$ is constant over a small temperature range, the above equation can be integrated to get,

$$\ln \frac{P_2}{P_1} = \frac{\hat{h}_{fg}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\text{or} \quad \ln P = -\frac{\hat{h}_{fg}}{RT} \text{ +constant}$$

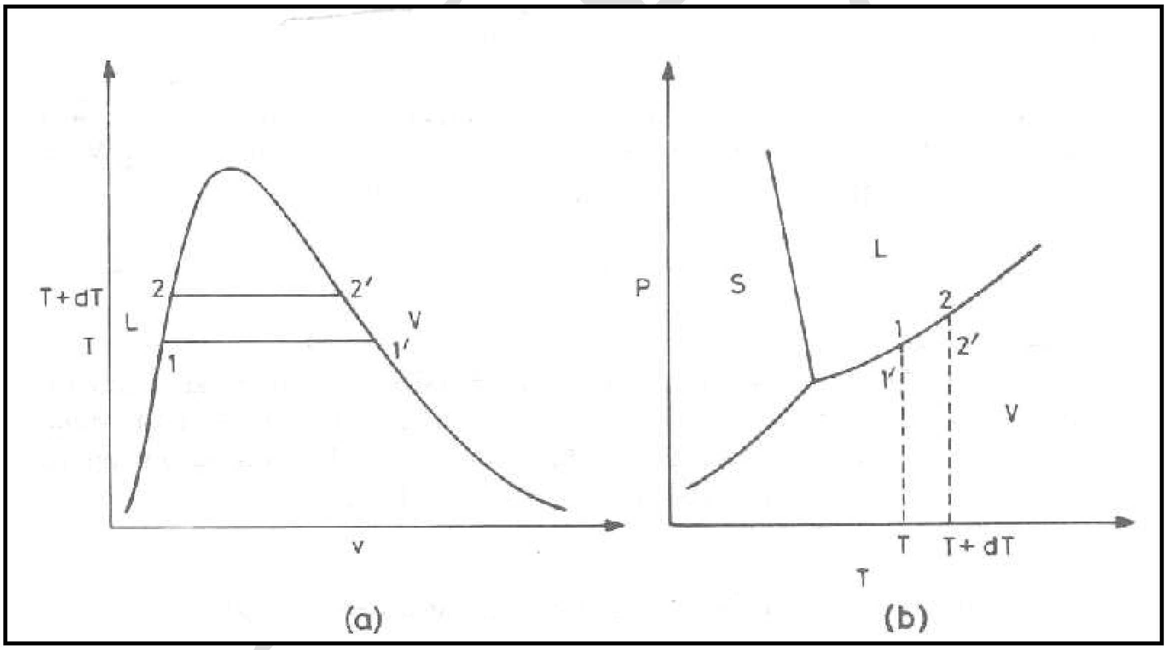
Hence, a plot of *lnP* versus *1/T* yields a straight line the slope of which is equal to –(h_{fg}/R).

Kirchoff Equation

Kirchoff relation predicts the effect of temperature on the latent heat of phase transition.

Consider the vaporization of a liquid at constant temperature and pressure as shown in figure. The latent heat of vaporization associated with the phase change 1 to 1’ is ($\hat{h}_{g1}$ - $\hat{h}_{f1}$) at temperature T. When the saturation temperature is raised to (T+dT), the latent heat of vaporization is ($\hat{h}_{g2}$ - $\hat{h}_{f2}$). The change in latent heat,

$$d\,\hat{h}_{fg} = d\,\hat{h}_{g} - d\,\hat{h}_{f}$$



(a) (b)

The variation in the enthalpy associated with the variation in the independent variables T and P is given by:

$$d\,\hat{h} = \hat{C}p\,dT + \hat{v}(1-\beta T)dP$$

or,

$$d\hat{h}_{fg} = (\hat{C}_{pg} - \hat{C}_{pf})dT + [(\hat{v}_g - \hat{v}_f) - (\hat{v}_g \beta_g - \hat{v}_f \beta_f)T]dP$$

$$\frac{\partial \hat{h}_{fg}}{\partial T} = (\hat{C}_{pg} - \hat{C}_{pf}) + [(\hat{v}_g - \hat{v}_f) - (\hat{v}_g \beta_g - \hat{v}_f \beta_f)T]\left(\frac{\partial P}{\partial T}\right)_{sat}$$

Substituting for $(dP/dT)_{sat}$ from the clapeyron equation,

$$\frac{\partial \hat{h}_{fg}}{\partial T} = (\hat{C}_{pg} - \hat{C}_{pf}) - \frac{(\hat{v}_g \beta_g - \hat{v}_f \beta_f)\hat{h}_{fg}}{(\hat{v}_g - \hat{v}_f)} + \frac{\hat{h}_{fg}}{T}$$

This is known as **Kirchoff relation**.

For a solid-to-liquid transition, it is a reasonably good approximation to assume that the molar heat capacity and the molar volume are constant in each phase and the coefficient of volume expansion β is negligible for each phase. Then,

$$\frac{\partial (\hat{h}_{sf}/T)}{\partial T} = \frac{\hat{C}_{pf} - \hat{C}_{ps}}{T}$$

where $\hat{h}_{sf}$ is the latent heat of fusion.

For the transition from liquid phase to vapour phase, the molar volume of the liquid phase can be neglected compared to the molar volume of the gas phase, and $\beta_g >> \beta_f$. The vapour phase may be approximated as an ideal gas. Then $\beta_g = 1/T$. It is clear that $v_g\beta_g > v_f\beta_f$. Hence,

$$\frac{\partial \hat{h}_{fg}}{\partial T} = (\hat{C}_{pg} - \hat{C}_{pf})$$

Phase Equilibrium- Gibbs Phase Rule

The number of independent variables associated with a multi component, multiphase system is given by the **Gibbs Phase Rule**, expressed as,

F=C+2-P

Where,

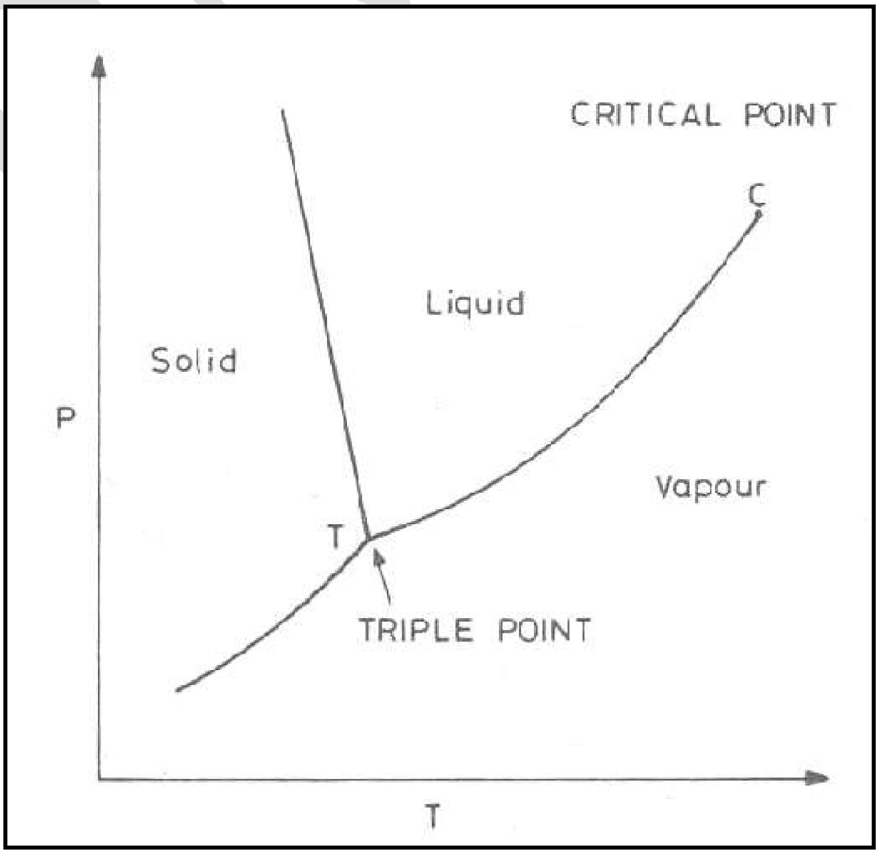
F= The number of independent variables

C= The number of components

P= The number of phases present in the equilibrium

- For a single component (C=1) two phase (P=2) system, one independent intensive property needs to be specified (F=1).
- At the triple point, for C=1, P=3 and thus F=0. None of the properties of a pure substance at the triple point can be varied.
- Two independent intensive properties need to be specified to fix the equilibrium state of a pure substance in a single phase.

Phase diagram for a single component system is given in figure.



Thermodynamics of electrochemical cells, solid electrolytes. Thermodynamics of point defects in solids.

Introduction to metallurgical kinetics: heterogeneous reaction kinetics: gas-solid, solid – liquid, liquid – liquid and solid-solid systems. Empirical and semi-empirical kinetics, concept of Johnson – Mehl equation, Thermal analysis.

Thermodynamics of electrochemical cells

THEORETICAL BACKGROUND

Electrochemistry:

Electrochemistry is the area of chemistry that deals with the relation between chemical changes and electrical energy. Chemical reactions can be used to produce electrical energy in *voltaic (galvanic) cells.* Electrical energy, on the other hand can be used to bring about chemical changes in what are termed *electrolytic cells.*

Oxidation- reduction reactions are those that involve the transfer of electrons from one substance to another. A *redox reaction* is the simultaneous occurrence of the two components or half reactions. *Oxidation* occurs when a chemical species loses or gives up electrons to another chemical species. *Reduction* occurs when a chemical species receives or gain electrons. The oxidation process provides the electrons necessary for reduction to occur. Therefore, the oxidized species is the *reducing agent.*, and the reduced species is the *oxidizing agent.*

For example, if a piece of zinc metal is immersed into a solution containing copper (II) ions, zinc will be oxidized by the copper (II) ions. Zinc loses electrons and it is oxidized while copper (II) ions gain electrons and are reduced. We can conveniently express these two processes by the following two half-reactions, which add to give the overall redox reaction.

$$\mathrm{Zn(s)} \longrightarrow \mathrm{Zn^{2+}(aq)} + 2e^- \qquad \text{(Oxidation)}$$

$$\mathrm{Cu^{2+}(aq)} + 2e^- \longrightarrow \mathrm{Cu(s)} \qquad \text{(Reduction)}$$

$$\mathrm{Zn(s)} + \mathrm{Cu^{2+}(aq)} \longrightarrow \mathrm{Zn^{2+}(aq)} + \mathrm{Cu(s)} \qquad \text{(Net Reaction)} \qquad (1)$$

The function of a voltaic cell is based upon reactions similar to the one illustrated in equation (1). The system Zn/Cu is called the Daniell cell in honor of John Frederick Daniell (1790-1845) who developed the cell for the first time. A salt bridge must be used to avoid polarization of the electrodes by facilitating the circulation of ions from both cell compartments. (see figure 1).

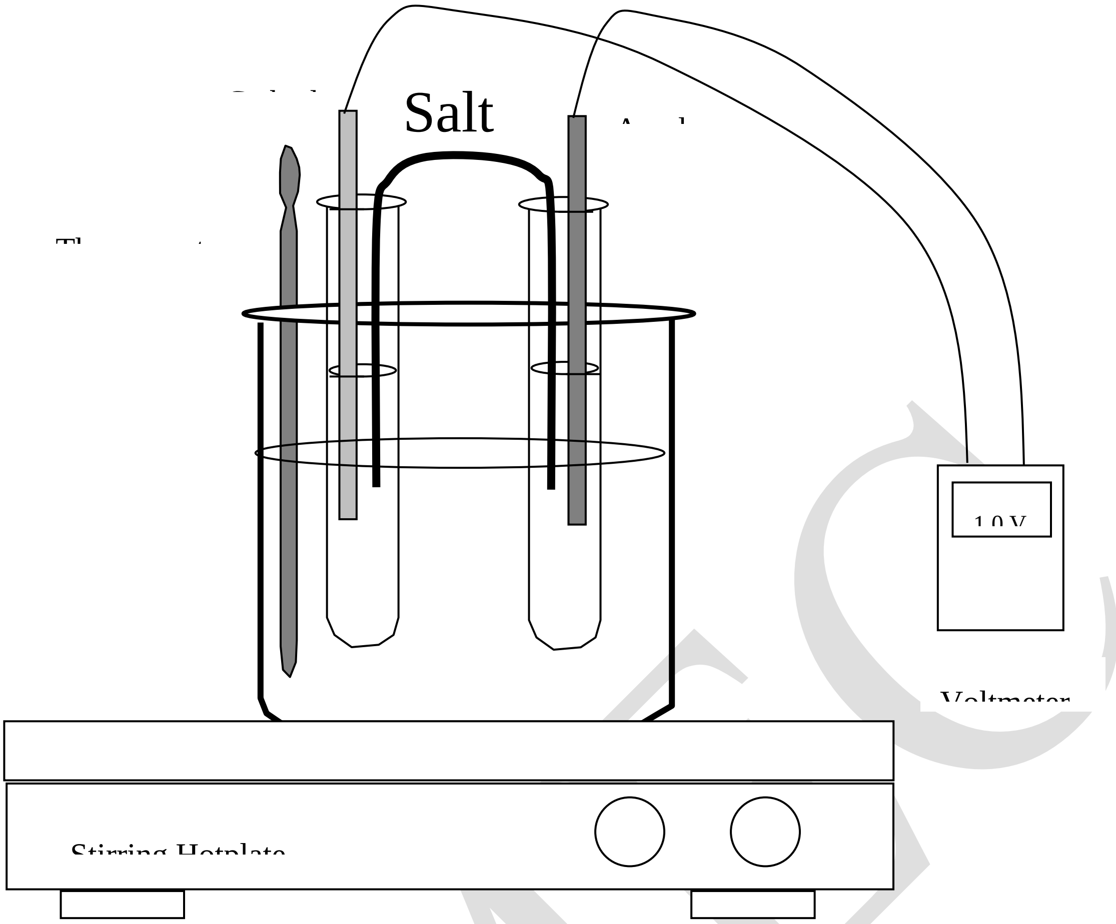


Figure 1 Electrochemical Cell

The cell voltage, or the electromotive force (abbreviated emf), is indicated on the voltmeter in volts. The cell emf is also called the cell potential. The magnitude of the emf is a quantitative measure of the driving force or thermodynamic tendency for the reaction to occur. In general, the emf of a voltaic cell depends upon the substances that make up the cell as well as on their concentrations. Hence, it is common practice to compare *standard cell potentials*, symbolized by E^{o}_{cell} . These potentials correspond to cell voltages under standard state conditions-gases at 1 atm pressure, solutions at 1 M concentration, and temperature at 25^{o}C.

Just as the overall cell reaction may be regarded as the sum of two half-reactions the overall cell emf can be thought of as the sum of two half-cell potentials, that is, the sum of the voltage of the oxidation half-reaction ($E^{o}_{(ox)}$) and the voltage of the reduction half-reaction ($E^{o}_{(red)}$)

$$E^{0}_{cell} = E^{0}_{(ox)} + E^{0}_{(red)} \qquad (2)$$

Because it is impossible to measure directly the potential of an isolated half-cell, the standard hydrogen half-reaction has been selected as a reference and has been assigned a standard reduction potential of exactly 0.000 V;

$$2H^{+}_{(1M)} \ + \ 2e^{-} \ = \ H_{2(1atm)} \quad (E^{o}_{red} \ = \ 0.00V) \qquad (3)$$

Let's look again at the Daniell cell described above. The standard half-cell potentials are:

$$\text{(Anode)} \ \ Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^{-} \quad (oxidation) \ \ E^{o}_{Zn/Zn^{2+}} \ = 0.76V$$

$$\text{(Cathode)} \ \ Cu^{2+} + 2e^{-} \ \rightarrow Cu_{(s)} \ (reduction) \ \ E_{Cu^{2+}/Cu} \ = 0.34V$$

Therefore,

$$E^{o}_{cell} = E^{o}_{(ox)} + E^{o}_{(red)}$$
$$E^{o}_{cell} = 0.76 + 0.34V$$
$$E^{o}_{cell} = 1.10V \qquad (4)$$

The complete notation scheme for a galvanic cell is written with the anode on the left and a double vertical line denoting the presence of a porous plate or salt bridge. For the Daniell cell:

$$\text{Zn} \mid \text{Zn}^{2+} \parallel \text{Cu}^{2+} \mid \text{Cu}.$$

Each electrode is connected to the voltmeter by alligator clips and metal wiring. The voltmeter measures the voltage generated by the redox reaction. The voltage reading will be positive when the electrodes are connected properly for spontaneous reaction. A spontaneous redox reaction occurs when the species with higher reduction potential is connected as the cathode. Otherwise, the voltage reading will be negative. The meter reading will be positive when the cathode is connected to the (+) outlet and the anode is connected to the (-) outlet. Physically, a negative voltage reading means that you have connected the wrong electrode as cathode. This is equivalent to reversing equation (1). When equation (1) is reversed, the measured cell potential difference becomes

E^{o}_{cell} = - 1.10 V. The absolute value of ΔE^{o}_{cell} is the same in both cases, but the sign is different. **The sign of ΔE^{o}_{cell} is positive for a spontaneous reaction and negative for non-spontaneous reaction.**

The Nernst Equation:

For measurements taken under standard conditions (1 atm, 1 M solutions), ΔE^{o}_{cell} measures the electric potential difference between the half- cells. For measurements taken under non-standard conditions (the usual laboratory situation), the Nernst equation is used to calculate ΔE_{cell}. The Nernst equation gives us the relationship between the overall cell potential difference for a redox reaction ΔE_{cell} and the concentrations of the metal-ion solutions. The Nernst equation is;

$$\Delta E_{cell} = \Delta E^{o}_{cell} - \frac{RT}{nF} \ln Q \tag{5}$$

where F is Faraday constant. R the universal gas constant, n the number of electrons transferred, and Q is the reaction quotient. When natural (ln) is converted to base ten (log) and (RT/nF) are evaluated using $R=8.315\ JK^{-1}mol^{-1}$, $T=295.15\ K$, and $F=96{,}485\ Cmol^{-1}$ the equation becomes;

$$\Delta E_{cell} = \Delta E^{o}_{cell} - \frac{0.0592V}{n} \log Q \tag{6}$$

In this form, galvanic cells are used to determine the concentration of the metal ions present under conditions other than standard conditions. If we apply the Nernst equation to equation (1) we will get

$$\Delta E_{cell} = \Delta E^{o}_{cell} - \frac{0.0592V}{n} \log \frac{[Zn^{2+}]}{[Cu^{2+}]} \tag{7}$$

Thermodynamics of Electrochemical Cell:

More than a century ago, scientists observed the effect of temperature on natural processes and formulated the laws of thermodynamics. Thermodynamics is the study of the flow of energy, especially in the form of heat, and its conversion from one form to another (for example, from chemical energy to heat energy). The laws of thermodynamics are a set of mathematical functions, which govern all forms of energy and their inter-conversion.

The *zeroth law* of thermodynamics is concerned with *temperature equilibrium;* it states that heat always flows from a hot to a cold body.

The *first law* of thermodynamics describes the *conservation of energy.* It states that energy cannot be created or destroyed; it can only be converted from one form to another.

The *second law* of thermodynamics is concerned with the *reversibility and direction* of natural events; it states that **the entropy of the universe tends to increase**. Therefore, **all spontaneous events are accompanied by an increase in the *entropy* of the universe.** Entropy (S) is a measure of disorder. The higher the entropy of a system, the lower the order of that system. For example, the entropy of helium sealed inside a balloon is lower than its entropy when is released to open space. When in the balloon, the individual helium atoms are confined to the space within the balloon. When the gas is released the atoms rush out into a less ordered state.

The *Third law* defines the *zero of entropy for a system*. It states that pure substances at *absolute zero* (0 Kelvin), the temperature at which all atomic motion ceases, have entropy of zero.

When these laws are applied to chemical reactions, they relate the equilibrium condition (whether the reaction is proceeding in the forward or reverse direction) and the temperature of the reaction to the thermodynamic functions, namely change in *enthalpy* (ΔH), change in entropy (ΔS), and change in free energy (ΔG). By studying the effect of temperature on the equilibrium condition for a chemical reaction, we can calculate these thermodynamic functions.

By examining ΔH, ΔS and ΔG in a chemical system, a wealth of information may be extracted. In thermodynamics a *system* is the particular part of the universe being studied.

Enthalpy describes changes of heat in a system. If the system absorbs heat during a given process, this process is said to be *endothermic*, and the change in enthalpy (ΔH) is greater than zero (□H > 0). On the contrary, if the system releases heat, the process is called *exothermic*, and (ΔH< 0).

As mentioned above, entropy is the measure of disorder or randomness in a system. The greater the order in a system, the lower the entropy. The lower the order in a system, the higher the entropy.

The *Gibbs Free Energy* (G) is the function derived from H and S. The change in free energy (ΔG) is a composite function that gives a measure of the spontaneity of a reaction. If ΔG < 0, a reaction will occur spontaneously. If ΔG > 0, the reaction is not spontaneous. If ΔG = 0 the system is at equilibrium. The mathematical form of ΔG is the following:

$$\Delta G = \Delta H - T\Delta S \tag{8}$$

Where T is the absolute temperature (in Kelvin). The effect of the sign of ΔH and ΔS and the effect of temperature on spontaneity of a reaction can be summarized as follows:

ΔH_{system}	ΔS_{system}	Process
-	+	Spontaneous at all temperatures
+	-	Non-spontaneous at all temperatures
+	+	Spontaneous at high temperatures
-	-	Spontaneous at low temperatures

Thermodynamics and Equilibrium:

For a general reaction or process of A and B giving products C and D :

$$aA \ + bB \quad \rightarrow \ cC \ + \ dD$$

the reaction quotient, Q, is:

$$Q \ = \frac{[c]^c[D]^d}{[A]^a[B]^b} \tag{9}$$

The ΔG of a process at any concentration of A, B, C, and D, is given by:

$$\Delta G \ = \ \Delta G^o + \ RT \ \ln \ Q \tag{10}$$

Where ΔG^O is the free energy of the reaction under the defined standard conditions of 1 atm and 1 M concentrations of reactants. ΔG is the observed change in free energy at conditions other than standard. At equilibrium Q = K_{eq}. The reaction favors neither products nor reactants at equilibrium, and ΔG = 0. Under these conditions equation (9) becomes:

$$\Delta G^o \ = -RT \ln \ K_{eq} \tag{11}$$

The cell potential of a redox process is related to the free-energy change as follows:

$$\Delta G^o \ = -nFE^o \tag{12}$$

In this equation, F is Faraday's constant, the electrical charge on 1 mol of electron 1F = 96,500 C/mol e^- = 96,500 J/V-mol e^- and n represents the number of moles of electrons transferred in the reaction. For the case when both reactants and products are in their standard states, equation (11) takes the following form:

$$\Delta G^o \ = -nFE^o \tag{13}$$

Laws of Electrolysis:

Electrolysis implies the processes which utilize electrical energy for extraction of metals (Example-Cu, Al, Zn etc) which known as **electro winning** and for purification of metals (Example-Cu, Al, Pb etc) which known as **electro refining**.

In case of electro winning, the anode is insoluble conductor while in electro refining, it is impure metal itself. The electrolyte in each case is a solution with sufficiently high electrical conductivity and solute concentration. The cathode may be pure metal or a blank of another metal.

Electrolytic dissociation of ionic media is governed by two laws, which are known as Faraday's laws of electrolysis.

Faraday's First Law:

It states that "The weight of material (W) deposited at an electrode is directly proportional to the quantity of electricity (Q) passed through the electrolyte".

Mathematically can be expressed as

$$W \propto Q \Rightarrow W \propto (c \times t) \quad [\text{Since } Q = c \times t] \tag{9.1}$$

$$\Rightarrow W = Z \times c \times t \tag{9.2}$$

[Where
c – Electric Current (in amp), t – Time (in sec.)
W – Weight deposited (in gm.), Z – Electrochemical Equivalent]

<u>**N. B.:**</u> Electrochemical Equivalent (Z): It is defined as the weight deposited by a current of 1 amp during its passage for duration of 1 sec.

Faraday's Second Law:

It states that "The weight of material (W) deposited at an electrode is directly proportional to the equivalent weight (E) of the material".

Mathematically can be expressed as

$$W \propto E \Rightarrow E \propto W \Rightarrow E = F \times W \tag{9.3}$$

$\Rightarrow F = E/W = (A/n)/W$,
$F \approx 96500$ Coulomb/gm. eq.
A – Atomic Mass, W – Weight deposited (in gm.)
n – Valency, E – Equivalent weight

Combined 1st and 2nd laws of Faraday, we have

$$W \alpha Q \times E \;\Rightarrow\; (Q \times E) \alpha W$$

$$\Rightarrow Q \times E = F \times W$$

Now putting $E = {}^{A}/_{Z}$ and $Q = (c \times t)$ in equation (9.6), we will get

$$W = Zct/nF$$

Some Important Parameters::

Current Efficiency: It is defined as the ratio of the actual mass of the substance (metal) liberated from an electrolyte by the passage of current to the mass of the substance liberated theoretically according to Faraday’s law.

Mathematically it is represented as

Current Efficiency = Theoritical amount of electricity required/Actual amount of electricity consumed

Electric Power: It is defined as the ratio of electric power used per day with actual weight of metal deposited.

Thermodynamics of Electrochemical Cells:

- An Electrochemical reaction involves coupling of chemical reaction with the flow of Electric current.
- Many metals are extracted and refined by electrolytic process (Zn, Al, Mg etc.).
- Electroplating and anodizing are employed for surface protection of metals and alloys from corrosion.
- Electrochemical reactions occur in Corrosion, Hydrometallurgy and slag-metal - reactions.
- Electrochemical method used for high temperature measurement tools.
- Batteries are Electrochemical cell.

Electrochemical cells are broadly classified into **two categories**

Galvanic Cells: In this case, stored chemical energy is converted into electrical energy.

Electrolytic Cells: In this case, stored electrical energy is used to do chemical work.

Thermodynamic studies/predictions/measurements can be done properly only for Galvanic cells. These are can be made to operate reversibly.

Daniel Cell:

Most common example of Galvanic cell is Daniel cell.

Overall Reaction: Zn(S) + CuS04(aq) = Cu(S) + ZnS04(aq)

Overall reaction (Ionic form): Zn(S) + Cu+2(aq) = Cu(S) + Zn+2(aq)

Reaction Consists of

Anodic Reaction: Zn(S) = Zn+2(aq) + 2e(0xidation) –

Cathodic Reaction: Cu+2(aq) + 2e = Cu (s) (Reduction) –

Electrolytes are ionic liquids or solids and classified as follows

Classification of Electrolytes

Sl. No.	**Electrolytes**	**Examples of current carrying Ions**
1	Aqueous Solutions	Na^+, H^+, Cl^- etc
2	Molten Salts	Na^+, K^+, Cd^+, Cl^-, F^-etc
3	Molten Slags	Ca^{+2}, Mn^{2+} etc
4	Solid Oxide Electrolytes	0^{2-}
5	Other Solid Electrolytes	Na^+, Ag^+, F^-, Li^+ etc

Aqueous solutions constitute the electrolytes in the Daniel cell. For example if we have considered aq. ZnSO4 solution, then add up some amount of H2SO4 to improve its electrical conductivity. Due to high mobility H+, it will carry major fraction of current. The reaction at cathode, primarily discharge of Zn2+ ions and deposition of Zn.

Similarly by taking molten salts at high temperature may consists of NaCl, KCl and CdCl2. But only Cd2+ will participate in electrochemical reaction.

Generally, for aqueous solutions as electrolyte, the electrochemical cell operated at room temperature. For molten salts, it is about (400-900) C. For molten slag case, it is about (1000-1500) C.

Solid Electrolyte:

In case of solid electrolytes, the operated temperature generally very high and it depends upon the nature of electrolytes. Out of many, **Zirconia (ZrO2)** is well known solid electrolyte. It is a high temperature ceramic material.

Zirconia is stable at high temperature but it undergoes some phase transformation during heating and cooling. Due to which there thermal stresses developed and that may be cause failure in service. To remove these chances, there are various oxides such as CaO, MgO and Y2O3 added and as a result melting point of ZrO2 get increased to approximately 2400 C.

Let us consider the example of ZrO2-CaO solid solution. In pure ZrO2, Zr^{4+} ions occupy cationic sites and O2- ions occupy anionic sites. So after the addition of CaO to ZrO2, some of Ca2+ replace the Zr2+ from the cationic sites and allows the movement of O2- ions. Since Ca2+ and Zr4+ are almost immobile around above (700-800) C. Thus the cell operated at high temperature.

Besides ZrO2-CaO solid electrolytes, other important solid electrolytes are ZrO2- Y2O3, ThO2-Y2O3, CaF2 doped with YF3 etc.

Thermodynamic of reversible galvanic cells:

Some electrical cell can be made to behave either as a Galvanic cell or as an electrolytic cell.

Example: Daniel Cell.

If external DC source connected to the cell having imposed voltage (Vext), that opposes that of the Daniel Cell voltage (Vcell). Then depending on magnitude of Vext and Vcell, we have two conditions

Condition-1:

Vest < Vce SS ⇒ Cell be*h*aves as Galvanic cell

Cell reaction is

Zn(S) + CuS04(aq) = ZnS04(aq) + Cu(S)

Condition-2:

$V_{est} > V_{ceSS} \Rightarrow$ Cell be*h*aves as elecrolytic cell

Cell reaction is

$\mathrm{Cu(S) + ZnS04(aq) = CuS04(aq) + Zn(S)}$

In an electrolytic cell, chemical reaction occurs only if current allowed to flow through the cell. But if no current flow i. e. circuit becomes open then at that time voltage is known as emf or electromotive force of the Galvanic cell.

Reversible Galvanic cell possible if and only

Use of a voltmeter of very high resistance makes current flow negligible.

Impose voltage from external source, $V_{est} \cong V_{ceSS}$ i. e. emf of the cell and as a result current flow is negligible.

Relation between cell emf (e) and free energy of cell reaction (∆g):

From a reversible process

$$dG = VdP - SdT - \eth W'$$

[Where, W’ – Work done other than work done against pressure]

At constant P and T,

$$dG = -\eth W'$$

In case of a reversible Galvanic cell,

$\eth W' = E\eth q$

$$(\text{Since } W = VIt = Eq \Rightarrow \eth W = E\eth q)$$

[Where

E – Cell Emf

$\eth q$ − Infinitesimal quantity of electric charge transformed across the cell due to the chemical reaction in the cell.]

Again from the Faraday's law of electrolysis,

$\eth q = ZFdn$

[Where, n – Number of moles]

Putting the value of ðq in the above equation, we get

$\eth W' = E \times (ZFdn) = ZFEdn$

Again putting this equation in free energy equation, we get

$dG = -\eth W' = -ZFEdn$

So for 1 mol of the above equation becomes

$dG = -ZFE \Rightarrow \Delta G = -ZFE$

Similarly, at standard state equation becomes

$dG^0 = -ZFE^0 \Rightarrow \Delta G^0 = -ZFE^0 \qquad (9.18)$

Since we know

$\Delta G = \Delta G0 + RT \ln J$

Now using the above equations we get

$-ZFE = -ZFE^0 + RT \ln J$

$\Rightarrow -E = -E^0 + (RT/ZF) \ln J$

$\Rightarrow E = E^0 - (RT/ZF) \ln J$ It is known as Nernst's equation. It can be written as

$E = E^0 - 2.303(RT/ZF) \log J$

Introduction to metallurgical kinetics: heterogeneous reaction kinetics: gas-solid, solid –liquid, liquid – liquid and solid-solid systems. Empirical and semi-empirical kinetics, concept of Johnson – Mehl equation, Thermal analysis.

TOPOCHEMICAL REACTION:

It is defined as the solid-gas reaction or phase boundary controlled reactions that **occur by the movement of well-defined interface**.

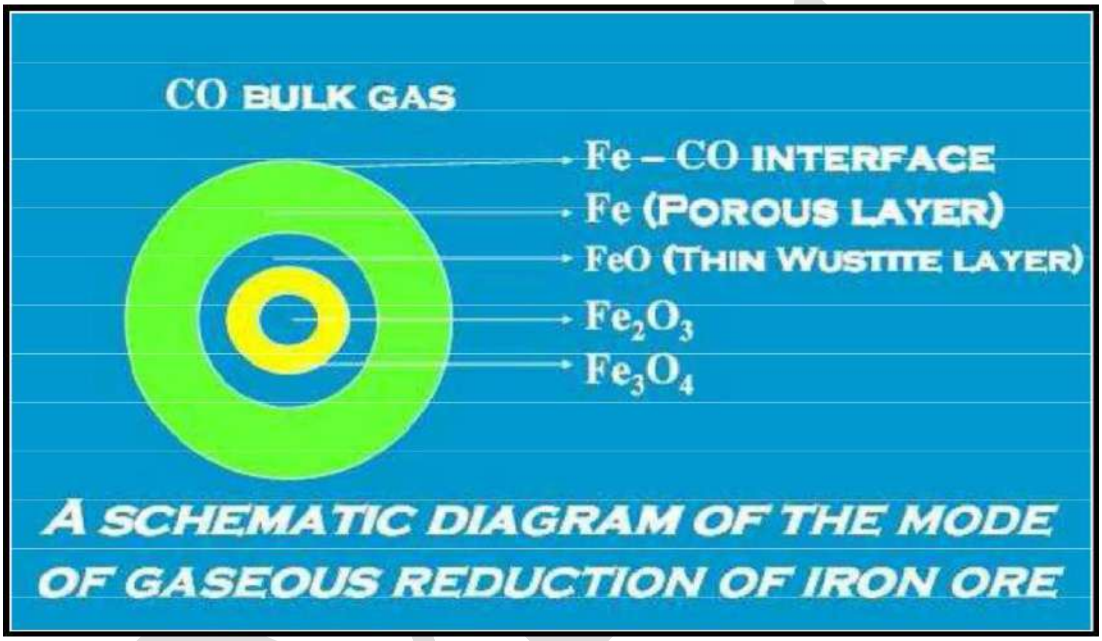


Fig represents a schematic diagram of Gaseous reduction of iron ore, where reduction occurs by using CO gas.

Steps of the topochemical reduction:

Diffusion of reduce gas (CO, H2) from the bulk gas phase to the ore-pellet through surface film.

i. Diffusion of reduce gas from ore-pellet to reductant layers.

ii. Chemical reaction at the interface

iii. Diffusion of product gas (CO2, H2O) from reductant layer to ore-pellet

iv. Diffusion of product gas from ore-pellet to surface film.

Most of the metallurgical reactions are heterogeneous. The main types of heterogeneous reactions are discussed below:

- **(i)** **Gas – Solid :** Reaction of hematite (Fe2O3) with CO or H2. Or Oxidation of Metals in atmosphere containing oxygen.
- **(ii)** **Gas –Liquid:** Gaseous reduction in hydro-metallurgy.
- **(iii)** **Liquid – Liquid:** Metal – slag reaction
- **(iv)** **Liquid – Solid:** Leaching and corrosion reactions
- **(v)** **Solid – Solid:** Metallothermic reductionic reaction

Dercivations

1. Spherical Particle (Topochemical reaction).

Rate of reaction $\propto$ Concentration of fluid.
$\propto$ Area of reaction.

$$-\frac{dW}{dt} \propto C$$
$$\propto A$$

$$\Rightarrow -\frac{dW}{dt} \propto CA$$

$$\Rightarrow -\frac{dW}{dt} = KCA$$ K is the reaction rate constant.

for Sphere, $A = 4\pi r^2$

$W = V \times \rho$.

$= \frac{4}{3}\pi r^3 \times \rho$.

Initially, reaction has not started, so $C = 1$.

Putting these values in above equation, we get

$$-\frac{d}{dt}\left[\frac{4}{3}\pi r^3 . \rho\right] = K . 4\pi r^2 . 1$$

$$\Rightarrow -\frac{dr}{dt} = \frac{3K}{\rho}$$

Initial radius of the unreacted reactant sphere is r_0. As the reaction takes place, the product layer develops and the reactant layer decreases. Let the final reactant sphere radius is r_f. So integrating the above equation from ~~to~~ $r = r_0$ $(t=0)$ to $r = r_f$ $(t=t)$ we have.

$$\int_{r_0}^{r} -dr = \frac{K'}{\rho}\int_0^t dt$$

$$\Rightarrow r_0 - r = \frac{K'}{\rho} . t \quad \text{———} ①$$

If the sphere is a metal oxide (e.g. reduction of hematite) and the fluid is a reductant, the weight of the spherical metal oxide decreases with time due to the loss of oxygen during reduction. So degree of reduction α =

$$\frac{\text{Weight loss}}{\text{Initial weight}} = \frac{W_0 - W_f}{W_0} = 1 - \frac{4/3\,\pi r^3 . \rho}{4/3\,\pi r_0^3\,\rho}$$
$$= 1 - \left(\frac{r}{r_0}\right)^3$$

$$\Rightarrow \left(\frac{r}{r_0}\right) = (1-\alpha)^{1/3} \Rightarrow r = r_0 (1-\alpha)^{1/3} \quad \text{——} ②$$

Putting eqn ② in eqn ①.

$$r_0\left[1-(1-\alpha)^{1/3}\right] = \frac{k't}{\rho} \quad ③$$

It is known as McKewan Model.

If the weight loss is measured for different times. measured from experimental data, and ~~as~~ $\left[1-(1-\alpha)^{1/3}\right]$ is plotted with time and it gives a straight line as per eqn ③, then it obeys the McKewan reaction model.

2. Flat Plate (Topo chemical)

Now, let us consider a flat plate of reactant having area A and thickness d. During the reaction, the product layer forms and it increases with increase in reduction.

So the rate of reaction can be written as.

$$\frac{dw}{dt} = \frac{DAC}{y}$$

where W is the weight of PRODUCT layer

D is Diffusion Coefficient

A is the Surface area of reaction.

C is Concentration.

$$W = v \times \rho.$$
$$= (A.y).\rho$$

Putting this value in above equation.

$$\frac{d(Ay\rho)}{dt} = \frac{DAC}{y} = \cancel{\left(\frac{DC}{\rho}\right)\frac{1}{Ay}}$$

where $K = \frac{DC}{\rho}$ = Constant

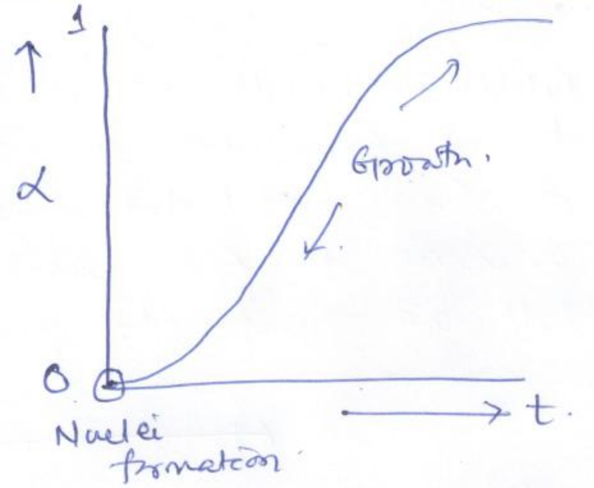
$$\Rightarrow \frac{dy}{dt} = \frac{K}{y}$$

$$\Rightarrow y\,dy = K.dt$$

$$\Rightarrow y^2 = K't.$$

It is called parabolic law.

3. Nucleation and Growth Model. or Johnson-Mehl's equation.



- First nuclei of product forms
- Then the nuclei of the product grows in size.

The relation between rate of reaction and time

$$\frac{d\alpha}{dt} = k^n t^{n-1} (1-\alpha)$$

$$\Rightarrow \int \frac{d\alpha}{1-\alpha} = k^n \int t^{n-\cancel{1}} \cdot dt$$

$$\Rightarrow -\ln(1-\alpha) = k^n \cdot \frac{t^n}{n} = \left(\frac{k^n}{n}\right) \cdot t^n$$

$$= k'^n t^n.$$

~~Taking~~

$$\Rightarrow \log\left(\frac{1}{1-\alpha}\right) = \frac{1}{2.303} \cdot (k't)^n$$

where $k' = \frac{k}{n^{1/n}}$

Taking log, $\log\log\left(\frac{1}{1-\alpha}\right)$

$$= n\log k' + n\log t - \log(2.303)$$

It is the expression for Johnson-Mehl equation.

Homogeneous	Heterogeneous
- Takes place within one phase Example :- $N_2 + H_2 = NH_3$	- Involves more than one Phase Example: Gas - Solid reaction. Reduction of Hematite ore by Co gas.
- Reaction occurs in bulk	- Reaction occurs at the interface.
- Rate of Chemical reaction is proportional to the volume of phase	- Rate is proportional to the area of the interface.
- No adsorption and desorption involved.	- Involves absorption of reactants into the interfacial layer.
- Reaction Mechanism is not Complex	- Reaction mechanism is Complex.

Molecularity	Order
- It is the number of reacting species	- It is the sum of the power of the Concentration terms in the rate expression.
- Theoretical value	- Experimentally determined.
- Positive integral value 1, 2, 3 --- n	- It can be negative, positive and fractional value.
- Doesn't tell about the Mechanism	- Gives clue about mechanism.
- Doesn't Change with temperature & pressure	- May change with temperature & pressure.

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B. Tech
PCMT 4202

Third Semester Regular Examination – 2014

METALLURGICAL THERMODYNAMICS AND KINETICS

BRANCH(S) : MM, MME

QUESTION CODE : H 412

Full Marks – 70

Time – 3 Hours

Answer Question No. **1** *which is compulsory and any* **five** *from the rest.*
The figures in the right-hand margin indicate marks.

1. Answer the following questions : 2×10
   - (a) What do you mean by Extensive and intensive properties ?
   - (b) Define Reversible and irreversible process.
   - (c) Define Activation energy and Internal energy.
   - (d) What is the basic principle of Differential Thermal Analysis (DTA) ?
   - (e) What do you mean by standard state of a system ?
   - (f) What is Electro Chemical Equivalent ?
   - (g) What is Limiting Current Density ?
   - (h) What is Henry's law ?
   - (i) What is phase rule ?
   - (j) State second law of thermodynamics.
2. Write short notes on any two : 5×2
   - (a) One weight percentage standard state
   - (b) Thermal Analysis
   - (c) Excess function
   - (d) Partial molal quantities
   - (e) Auxiliary functions.

P.T.O.

(a) Derive Gibbs Helmholtz equation $\left[\frac{\partial(\Delta G/T)}{\partial T}\right]_P = -\Delta H/T^2$ 5

(b) Calculate the standard heat of formation of solid PbO produced from liquid Pb and O_2 gas at 800 K. The melting point of Pb is 600 K and its latent heat of fusion is 4.81 kJ/mol. 5

Given :

$\Delta H^\circ_{f}, 298, Cr_2O_{3(s)} = -1120.3$ kJ/mol,

$\Delta H^\circ_{f}, 298, Al_2O_{3(s)} = -1674.0$ kJ/mol

$Cp, Al_{(s)} = 20.7 + 12.4 \times 10^{-3}T$ J/K/mol

$Cp, Al_2O_{3(s)} = 106.6 + 17.8 \times 10^{-3}T - 28.5 \times 10^{5}T^{-2}$ J/K/mol

$Cp, Cr_{(s)} = 24.4 + 9.87 \times 10^{-3}T - 3.7 \times 10^{5}T^{-2}$ J/K/mol

$Cp, Cr_2O_{3(s)} = 119.4 + 9.2 \times 10^{-3}T - 15.6 \times 10^{5}T^{-2}$ J/K/mol

$2Pb + O_2 = 2PbO$

$\Delta H^\circ_{T} = \Delta H_{T_1} + \int_{T_1}^{T_n} Cp$

4. (a) What is an ideal solution ? Explain the important characteristics of an ideal solution in terms of : 5

(i) Thermodynamic chemical potential

(ii) Enthalpy.

(b) Calculate the standard heat of reaction of $Fe_2O_3 + 3CO = 2Fe + 3CO_2$ from the following data : 5

$3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2$;

$\Delta H^\circ_{298} = -12.7$ k.Cal

$Fe_3O_4 + CO = 3FeO + CO_2$;

$\Delta H^\circ_{298} = +9.8$ k.Cal

$FeO + CO = Fe + CO_2$;

$\Delta H^\circ_{298} = -4.4$ k.Cal

5. (a) Discuss topo-chemical pattern of iron ore reduction. Discuss the significance of activation energy in a chemical reaction. 6

(b) Calculate the entropy of liquid iron at its melting point, 1808 K, given that for iron : 4

$L_f = 15.4$ KJ/mol, $S^\circ_{298, Fe(s)} = 27.9$ J/K/mol and Cp = 25.2 J/K/mol.

OR (of b.)

Contd.

Calculate the standard entropy change for the reaction

$Cr_2O_3(s) + 3C(s) = 2Cr(s) + 3CO(g)$

Given :

S°_{298}, $Cr_2O_{3(s)}$ = 83.17 J/K/mol

S°_{298}, $C_{(s)}$ = 5.69 J/K/mol

S°_{298}, $Cr_{(s)}$ = 23.76 J/K/mol

S°_{298}, $CO_{(g)}$ = 197.90 J/K/mol

6. (a) What is fugacity ? What do you mean by standard state of a system ? 5

   (b). State Henry's Law. Justify "the fugacity of the solute in real dilute solution is proportional to its mole fraction". 5

7. Derive the following thermodynamic relations (any two) : 5×2

   (a) $Cp - Cv = R$

   (b) $P_1(RT_1/P_1)^\gamma = P_2(RT_2/P_2)^\gamma = \text{Constant}$

   (c) $dU = T.dS - P.dV$

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

8. What is entropy ? Discuss important characteristics of entropy. Derive expression for entropy of a perfect gas ($S = Cp \ln V + Cv \ln P + \text{constant}$). 2+4+4

OR

Derive Maxwell's Relations. From the following data determine which metal has greater probability of oxidation in presence of steam at 827°C and 1 atm pressure. 6+4

(a) $NiO(s) + H_2(g) = Ni(s) + H_2(g)$, $\Delta G^\circ = (-2301 - 42.59\,T)$ J

(b) $1/3\, Cr_2O_3(s) + H_2(g) = 2/3 Cr(s) + H_2O(g)$, $\Delta G^\circ = (126{,}566 - 30.67T)$ J

Registration No: | | | | | | | | | | |

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B.TECH
PMT3I102

3rd Semester Regular Examination 2016-17
METALLURGICAL THERMODYNAMICS AND KINETICS
BRANCH(S): METTA, MME
Time: 3 Hours
Max Marks: 100
Q.CODE: Y546

Answer Part-A which is compulsory and any four from Part-B.
The figures in the right hand margin indicate marks.

Part – A (Answer all the questions)

Q1 **Answer the following questions:** (2 x 10)

a) In an Ellingham diagram, the standard free energy change ΔG^0 for the oxidation reaction of a metal M given by: $xM_{(s)} + O_2 = M_xO_2(S)$, is plotted as a function of temperature. The slope of this line is positive because
[✓ (A)] ΔS^0 is positive (B) ΔS^0 is negative (C) ΔH^0 is positive (D) ΔH^0 is negative

b) The entropy becomes zero at 0^0C for a
(A) Pure element [✓ (B)] perfect crystal [✓ (C)] random solid solution (D) none of these

c) The slope of the Gibbs energy G versus T curve at 0K and constant pressure is
(A) 0 (B) H_0 [✓ (C)] S_0 (D) - H

d) Which one of the following is NOTan intensive property?
(A) Temperature(B) Pressure[✓ (C)] Volume(D) Refractive index

e) The specific heat (Cp) of pure iron expressed in J/(mol.K) as a function of temperature T (in K) is given as:
$Cp = 17.49 + 24.77 \times 10^{-3}\, T$
What is the change in the enthalpy of pure iron (in J/mol) when it is heated from 25°C to 700°C? ...11806.045J/mol

f) If two systems P and Q are in thermal equilibrium with a third system M, then P and Q will also be in thermal equilibrium with each other. This is following
(A) First law of Thermodynamics (C) Third law of Thermodynamics (B) Second law of Thermodynamics [✓ (D)] Zeroeth law of Thermodynamics

g) A heat engine takes in 900 J of heat from a high temperature reservoir and produces 300 J of work in each cycle. What is its efficiency?...33.33%

h) Entropy change for a reversible process is ..zero (0).

i) Enthalpy change during a constant-pressure process is equal to ..$dq = du + dw$

j) The value of activity coefficient for ideal Raoultian behaviour is ....1.....

$F = U - TS$

$U = \boxed{F} + TS$

Q2 **Answer the following questions:** **(2 x 10)**

a) Define Henry's law.

b) Draw the curve showing variation of (i) C_p~T, (ii) H~T(iii) G~T.

$C_p = \left(\frac{\partial H}{\partial T}\right)_p$

c) Define activity of a component.

d) What is Helmholtz free energy?

$y = \cancel{mx} + C$

e) Draw the schematic of a heat engine.

$\Delta U = T_H - T_L$

f) What is spontaneous process?

g) Define second law of thermodynamics in terms of entropy

h) Define thermal analysis? What are the different techniques of thermal analysis?

i) A first-order reaction proceeds until 75% of reactant A is consumed within 10 min. Determine the rate constant.

j) What is the significance of Johnson-Mehl equation?

Part – B (Answer any four questions)

Q3 a) Ten litres of a monatomic ideal gas at 25^0C and 10 atm pressure are expanded to a final pressure of 1atm. The molar heat capacity of the gas at constant volume, C_v is 3/2R and is independent of temperature. Calculate the work done, the heat absorbed and the change in U and in H for the gas if the process is carried out (1) isothermally and reversibly, and (2) adiabatically and reversibly. Having determined the final state of the gas after reversible adiabatic expansion, verify that the change in U for the process is independent of the path taken between the initial and final states by considering the process to be carried out as **(10)**

i. An isothermal process followed by a constant volume process

ii. A constant volume process followed by an isothermal process

iii. An isothermal process followed by a constant pressure process

iv. An constant volume process followed by a constant pressure process

v. A constant pressure process followed by a constant volume process

b) Draw the phase diagram for a one component system and explain the various regions in the curve **(5)**

Q4 a) Ten moles of ideal gas, in the initial state P_1= 10atm, T_1= 300K are taken round the following cycle: **(10)**

i. A reversible change of state along a straight line path on the P-V diagram to the state P=1atm, T=300K,

ii. A reversible isobaric compression to V=24.6 liters

iii. A reversible constant volume process to P=10atm.

How much work is done on or by the system during the cycle? Is this work done on the system or by the system?

b) Two moles of a monoatomic ideal gas are at contained at a pressure of 1atm and a temperature of 300K. 34,166 joules of heat are transferred to the gas, as a result of which the gas expands and does 1216 joules of work against its surroundings. The process is reversible. Calculate the final temperature of the gas. **(5)**

(10)

Q5 a) Five moles of an ideal gas are contained adiabatically at 50atm pressure and 300K. The pressure is suddenly released to 10atm, and the gas undergoes an irreversible expansion during which it performs 4000 joules of work. Shoe that the final temperature of gas after the irreversible expansion is greater than that which the gas would attain if the expansion from 50 to 10 atm has been conducted reversibly. Calculate the entropy produced as a result of the irreversible expansion.

The constant volume molar heat capacity of the gas C_v has the value 1.5R.

(5)

b) The initial state of one mole of a monoatomic ideal gas is P=10 atm and T= 300K. Calculate the change in entropy of the gas for (a) an isothermal decrease in the pressure to 5atm, (b) a reversible adiabatic expansion to a pressure of 5atm, (c) a constant volume decrease in the pressure to 5 atm.

(10)

Q6 a) Calculatetheheatofreactionofchlorinationofzirconiumoxideat25°C (298K)and777°C(1050K),accordingtothefollowingreaction:

$ZrO_2+2Cl_2+C=ZrCl_4+CO_2$.

Given:For $ZrCl_4$:ΔH°_{298}=-234.7kcal/mole(-931.98kJ/mol)

Cp= 133.55-12.18X 10^5T^{-2}J/K/mol).

For CO_2:ΔH°_{298}=-94.05kcal/mole(-393.50kJ/mol)

Cp= 44.14+9.04X10^{-3}T-8.58X10^5T^{-2}J/K/mol).

ForZrO_2: ΔH°_{298}=-259.5kcal/mole (-1,085.75kJ/mol).

Cp= 69.62+7.53X10^{-3}T-14.06x10^5T^{-2}J/K/mol)

ForCl_2:Cp= 36.90-0.25x10^{-3}T-2.85x 10^5T^{-2}J/K/mol).

ForC:Cp= 17.15+4.27x10^{-3}T-8.79x10^5T^{-2}J/K/mol

(5)

b) Calculate the entropy change of the Universe in isothermal freezing of 1g-mole of super cooled liquid gold at 1250 K, from the following data for gold.

T_m= 1336K, ΔH_m^0 (at 1336K)= 12.36 x 10^3 J/mol

$C_p(S)$= 23.68 + 5.19 x 10^{-3} T J/mol/K

$C_p(S)$= 29.29 J/mol/K

(10)

Q7 a) Al_2O_3 which melts at 2324K, and Cr_2O_3, which melts at 2538K form complete ranges of solid and liquid solutions. Assuming that $\Delta S_m{}^0{}_{Cr2O3}$= $\Delta S_m{}^{0Al2O3}$, and that the solid and liquid solution in the system Al_2O_3-Cr2O3 behave ideally, calculate

i. The temperature at which equilibrium melting begins when an alloy of X_{Al2O3}=0.5 is heated

ii. The composition of the melt which first forms

iii. The temperature at which equilibrium melting is complete

iv. The composition of last formed solid.

(5)

b) The isotropic composition of lead in atomic percent is

Atomic weight	Atomic percent
204	1.5
206	23.6
207	22.6
208	52.3

Calculate the molar configurational entropy of lead.

Q8 **a)** At 700K, the activity of Ga in a liquid Ga-Cd solution of composition X_{Ga}=0.5 has the value 0.79. On the assumptions that liquid solutions of Ga and Cd exhibit regular solution behaviour, estimate the energy of the Ga-Cd bond in the solution. The molar enthalpies of evaporation of liquid Ga and liquid Cd at their melting temperatures are, respectively, 270000 and 100000J. **(10)**

b) At 1300K, the Emf of the following cell is 0.60 V. **(5)**

Pb(pure liquid)/ Liquid(PbO-SiO_2)/Pt(s), O_2(g)(P_{O_2}= 1atm)

Given: $\Delta G^0 = -$ 88,800J mol^{-1} at 1300K for the reaction

Pb(l) + ½ O_2(g) = (PbO)

Calculate the activity and the activity coefficient of PbO in the PbO-SiO_2 electrolyte.

Q9 **a)** With the help of a PV diagram of a Carnot cycle derive the efficiency of Carnot cycle taking ideal gas as the working substance. With the help of the efficiency derive the definition of second law of thermodynamics.You are now operating a Carnot engine at 40% efficiency, which exhausts heat into a heat sink at 298 K. If you want to increase the efficiency of the engine to 65%, to what temperature would you have to raise the heat reservoir? **(10)**

b) Derive the Maxwell relations. **(5)**