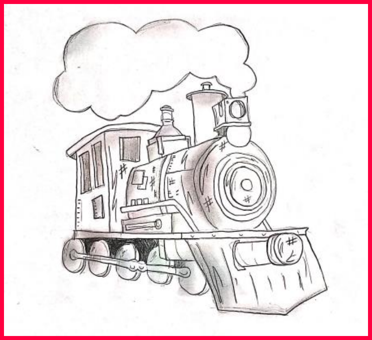
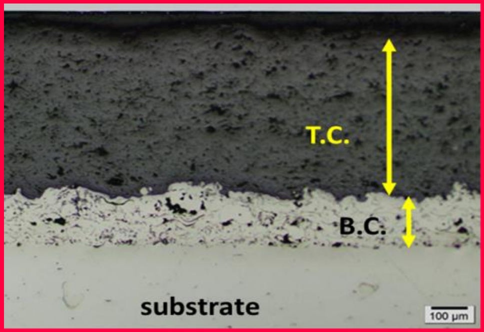
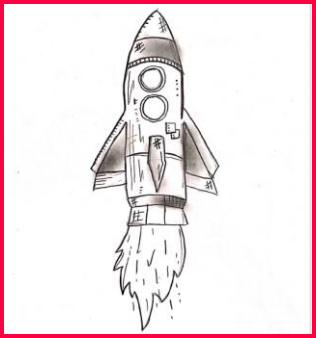
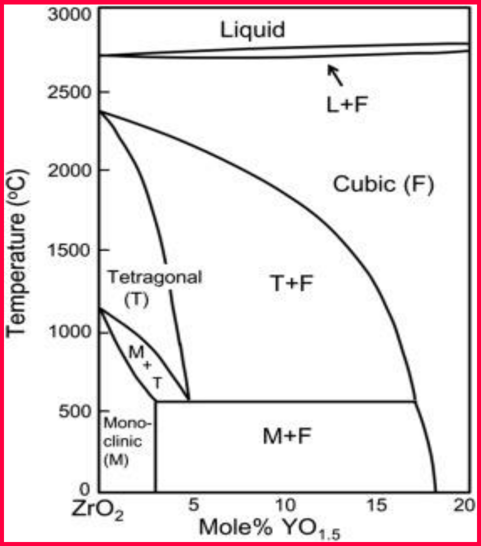
Basics of
Materials Thermodynamics









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To

Our parents

Itaet Husain & Asia Begum
Qamar-ud Din & Bilquees Akhter

And

Our grand children

Maryam, Mustafa, Rayan, Baaqir, Rania
Zoya, Osman

Preface

While teaching thermodynamics to the engineering students for almost a decade, authors felt that students regard Materials Thermodynamics as a difficult subject. This is partly due to the non-availability of books dealing with the basics of this subject without going into the details not required by the beginners. Keeping this in mind, authors have prepared this book which can provide sound footing to the students beginning their studies in this subject. This book, which may be treated as a textbook for the first course in Materials Thermodynamics, focuses on the basic principles with practical applications. Extensive illustrations have been included to explain the concepts involved. A large number of practice problems have been provided to facilitate the students in understanding the concepts.

We would like to express our gratitude to all our students whose inquisitiveness helped us in preparing this book. Our special thanks to the engineers at the Propulsion Engineering And Research Lab (PEARL), in particular Abdul Moeez, Ali Asgher, Muzna Tariq and Suniya Sadullah Khan whose keen interest was a great help in preparation of the manuscript.

Contents

Chapter 1

Thermodynamics of Materials

Learning Outcomes:

Student should be able to explain

- What is Materials Thermodynamics.
- What are the main objectives of Materials Thermodynamics.
- Why Materials Thermodynamics is a relatively new subject.
- The basic concepts like system, surrounding, component, phase.

We start with a brief on the need of materials thermodynamics. Then we discuss few concepts necessary for the building of further understanding of materials behavior. Basic definitions of system and its surrounding, state of a system, intensive and extensive properties, components and phases in a system will be stated.

1.1 Introduction

The word 'Thermodynamics' consists of two parts: 'thermo-' meaning heat and '-dynamics' meaning power or work. So, it is the relation between heat (Q) and work (W). For this interaction, we require a system whose internal energy (U) may also change in the process. So, thermodynamics is the relationship in Q, W and U. Realizing that U may not be useful in most situations, concepts of other energy terms like enthalpy and free energy (H, A, G) and entropy (S) are introduced.

Thermodynamics may, therefore, be regarded as the study of changes in heat and various other forms of energy during different processes. Thermodynamics of materials is basically the study of the behavior of materials and the effect of external influences on their characteristics.

A basic question we confront in Physical Sciences is, “Will a process occur?” Thermodynamics tells us whether a process can occur or not under the given conditions. A 'Process' is a much-generalized term which may include physical changes (such as melting, boiling, mixing, etc.) or chemical changes (such as decomposition, oxidation, reduction, etc.). If thermodynamics says that a process cannot occur, it will never occur and we have to change the conditions if we are interested in that particular process. On the other hand, if thermodynamics says that a process can occur, it may or may not occur. Sometimes kinetic factors may be limiting the process and some activation energy may be required to initiate the process or a catalyst may be required to alter the rate of change.

For some processes, it is easy to determine whether they will occur or not. For example, water will flow from a higher point to a lower point or iron will get rusted if left in moist air. However, most of the processes need criteria to find whether a process can occur or not under the given conditions and if not, what conditions should be changed so that it could occur. This is the main objective of the materials thermodynamics.

While thermodynamics generally deals with the interplay of heat and work, materials thermodynamics covers the phase equilibria in single and multicomponent systems, the behavior of solutions, metal extraction and refining, the interaction of materials with the environment, defects in materials, the behavior of surfaces, interfaces and other phase boundaries, etc. It is a relatively new subject as it stemmed from Chemical Thermodynamics after its firm establishment. In addition, many processes in Materials Engineering occur at high temperature and generating data for such processes is generally difficult and has remained a slow process.

Materials Thermodynamics is the scientific study that overlaps the areas of materials science and thermodynamics. Materials science is the study of relationships among the compositions, processing, structures, properties, and performance of materials. If we know this relationship, we can critically analyze the relative performance of materials in a given application. The main characteristics of the structure of a material and the processing method taken together and related through the laws of thermodynamics and kinetics, govern a material's microstructure, and dictate its properties and performance. Thermodynamics of materials defines the relationships between material and energy and describes how the properties of materials are controlled by thermodynamic principles. Thermodynamics of materials is thus a vital aspect of materials science and engineering.

Before the works of Gibbs and Maxwell, chemistry was considered an empirical science. These two scientists changed the very nature of chemistry by "deriving mathematical laws governing behavior of matter undergoing physical or chemical change". J. W. Gibbs was a professor of Mathematical Physics at Yale (1871-1903). In 1876-78, Gibbs published a series of papers entitled 'On the equilibria of heterogeneous substances'. This work established the foundations of chemical thermodynamics. Gibbs introduced the terms of maximum work and free energy. He talked about spontaneity criteria, chemical equilibrium, phase equilibria, solutions, adsorption, energy changes in electrochemical cells, etc.

1.2 Some Basic Concepts

Some concepts which are necessary to understand the basics of materials thermodynamics are now described.

1.2.1 System & Surroundings

A portion of matter under consideration is known as a system and everything around the system is known as its surroundings, Figure 1.1. The system is separated from its surrounding by a boundary.

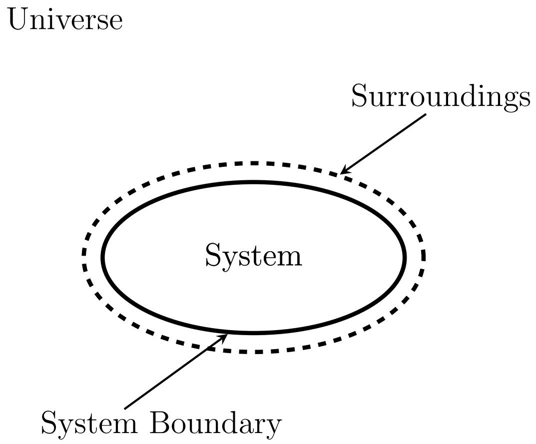


Figure 1.1: Illustration of System, Boundary, and Surrounding

The system may be an open system, closed or isolated type as depicted in Figure 1.2. An open system allows the exchange of mass and energy with its surroundings. A closed system only allows the exchange of energy. In an isolated system, neither mass nor energy is allowed to flow from or into the system.

We are basically interested in changes occurring in a system and would like to restrict our calculations to the system only. Accompanying changes in the surroundings are difficult to handle and thus we would like to develop mathematical relations describing the behavior of the system only. In this contest, we first deal with a simple closed system such as a cylinder with movable piston containing one mole of an ideal gas. After developing basic thermodynamic relations and criteria, we open the system where quantities (moles) of various species may change such as mixing or solution making. Here the concept of chemical potential is introduced and the principles governing the equilibrium of phases in contact are discussed. Next, we deal with reacting systems. At this stage, we will have sufficient capability to deal with electrochemical processes, surface energies, defects in solids, etc.

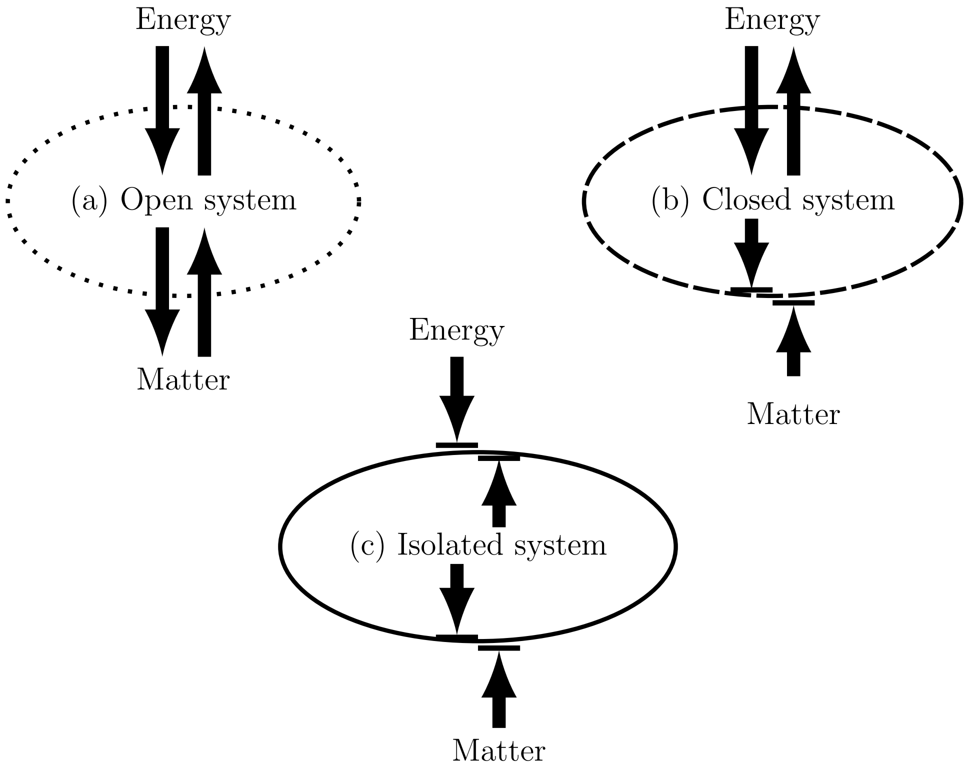


Figure 1.2: (a) Open System may transfer energy and mass to the surrounding, (b) closed system may transfer only energy to the surrounding and (c) isolated system neither exchanges energy nor matter with the surrounding.

1.2.2 State of a system

State is the condition of a system described by its properties. State of a system is generally described by the state variables such as Pressure (P), Temperature (T), Volume (V).

Microscopic State: If properties of the constituents of a system like atoms, molecules, etc., are known, these detailed properties would describe the microscopic state of the system. This may include the nature and number of various types of particles, their energy distribution and interactions among the particles. The microscopic state is then related to the overall behavior of the system. Since the statistical means are used to compute the average behavior of particles in this case, this type of thermodynamics is known as statistical thermodynamics.

Macroscopic State: When properties of the constituent particles are not available, the system may be treated as a continuum and is described macroscopically through bulk properties like pressure, volume, temperature, and compositions. These properties are easy to visualize and measure. The type of thermodynamics in which macroscopic properties are dealt is known as classical thermodynamics. We will generally be dealing with classical thermodynamics which involves easily measurable properties. Only in some cases (such as entropy of mixing and defects in solids), reference will be made to the statistical thermodynamics involving microscopic states. It should be noted that both the approaches lead to the same conclusions in a given situation and various attempts are made to show that both the approaches provide similar results.

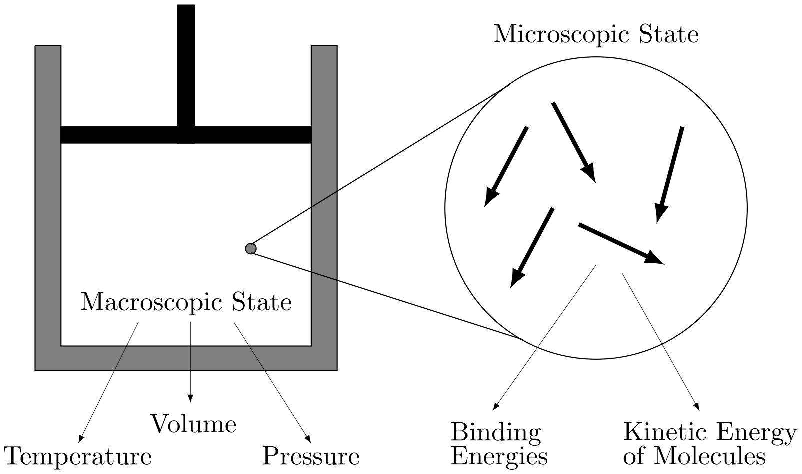


Figure 1.3: An illustration to describe macroscopic and microscopic states of a system

A relation among the state variables is referred to as the Equation of State.

$$P = f(V, T, n)$$

The ideal gas law and the Van der Waal equation are examples of the equation of state for ideal gases and real gases, respectively and are given below

$$PV = nRT \tag{1.1}$$

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \tag{1.2}$$

Where P = Pressure, V = Volume, T = Temperature, n = number of moles, R = gas constant, 'a' and 'b' are Van der Waal's constants related to molecular attractions and volume of molecules, respectively. It may be noted that, in general, for a system of fixed composition, we need to describe only two variables and the third one is automatically fixed. In other words, thermodynamic state of a given system is completely described when values of two independent state variables are fixed.

1.2.3 Extensive Properties

These are the properties that depend upon the EXTENT (amount and size) of the system. Some examples of extensive properties include mass, volume, energy, entropy, etc. Extensive properties can be easily handled using rules of algebra. For example, if enthalpy of one mole of aluminum oxide is -1687 kJ then the enthalpy of two moles of aluminum oxide will be -3374 kJ.

1.2.4 Intensive Properties

The properties which are independent of the amount or size of the system are called intensive properties. Density, pressure, temperature, etc. are some examples of intensive properties. It should be noted that whereas volume, mass, heat capacity are extensive properties; molar volume, density (mass/volume), molar heat capacity are intensive properties, as the ratio of two extensive properties will provide an intensive property.

1.2.5 Components

Chemical Species of the fixed composition are known as components in a thermodynamic system. The component may be an element such as Fe, C, or compound such as H_2O, Fe_3C, $NaCl$, Cr_2O_3 and Al_2O_3. Solutions are not regarded as components. Unary systems have only one component e.g., water, CO_2 . Binary system is the one having two components as its constituents, for example, $Fe - Cr$, $H_2O - NaCl$. Ternary systems have three components, e.g. austenitic stainless steel may be regarded as a three component ($Fe - Cr - Ni$) system.

1.2.6 Phase

A finite volume (portion) in a physical system within which properties are uniform is called a phase. Within a phase there are no abrupt changes in properties from one point to another. Two phases are separated by a phase boundary. In simple terms, a phase is a portion of matter having uniform properties. The system having one phase is termed as homogeneous while a system having more than one phase is termed as a heterogeneous system. Whereas gases generally constitute single phase, homogeneous liquid solution and solid solution are also regarded as single phase. For a single phase, we need homogeneous distribution at molecular or atomic level. In solids, each crystal structure will constitute a separate phase and different crystal structures mean different phases. For instance α $Pb - Sn$ alloy is a homogeneous system and has only one phase α whereas the Eutectic $Pb-Sn$ alloy is heterogeneous system and has two phases α and β which generally occur as alternating layers as shown in Figure 1.4.

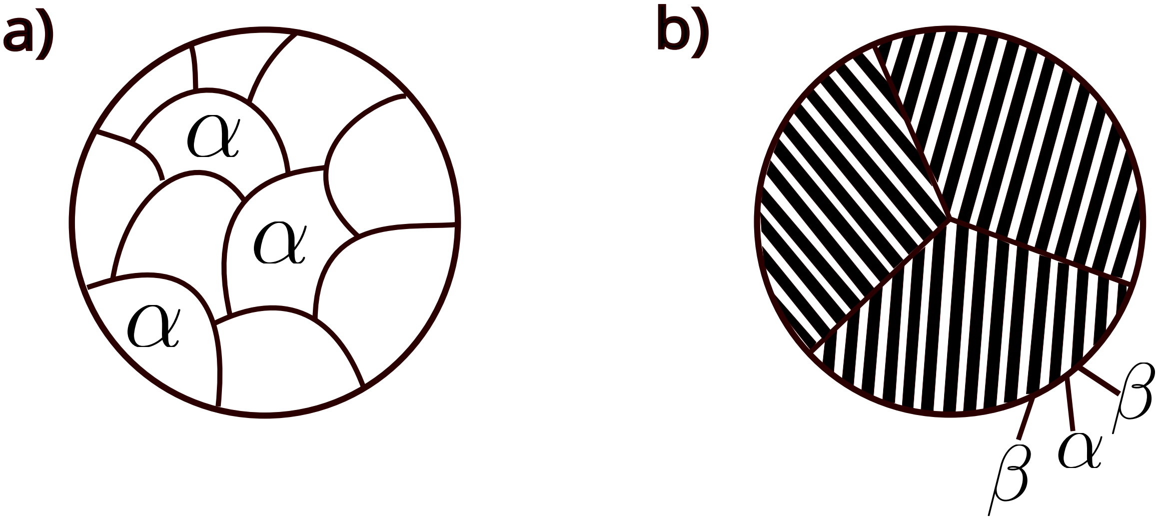


Figure 1.4: a) Homogeneous $Pb - Sn$ alloy and b) heterogeneous eutectic $Pb - Sn$ alloy

1.2.7 Some Examples of Components and Phases

1. We dissolve common salt in water. This solution is a two-component system ($H_2O - NaCl$) but is a homogenous system having one phase (aqueous solution – brine). Now if we add ice cubes in it, we get two phases (aqueous solution and solid ice) but the components remain two ($H_2O - NaCl$). If we add kerosene in it, we get three phases (aqueous solution, Oil, and solid ice) and three components (H_2O, $NaCl$, kerosene). Strictly speaking, kerosene itself is a solution of many hydrocarbons.

2. Ordinary steel is considered a two-component (Fe, C) and a two-phase structure (Ferrite + Carbide). Remember Pearlite is not a single phase, Figure 1.5. It is a mixture of two phases (Ferrite + Carbide) in a fixed ratio and in a definite pattern. Ferrite (α) is a solid solution of C in Fe and has BCC structure. Iron carbide (Fe_3C) is an intermetallic compound having 6.67% C in Fe with orthorhombic structure.

3. Ordinary Cast iron is generally considered a three component (Fe, C, and Si) and a three-phase structure (Ferrite + Carbide + Graphite). Graphite is the stable allotropic form of carbon having hexagonal structure.

4. Ferritic stainless steel may be considered as a two-component (Fe, Cr) system and has single-phase structure (Ferrite).

5. Austenitic stainless steel may be considered as a three component (Fe, Cr, and Ni) system and has single-phase structure (Austenite). Austenite (γ) is a solid solution of C in Fe having FCC structure.

6. Mullite is a ceramic having a single phase and is a two-component (SiO_2, Al_2O_3) system.

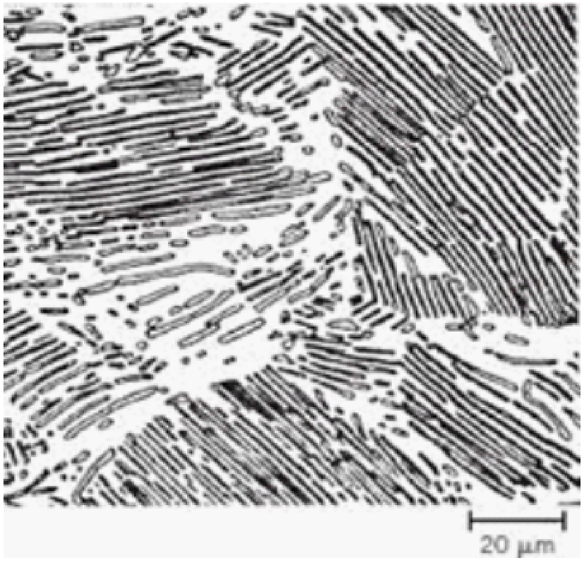


Figure 1.5: Pearlite in steel consists of two phases, ferrite and carbide.

1.3 Objectives of Studying Materials Thermodynamics

Here we summarize the basic objectives:

- To learn why some processes occur and some do not occur under the given conditions
- To learn to apply simple thermodynamic principles governing the behavior of materials
- To understand behavior of various metals and alloys under various conditions
- To understand principles of extraction and refining of various materials
- To understand various metallurgical processes and the variables affecting these processes

After studying this basic course, we will be able to answer the questions like:

- Will a solid melt – or a liquid solidify?
- Will A dissolve B – to what extent and how it affects properties of the solution?
- Why some undesirable elements cannot be removed, e.g., the removal of S & P from pig iron is difficult in a Blast furnace?
- How can we remove unwanted elements in refining operations, e.g., S & P in steel making?
- Will an electrochemical setup provide electrical energy or consume energy?

- Will a piece of metal get rusted or its oxide will decompose?
- Under what conditions a compound (e.g.,$CaCO_3$) will decompose?
- Could some defects be considered part of equilibrium structure?
- How external factors may help in achieving equilibrium structure?

Summary

1. Thermodynamics is the relation between heat (Q) and work (W) affecting the internal energy (U) of a system. Concepts of other energy terms like enthalpy and free energy (H, A, G) and entropy (S) are introduced to facilitate the discussion.

2. Thermodynamics gives the answer to the question whether a process can occur or not under the given conditions.

3. Materials science is the study of relationships among the compositions, processing, structures, properties, and performance of materials and Materials Thermodynamics helps in understanding these relationships. Materials thermodynamics covers the phase equilibria, solutions, extraction and refining, effect of environment on materials, defects, the behavior of surfaces, interfaces and other phase boundaries, etc.

4. Materials Thermodynamics is relatively a new subject stemming from Chemical Thermodynamics. Generating data for many processes in Materials Engineering which occur at high temperature is difficult and has remained a slow process.

5. Gibbs and Maxwell revolutionized the subject by deriving the mathematical laws governing the behavior of matter undergoing physical or chemical change.

6. A system is a portion of matter under consideration and everything around the system is known as its surroundings. An open system allows the exchange of mass and energy with its surroundings. A closed system only allows the exchange of energy. In case of an isolated system, neither mass nor energy is allowed to flow from or into the system. We are basically interested in changes occurring in the system and would like to restrict our calculations to the system only.

7. We first develop basic thermodynamic relations and criteria using a simple closed system such as a cylinder with movable piston containing ideal gas. After that, we open the system introducing the concept of chemical potential and the principles governing the equilibrium of phases. Next, we deal with reacting systems. Then we discuss electrochemical processes, surface energies, defects in solids, etc.

8. The properties of the constituent particles such as nature and number of particles, their energy distribution and interactions among the particles, describe the microscopic state of the system and this type of thermodynamics is known as statistical thermodynamics. On the other hand, we may treat a system as a continuum and describe it through bulk properties like pressure, volume, temperature, and compositions. This treatment is known as classical thermodynamics.
9. Extensive properties depend upon the extent (amount and size) of the system. Intensive properties are independent of the amount or size of the system.
10. Chemical Species of fixed composition are known as components in a thermodynamic system. A portion within which properties are uniform is called a phase. Within a phase there are no abrupt changes in properties from one point to another. Two phases are separated by a phase boundary.

Practice Problems

1. Evaluate the following statements.
    - i) Materials Science cannot be understood nor can it progress without understanding of thermodynamics.
    - ii) Steel and cast iron are multicomponent, multiphase systems.
    - iii) Austenitic stainless steels and Ferritic stainless steels are multicomponent, single phase systems.
    - iv) Pearlite is not a phase.
    - v) Ti-6Al-4V alloy has 3 components and 2 phases.
    - vi) Mullite is a single phase binary system.
    - vii) Volume of an ideal gas and its entropy could be treated as intensive as well as extensive property.
2. Explain the terms ‘component’ and ‘phase’ with examples.
3. Mention the components and phases in the following:
    - i) Molten material in the hearth of a pig iron Blast Furnace
    - ii) α/β brass
    - iii) A composite with Kevlar fibers in epoxy matrix
    - iv) Electrolytic bath for aluminum extraction
    - v) Age hardened Aluminum alloy
    - vi) Wind shield glass of an automobile
4. How would you show that Pearlite is a mixture of two phases?

Chapter 2

First Law of Thermodynamics and its Applications

Learning Outcomes:

Student should be able to explain

- First law of thermodynamics with sign convention
- Difference between the First law of thermodynamics and the law of conservation of energy
- How to write differential of a state function
- What is enthalpy? Why enthalpy is more useful than internal energy?
- What is molar heat capacity and how it varies with temperature?
- Expression for enthalpy as a function of temperature
- Limitations of first law and the need for second law

Invention of machines used to extract water from mines initiated investigations about relationship between heat and work. Early contributions only focused on improving the efficiency and output of engines and machines and advancements of thermodynamics were slow in that era. Simple yet powerful, the first law lays the foundations of thermodynamics. There are various useful ideas in materials thermodynamics which stem from the first law. Concepts like state functions will be introduced which make it easy to apply mathematics in order to derive useful conclusions.

2.1 Internal Energy

We may consider the total energy of a system as comprising of three components:

1. Macro Potential Energy (P.E.) describes the work done against gravity with respect to a certain reference point. Mathematically the change in PE is given as;

   $$\Delta P.E. = (mgh_2 - mgh_1)$$

   This equation represents the work done against gravitational force in moving the system from height h_1 to h_2 which results in increase in potential energy of the system.

2. The macro Kinetic Energy (K.E.) describes the work done to change the velocity of the system from v_1 to v_2.

   $$\Delta K.E. = \left(\frac{1}{2}mv_2^2 - \frac{1}{2}mv_1^2\right)$$

3. When the position and velocity of a system do not change ($\Delta P.E. = 0, \Delta K.E. = 0$), work done on the system would result in change in internal energy (ΔU) of the system. Internal energy represents all types of energies within the system including binding energies within molecules, intermolecular energies, kinetic energies of molecules, etc. Calculations of absolute values of internal energy are very difficult. Fortunately, we are not interested in absolute values of such energy but in the change in internal energy, ΔU, of the system. Like kinetic and potential energy, the internal energy of a system is also an extensive property.

2.2 First Law of Thermodynamics

The first law of thermodynamic says, "Change in internal energy of a system is equal to the difference between heat absorbed and work done by the system."

Mathematically,

$$\Delta U = Q - W \tag{2.1}$$

For a given system, the first law of thermodynamics is the relationship between Q (heat), U (internal energy) and W (work done). It is a subset of the law of conservation of energy for an isolated system. According to this, heat, work and internal energy are inter-convertible but overall energy of the system will remain constant.

It should be noted that, in addition to mechanical work, 'W' could also represent chemical work, electrical work, etc.

1st Law of thermodynamics is similar to the law of conservation of energy but 1st Law deals only with Q, W and U while law of conservation of energy deals with many types of energies.

2.2.1 Sign Convention

Conventionally the work done BY the system is taken as positive and the work done ON the system as negative. When some work is done on the system, its internal energy increases, i.e.,

$$\Delta U = -W \tag{2.2}$$

If heat Q is added to a system without any work, heat absorbed by the system would be equal to increase in its internal energy

$$\Delta U = Q \tag{2.3}$$

Combining Equation 2.2 and Equation 2.3, we get

$$\Delta U = Q - W \tag{2.1}$$

For infinitesimal changes, we write

$$dU = \delta Q - \delta W \tag{2.4}$$

Depending on the relative arrangements, 1st Law of thermodynamics may be stated in three possible ways;

i) Increase in internal energy is equal to heat *absorbed* by the system minus work done *by* the system.

$$dU = \delta Q - \delta W$$

ii) Work done *by* the system is equal to heat *absorbed* by the system minus *increase* in internal energy.

$$\delta W = \delta Q - dU$$

iii) Heat *absorbed* by the system is equal to work done *by* the system plus *increase* in internal energy.

$$\delta Q = dU + \delta W$$

Remember, we use algebraic methods for calculations. Equation 2.4 remains the same and we follow sign convention for heat changes and work as explained below.

i. If heat *absorbed* by system is Q = 15 J and the work done *by* the system is W = 12 J, the internal energy of the system will *increase* by 3 J.

$$\Delta U = Q - W = 15 - 12 = 3J$$

ii. If heat *released* by system is Q = -25 J and the work done *on* the system is W = -16 J, the internal energy of system will *decrease* by 9 J.

$$\Delta U = Q - W = (-25) - (-16) = -9J$$

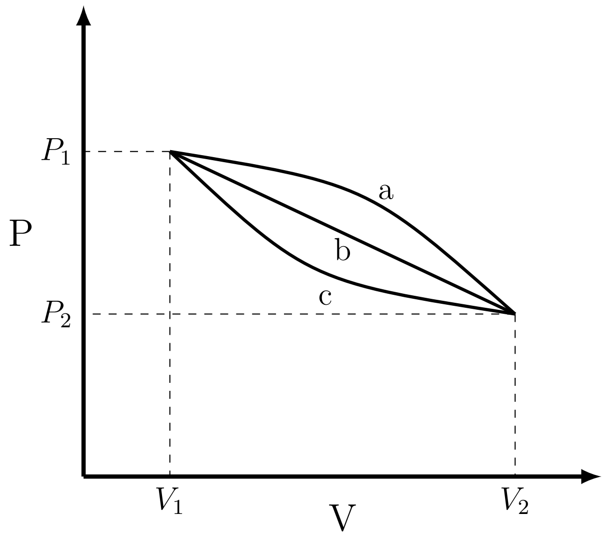


Figure 2.1: Path dependent functions have different values for paths a, b and c. State functions are defined by initial and final state only.

iii. If heat *absorbed* by system is Q = 15 J and work done *on* the system is W = -16 J, the internal energy of system will *increase* by 31 J

$$\Delta U = Q - W = 15 - (-16) = 31J$$

iv. If heat *released* by system is Q = -25 J and the work done *by* the system is W = 12 J, the internal energy of system will *decrease* by 37 J

$$\Delta U = Q - W = (-25) - (12) = -37J$$

2.2.2 State Function

A state function depends upon the state of a system only. It does not depend on the path followed while going from one state to another state. In a cyclic process the change in a state function would be zero since the system comes back to its original state after a complete cycle. Work done and Heat absorbed depend upon the path followed so these are not state functions. Fig. 2.1 shows expansion of ideal gas from state 1 to state 2. The work done by the gas and heat absorbed by the gas are different for paths a, b, c.

Hence, a state function or property is independent of the path followed in going from state 1 to state 2, and only depends on the initial and final conditions. Common state functions in thermodynamics are; Internal Energy (U), Enthalpy (H), Entropy (S), Gibbs Free Energy (G) and Helmholtz Free Energy (A). The change in a state function is expressed by "Δ", such as ΔU, while the infinitesimal change is written as dU. Work and heat are dependent upon path followed so they are path-dependent functions (non-state functions). The infinitesimal change in a non-state function is expressed by "δ", such as δW.

From the first law, we note that $dU = \delta Q - \delta W$

This relation describes the change in a state function as the difference of two non-state functions. This means that the change in the state function U remains the same as long as the difference between two non-state functions remains the same while their individual values may differ.

i. $dU = \delta Q_1 - \delta W_1$

ii. $dU = \delta Q_2 - \delta W_2$

iii. $dU = \delta Q_3 - \delta W_3$

Depending on how we take the system from state 1 to state 2, the heat and work interaction would change, but their difference would be the same, as their difference represents the change in internal energy. This means that the change in the state function U remains the same as long as the difference between two non-state functions remains the same although the individual values may differ.

The concept of state functions makes it possible to apply mathematics to follow changes in a system. In case of non-state functions, there could be infinite number of possible paths and a specific mathematical function cannot describe the change. It should be noted that once the path is defined, functions like heat and work become uniquely defined. Examples are heat change or work done in an isothermal change or adiabatic change.

The change in a state function can be expressed as the sum of partial differentials. If we treat internal energy as a function of volume and temperature,

$$U = U(V, T)$$

The change in internal energy is then given by

$$dU = \left(\frac{dU}{dV}\right)_T dV + \left(\frac{dU}{dT}\right)_V dT \tag{2.5}$$

Note that the partial differential $\left(\frac{dU}{dV}\right)_T$ indicates the rate at which internal energy changes with volume at constant temperature.

Let us take another example. We take G as a function of P and T

$$G = G(P, T)$$

then

$$dG = \left(\frac{dG}{dP}\right)_T dP + \left(\frac{dG}{dT}\right)_P dT$$

$\left(\frac{dG}{dP}\right)_T$ represents the rate at which Free energy (G) changes with pressure at constant temperature.

If we maintain constant temperature, dT would be zero. Then

$$dG = \left(\frac{dG}{dP}\right)_T dP$$

Or

$$\Delta G = \int dG = \int \left(\frac{dG}{dP}\right)_T dP$$

Recall from calculus

$$\frac{dy}{dx} = a$$

$$\Delta y = \int dy = \int a\ dx$$

Now we give some examples of defining the path to make mathematics easy.

a. Constant Volume Process

As we know that, the work done is given by

$$dW = PdV$$

$$W = \int PdV$$

For a constant volume process, $dV = 0$, hence work done would be zero

$$dW = 0$$

According to the first law of thermodynamics

$$\Delta U = Q_V - W$$

Where Q_V is heat absorbed at constant volume. Here $W = 0$ so,

$$\Delta U = Q_V \tag{2.6}$$

This means that the change in internal energy is equal to the heat absorbed at constant volume.

b. Constant Pressure Process

In this case, if we keep the pressure P constant and the volume changes from V_1 to V_2 and consequently internal energy changes from U_1 to U_2. Then work done is given by

$$W = \int_1^2 PdV$$

$$W = P\int_1^2 dV$$

$$W = P(V_2 - V_1) \tag{2.7}$$

According to the first law of thermodynamics

$$\Delta U = Q_P - W$$

$$U_2 - U_1 = Q_P - P(V_2 - V_1)$$

$$Q_P = (U_2 + PV_2) - (U_1 + PV_1) \tag{2.8}$$

Since the combination of U and PV is frequent in thermodynamics, a new energy function Enthalpy (H) is defined as,

$$H = U + PV \tag{2.9}$$

So heat absorbed at constant pressure becomes difference in enthalpy between two states,

$$Q_P = H_2 - H_1$$

$$\Delta H = Q_P \tag{2.10}$$

Hence the change in enthalpy is equal to the heat absorbed at constant pressure.

Conventionally, the enthalpy of pure elements in the stable state at room temperature is taken as zero. Therefore, for each of these pure elements Fe, Cr, Hg, O_2, H_2, the enthalpy at 298 K is taken as zero. Graphite has zero enthalpy because it is thermodynamically stable state of carbon at room temperature while another form of carbon (diamond) has enthalpy of 2.4 kJ/mole at 298 K.

As most of the processes occur at atmospheric pressure, Q_P (heat absorbed at constant pressure) is more useful than Q_V (heat absorbed at constant volume). Therefore, enthalpy (H) has more practical significance than internal energy (U). Note that the difference in H and U would be significant only in the processes involving gases. Sometimes, enthalpy is referred to as the total heat content.

2.3 Heat Capacity

Heat capacity of a substance is the amount of heat required to raise its temperature by one degree. In materials thermodynamics, we use the term Molar Heat Capacity which is given by

$$C = dQ/dT$$

$$dQ = C\ dT \tag{2.11}$$

At constant volume,

$$dQ_V = C_V dT \rightarrow dU = C_V dT \quad (\therefore dQ_V = dU) \tag{2.12}$$

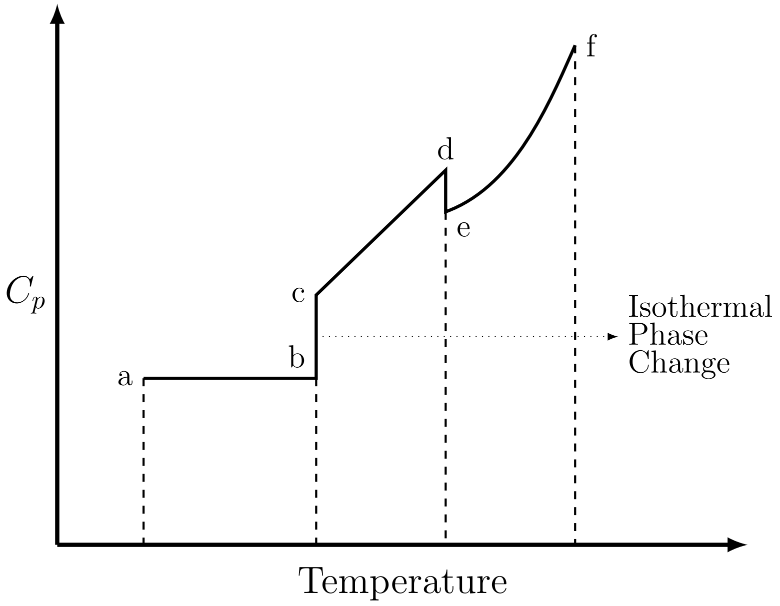


Figure 2.2: Variation of C_P as a function of temperature for a hypothetical element. Jumps indicate isothermal phase changes (allotropic change, melting, boiling).

And at constant pressure,

$$dQ_P = C_P dT \rightarrow dH = C_P dT \quad (\therefore dQ_P = dH) \tag{2.13}$$

$$\Delta H = \int C_P dT \tag{2.14}$$

Molar heat capacity is one of the most important thermodynamic properties of substances and C_P represents a frequently listed property in tables of thermodynamic data. It is usually tabulated as a function of T as

$$C_P = a + bT + cT^{-2} \tag{2.15}$$

As an example, for solid chromium, $C_P = 24.43 + (9.87\times10^{-3})T + (-3.68\times10^{5})T^{-2}$. If b and c are zero, C_p does not change with temperature. If only c is zero, C_P varies linearly with temperature. Note that C_P will have different values for different phases, i.e., for each allotrope, liquid and vapor. A jump will be observed at the transformation temperature. This is illustrated in Figure 2.2.

Let us take the example of various phases of iron.

For liquid $Fe, C_P = 41.8 J/mol.K$

For γ $Fe, C_P = 24.47 + (8.45 \times 10^{-3})T$

For α/δ $Fe, C_P = 37.12 + (6.17 \times 10^{-3})T$

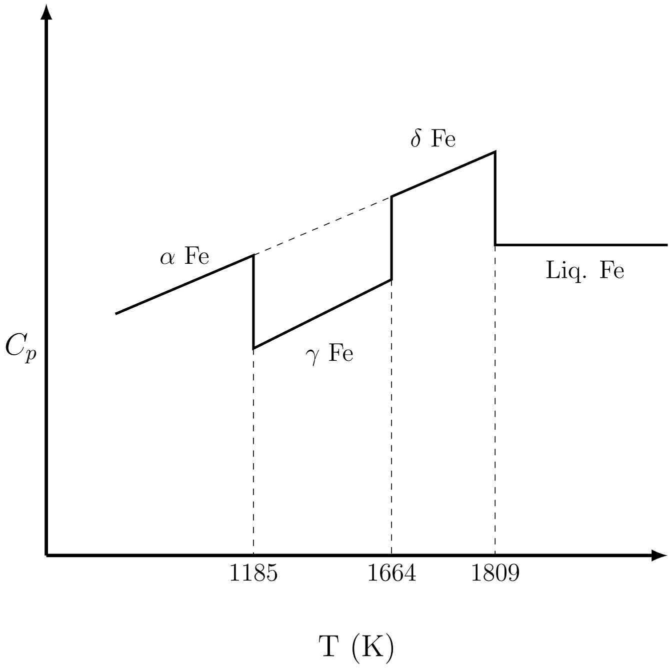


Figure 2.3: Graph of C_P as a function of temperature for iron

At 1185 K C_P of α Fe = 44.43 J/mol.K
At 1185 K C_P of γ Fe = 34.48 J/mol.K
At 1664 K C_P of γ Fe = 38.53 J/mol.K
At 1664 K C_P of δ Fe = 47.38 J/mol.K
At 1809 K C_P of δ Fe = 48.28 J/mol.K
At 1809 K C_P of liquid Fe = 41.8 J/mol.K

Figure 2.3 shows graph of C_P as a function of temperature for iron.

Now let us see how C_p values are used in enthalpy calculations.
Example: Calculate enthalpy of Pure Al at 600 K

$$\Delta H = \int C_P dT$$

$$\Delta H = H(600) - H(298) = \int C_P dT$$

$$H(600) = H^0_{298} + \int_{298}^{600} C_P dT$$

Note that, as per convention, we take $H^0_{298} = 0$

Example: Calculate enthalpy of Pure Al at 1000 K. The melting point of pure aluminum is 933K.

$$H(1000) = H^0_{298} + \int_{298}^{933} C_{P_s} dT + \Delta H_m + \int_{933}^{1000} C_{P_l} dT$$

Example: Calculate enthalpy of Pure Fe at 3500 K

$$\begin{aligned} H_{3500} = H^0_{298} + \int_{298}^{T_1} (C_P)_\alpha dT + \Delta H_{tr(\alpha/\gamma)} \int_{T_1}^{T_2} (C_P)_\gamma dT \\ + \Delta H_{tr(\gamma/\delta)} \int_{T_2}^{T_m} (C_P)_\delta dT + \Delta H_m \\ + \int_{T_m}^{T_b} (C_P)_{liquid} dT + \Delta H_b + \int_{T_b}^{3500} (C_P)_{vapors} dT \end{aligned} \quad (2.16)$$

For pure iron, we take $\Delta H^0_{298} = 0$
ΔH_{tr} = enthalpy change in allotropic transformation
ΔH_m = enthalpy change in melting
ΔH_b = enthalpy change in boiling
T_1 and T_2 are temperatures of allotropic transformations.
T_m and T_b are melting and boiling temperatures.
C_P values for each phase are tabulated.
All these values are available in the thermodynamic data book.

Example: Heat of formation of a compound
ΔH°_{298} for the reaction $Ba + 1/2O_2 = BaO$ is -548,100 J/mol.
Calculate the heat of formation of BaO.
$\Delta H^\circ_{298} = H_{products} - H_{reactants}$
$\Delta H^\circ_{298} = H(BaO) - [H(Ba) + 1/2H(O_2)]$
$-548,100 = H(BaO) - 0$
$H(BaO) = -548,100J/mol$
Note that we have taken enthalpy of pure elements at room temperature as zero.

The heat of formation of BaO is -548,100 J/mol. It is necessary to give units as J/mol

2.4 Work Done in a Simple Thermodynamic System

Let us do some calculations related to the work done in a simple system containing ideal gas. Here the work done is mechanical and is related to change in volume. The term reversible is used to indicate that we are assuming there are no losses in such a process.

2.4.1 Work done in a Reversible Isothermal Process

In an isothermal process, temperature of the system remains constant and as a result there will be no change in internal energy. As mathematically shown in Equation 2.12

$$dU = C_V dT$$

When $dT = 0$, we have $dU = 0$
The first law then says

$$dW = dQ$$

As we consider a simple system consisting of a cylinder with piston containing ideal gas. In such case

$$dW = PdV = dQ$$

For an ideal gas,

$$PV = nRT$$

So,

$$W = \int PdV = \int \frac{nRT}{V} dV \tag{2.17}$$

By integrating, we get

$$W = Q = nRT\ ln\left(\frac{V_2}{V_1}\right) = nRT\ ln\left(\frac{P_1}{P_2}\right) \tag{2.18}$$

Since, for isothermal change in an ideal gas $V_2/V_1 = P_1/P_2$
Note that, for an isothermal process, work done by the system is equal to heat absorbed by the system at constant internal energy. Here, work done by the system is positive in case of expansion when $V_2 > V_1$ which means $P_2 < P_1$. In case of compression, the work is done on the system and is negative since $V_2 < V_1$ which means $P_2 > P_1$.

2.4.2 Work done in a Reversible Adiabatic Process

In an adiabatic process, the heat exchange across the system boundary is zero i.e. $dQ = 0$.

According to the first law of thermodynamics,

$$dU = dQ - dW$$

For an adiabatic process, it becomes,

$$dU = -dW$$

At constant volume, the molar heat capacity is given by Equation 2.12

$$dU = C_V dT$$

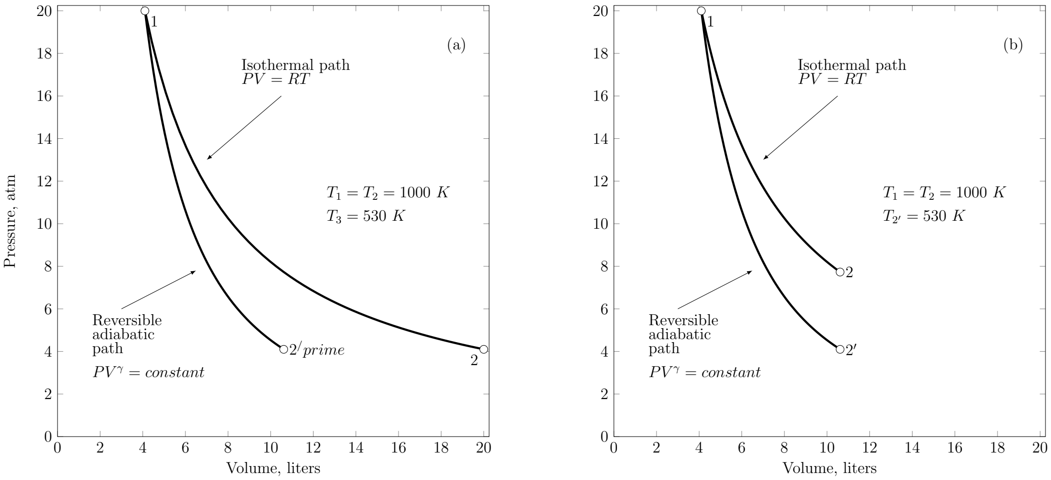


Figure 2.4: Work done during reversible isothermal and adiabatic expansion of an ideal gas

$$\Delta U = \int C_V dT$$

When C_V does not change with temperature,

$$\Delta U = C_V(T_2 - T_1) \tag{2.19}$$

Note that internal energy will decrease if temperature decreases.

Work done for an adiabatic process can also be calculated as

$$W = \int P dV$$

For adiabatic process of an ideal gas, $PV^\gamma = constant$ where

$$\gamma = \frac{C_P}{C_V}$$

For monoatomic ideal gas $\frac{C_P}{C_V} \approx 1.5$

The work would be positive in case of expansion which will occur only when temperature of system decreases.

Now the question arises as to why the work done in isothermal process is greater than work done in adiabatic process? This is illustrated in Figure 2.4. The answer lies in the fact that for isothermal process, $dW = dQ$. The heat supplied in an isothermal process is totally converted into work. In comparison, for an adiabatic process, as dQ is zero, $dW = -dU$. The system in adiabatic process will do work only when internal energy decreases i.e., the temperature is decreasing. In other words, the work is done by the system at the expense of its internal energy.

2.5 $(C_P - C_V)$ for an Ideal Gas

We start with the definition of enthalpy

$$H = U + PV$$

Differentiating this equation

$$dH = dU + PdV + VdP$$

$$dH - dU = PdV + VdP$$

By putting the values of dH and dU from Equation 2.12 and Equation 2.13 in this equation, we get

$$C_P dT - C_V dT = PdV + VdP$$

From ideal gas equation for one mole gas

$$PV = RT$$

Differentiating

$$PdV + VdP = RdT$$

Thus by comparing section 2.5 and section 2.5 we get

$$C_P dT - C_V dT = RdT$$

or

$$C_P - C_V = R \tag{2.20}$$

2.6 Use of Enthalpy Data - Metallothermic Reduction

There are many uses of enthalpy data such as determination of adiabatic flame temperature, energy balance in industrial reactions, etc. Here we describe the use of such data in Metallo-thermic Reduction.

Carbon is regarded as a universal reducing agent as it can reduce most of the metals from their oxides. However, reduction of very reactive metals by carbon may require impractically high temperatures. In some cases, a highly reactive metal such as calcium or magnesium may be used for reduction. Such processes generally evolve a lot of heat. Therefore, these processes are termed as Metallo-thermic Reduction. The well-known example is Thermit Welding in which aluminum is used to reduce iron oxide. This generates so much heat that the reduced iron gets melted and is used to join steel parts.

Metallothermic reduction is used in an exotic way to reduce metals like U, Zr and Ti, in a process known as Kroll Process. If the oxides of these metals are reduced using Ca or Mg, the oxides which are produced (CaO and MgO) have very high melting points. For a proper separation of resulting metal and oxide, we would like to have both of these phases in molten condition. Hence, metallo-thermic reduction of oxides in these cases is not feasible. In Kroll process, we first convert the oxide in some halide (fluoride or chloride) which is then reduced using Ca or Mg. This process has additional advantage that most of the impurities get removed during the halide formation.

Let us analyze the reduction of ZrF_4 using Mg. The question is whether we get sufficient heat in the reduction process so that the products reach the temperature which is sufficiently higher than the MP of Zr. While the MP of MgF_2 is much lower, the MP of Zr is 1858 C and we aim to get an adiabatic temperature of 2000 C.

The data required for this calculation is :

$H_f(298)$ for ZrF_4 = - 1,911,251 J/mol

$H_f(298)$ for MgF_2 = -1,124,200 J/mol

So heat released in the reaction

$$ZrF_4 + 2Mg \rightarrow Zr + 2MgF_2$$

would be

$\Delta H = H(products) – H(reactants)$

$\Delta H = 2H_f(298) for MgF_2 - H_f(298) for ZrF_4$

$\Delta H = 2 \times (-1124200) – (1911251) = -337,149 J$

Note that Zr and Mg are pure elements and their enthalpies at 298 K are taken as zero.

Now we want to check whether this heat is sufficient to raise the temperature of products to 2000 C (2273 K).

a. Heat required by Zr

$$\begin{aligned} H_{2273}(Zr) = \;& H^\circ_{298} + \int_{298}^{T_1} (C_P)_\alpha dT + \Delta H_{tr(\alpha/\beta)} + \int_{T_1}^{T_2} (C_P)_\beta dT \\ & + \Delta H_m + \int_{T_m}^{T} (C_P)_{liquid} dT \end{aligned}$$

$(C_p)_\alpha = 21.97 + 11.63 \times 10^{-3} T, \quad J/K/mol$

$(C_p)_\beta = 23.22 + 4.64 \times 10^{-3} T, \quad J/K/mol$

$(C_p)_{liquid} = 39.72, \quad J/K/mol$

For pure Zr, we take $H^\circ_{298} = 0$

ΔH_{tr} = enthalpy change in allotropic transformation = 3770 J/mol

ΔH_m = enthalpy change in melting = 19246 J/mol

T_{tr} is temperature of allotropic transformations = 852 C = 1125 K

T_m is melting temperature = 1857 C = 2130 K

$$\begin{aligned}
H_{2273}(Zr) &= 0 + \int_{298}^{1125} (21.97 + 11.63 \times 10^{-3}T)dT + 3770 \\
&\quad + \int_{1125}^{2130} (23.22 + 4.64 \times 10^{-3}T)dT + 19246 + \int_{2130}^{2273} (39.72)dT \\
&= [21.97T + 11.63 \times 10^{-3}T^2/2] + 3770 + \\
&\quad [23.22T + 4.64 \times 10^{-3}T^2/2] + 19246 + [39.72T] \\
&= [21.97 \times (1125 - 298) + 11.63 \times 10^{-3}/2 \times (11252 - 2982)] + \\
&\quad 3770 + [23.22 \times (1125 - 298) + 4.64 \times 10^{-3}/2 \times \\
&\quad (11252 - 2982)] + 19246 + [39.72 \times (1125 - 298)] \\
&= 84633\ J
\end{aligned}$$

b. Heat required by MgF_2

$$\Delta H(MgF_2) = \int_{298}^{1536} (C_P)_s\ dT + \Delta H_m + \int_{1536}^{2273} (C_P)_{liquid}\ dT$$

$$\begin{aligned}
\Delta H(MgF_2) =& \int_{298}^{1536} (77.11 + 3.89 \times 10^{-3}T - 14.94 \times 10^5 T^{-2})\ dT \\
&+ 58600 + \int_{1536}^{2273} 94.56\ dT \\
=&[77.11T + 3.89 \times 10^{-3}T^2 + 14.94 \times 10^5 T^{-1}] + 58600 + [94.56T] \\
=&[77.11 \times (1536–298) + 3.89 \times 10^{-3}(15362 - 2982)/2 + \\
&14.94 \times 10^5 \times (1536^{-1} - 298^{-1})] + 58600 + [94.56(2273–1536)] \\
=&224128\ J/mol
\end{aligned}$$

Total heat required = 84633 + 2× 224128 = 532889 J

Additional heat required is = 532889 – 337149 = 195745 J

Thus, in order that the stoichiometric product mixture reaches a temperature of 2000 °C, neglecting losses, we need to provide 195745 Joules in addition to the heat released in the reaction. It is convenient to heat the reactants before the reaction starts. This is called Preheating. Also, it is difficult to measure the amount of heat provided while temperature measurement is much easier. So, now we would like to find the temperature which reactants will attain when we provide 195745 Joules as preheat. Our reactants are 2 moles of Mg and one mole of ZrF_4.

Heat gained by ZrF_4

$$\begin{aligned}
&= \int_{298}^{T_1} (C_P)_s \; dT \\
&= \int_{298}^{T_1} [117.27 + 18.55^{-3}T - 17.22 \times 10^5 T^{-2}] dT \\
&= [117.27 \times T + 18.55 \times 10^{-3} T^2/2 - 17.22 \times 10^5(-T^{-1})] \\
&= [117.27 \times (T–298) + 18.55 \times 10^{-3}(T^2–298^2)/2 \\
&\quad + 17.22 \times 10^5(T^{-1} - 298^{-1}) \\
&= 117.27T + 9.27 \times 10^{-3}T^2 + 17.22 \times 10^5 T^{-1}–41548.7
\end{aligned}$$

Heat gained by Mg

$$\begin{aligned}
&= \int_{298}^{T_1} (C_P)_s \; dT \\
&= \int_{298}^{T_1} [21.12 + 11.92 \times 10^{-3}T + 0.15 \times 10^5 T^{-2}] dT \\
&= [21.12 \times (T) + 11.92 \times 10^{-3} T^2/2 + 0.15 \times 10^5(-T^{-1})] \\
&= [21.12 \times (T–298) + 11.92 \times 10^{-3}(T^2–298^2)/2 \\
&\quad - 0.15 \times 10^5(T^{-1} - 298^{-1}) \\
&= 21.12T + 5.96 \times 10^{-3}T^2 - 0.15 \times 10^5 T^{-1}–6773
\end{aligned}$$

Total Heat gained by one mole of ZrF_4 and two moles of Mg

$$\begin{aligned}
&= 117.27T + 9.27 \times 10^{-3}T^2 + 17.22 \times 10^5 T^{-1}–41548.7 \\
&\quad + 2 \times [21.12T + 5.96 \times 10^{-3}T^2 - 0.15 \times 10^5 T^{-1}–6773] \\
&= 159.51T + 21.19 \times 10^{-3}T^2 + 16.92 \times \times 10^5 T^{-1}–48321.7
\end{aligned}$$

This should be equal to the heat provided in preheating, i.e., 195745 Joules.

$$159.51T + 21.19 \times 10^{-3}T^2 + 16.92 \times 10^5 T^{-1}–48321.7 = 195745$$

On solving, we get T = 1298 K or 1025 °C.

This is too high a temperature, much above the melting point of Mg. Such preheating would be impractical. So we have to explore other possibilities, such as:

i. Use of Ca for reduction instead of Mg

$$\begin{aligned}
&ZrF_4 + 2Ca \rightarrow Zr + 2CaF_2 \\
&\Delta H = H(products)–H(reactants) \\
&\Delta H = 2H_f(298) forCaF_2 - H_f(298) forZrF_4 \\
&\Delta H = 2 \times (-1219636)–(1911251) = -528,021J
\end{aligned}$$

Heat released in this reaction is much higher and the requirements of preheating are minimal.

ii. Incorporating ZnF_2 in the reduction charge.

This has two effects. Additional heat is released on reduction of ZnF_2 and we get alloy of Zr and Zn. Whereas pure Zr has MP of 1858 °C, the eutectic (Zr – 37%Zn) has MP of 1022 °C only. Zn can later be removed by heating the alloy in a vacuum furnace. Since Zn has very high vapor pressure, it is easily distilled out.

2.7 Limitations of the First Law

Limitations of the 1st law may be summarized as follows:

- 1st Law does not prohibit flow of heat from low T to high T
- 1st Law does not put any restriction on the amount of heat which can be converted into work.
- 1st Law does not describe the maximum work which can be obtained from a system (Spontaneous Process), or the minimum work required to cause a desired change (Non-Spontaneous Process)

Hence, 2nd Law is required and there is a need to understand reversible and irreversible processes. In an irreversible process, degradation occurs and energy is converted into its lowest form, i.e., heat, and is not able to do useful work.

We say that the first law of thermodynamics provides base for some useful relations which could be further developed to get a better understanding of the behavior of matter with the help of the second law of thermodynamics.

Summary

- First law of thermodynamic is a subset of law of conservation of energy which deals with interchange of heat, work and internal energy of a thermodynamic system.

$$\Delta U = Q - W$$

- All types of energies (bonding energies, intermolecular energies, K.E. of molecules etc.) other than macro potential energy and K.E. collectively represent internal energy U of a system.
- In an isothermal process, change in internal energy becomes zero, $\Delta U = C_v(T_2 - T_1) = 0$, and work output becomes equal to the heat provided to the system. There is no limit to this, system will continue to do work as long as heat is given to the system.

- In an adiabatic process, work done becomes equal to the decrease in internal energy. Work output is limited to the decrease in internal energy of the system.
- At constant pressure, change in heat of the system is equal to the change in enthalpy of the system with respect to temperature.
- If there is no transformation, enthalpy change is simply given by

$$\Delta H = \int C_p \, dT$$

- For an isothermal reversible process, work done by the system is function of either volume or pressure:

$$W = RT \, ln\left(\frac{V_2}{V_1}\right) = RT \, ln\left(\frac{P_1}{P_2}\right)$$

- Difference in heat capacity at constant pressure and heat capacity at constant volume, for an ideal gas, is equal to the gas constant (R = 8.314 J/mol.K).

$$C_P - C_V = R$$

Practice Problems

1. Evaluate the following statements.
    i. Concept of state function is important in thermodynamics.
    ii. Uranium oxide is not reduced by carbon or magnesium.
    iii. Magnesium can directly reduce zirconium oxide but we don't like this reduction. Instead, we convert zirconium oxide into fluoride and then reduce it to get Zr metal.
    iv. Heat and work can be state functions.
2. Write an essay on the first law of thermodynamics. The essay should cover the following:
    a. Description of the law emphasizing the sign convention
    b. Some useful concepts derived from the law
    c. Limitations necessitating the advent of second law
3. Calculate the work done when two moles of an ideal gas, initially at 50°C, are compressed from 2 atmosphere pressure to 5 atmosphere pressure. What is the amount of heat absorbed /released? Carry out these calculations for a) Isothermal Process b) Adiabatic Process.

4. Following information about pure iron is available.

   Low temperature phase α transforms to γ at 910°C, γ transforms to δ at 1410°C and δ melts at 1539°C. Normal boiling point is 2862°C.

   Write an expression for enthalpy of Fe vapors at a temperature 'T' above the boiling point.

5. Find whether the heat released in metallothermic reduction of UF_4 by Ca is sufficient to raise the temperature of products to 1500°C.

   Data for CaF_2 :
   $C_p(\alpha) = 59.83 + 30.46 \times 10^{-3}\ T + 1.97 \times 10^{5}\ T^{-2}$ (298 – 1424 K)
   $C_p(\beta) = 108 + 10.46 \times 10^{-3}\ T$ (1424 - 1691K)
   $C_p(l) = 100.2$ J/mole.K
   $\Delta H\ (\alpha/\beta) = 4000$ J/mole, $\Delta H\ (m) = 29706$ J/mole
   $H(298) = -1919.6$ kJ/mole

   Data about UF_4 and U may be obtained from any thermodynamics book.

6. What do jumps or steps indicate in graph of $C_P = f(T)$?
   Manganese exhibits 4 allotropic transformations. Write expression for enthalpy of Mn vapors at T above its boiling point.

7. Given Helmholtz free energy as a function of volume and temperature, write an equation for change in free energy.

Chapter 3

Second Law of Thermodynamics

Learning Outcomes:

Student should be able to explain

- Concept of a reversible process and its importance
- Entropy change in a reversible process
- Entropy change in irreversible, spontaneous or natural process
- Entropy change as a criterion of spontaneity
- Maximum work by the system and Minimum work on the system
- Heat engine and its efficiency
- Thermodynamic and ideal gas temperature scale
- Why efficiency of heat engine is very low
- Various statements of second law
- Third law and Zeroth law of thermodynamics

Introduction

The limitations of the first law necessitated the introduction of the second law of thermodynamics which has much more practical applicability. It was quickly realized that while mechanical energy could be completely converted into heat (heat is the lowest form of energy), heat cannot be completely converted into the work. Every form of energy tends to go into heat energy. These observations were explained by the second law. The concepts of entropy, spontaneous and reversible process are necessary for further development of materials thermodynamics. A reference to heat engines helps in understanding of thermodynamic temperature scale. Finally the third law of thermodynamics leads to the concept of absolute values of entropy of materials.

3.1 Need for the Second Law of Thermodynamics

First law of thermodynamics is a subset of the law of conservation of energy. Though a universal law, it is somewhat passive as far as the applications are concerned. It does not specify the direction of any process. For example, we know that heat cannot flow from a cold body to hot body although it is not prohibited by the first law. In general, the first law does not help us in defining the direction of any spontaneous process. This is not the failure of the first law, it is rather its limitation. It is the second law which provides a means to predict whether a particular process could take place under certain conditions and this leads us to the criteria of spontaneity.

Second law of thermodynamics asserts that processes occur in a particular direction and that the energy has quality as well as quantity. A process occurs when it satisfies both laws of thermodynamics.

First Law was merely a statement of energy conservation

$$dU = \delta Q - \delta W$$

For adiabatic process $\delta Q = 0$

$$dU = -(\delta W)$$

$$\delta W = -dU$$

If work is done by the system, its internal energy decreases and work done on the system is equal to increase in its internal energy.

If no work is done, $\delta W = 0$, then

$$dU = \delta Q$$

What happens when a process is neither adiabatic nor isochoric (constant volume)? In such a case we would be interested in finding the maximum work which is obtainable in a process. The second law answers these questions.

3.2 Spontaneous Process

A process which requires no external agency to occur is called a spontaneous process. Left to itself, a system will do one of the two things; it will remain in the state in which it happens to be, or it will move, on its own accord, to another state which will be its equilibrium state. Such a process that involves spontaneous movement of a system from non-equilibrium to equilibrium state is also referred to as a natural process or irreversible process. Spontaneous processes are thermodynamically irreversible. In undergoing spontaneous process, a system may be made to do useful work. Whereas the spontaneous process releases energy (can do useful work), work has to be done for the reverse process to occur. Every system tends to be in equilibrium and its capability of doing work decreases as it approaches equilibrium. Some examples of spontaneous processes are given below:

1. Ice cube melts at room temperature while water freezes in the freezer.

2. Iron exposed to moist air gets rusted.
3. Glucose burns in air when reaction is started,

$$C_6H_{12}O_{6_{(aq)}} + 6O_{2_{(g)}} \rightarrow 6CO_{2_{(g)}} + 6H_2O_{(l)}$$

4. Hot tea cools down, heat flows from high temperature (system) to low temperature (surrounding), down the thermal potential gradient.
5. An object falls, down the gravitational potential gradient.
6. A test charge moves, down the electrical potential gradient.
7. Chemical species move (diffuse), down the chemical potential gradient.
8. Various components mix to form solutions.

Work has to be done or energy has to be provided to make a non-spontaneous process to occur. In other words, we want to reverse a natural process. Some examples of non-spontaneous processes, which can be made to occur by changing the conditions, are given below:

1. We can melt ice cube at -2 ^{o}C by applying pressure.
2. We can get Fe from iron oxide by heating it with C.
3. Photosynthesis – formation of glucose occurs using sunlight (in presence of chlorophyll).
$$6CO_{2_{(g)}} + 6H_2O_{(l)} \rightarrow C_6H_{12}O_{6_{(aq)}} + 6O_{2_{(g)}}$$
4. We can extract heat from a cool object using heat pump (Refrigeration)
5. We can take an object to a higher place by doing work against gravitational field.
6. We can move a test charge from low to high potential by doing work against electric field.
7. Chemical species could be moved against chemical potential gradient by doing work.
8. We can separate (unmix) components using chromatography, distillation, etc.

As a material scientist/engineer, we are interested in both spontaneous as well as nonspontaneous processes. If spontaneous process is useful, we may want to control its rate. If spontaneous process is not useful, we would like to stop it. If a non-spontaneous process is useful, we would like to find the conditions in which it could be made to occur.

3.3 Entropy

Entropy, in simple terms, is a measure of disorder in a system. Entropy 'S' of a system is a state function. The disorder in turn is defined by how many species are there in the system, how they are distributed and what kind of freedom of movement do they possess. Solids have less entropy than liquids as the atoms in solids are tightly packed and are allowed to move in a specific manner only. While, in liquids the atoms or molecules are free to move in any direction within the volume. Gases have even higher entropy as particles can move in any manner or direction within the container.

Two types of entropies are thermal entropy (heat) and configurational entropy (mixing). Thermal entropy is concerned about increasing vibrational, rotational or translational motion of the particles in the system, while configurational entropy is related to the arrangement or position of particles in the system.

Mathematically, thermal entropy is defined as

$$\Delta S = \frac{Q}{T} \tag{3.1}$$

For infinitesimal changes,

$$dS = \frac{\delta Q}{T} \tag{3.2}$$

Equation 3.1 may be written as

$$Q = (\Delta S)T$$

The above equation shows that if temperature is low, less amount of heat is needed to create same extent of disorder. Entropy changes are calculated through reversible path only. The net increase in entropy (entropy of system and surrounding), during a process is a measure of the degree of irreversibility of the process.

3.4 Reversible Process

For the mathematical treatment, the quantities involved must have well defined values or relations. Unfortunately, losses in a process are difficult to quantify. One way to overcome this difficulty is to conceptualize a process with zero losses. In thermodynamics, such a process is called a reversible process. This makes mathematics easy. Once the conclusions are obtained as the limiting case, the reasonable losses could be incorporated to get the practical results.

Since the degree of irreversibility is variable, it is possible for a process to be conducted such that the degree of irreversibility is minimized. The ultimate of this minimization is a process in which the degree of irreversibility is zero and in that case no degradation occurs. This limit, towards which the behavior of real systems can be made to approach, is the reversible process. For a reversible process, the concept of spontaneity is no longer applicable. If the spontaneity is not there, it is apparent that, at all times during the process, the system is at equilibrium. Thus a reversible

Table 3.1: Vapor pressure of water at various temperatures

Temperature (°C)	P_{H_2O} (mm Hg)
0	4.5
25	23.8
90	525
100	760

process is the one during which the system is never away from equilibrium. Such a path, of course, is imaginary but it is possible to conduct an actual process in such a manner that it is virtually reversible.

To understand the concept of a reversible process, we take an example of a system consisting of water in equilibrium with its vapors.

Remember, the vapor pressure of a substance is a function of temperature.

$$P = f(T)$$

For water,

$$log\ P_{H_2O} = \frac{-2900}{T} - 4.65\ log\ T + 22.613$$

Here, the vapor pressure is in mm of Hg. Table 3.1 gives vapor pressure of water at several temperatures,

Boiling point of a liquid is the temperature at which its vapor pressure becomes equal to the external pressure. The normal boiling point of water at sea level is 100 ^{o}C. At high altitudes, water boils at a lower temperature which makes cooking difficult. In that case we increase the pressure by using a pressure cooker.

In order to understand a reversible process, we make a system of water and its vapors in a container in which we keep the temperature constant and can vary the pressure at will. Note that the space above water has only water vapors (no air).

In the equilibrium condition, the piston will not move as $P_{ext} = P_{H_2O}$.

If we decrease the pressure by a small amount ΔP, the piston will move upward. Water, in an attempt to keep its vapor pressure constant (which is defined by temperature), will evaporate. For this vaporization, heat is absorbed from the constant temperature source (surrounding). We continue this expansion until one mole water has evaporated. Volume of one mole of water vapors is V which is much larger than the volume of one mole liquid water. Thus the change in volume in this process is taken as V. Work is done by the system and heat is absorbed from the surrounding. Work done by the system is

$$W_1 = (P_{H_2O} - \Delta P)V$$

Note that here $(P_{H_2O} - \Delta P)$ is the constant pressure against which expansion has occurred while V is the change in volume when one mole of water is converted into vapors. Since the work is done by the system, it is positive. Now if we increase

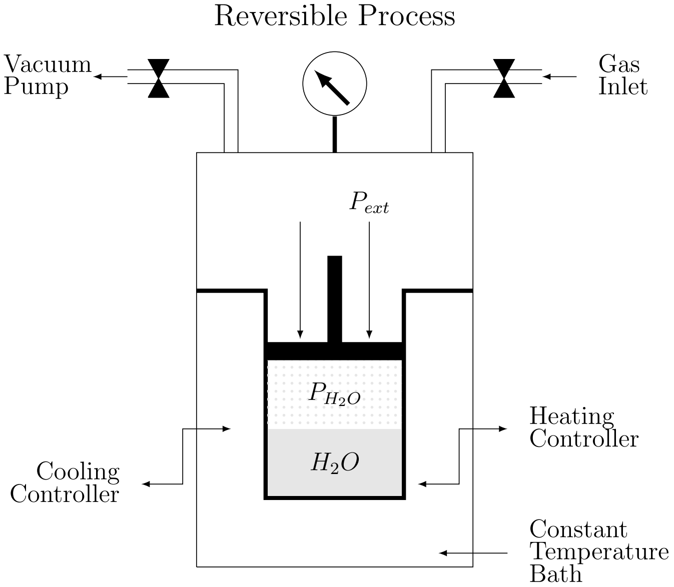


Figure 3.1: A system containing water and its vapors used to illustrate a reversible process. In this system, we can maintain constant 'T' and can control 'P'.

the pressure by a small amount ΔP, the piston will move downward. Water, in an attempt to keep its vapor pressure constant, will condense by releasing heat to the surroundings. We continue until one mole water vapor has condensed having volume equal to V. The system releases heat to the surrounding and the work done on the system in this process is

$$W_2 = (P_{H_2O} + \Delta P)V$$

Note that here $(P_{H_2O} + \Delta P)$ is the constant pressure causing compression while V is the change in volume when one mole of water vapors are converted into liquid. Since the work is done on the system, it is negative.

Net work done on the system in this process then will be,

$$W_2 - W_1 = (P_{H_2O} + \Delta P)V - (P_{H_2O} - \Delta P)V$$

$$W_2 - W_1 = 2(\Delta P)V$$

The system has come back to its original position, but in the process we have done some net work on the system. This net work done on the system represents loss. The process with finite driving force, ΔP, results in degradation of mechanical energy (work) into heat which is released to the surrounding.

For smaller pressure difference, δP, the loss would be less.

$$W_2 - W_1 = 2(\delta P)V$$

According to the above equation, as δP approaches zero, the net work done approaches zero which means the loss approaches zero. Such a process is called a

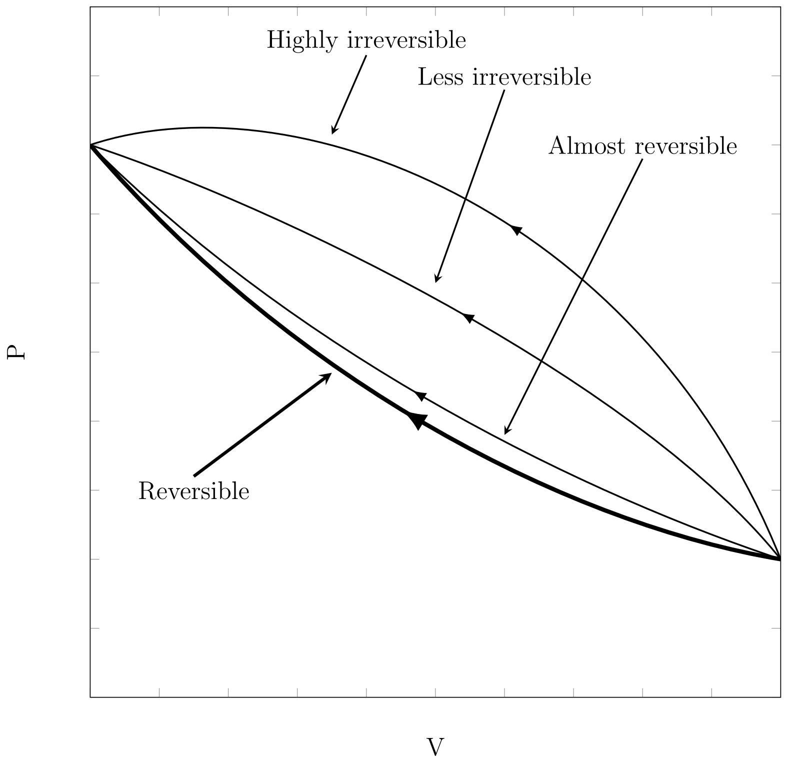


Figure 3.2: Effect of irreversibility during isothermal compression of an ideal gas

reversible process. In a reversible process, the driving force must be infinitesimally small, approaching zero. In the above equations, δP was the driving force. As the driving force approaches zero, the heat/energy loss also approaches zero. The disadvantage is that the reversible process will be extremely slow and impractical. However, the mathematics becomes simple. As noted above, the work done by the system in a reversible process is maximum. It decreases as the irreversibility increases. Similarly, the work done on the system will be minimum in a reversible process. It increases as the irreversibility increases. Remember, our aim is to get maximum work when the system is doing work and we want to keep it minimum if we have to do work on the system. This means that the maximum output can be taken out of the system only in a reversible process in which the system passes through a series of equilibrium stages and is never away from equilibrium. Though such a process appears impractical, we will see later that in electrochemical processes, reversibility could be approached.

Figure 3.2 illustrates the effect of irreversibility during isothermal compression of an ideal gas. As we approach reversibility, the work done on the system decreases. Figure 3.3 illustrates that the work done by a system in an irreversible process is less than that in a reversible process. On the other hand, the work done on the system in an irreversible process is more than that in a reversible process. Thus we incur losses in irreversible processes.

We may summarize the above discussion as follows:

- When we decrease the degree of irreversibility (decreasing degradation), we increase the degree of reversibility.

- In the limiting case, when the degree of irreversibility is zero, the process is completely reversible.

- In such case, the system passes through continuum of equilibrium states – It is never away from equilibrium state.

- We could approach reversibility by making the driving force as small as possible.

- If the direction of this infinitesimal force is reversed, the direction of the process is reversed.

- Such process will be extremely slow – Impractical.

- However, it is important since it is easy to understand and the math involved is simple.

- Just like in physics, we solve problems by neglecting friction. Then we may incorporate friction also.

- Concept of streamline flow vs turbulent flow helps in understanding of a reversible process.

Some people get confused between a reversible chemical reaction and a thermodynamically reversible process. A reversible reaction is the one which occurs in both forward and backward directions. State of equilibrium is achieved when the rate of forward reaction becomes equal to the rate of backward reaction. At this stage, the direction of reaction can be changed by changing suitable parameters. Thus a reversible chemical reaction under equilibrium condition represents a reversible process. However, a thermodynamically reversible process could be any physical or chemical process.

3.5 Degree of Irreversibility

We now analyze the evaporation process in the above example. The work done by the system during the evaporation of 1 mole water is seen to have its maximum value in the reversible process. In case of irreversible evaporation, system will perform less work that is given by

$$W = (P_{H_2O} - \Delta P)V$$

For the reversible process, ΔP would approach zero and the maximum work done by the system is given by

$$W_{max} = P_{H_2O}V$$

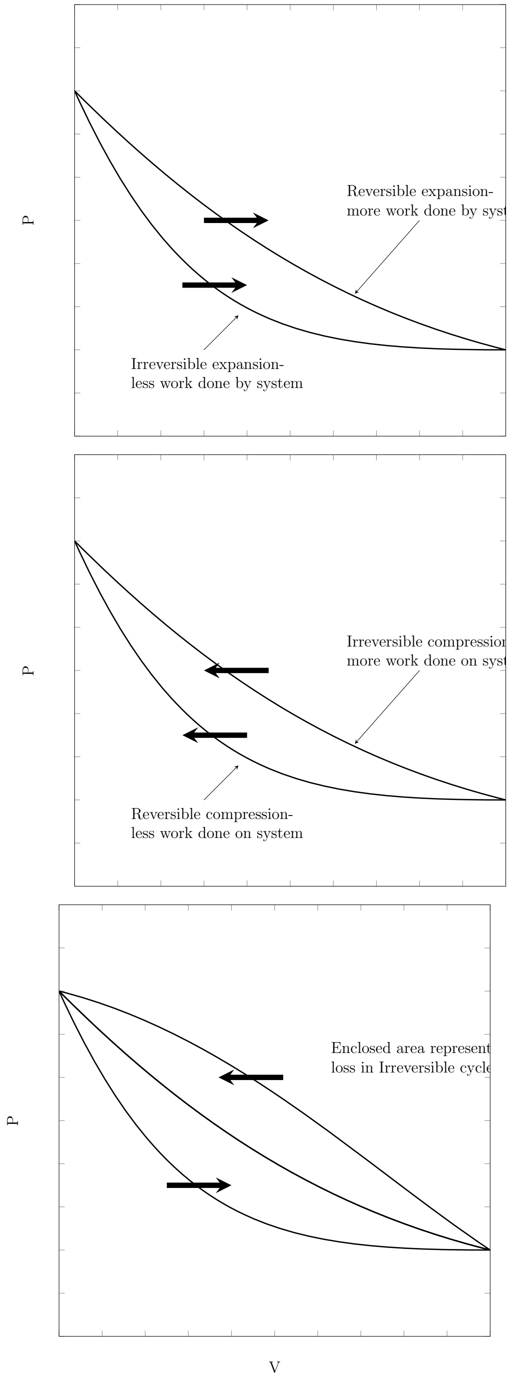


Figure 3.3: Illustration to show that irreversibility results in loss

It means that in case of reversible process the amount of heat system absorbed was totally converted to work. According to the first law of thermodynamics

$$Q_{rev} = \Delta U + W_{max}$$

Q_{rev} is the maximum heat absorbed by the system

ΔU for the system caused by the evaporation of 1 mole of water is independent of whether the process is carried out reversibly or irreversibly. For the irreversible process

$$Q = \Delta U + W$$

Where

Q = heat absorbed by the system (which is less than Q_{rev}),

W = work done by the system (which is less than W_{max}) while ΔU remains constant.

The difference between the work done during the reversible process and that done during the irreversible process, (W_{max}–W) represents the loss. In other words, the mechanical energy is degraded to heat in the system due to irreversibility. When we tend to make the process reversible, the loss also approaches zero and $W \to W_{max}$.

Now,

$$Q_{rev} - Q = \text{heat produced by degradation}$$

This heat is produced by degradation, which is given as

$$Q_{rev} - Q = W_{max} - W,$$

and signifies that less heat is transferred to the cylinder from the reservoir during the irreversible process than is transferred during the reversible process. The difference is generated within the system by degradation.

During the reversible expansion, heat is lost from the surrounding, the entropy change is given as

$$\Delta S_{surrounding} = -\frac{Q_{reversible}}{T}$$

Negative sign corresponds to the heat leaving the surrounding which results in the decrease in entropy of surrounding.

The change in entropy for the water and water vapor system in the cylinder is given by:

$$\Delta S_{System} = +\frac{Q_{reversible}}{T}$$

Positive sign corresponds to the heat entering the system and entropy content of the system increases. As entropy of the system is increasing and the entropy of surrounding is decreasing by equal amount, the total entropy change will be zero. Therefore, in a reversible process

$$\Delta S_{Total} = \Delta S_{Surrounding} + \Delta S_{System} = 0$$

Hence, in a reversible process, the entropy changes of the system and the surrounding are equal and opposite. If entropy of the system decreases, there will be an equal increase in the entropy of surrounding and vice versa.

If the evaporation process occurs irreversibly, then the heat $Q(Q < Q_{reversible})$ is transferred from the reservoir to the cylinder. Thus change in entropy of the *surrounding* is given by:

$$\Delta S_{surrounding} = -\frac{Q}{T}$$

Where $Q < Q_{reversible}$

The total heat appearing in the cylinder equals the heat 'Q' transferred from the heat reservoir (surrounding) plus the heat which is produced by degradation of the work due to the irreversible nature of the process. Less heat is absorbed from the reservoir as heat is generated in the system due to irreversibility. The entropy change of the system is thus given by the following equation

$$\Delta S_{System} = \frac{\text{Heat absorbed from reservoir}}{T} + \frac{\text{Heat produced due to degradation}}{T}$$

$$\Delta S_{System} = \frac{Q}{T} + \frac{(Q_{reversible} - Q)}{T}$$

$$\Delta S_{System} = \frac{Q_{reversible}}{T}$$

It is seen that, whether the process is reversible or irreversible, the entropy change for the system will be same. This is due to the fact that entropy of the system is a state function, while entropy of surrounding will be different. The entropy of system does not depend upon the path followed whether the process is reversible or irreversible. Thus for the evaporation process, irrespective of the degree of irreversibility,

$$\Delta S_{System} = \frac{Q}{T} + \Delta S_{irreversible}$$

Where

$$\Delta S_{irreversible} = \Delta S_{Total} = \frac{Q_{reversible} - Q}{T}$$

As the degree of irreversibility decreases, the process gets closer to reversibility,

$$Q \rightarrow Q_{reversible}, \qquad \Delta S_{irrevesible} \rightarrow 0$$

As $Q_{reversible} > Q$, this entropy change is positive, and thus entropy has been produced as a result of the occurrence of an irreversible process. The entropy produced $\left(\frac{Q_{reversible}-Q}{T}\right)$ is termed as $\Delta S_{irreversible}$ and is the measure of degradation which has occurred as a result of the irreversible process. Through similar arguments, it can be shown that in the reversible condensation, decrease in entropy of the system is equal to increase in the entropy of surrounding while in the irreversible condensation, there is a net increase in entropy. Entropy change in the system remains the same while there is additional increase in the entropy of the surrounding in the irreversible condensation.

This gives us mathematical expression for the 2^{nd} Law of Thermodynamics:

$$\Delta S_{Total} \geq 0 \tag{3.3}$$

or

$$\Delta S_{irreversible} \geq 0$$

In a process, there will be no change in total entropy if it occurs reversibly and the total entropy will increase if the process is irreversible. The irreversible process can also be described as spontaneous or natural process. This also leads to another statement of the second law of thermodynamics, 'Entropy of universe is increasing'.

As the degree of irreversibility increases, the entropy produced increases and thus we say that entropy is a measure of irreversibility. This also gives us a criterion for spontaneity. A process will be spontaneous if it is accompanied by increase in entropy. However, there is one problem. The subscript "Total" in ΔS calculation signifies that we have to calculate change in entropy of the system as well as that of the surrounding. This makes the job of determining spontaneity of a process difficult. We would like to have spontaneity criteria where we are interested in changes in the system only.

Example. *Entropy production in irreversible freezing (Freezing of undercooled melt)*

Calculate the entropy change of the universe in isothermal freezing of 1 g.mole of supercooled liquid gold at 1250K.

Data for gold:

Tm = *1336K*, ΔH_m^o = *12.36*$\times 10^3$ *J/mol*
$C_{p_{solid}} = 23.68 + 5.19 \times 10^{-3} T$ *J/mol/K,*
$C_{p_{liquid}} = 29.29$ *J/mol/K*

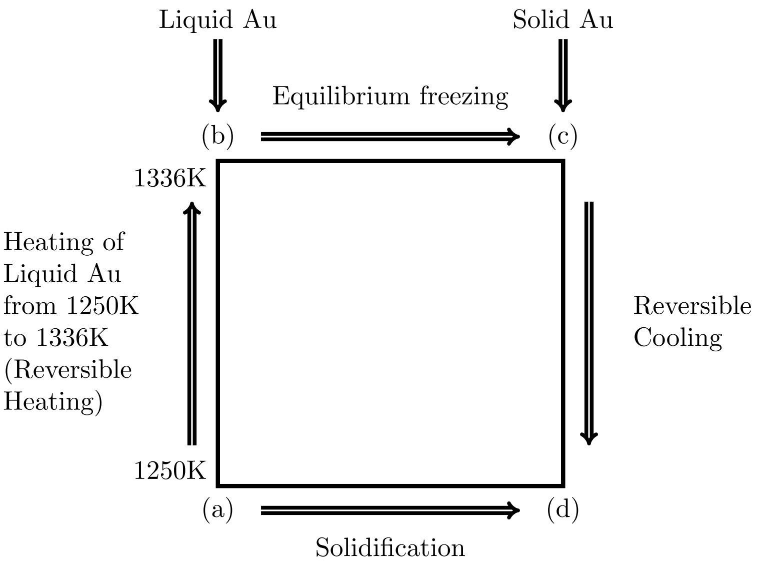
Solution. The freezing which occurs at normal freezing point would be reversible freezing. In practice, freezing generally occurs at lower temperatures. The liquid at a temperature below the freezing point is called the undercooled melt which will spontaneously freeze when nucleation barrier is overcome.

We need to calculate separately, entropy change of the system and entropy change of the surrounding.

Entropy of system is a state function. So, we can design the process such that the system reaches the final stage through a series of reversible steps. This will make our calculations easy.

The entropy of surrounding increases because the heat released by the system in freezing is absorbed by the surrounding. For entropy change of surrounding we will calculate heat released by the system and then divide it by the temperature of surrounding.

Let us draw a sketch to show various steps.



1. Process a to b is the heating of liquid Au from 1250 K to its freezing point 1336 K. This process can be carried out reversibly and we call it reversible heating.
2. Process b to c is the freezing of liquid Au at its freezing point 1336 K. This process can be carried out reversibly and we call it reversible freezing.
3. Process c to d is the cooling of solid Au from 1336 K to 1250 K. This process can be carried out reversibly and we call it reversible cooling.
4. Process a to d is the irreversible freezing of liquid Au below its freezing point.

First we calculate entropy change of the system in going from a to d through reversible path via b and c.

$$\Delta S_{sys} = \Delta S_{a\to b} + \Delta S_{b\to c} + \Delta S_{c\to d}$$

$$\Delta S_{a\to b} = \int_{1250}^{1336} \frac{Cp(l)}{T} dT = \int_{1250}^{1336} \frac{29.29}{T} dT$$

$$\Delta S_{b\to c} = \frac{-\Delta H_m}{1336} = \frac{-12.36\times 10^3}{1336}$$

$$\Delta S_{c\to d} = \int_{1336}^{1250} \frac{C_p(s)}{T} dT = \int_{1336}^{1250} \frac{23.68 + 5.19\times 10^{-3}T}{T} dT$$

$$\Delta S_{sys} = \int_{1250}^{1336} \frac{29.29}{T} dT - \frac{12.36\times 10^3}{1336} + \int_{1336}^{1250} \frac{23.68 + 5.19\times 10^{-3}T}{T} dT$$

$$\boxed{\Delta S_{sys} = -9.327\ J/K/mol}$$

To find entropy change of surrounding, we calculate enthalpy change of the system. As the enthalpy of system is a state function, the calculations can be carried out through reversible path.

$$\Delta H_{system} = \Delta H_{a \to b} + \Delta H_{b \to c} + \Delta H_{c \to d}$$

$$\Delta H_{system} = \int_{1250}^{1336} Cp(l)dT + (-\Delta H_m^o) + \int_{1336}^{1250} Cp(s)dT$$

$$\Delta H_{system} = \int_{1250}^{1336} (29.29)dT - 12,36 \times 10^3 + \int_{1336}^{1250} (23,68 + 5.19 \times 10^{-3})dT$$

$$\Delta H_{system} = -12.46 \times 10^3 J/mol$$

This is the heat released by the system which is equal to the heat absorbed by the surrounding.

$$\Delta S_{surrounding} = \frac{+\Delta H_{system}}{1250}$$

$$\Delta S_{surrounding} = \frac{12.46 \times 10^3}{1250} = +9.967 J/K/mol$$

$$\Delta S_{universe} = \Delta S_{sys} + \Delta S_{surrounding}$$

$$\Delta S_{universe} = -9.327 + 9.967 = +0.64 J/K/mol$$

So, the irreversible freezing has resulted in increase in entropy. The magnitude of this entropy change is small as the process involves condensed phase (liquid and solid) only. □

3.6 Heat Engine

A good understanding about heat-work relation and entropy changes can be obtained from the consideration of heat engines. It was realized that while work may be completely converted into heat, heat cannot be completely converted into work. Thus heat engines had low efficiencies. Later we will see that we could achieve much higher efficiencies in electrochemical processes.

A heat engine is a device which takes heat from a high temperature source, converts some part of it into work and rejects the remaining amount of heat into a low temperature sink. We would be happy if we could completely convert heat into work. The first law of thermodynamics does not put any restriction on complete conversion of heat into work. However, this is forbidden by the second law of thermodynamics. One of the statements of second law in this respect is, 'It is impossible, by means of

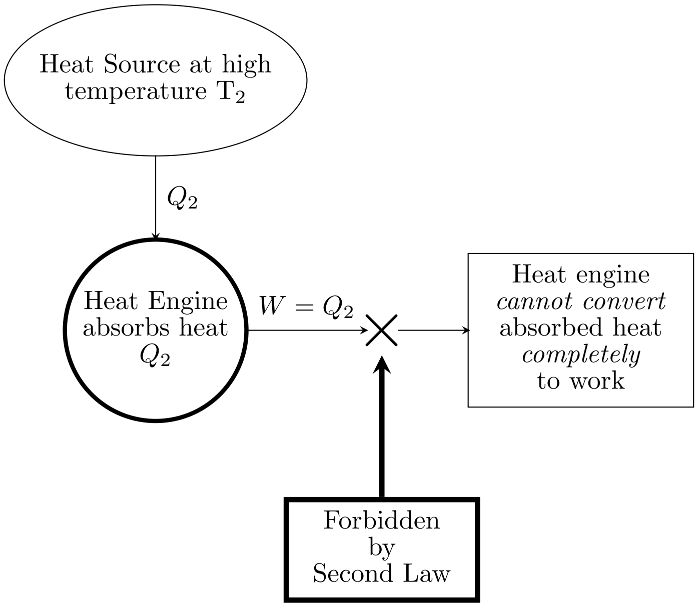


Figure 3.4: Restriction imposed by second law of thermodynamics on a heat engine

a cyclic process, to take heat from a reservoir and convert it to work without, in the same operation, transferring heat to a cold reservoir.'

Figure 3.4 describes the restriction by second law and Figure 3.5 schematically describes the working of a heat engine.

The reservoir at high temperature is called source while the low temperature reservoir is called sink. It is desirable to look at the efficiency of a heat engine.

$$\text{efficiency} = \frac{\text{Work done by heat engine}}{\text{Heat absorbed from the source}}$$

In the present case,

$$\text{efficiency}, \quad \eta = \frac{W}{Q_2} \tag{3.4}$$

For a continuous operation, it is necessary for the system to carry out cyclic operation. One convenient cycle is the Carnot cycle. This cycle consists of four steps and it is assumed that all the processes are reversible:

1. Absorption of heat Q_2 at T_2 resulting in isothermal expansion (work done by system W_1)

2. Adiabatic expansion (work done by the system W_2 at the expense of its energy decreasing temperature to T_1)

3. Rejection of heat Q_1 to sink at temperature T_1 during isothermal compression (work done on system W_3)

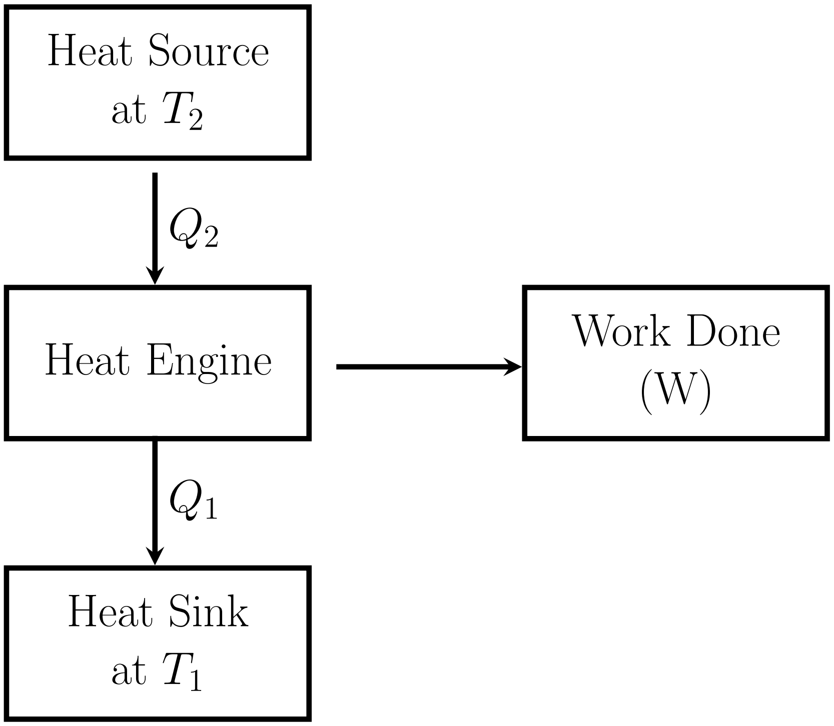


Figure 3.5: Schematic representation of a Heat Engine

4. Adiabatic compression (work done on system W_4 which increases its internal energy, increasing the temperature to T_2)

By using Carnot cycle
Entopy Change in reversible isothermal expansion = $\frac{Q_2}{T_2}$
Entropy Change in reversible isothermal compression = $-\frac{Q_1}{T_1}$
Adiabatic expansion and compression is isentropic.
Total change in entropy of the system in a cycle is

$$\Delta S = \frac{Q_2}{T_2} - \frac{Q_1}{T_1}$$

Since entropy is a state function, the total change in entropy of the system in a cycle would be zero,

$$\Delta S = 0$$

$$\frac{Q_2}{T_2} - \frac{Q_1}{T_1} = 0$$

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

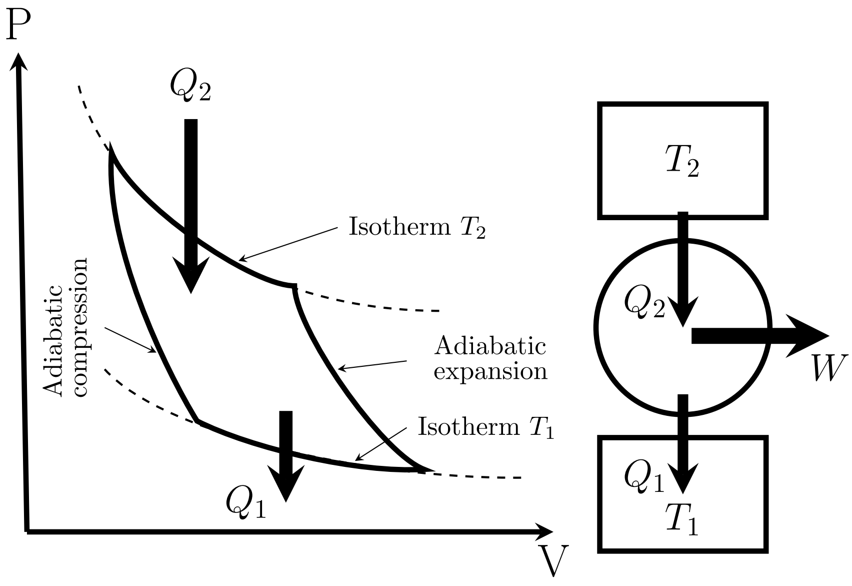


Figure 3.6: P-V diagram for Carnot Cycle

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \tag{3.5}$$

As

$$W = Q_2 - Q_1$$
$$\eta = \frac{W}{Q_2} = \frac{Q_2 - Q_1}{Q_2} = 1 - \frac{Q_1}{Q_2}$$

Hence, we get

$$\eta = 1 - \frac{T_1}{T_2} \tag{3.6}$$

If we assume that the working substance in the heat engine is one mole of ideal gas, we can obtain efficiency using gas laws as follows.

From the first law of thermodynamics,

$$\sum_{cycle} \Delta U = 0 = \text{heat absorbed - work done}$$
$$0 = (Q_2 - Q_1) - W$$
$$W = Q_2 - Q_1$$
$$\eta = \frac{W}{Q_2} = \frac{Q_2 - Q_1}{Q_2}$$
$$\eta = \frac{RT_2\ ln\ (V_2/V_1) - RT_1\ ln\ (V_4/V_3)}{RT_2\ ln\ (V_2/V_1)}$$

As $V_2/V_1 = V_4/V_3$, we get

$$\eta = 1 - \frac{T_1}{T_2}$$

Which is the same as before.

3.7 Thermodynamic Temperature Scale

The above discussion shows that the maximum efficiency is independent of the working substance and is the function of the working temperatures only. Before the application of gas laws to this problem, Kelvin had proposed that

$$\frac{Q_1}{Q_2} = \frac{f(t_1)}{f(t_2)}$$

Here ‘t’ is the temperature in Celsius scale.

Kelvin took these functions to have a simple form, i.e.,

$$f(t_1) = t_1 + 273.16 = T_1$$
$$f(t_2) = t_2 + 273.16 = T_2$$

So

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

or

$$1 - \frac{Q_1}{Q_2} = 1 - \frac{T_1}{T_2}$$

The relation

$$f(t) = t + 273.16 = T$$

defines an absolute thermodynamic scale of temperature. It may be noted that the zero of this temperature scale is that temperature of a cold reservoir which makes the efficiency 100%.

Later, it was shown using ideal gas law that

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

where ‘T’ is the temperature in the ideal gas temperature scale. Hence, it was concluded that the thermodynamic temperature scale and the ideal gas temperature scale are the same. Remember, ideal gas temperature scale was defined based on Charles Law, where it was noted that when the volume of ideal gas is extrapolated to low temperatures, it becomes zero at -273.16 ^{o}C. This temperature was then defined as zero on absolute temperature scale.

From the above discussion regarding heat engines, the following points may be noted:

1. Efficiency of a heat engine cannot be 100% as some heat must be rejected to continue a cyclic operation. Recall a piston of an engine along with a flywheel. After the expansion, the piston has to come back to its original position. That requires compression part of the cycle associated with heat rejection. Modern cycles use Combined Heat and Power (CHP) cycle in which heat rejected by the first system is further utilized to generate power thereby increasing overall efficiency.

2. As

   $$\eta = 1 - \frac{T_1}{T_2}$$

   In order to have

   $$\eta = 1$$

   we need to obtain value of T_1= 0 K, or to get infinite value of T_2, both of which are not possible.

3. From the above equation we can see that, for maximum efficiency, we need the highest possible value of T_2, i.e., temperature of the source, and the lowest possible value of T_1, i.e., temperature of the sink.

4. Practical engines have efficiencies less than the theoretical value obtained from the above equation, as in practical cases the processes cannot be reversible (which is the assumption in calculating η above). Remember, to apply math we assume that all the expansion and compression processes in the cycle are reversible.

3.8 The Third Law of Thermodynamics

As per Planck's statement, the third law of thermodynamics says, 'Entropy of any homogeneous substance which is in complete internal equilibrium may be taken to be zero at 0 K.'

Homogeneous substance with internal equilibrium basically means a pure element in crystalline structure with no defect. When we have more than one element, entropy of mixing (configurational entropy) must be considered. Even in case of pure element, there may be configurational entropy because of isotopes. Glassy structure, presence of dislocations, vacancies and interstitials all contribute positively towards entropy.

It should be noted that the third law of thermodynamics can be verified experimentally.

Third law provides the basis to calculate absolute values of entropy of substances. Remember, in case of enthalpy, we arbitrarily take enthalpy of pure elements in stable form at room temperature to be zero. This is an assumed reference. However, entropy of pure defect free crystalline element is zero is not an assumption but a fact as per third law.

3.9 Zeroth Law of Thermodynamics

According to the *zeroth law of thermodynamics*, if two substances A and B are in thermal equilibrium with a third substance C, then A and B are in thermal equilibrium with each other.

Zeroth Law provides the concept of temperature and provides a basis for temperature measurement.

Why is it called the zeroth law of thermodynamics? Three laws of thermodynamics were already established and named as the first, second and third law. This law is the fundamental one, it was given a lower number, i.e., zero and the law is called the "Zeroth law".

Summary

- The total entropy change is a measure of irreversibility.
- $dS = \delta Q/T \rightarrow \Delta S = \delta Q_{reverible}/T$ for measurement we need reversible path as we cannot do calculation along irreversible path.
- Entropy of the system is a state function, while entropy of the surrounding is not a state function. Thus we say that the entropy change of system does not depend upon the path followed whether it is reversible or irreversible.
- In a reversible process, the driving force is infinitesimally small and
    - Maximum work is done by the system (Minimum work done on the system)
    - System will pass through a series of equilibrium stages
    - No loss or degradation of energy occurs.
- Disadvantage of this consideration is that the driving force needs to approach zero and the process will be extremely slow and impractical.
- Advantage of this consideration is that the losses in the process approach zero and the mathematical calculations become easy.
- $\Delta S_{Total} = 0$ for reversible process
- $\Delta S_{Total} > 0$ for irreversible, spontaneous or natural process

Practice Problems

1. Evaluate the following statements:

    i. Though impractical, the concept of a reversible process is useful.
    ii. Entropy of universe is increasing.
    iii. If we find that any thermodynamic law is being violated, something is wrong with us.
    iv. Talking about a reversible process is a waste of time.
    v. We can cool a room by keeping the door open of a refrigerator, kept in the room.
    vi. Heat engines have very low efficiencies.
    vii. There was a logical need of the second law of thermodynamics.
    viii. Thermodynamic temperature scale and Ideal gas law temperature scale are the same.

2. Give some statements of the second law which tell us that it is more practical than other laws of thermodynamics.

3. One statement of third law is, ‘Entropy of a pure crystalline solid in complete equilibrium at 0 K may be taken as zero’. It is generally said that all these requirements are very difficult to be met. Comment.

4. Evaluate the statement, ‘The concepts of State Function and Reversible Process have greatly helped advancement of thermodynamics’.

5. Thermodynamics revolves around four laws. Briefly discuss these laws w.r.t. their usefulness and limitations.

6. Evaluate *reversibility* in terms of the concept, its usefulness and limitations.

Chapter 4

Maximum Work, Spontaneity Criteria and Entropy

Learning Outcomes:

Student should be able to explain

- Maximum work available from a system
- Concept of Free energy
- Energy and Entropy criteria of spontaneity
- Most suitable criterion of spontaneity
- Entropy changes in various physical and chemical processes
- Statistical approach to entropy
- Chemical potential
- Uphill diffusion

We have seen that the total entropy increases in a spontaneous process. Hence entropy change could be used as a criterion for spontaneity. The problem we noticed is that we have to calculate entropy change of the system as well as the surrounding and then find the net change. Our interest is in the changes within the system only as changes in surrounding are difficult to calculate. So, we start with the concept of maximum work a system can do. This will lead to the concept of free energy and then we can get to useful spontaneity criteria.

4.1 Maximum Work

Recall that the work done by a system is maximum only in a reversible process. This also corresponds to the maximum heat absorbed by the system. In other words,

$$W_{max} \textit{ corresponds to } Q_{max} \textit{ which is } Q_{rev}$$

If δQ_{rev} is the heat absorbed, the increase in entropy of the system is

$$dS = \frac{\delta Q_{rev}}{T}$$

Hence the 2$^{\text{nd}}$ law of thermodynamics gives us

$$\delta Q_{rev} = TdS \tag{4.1}$$

From the first law of thermodynamics

$$\delta W_{max} = \delta Q_{rev} - dU$$

Combining both equations

$$\delta W_{max} = TdS - dU \tag{4.2}$$

$$\delta W_{max} = -(dU - TdS)$$

This means that the maximum work is given by decrease in an energy function denoted by 'A' such that

$$dA = (dU - TdS) \tag{4.3}$$

And hence

$$\delta W_{max} = -(dA) \tag{4.4}$$

Maximum work done by a system is equal to the decrease in 'A'. This function is called the Helmholtz Free Energy. Remember, maximum work is available during the reversible process only. The irreversible process will entail losses thus decreasing the available useful work.

For an irreversible process, heat absorbed by the system is less

$$\delta Q = TdS - TdS_{irrev}$$

Using first law

$$\delta W = \delta Q - dU$$

We get

$$\delta W = (TdS - TdS_{irrev}) - dU$$

$$\delta W = (TdS - dU) - TdS_{irrev} \tag{4.5}$$

This means that the maximum work would always be less than $(TdS–dU)$

$$\delta W \leq TdS - dU$$

So, the maximum work is

$$\delta W_{max} = -(dU - TdS)$$

$$\delta W_{max} = -(dA)$$

Note that, for reversible isothermal process,

$$\delta W_{max} = TdS$$

And for reversible adiabatic process,

$$\delta W_{max} = -(dU)$$

And for a general process,

$$\delta W_{max} = -(dU - TdS)$$

For finite changes,

$$W_{max} = -(\Delta U - T\Delta S)$$

Here

W_{max} = Max work done by the system
$T\Delta S$ = Energy change of the system associated with entropy change
ΔU = Change in internal energy of the system

So the useful work available depends on two factors, ΔU and $T\Delta S$. Thus a process is favored by a decrease in 'U' and/or an increase in 'S'.

4.2 Spontaneity Criteria

As per our basic understanding, a system will have a tendency to move towards the stable state. If we talk about the energy, it will be the minimum energy state. If we talk about entropy, it will be the maximum entropy state. So, if a system is at equilibrium, it will be either in the minimum energy state or maximum entropy state. If the system is not in equilibrium state, it will have tendency to spontaneously move to the equilibrium state. In this process, energy term (U, H, G, A) will tend to decrease while entropy will tend to increase.

Keeping this naive understanding in mind, let us look at various spontaneity criteria. We need to keep in mind that, for the development of basic concepts,

1. We are considering a closed system consisting of ideal gas in which heat, internal energy and work are interplaying. Work here is basically PV work.

2. The thermodynamic variables are P, V and T. Entropy and internal energy of the system is under consideration. For convenience, enthalpy and free energy functions have been introduced.

3. We are interested in changes in the system and are not worried about changes in the surrounding.

4. In the later chapters, the discussion is extended to open systems, to system undergoing chemical reactions, to incorporate other energies like surface energies, other types of works like electrochemical work and so on.

4.2.1 Internal Energy Criterion

The first law of thermodynamics states that

$$dU = \delta Q - \delta W$$

Combining second law and considering PV work only, we get

$$dU = TdS - PdV \tag{4.6}$$

From calculus, we know that minima or maxima of a function requires the first derivative to be zero. The minima in internal energy would occur when derivative of U is zero. dU will be zero when both dS and dV are zero. dS and dV zero mean that S and V are not changing, i.e., S and V are constant.

$$dU = 0 \text{ requires } dS = 0 \text{ and } dV = 0$$

For equilibrium we get the condition that, at constant S and V, U should be the minimum.

$$(dU)_{S,V} = 0$$

If it is not, the system will undergo spontaneous change to reduce U,

$$(dU)_{S,V} < 0$$

Combining these two, we can write that

$$(dU)_{S,V} \leq 0$$

At constant volume and entropy, the system will either decrease its internal energy (spontaneous process) or keep it constant (equilibrium).

This means that the internal energy of a system, keeping entropy and volume constant, must decrease for the process to occur spontaneously. This is illustrated in Figure 4.1. The use of this spontaneity criterion is not desirable since the entropy need to be kept constant which is difficult to control.

Now let us determine the behavior of entropy. Rearranging the above equation, we get

$$dS = \frac{1}{T}dU + \frac{P}{T}dV \tag{4.7}$$

For maxima in entropy, its differential dS need to be zero. dS would be zero when both dU and dV are zero. This means that U and V are constant.

$$(dS)_{U,V} = 0$$

This is the condition for equilibrium. If entropy is not maximum, the system will have tendency to go in the direction of increasing entropy.

$$(dS)_{U,V} > 0$$

As illustrated in Figure 4.2, this is entropy criterion for spontaneity. When the internal energy and volume of a system are kept constant, its entropy must increase for the process to be spontaneous. This criterion is also not desirable since controlling internal energy is difficult.

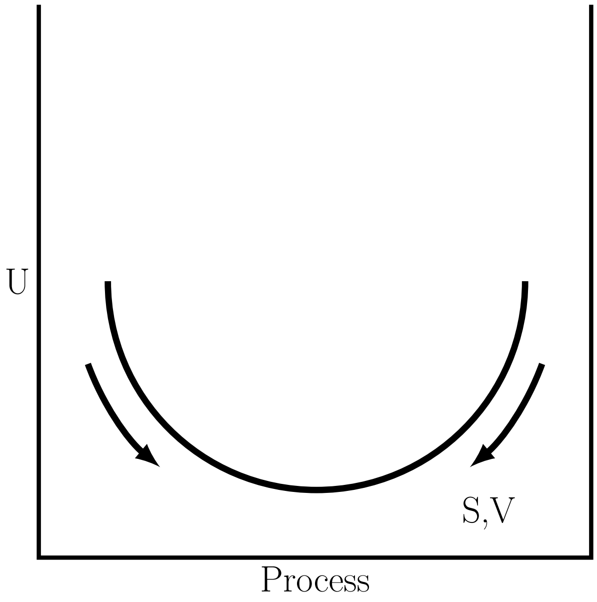


Figure 4.1: Internal energy criterion for spontaneity

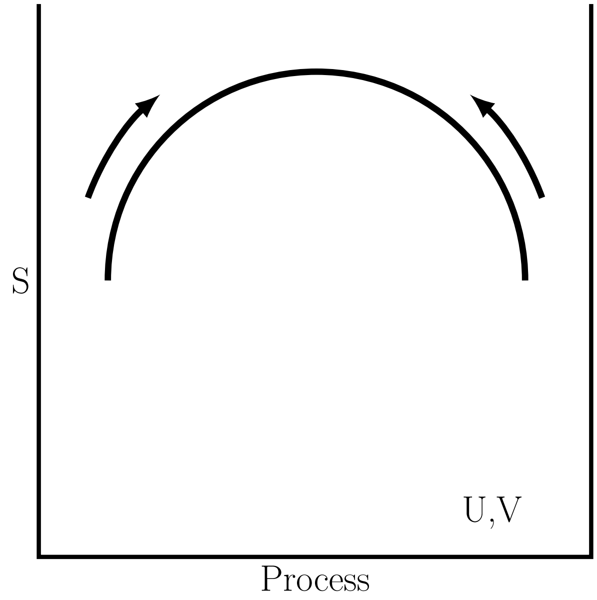


Figure 4.2: Entropy criterion for spontaneity

4.2.2 Enthalpy Criterion

Now, we use the definition of enthalpy

$$H = U + PV$$

On differentiating, we get

$$dH = dU + PdV + VdP$$

Using the expression for combined first law and second law

$$dH = [TdS - PdV] + PdV + VdP$$

$$dH = TdS + VdP \tag{4.8}$$

$$(dH)_{S,P} = 0$$

This is the condition for equilibrium. If entropy and pressure of the system are kept constant and it has no desire to change its enthalpy, the system would be in equilibrium with minimum enthalpy. If the system wants to undergo some change at constant S and P, its enthalpy will decrease.

$$(dH)_{S,P} < 0$$

As illustrated in Figure 4.3, this is enthalpy criterion for spontaneity where entropy and pressure need to be kept constant but since entropy is difficult to control, this criterion is again not desirable.

Now let us determine the behavior of entropy. Rearranging the above equation, we get

$$dS = \frac{1}{T}dH - \frac{V}{T}dP \tag{4.9}$$

For maxima in entropy, its differential dS need to be zero. dS would be zero when dH and dP are zero. This means that H and P are constant.

$$(dS)_{H,P} = 0$$

This is the condition for equilibrium. If entropy is not maximum, the system will have tendency to go in the direction of increasing entropy.

$$(dS)_{H,P} > 0$$

This is entropy criterion for spontaneity. When the enthalpy and pressure of a system are kept constant, its entropy must increase for the process to be spontaneous. This criterion is also not desirable since controlling enthalpy is difficult.

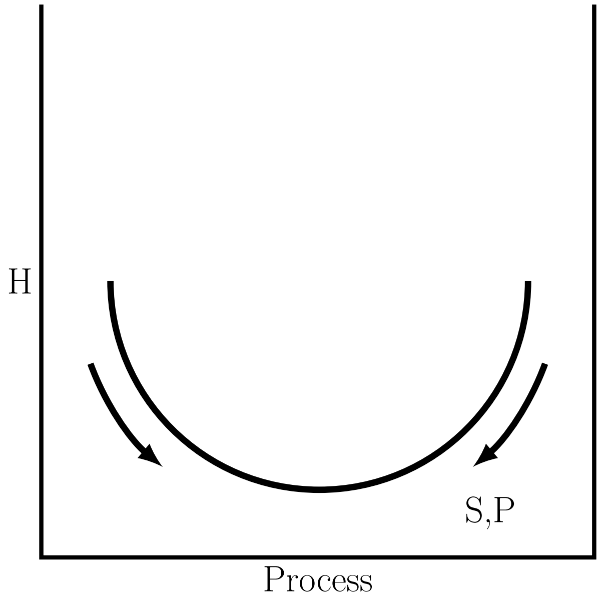


Figure 4.3: Enthalpy criterion for spontaneity

4.2.3 Helmholtz Free Energy Criterion

Now, another energy function, Helmholtz Free Energy, is defined as

$$A = U–TS \tag{4.10}$$

On differentiating

$$dA = dU - TdS - SdT$$

Since

$$dU - TdS = -PdV$$

We get

$$dA = -PdV - SdT \tag{4.11}$$

$$(dA)_{V,T} < 0$$

This criterion for spontaneity is useful. As illustrated in Figure 4.4, process will be spontaneous if there is decrease in Helmholtz free energy keeping volume and temperature constant. This is considered as the second best criterion for spontaneity since volume and temperature of the system can be easily controlled.

4.2.4 Gibbs Free Energy Criterion

Now, another energy function, Gibbs Free Energy, is defined as

$$G = H–TS \tag{4.12}$$

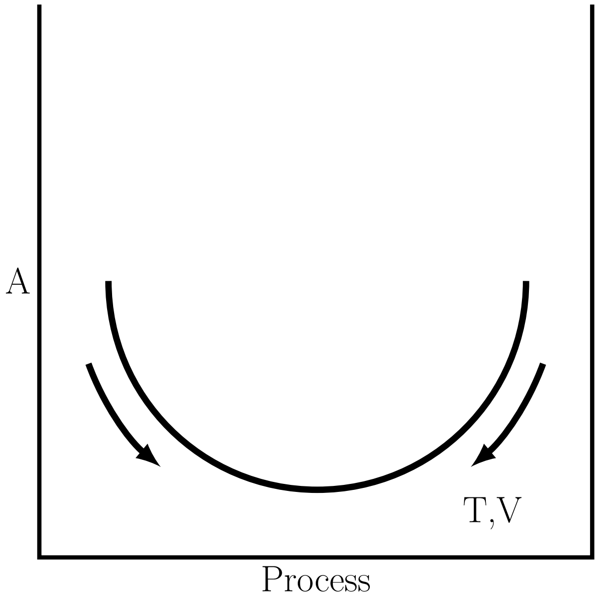


Figure 4.4: Helmholtz free energy criterion for spontaneity

On differentiating

$$dG = dH - TdS - SdT$$

Since

$$dH = TdS + VdP$$

We get

$$dG = -SdT + VdP \tag{4.13}$$

Following the same arguments, we get the condition for equilibrium as

$$(dG)_{P,T} = 0$$

And condition for spontaneity as

$$(dG)_{P,T} < 0$$

This is the best and the most useful criterion for spontaneity since keeping temperature constant is not difficult and most of the metallurgical processes occur at constant pressure i.e., atmospheric pressure. Gibbs free energy criterion in illustrated in Figure 4.5.

Spontaneity criteria are summarized in Table 4.1.

4.2.5 Spontaneity Criteria – Historical Perspective

We want to know whether a process is spontaneous or not.

In simple systems, it is easy to predict direction. e.g.,

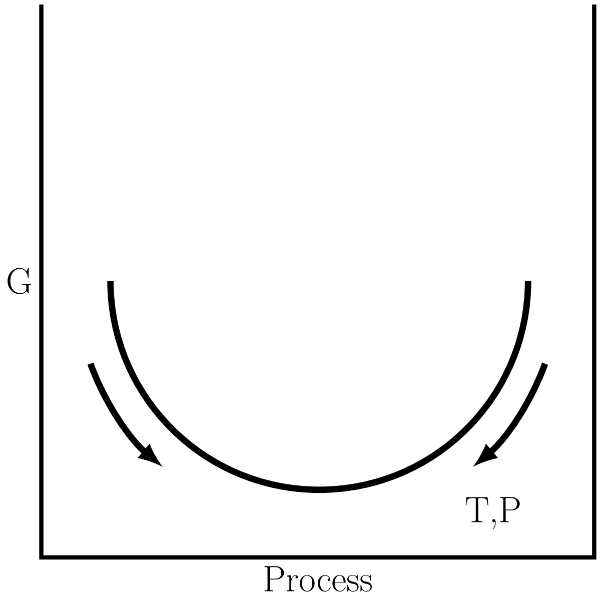


Figure 4.5: Gibbs Free Energy Criterion for Spontaneity

i) We can tell direction of heat flow by touching two objects at different temperatures

ii) When partition between two gases is removed, we know that they will mix spontaneously.

In less simple systems, direction of process is difficult to predict and we need criteria of spontaneity.

Suppose we want to explore the following reaction

$$CO_{(g)} + NO_{(g)} \rightarrow CO_{2_{(g)}} + \frac{1}{2}N_{2_{(g)}}$$

If we can show this reaction to be spontaneous, it is excellent way to remove air pollutants. We can spend time to find how to initiate it or catalyze it. If not, we should not waste time.

Since long, a naive understanding has been:

A) A process will occur when there is decrease in energy. For example, a reaction will occur when energy of products is less than energy of reactants – say $\Delta H < 0$ i.e., exothermic process. This is true in many cases, but fails in various situations, for example,

    - Melting of ice at room temperature
    - Dissolution of KNO_3 in water

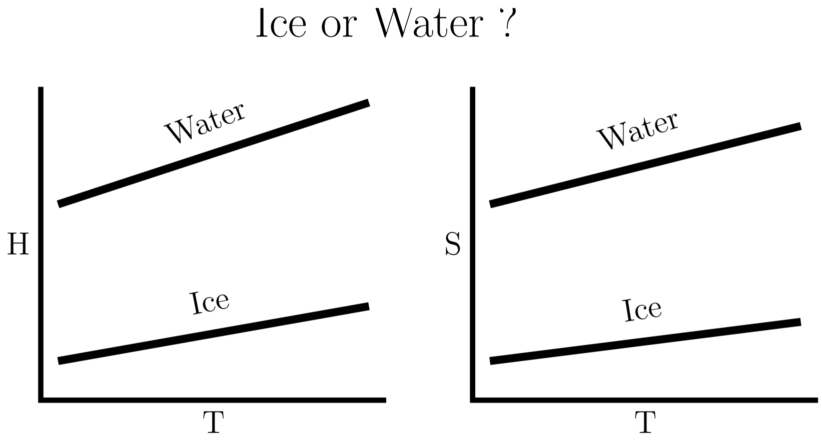


Figure 4.6: Variation of enthalpy and entropy of water and ice as a function of temperature

B) A process will occur if entropy increases - $\Delta S > 0$. In many cases this is true such as melting of ice at room temperature or mixing of two gases. However, we can find instances where this is not true such as the oxidation of iron,

$$Fe_{(s)} + \frac{1}{2}O_{2_{(g)}} \rightarrow FeO_{(s)}$$

Let us discuss example of water and ice.

- When water at -4 ^{o}C spontaneously freezes, we note

  . $\Delta H < 0$ Exothermic, Enthalpy decreases

  . $\Delta S < 0$ Entropy decreases

- When ice at 4 ^{o}C spontaneously melts, we have

  . $\Delta H > 0$ Endothermic, Enthalpy increases

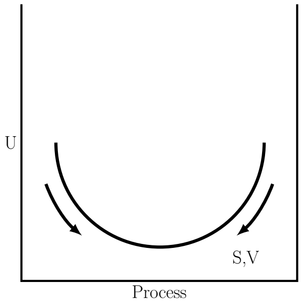
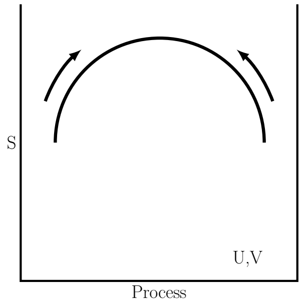
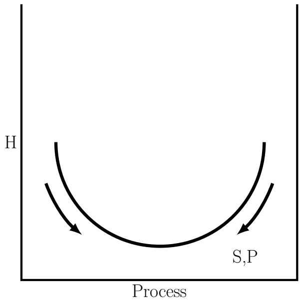
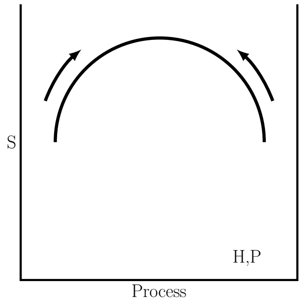
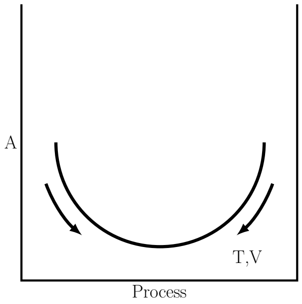
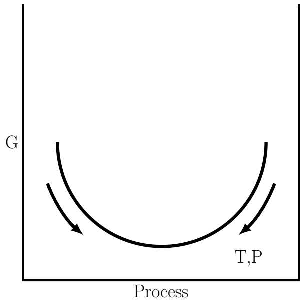
  . $\Delta S > 0$ Entropy increases

Figure 4.6 shows the variation of enthalpy and entropy of water and ice as a function of temperature.

If we consider enthalpy, ice should be stable at all temperatures. If we consider entropy, water should be stable at all temperatures. The puzzle is solved by Gibbs free energy.

If we plot G = f(T), as shown in Figure 4.7, for both water and ice, we find cross over at the normal freezing point (273K). Below this temperature, ice is stable and above this temperature, water is stable.

Table 4.1: Summary of Spontaneity Criteria

$dU = TdS - PdV$ $(dU)_{S,V} < 0$  	$dS = \frac{1}{T}dU + \frac{P}{T}dV$ $(dS)_{U,V} > 0$ 
$dH = TdS + VdP$ $(dH)_{S,P} < 0$  	$dS = \frac{1}{T}dH - \frac{V}{T}dP$ $(dS)_{S,P} > 0$ 
$dA = -SdT - PdV$ $(dA)_{V,T} < 0$  	$dG = -SdT + VdP$ $(dG)_{P,T} < 0$ 

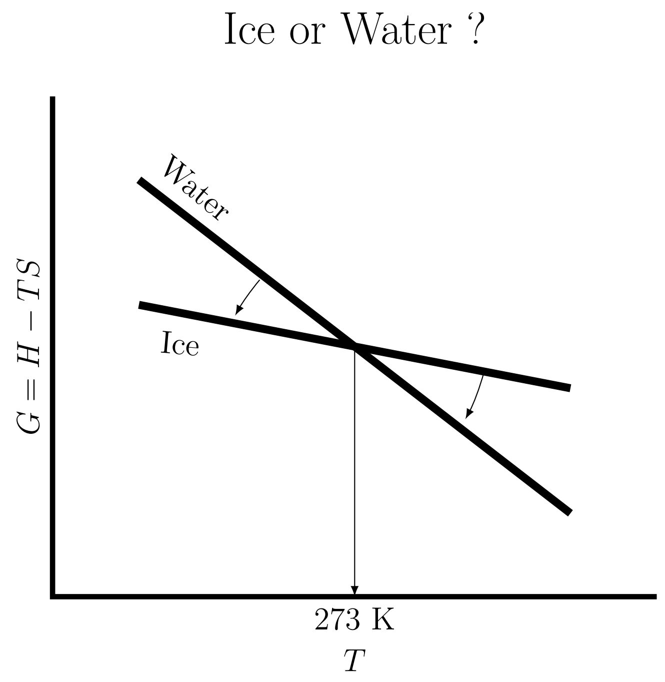


Figure 4.7: Variation of Free Energy of water and ice as a function of temperature

4.3 Use of Gibbs Free Energy Criterion for a Process

Now we have a very useful criterion. At constant T and P,

1. A process will occur if it results in decrease in Free Energy 'G' of the system.
2. A process cannot occur if it results in increase in 'G'.
3. The system would be in equilibrium (no tendency to change) if there is no change in 'G'.

Importance of Gibbs free energy as a criterion can be summarized as:

- Although all of the criteria tell us the direction of the process and the conditions needed, Gibbs Free Energy is the most useful. This is due to its practicality. Keeping pressure and temperature constant is very easy as compared to entropy and internal energy which are difficult to control. Most metallurgical operations occur at atmospheric pressure. We just have to maintain constant temperature to apply this criterion.
- Maximum useful work which we can get from a system is
  - $\delta W_{max} = -(dU - TdS) = -dA$
  - $\delta W_{max} = -(dH - TdS) = -dG$

- ◦ If no work done other than PV work
  - i) If PV work is zero (constant volume) $dA \leq 0$
  - ii) At constant P (including PV work) $dG \leq 0$

The definition of Gibbs Free energy,

$$G = H – TS$$

at constant P and T gives

$$\Delta G = \Delta H - T\Delta S \tag{4.14}$$

This equation is one of the most important relations in the thermodynamics of materials. In order to determine whether a process is spontaneous or not we need to calculate ΔG

$$\Delta G = G(final\ state) - G(initial\ state)$$

This may be calculated from ΔH and ΔS which use C_p values. Electrochemical means provide a very convenient way to find ΔG, using EMF 'E' of an appropriate cell (discussed in chapter 8).

$$\Delta G = -n\ F\ E$$

The equation

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

provides answers to two basic questions.

1. Can a process occur if enthalpy increases? Yes, for endothermic process the enthalpy increases. We need to ensure that the free energy decreases. For this, we require that entropy should sufficiently increase.

2. Can a process occur if entropy decreases? Yes, the process could occur if the entropy of the system decreases. We need to ensure that the free energy decreases. For this, we require that enthalpy should sufficiently decrease.

The relation $\Delta G = \Delta H – T\Delta S$ may be visualized as follows:

$\Delta G = \Delta H$ (Energy change due to change in chemical species bond energy)
$–T\Delta S$ (Energy associated with entropy change)

In other words, the driving force for a chemical reaction (ΔG) depends on two quantities:

- the energy change due to making and breaking of bonds (ΔH)
- the product of T and the change in randomness (ΔS)

ΔG represents the maximum (useful) work available from the system,

- if entropy decreases, available work is less than ΔH
- if entropy increases, available work is more than ΔH

- entropy contribution increases as T increases

According to the above equation, the following possibilities can occur:

1. ΔH decreases, ΔS increases. The process can occur at any temperature.
2. ΔH increases, ΔS decreases. The process cannot occur at any temperature.
3. ΔH increases, ΔS increases. This process will depend upon the relative magnitudes. Magnitude of ΔS should be high and magnitude of ΔH should be low. The process is favored at high temperature.
4. ΔH decreases, ΔS decreases. This process will also depend upon the relative magnitudes. ΔS should have low magnitude, ΔH should have high magnitude. The process is favored at low temperature.

Let us see some examples.

1. Oxidation of Silver

$$2Ag_{(s)} + \frac{1}{2}O_{2_{(g)}} \rightarrow Ag_2O_{(s)}$$

For the above chemical reaction

$$\Delta G^\circ = -30,540 + 66.11T$$

Comparing this equation with equation for Gibbs free energy change, we get

$$\Delta H^\circ = -30,540 J/mole$$

$$\Delta S^\circ = -66.11 J/K/mole$$

For a process to occur

$$\Delta G < 0$$

$$-30,540 + 66.11T < 0$$

Solving for T

$$T < 462K$$

It should be kept in mind that the value given is that for standard free energy change (and standard enthalpy change and standard entropy change). ΔG° means the difference in free energy of products and reactants when all of them are in their standard states.

2. Oxidation of Iron

$$Fe_{(s)} + \frac{1}{2}O_{2_{(g)}} \leftrightarrow FeO_{(s)}$$

The standard free energy equation is given as

$$\Delta G^\circ = -263,700 + 64.35T$$

For reaction to occur $\Delta G < 0$

$$-263,700 + 64.35T < 0$$

$$T < 4100K$$

3. Decomposition of HI

$$2HI_{(g)} \leftrightarrow H_{2_{(g)}} + I_{2_{(g)}}$$

The free energy equation for above chemical reaction is given as

$$\Delta G^\circ = 8370 + 17.65T$$

For reaction to occur $\Delta G < 0$

$$8370 + 17.65T < 0$$

$$T < -500K$$

Notice that the value of temperature comes out to be negative. However, temperature in Kelvin scale can never be negative. For any value of temperature, ΔG° would always be a positive value for the above equation. Therefore, the above reaction is not possible at any temperature when the reactants and products are present in their standard states.

4. Formation of Iron carbide

$$3Fe_{(s)} + C_{(s)} \leftrightarrow Fe_3C_{(s)}$$

The free energy equation for this chemical reaction is given by

$$\Delta G^\circ = 29040 - 28.03T$$

$$\Delta G < 0$$

Solving for T we get

$$T > 1036K$$

Iron carbide will have a tendency to decompose at lower temperatures. Given sufficient time and temperature (for atomic mobility) iron carbide will decompose to give ferrite and graphite. This is what we observe when we heat treat white cast iron to make malleable cast iron.

5. Reactions in Carbon / Oxygen System

$$C_{(s)} + \frac{1}{2}O_{2_{(g)}} \leftrightarrow CO_{(g)} \qquad \Delta G^\circ = -111,700 - 87.65T$$
$$C_{(s)} + O_{2_{(g)}} \leftrightarrow CO_{2(g)} \qquad \Delta G^\circ = -394,100 - 0.84T$$

If we multiply first equation by 2 we get

$$2C_{(s)} + O_{2_{(g)}} \leftrightarrow 2CO_{(g)} \qquad \Delta G^\circ = -223,400 - 175.30T$$

The value of ΔG° for $C + CO_2 \leftrightarrow 2CO$ can be calculated using this data.

$$2C_{(s)} + O_{2_{(g)}} \leftrightarrow 2CO_{(g)} \qquad \Delta G^\circ = -223,400 - 175.30T \tag{4.15}$$
$$C_{(s)} + O_{2_{(g)}} \leftrightarrow CO_{2_{(g)}} \qquad \Delta G^\circ = -394,100 - 0.84T \tag{4.16}$$

Subtracting Equation 4.16 from Equation 4.15, we get

$$C_{(s)} \to 2CO_{(g)} - CO_{2_{(g)}} \qquad \Delta G^\circ = 170,400 - 174.46T$$

Or

$$C_{(s)} + CO_{2_{(g)}} \to 2CO_{(g)} \qquad \Delta G^\circ = 170,400 - 174.46T$$

For reaction to proceed in the forward direction, $\Delta G^\circ < 0$

Solving for T we get

$$T > 978K$$

At temperature higher than 978 K, CO_2 will react with C to form CO while at lower temperatures, CO will decompose to deposit C. The forward reaction is important in blast furnace for reduction of iron oxide while the reverse reaction is of significance in carburizing of steel.

4.4 Maxwell's Relations

Basic principles of calculus can be used to obtain various useful relations in thermodynamics. In order to derive Maxwell's relations, let us rewrite the basic equations for Internal Energy, Enthalpy, Helmholtz Free Energy and Gibbs Free Energy as stated earlier in this chapter. Remember, for simplicity we are dealing with the variations in the state variables P, V and T only.

$$dU = TdS - PdV \tag{4.17}$$
$$dH = TdS + VdP \tag{4.18}$$
$$dA = -SdT - PdV \tag{4.19}$$
$$dG = -SdT + VdP \tag{4.20}$$

Using Equation 4.17, we get

$$\left(\frac{\partial U}{\partial S}\right)_V = T \tag{4.21}$$

and

$$\left(\frac{\partial U}{\partial V}\right)_S = -P \tag{4.22}$$

Using Equation 4.18, we get

$$\left(\frac{\partial H}{\partial S}\right)_P = T \tag{4.23}$$

and

$$\left(\frac{\partial H}{\partial P}\right)_S = V \tag{4.24}$$

Using Equation 4.19), we get

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \tag{4.25}$$

and

$$\left(\frac{\partial A}{\partial V}\right)_T = -P \tag{4.26}$$

Using Equation 4.20), we get

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \tag{4.27}$$

and

$$\left(\frac{\partial G}{\partial P}\right)_T = V \tag{4.28}$$

By comparing Equation 4.21 and Equation 4.23

$$\left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P \tag{4.29}$$

By comparing Equation 4.22 and Equation 4.26

$$\left(\frac{\partial U}{\partial V}\right)_S = \left(\frac{\partial A}{\partial V}\right)_T \tag{4.30}$$

By comparing Equation 4.24 and Equation 4.28

$$\left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial G}{\partial P}\right)_T \tag{4.31}$$

By comparing Equation 4.25 and Equation 4.27

$$\left(\frac{\partial A}{\partial T}\right)_V = \left(\frac{\partial G}{\partial T}\right)_P \tag{4.32}$$

4.5 Entropy-A Measure of Disorder

Entropy in simple terms may be regarded as a measure of disorder. Here, we will see that the magnitude of entropy change very nicely depicts extent of disorder in various processes.

In a given system, we can increase disorder through two ways:

- By providing heat
- By mixing

When heat is provided, there are two possibilities

- Temperature increases, the entropy change is $\Delta S = \int (\delta q/T)$
- Structural rearrangement without temperature change such as isothermal phase transformation, here, $\Delta S = (\Delta H/T_{tr})$

In case of reactions, we may have

- Changes in structure of molecules which results in small changes in entropy
- Change in moles of gases which results in large change in entropy. A rule of thumb is that for increase in one mole of a gas, the entropy increases by about 150 J/K/mole.

4.5.1 Richard's Rule

Richard noted that the values for molar entropy for melting of metals fall in a narrow range.

For Face Centered Cubic (FCC) metals $\quad \Delta S_m = \dfrac{\Delta H_m}{T_m} \approx 9.6 J/(K.mol)$

For Body Centered Cubic (BCC) metals $\quad \Delta S_m = \dfrac{\Delta H_m}{T_m} \approx 8.3 J/(K.mol)$

The similar values for entropy change on melting for various metals can be explained by considering the melting process. Regardless of the type of metal, on melting of one mole, Avogadro number of atoms which were vibrating on lattice points are now free to move within the liquid phase. Hence, the extent of disorder on melting is almost same in case of any metal. The value for FCC metals is a little higher because in this case a more compact structure is being converted into liquid form in comparison to BCC which is relatively an open structure.

This rule is sometimes used for estimation of enthalpy of melting using the melting point.

$$\Delta H_m = T_m \times \Delta S_m$$

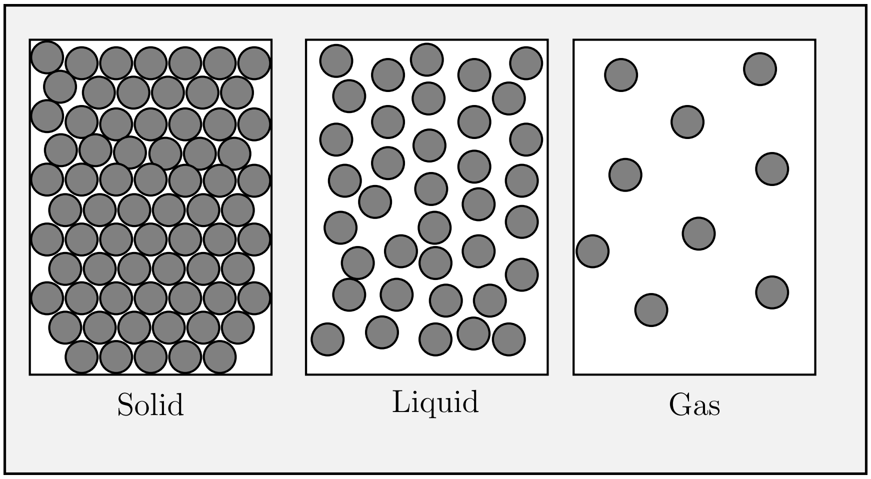


Figure 4.8: Comparison of disorder in solids, liquids and gases

4.5.2 Trouton's Rule

Trouton's rule states that molar entropy for boiling of metals is $88J/(K.mol)$. Again, we are freeing one mole particles from liquid state and converting them into vapor state. Therefore, the extent of disorder is same for every metal. However, in comparison to melting, the extent of disorder is much higher. This rule is sometimes used for estimation of enthalpy of boiling using the boiling point.

$$\Delta H_b = T_b \times \Delta S_b$$

Figure 4.8 compares the disorder in solid, liquid and vapor phases.

4.5.3 Entropy Changes in Chemical Reactions

Entropy changes when condensed phases (solids and liquids) are involved are small. Entropy changes are significant when number of moles of gases change during any process. As a rule of thumb, entropy increases by about 150 J/K if one mole gas is produced.

$$MO_{2_{(s)}} \rightarrow M_{(s)} + O_{2_{(g)}} \qquad \Delta S = +150J/K \qquad \text{(One mole gas evolved)}$$
$$M_{(s)} + \frac{1}{2}O_{2_{(g)}} \rightarrow MO_{(s)} \qquad \Delta S = -75J/K \qquad \text{(Half mole gas consumed)}$$

In the following, we compare actual values of entropy change in reactions involving net production or consumption of various amounts of gases.

$$2Cu_{(s)} + \frac{1}{2}O_{2_{(g)}} \rightarrow Cu_2O_{((s)} \qquad \Delta S = -69J/K\text{(Half mole gas consumed)}$$
$$Ni_{(s)} + O_{2_{(g)}} \rightarrow NiO_{(s)} \qquad \Delta S = -172J/K\text{(One mole gas consumed)}$$
$$C_{(s)} + \frac{1}{2}O_{2_{(g)}} \rightarrow CO_{(g)} \qquad \Delta S = +87J/K\text{(Half mole gas produced)}$$

When, in a reaction, moles of gases on both sides remain the same, entropy change is small.

$$C_{(s)} + O_{2_{(g)}} \rightarrow CO_{2_{(g)}} \qquad \Delta S = +0.084 J/K$$
$$H_{2_{(g)}} + Cl_{2_{(g)}} \rightarrow 2HCl_{(g)} \qquad \Delta S = +12.8 J/K$$
$$2MgO_{(s)} + SiO_{2_{(s)}} \rightarrow Mg_2SiO_{4_{(s)}} \qquad \Delta S = -4.32 J/K$$

4.5.4 Examples of Entropy Calculations:

Reversible isothermal compression of one mole of ideal gas

Using first law of thermodynamics

$$Q = \Delta U + W$$

In isothermal process, $\Delta U = 0$, so $W_{max} = Q_{rev}$

$$W_{max} = \int_{V_A}^{V_B} PdV = \int_{V_A}^{V_B} \frac{RT}{V} dV = RT\ ln\frac{V_B}{V_A}$$

So,

$$Q = RT\ ln\frac{V_B}{V_A}$$

For compression $V_B < V_A$ as the work is done on the system (negative). The transfer of heat from the gas to the reservoir causes decrease in the entropy of the gas.

$$Q_{reversible} = W_{maximum} = \text{heat given out by the system}$$
$$\Delta S_{gas} = \frac{Q_{rev}}{T} = \frac{W_{max}}{T} = \frac{RT}{T} ln\frac{V_B}{V_A} = R\ ln\frac{V_B}{V_A}$$

Which is a negative quantity. Since the process is reversible, there is no change in total entropy and the entropy change of surrounding is given by

$$\Delta S_{surrounding} = -\Delta S_{gas} = R\ ln\frac{V_A}{V_B}$$

$$\Delta S_{Total} = 0$$

Reversible adiabatic expansion of a gas

In an adiabatic process, no heat enters or leaves the system. Therefore,

$$\Delta S_{system} = 0$$

A reversible adiabatic process is thus an isentropic process. During a reversible adiabatic expansion, the work done by the gas, W_{max} is equal to the decrease in the internal energy of the gas.

$$\Delta U = \delta Q - \delta W$$

$$dU = TdS - \delta W, \qquad \text{since } \Delta S = 0$$

we have

$$\boxed{W_{max} = -dU}$$

Entropy of a substance as a function of temperature

Thermal Entropy for a process occurring at constant pressure in which temperature changes would be

$$dS = \frac{\delta Q_p}{T}$$

or

$$dS = \frac{dH}{T}$$

Hence,

$$\Delta S = \int \frac{C_P dT}{T}$$

While in any isothermal transformation (allotropic transformation, melting, boiling, etc.) at constant pressure, it would be,

$$\Delta S = \frac{\Delta H_{tr}}{T_{tr}}$$

Example: Write expression for entropy of uranium vapors above the boiling point. Uranium undergoes three allotropic transformations before melting.

$$\begin{aligned} S_{U,T} = & S_{U,298} + \int_{298}^{941} (C_p)_\alpha dT/T + \Delta H_{\alpha/\beta}/T_{\alpha/\beta} \\ & + \int_{941}^{1049} (C_p)_\beta dT/T + \Delta H_{\beta/\gamma}/T_{\beta/\gamma} + \int_{1049}^{1408} (C_p)_\beta dT/T \\ & + \Delta H_m/T_m + \int_{1408}^{1773} (C_p)_l dT/T + \Delta H_b/T_b + \int_{1773}^{T} (C_p)_v dT/T \end{aligned}$$

where 941 K, 1049 K, 1408 K and 1773 K are the respective transformation temperatures. C_p values for all the phases are available as well as the enthalpies and temperatures of various transformations. Here we start with $S_{U,298}$ which is not zero. We may also use $S_{U,0}$ and use 3^{rd} law of Thermodynamics, according to which pure crystalline uranium at 0 K has zero entropy.

4.6 Entropy from Statistical Point of View

Classical thermodynamics deals with the measureable bulk properties like volume, pressure, temperature, etc. However, statistical thermodynamics which is evolved through the concept of quanta (discrete energy packets) concerns with the atoms, molecules or simply particles and their random arrangement. In statistical thermodynamics, the equilibrium state is referred to as the most probable state. The concept

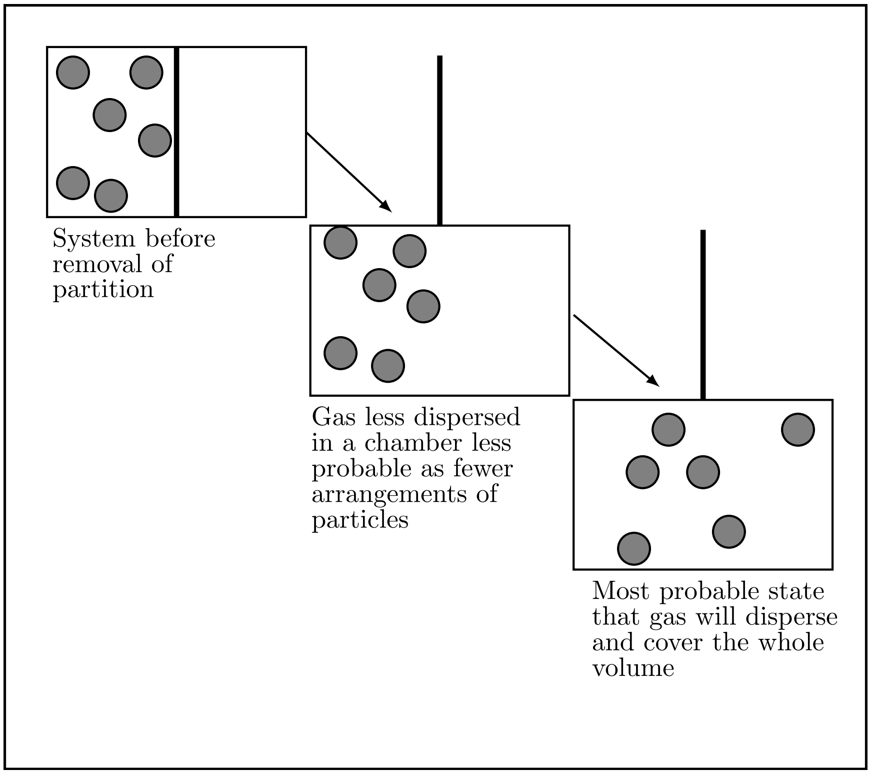


Figure 4.9: Entropy of the most probable state

is illustrated in Figure 4.9. Entropy at atomic or molecular level is defined as the degree of mixed-up-ness i.e., more the molecules are mixed, more the entropy they possess.

The most probable distribution of N particles is obtained by determining the set of numbers n_0, $n_1 \ldots n_r$ that maximizes the value of Ω, the degree of mixed-up-ness,

$$\Omega = \frac{N!}{n_0!\ n_1!\ ...\ n_r!} \tag{4.33}$$

The Boltzman equation for entropy is

$$S = k\ ln\ \Omega \tag{4.34}$$

Where

$$\Omega = \Omega_{thermal} \times \Omega_{configurational}$$

$$S = k\ ln\ \Omega_{thermal} + k\ ln\ \Omega_{configurational}$$

k is the Boltzmann constant which is gas constant per molecule, i.e., $k = R/N_A$ where N_A is the Avogadro's number.

For Ω, we have two categories:

1. $\Omega_{thermal}$: Number of ways in which energy is distributed among particles

2. $\Omega_{configurational}$: Number of ways in which particles are arranged (permutations)

Entropy of mixing (configurational entropy) is given by

$$S = k\ ln\ \Omega_{configurational}$$

The most probable state of the system is that in which Ω has a maximum value, consistent with the fixed values of U, V and n. Thus, the equilibrium state of the system is that in which S is a maximum, consistent with the fixed values of U, V and n. The Boltzmann equation thus provides a physical quality to entropy.

When two types of particles are mixed, the entropy calculation is simply as described below:

For

$$n_A = \text{Number of molecules of A}$$
$$n_B = \text{Number of molecules of B}$$

Using permutation formula, we get

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

For large numbers, we use Stirling's approximation

$$ln(X)! = XlnX - X$$

Example. *Find entropy of mixing 3 A atoms and 2 B atoms*

Solution.

$$\Omega = \frac{(5)!}{(3)!(2)!} = 10$$

$$S = kln\Omega = [8.314/(6.02 \times 10^{23})]ln10 = 3.177 \times 10^{-23} J/K$$

□

Example. *Find entropy of mixing 1 mole A and 2 moles B*

Solution.

$$n_A = 1\text{ mole}$$

$$n_B = 2\text{ mole}$$

$$\Omega = \frac{(3N_A)!}{(N_A)!(2N_A)!}$$

$$ln\Omega = ln(3N_A)! - ln(N_A)! - ln(2N_A)!$$

Using Stirling's Approximation, we get

$$ln\Omega = [3N_A ln(3N_A) - 3N_A] - (N_A lnN_A - N_A) - [2N_A ln(2N_A) - 2N_A]$$

Simplifying the equation, we get

$$ln\Omega = 3N_A ln3 - 2N_A ln2 - N_A ln1$$

$$ln\Omega = N_A[3ln3 - 2ln2 - ln1]$$

$$ln\Omega = N_A[1.9095]$$

Now

$$S = k\ ln\ \Omega$$

$$S = \frac{R}{N_A} ln\Omega$$

$$S = \frac{R}{N_A} N_A[1.9095]$$

Or

$$S = R[3ln3 - 2ln2 - 1ln1] = 15.87J/K$$

□

4.6.1 Entropy of Mixing of a Binary Solution

Let us find the entropy of mixing of n_1 moles of A and n_2 moles of B gas:

We use the Boltzman equation

$$S = k\ ln\ \Omega$$

where

$$\Omega = \frac{(n_1 N_A + n_2 N_A)!}{(n_1 N_A)!(n_2 N_A)!}$$

$$ln\Omega = ln[n_1 N_A + n_2 N_A]! - [ln(n_1 N_A)! + ln(n_2 N_A)!]$$

Using Stirling's approximation

$$\begin{aligned} ln\Omega = &[(n_1 N_A + n_2 N_A) ln(n_1 N_A + n_2 N_A) - \\ &(n_1 N_A + n_2 N_A)] - [(n_1 N_A ln(n_1 N_A) - n_1 N_A) + \\ &(n_2 N_A ln(n_2 N_A) - n_2 N_A)] \end{aligned}$$

Simplifying the above equation, we get,

$$\begin{aligned} ln\Omega = &(n_1 N_A + n_2 N_A) ln N_A + (n_1 N_A + n_2 N_A) ln(n_1 + n_2) - \\ &n_1 N_A ln(n_1 N_A) - n_2 N_A ln(n_2 N_A) \end{aligned}$$

$$ln\Omega = N_A[(n_1 + n_2) ln(n_1 + n_2) - n_1 ln n_1 - n_2 ln n_2]$$

$$ln\Omega = -N_A \left[n_1 ln \frac{n_1}{n_1 + n_2} + n_2 ln \frac{n_2}{n_1 + n_2} \right]$$

$$ln\Omega = -N_A[n_1 ln X_1 + n_2 ln X_2]$$

$$S = k\ ln\ \Omega$$

$$S = \frac{R}{N_A}[-N_A(n_1 lnX_1 + n_2 lnX_2)]$$

$$S = -R[n_1 lnX_1 + n_2 lnX_2]$$

In general,

$$S = -R\left[\sum n_i lnX_i\right] \tag{4.35}$$

Which is same as obtained from the classical thermodynamics as we will see later in the chapter on solutions.

4.7 Chemical Potential

In a physical field, we use the term potential for the driving force which causes the spontaneous movement. Some examples are given below:

1. Electric charge (+) flows from a region of high electric potential (voltage) to a region of low electric potential.
2. Matter moves from a position of high gravitational potential (height) to low gravitational potential.
3. Heat flows from high thermal potential (Temperature) to low thermal potential.

In a similar sense, the chemical potential governs the flow of chemical species which move spontaneously from a region of high chemical potential to a region of low chemical potential. When the chemical potentials in the two regions are equal, they are in diffusive equilibrium with respect to that specie and there is no net movement.

The chemical potential can, therefore, be used to determine whether a system is in equilibrium or not. When the system is in equilibrium, the chemical potential of each component will be the same in all the phases in the system. This is the Principle of Phase Equilibria. In thermodynamics, chemical potential of a component 'i' is also called as its partial molar free energy. It is the free energy per mole of a component 'i' in a given system.

So far, we have considered closed systems in which the number of components and their amounts do not change. We have also concluded that the best criterion for spontaneity is Gibbs Free Energy. So, we would like to find how the free energy of a system changes when amount of a particular component in the system is changed.

For a closed system, we write

$$G = G(T, P)$$

Then

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$$

or

$$dG = (-S)dT + (V)dP$$

For variation in the composition and size of a system, Gibbs free energy is represented as

$$G(T, P, n_i, n_j, n_k \ldots)$$

Where i, j and k are the components and n_i , n_j , n_k represent number of moles of these components, respectively. The 'n' represents the total size of the system where,

$$n = n_i + n_j + n_k \ldots$$

The fundamental equation for change in Gibbs free energy then becomes,

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_i,n_j,n_k} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_i,n_j,n_k} dP + \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j,n_k} dn_i + \left(\frac{\partial G}{\partial n_j}\right)_{T,P,n_i,n_k} dn_j + \ldots \quad (4.36)$$

The third term in the above equation represents free energy change when the number of moles of component 'i', i.e., n_i changes, keeping all other terms constant. This then defines the chemical potential μ_i of the component 'i' and is mathematically represented as

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j,n_k,\ldots} \quad (4.37)$$

This is the free energy change when 1 mole of component ' i' is added to the system keeping T, P and moles of other components constant. So, we can write

$$dG = -SdT + VdP + \mu_i dn_i + \mu_j dn_j + \mu_k dn_k + \ldots$$

or

$$dG = -SdT + VdP + \sum_{i}^{k} \mu_i dn_i \quad (4.38)$$

The last term of the above equation is termed as the chemical work done.

In a similar manner, chemical potential could be defined in terms of Helmholtz free energy, enthalpy and internal energy where thermodynamic variables which are kept constant are different in each case.

$$\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j,n_k}$$

$$\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j,n_k}$$

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j,n_k}$$

Using the following equations for closed system:

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

$$dG = -SdT + VdP$$

$$dA = -SdT - PdV$$

We can now write for an open system,

$$dG = -SdT + VdP + \sum_i^k \mu_i dn_i$$

$$dA = -SdT - PdV + \sum_i^k \mu_i dn_i$$

$$dH = TdS + VdP + \sum_i^k \mu_i dn_i$$

$$dU = TdS - PdV + \sum_i^k \mu_i dn_i$$

Note that these concepts continue to grow and we get various types of energies involved in the system. For example, if surface energy and electric energy are also involved, we will write

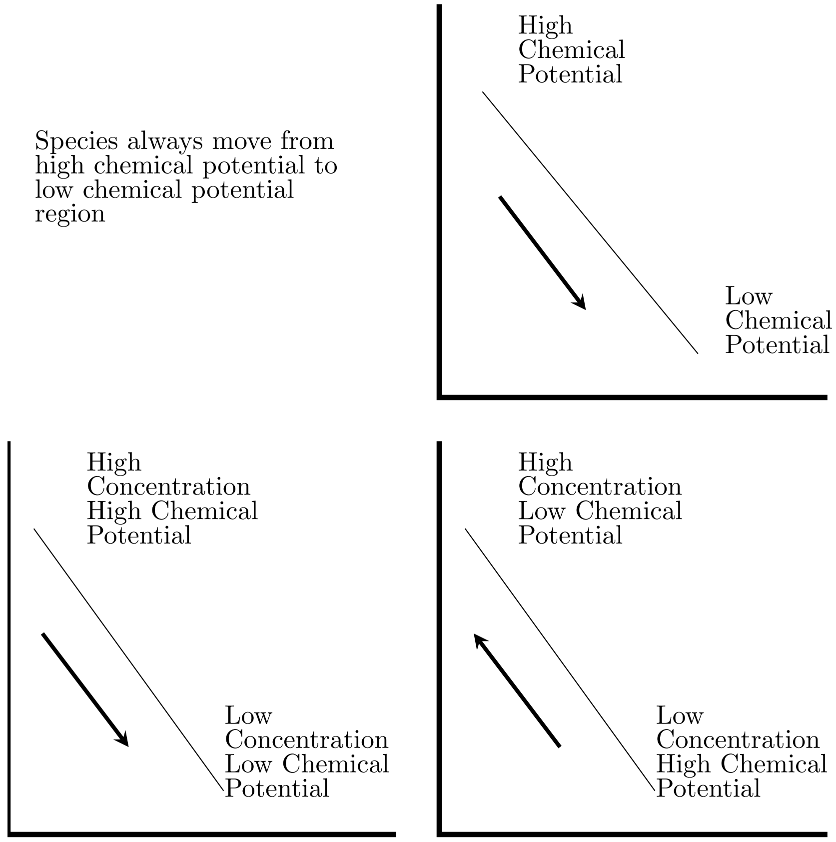
$$dG = -SdT + VdP + \sum_i^k \mu_i dn_i + Vdq + \gamma d\overline{A}$$

Where V is electric potential, q is charge, γ is surface energy and $\overline{A}$ is the area. Both of these will be discussed later; surface energy when we discuss adsorption and electric energy when we develop an important relation, $\Delta G = -zFE$.

4.7.1 Diffusion – The Movement of Chemical Species

Remember the electrical potential is the driving force for the movement of an electric charge in an electrical field and represents ability of electric charge to do work. Gravitational potential is the driving force for movement of mass in the gravitational field and represents the ability of a mass to do work. Similarly, chemical potential is the driving force due to which chemical species will move from higher potential to lower potential. A region having attraction for a given species represents lower potential while a region having repulsion for a given species represents higher potential.

The movement of chemical species is always controlled by chemical potential. Normally, when interactions could be neglected, the chemical potential of any specie



Normal Diffusion

Uphill Diffusion

Figure 4.10: Species always move from high chemical potential to low chemical potential region whether it is normal diffusion or uphill diffusion.

would be proportional to its concentration. Therefore, a region having higher concentration will have higher chemical potential for that specie and a region having lower concentration will have lower potential. Hence, a species will move from higher concentration to lower concentration region. This is the normal diffusion.

In presence of interactions, the chemical potential of a specie may not be proportional to its concentration. The region having attraction will be low potential region and the species will move to this region even if the concentration is already higher in this region. In this case, specie will move from low concentration region to high concentration region. Movement against the concentration gradient is termed as Uphill Diffusion. In other words, uphill diffusion is the movement of species from a region of lower concentration to a region of higher concentration. Even in this case, species are moving from higher chemical potential region to lower chemical potential region and chemical potential remains the driving force. Figure 4.10 illustrates the role of chemical potential in the movement of chemical species.

Some examples of uphill diffusion are given below.

1. If we have oil and water in a container, oil will form a separate phase on top of water. If a drop of oil is placed in water it will move from water to oil phase.
2. Magnetic particles move in a magnetic field irrespective of concentration of the particles.
3. During steel making, we blow oxygen in molten iron to remove impurities by making their oxides. Initially FeO is formed. Part of it is used in oxidizing the impurities. The remaining FeO moves towards slag. Slag already has FeO, Still it moves from molten iron to slag, towards the higher concentration region from lower concentration. The chemical potential of oxide in slag is low due to attractions of other oxides.
4. On cooling a eutectoid steel, austenite decomposes to form ferrite and carbide. In this process, carbon diffuses from 0.8% C region (austenite) to 6.67% region (carbide). Carbon in carbide has much lower chemical potential.

$$\gamma_{(0.8\%\ C)} \rightarrow \alpha_{(0.02\%\ C)} + Fe_3C_{(6.67\%\ C)}$$

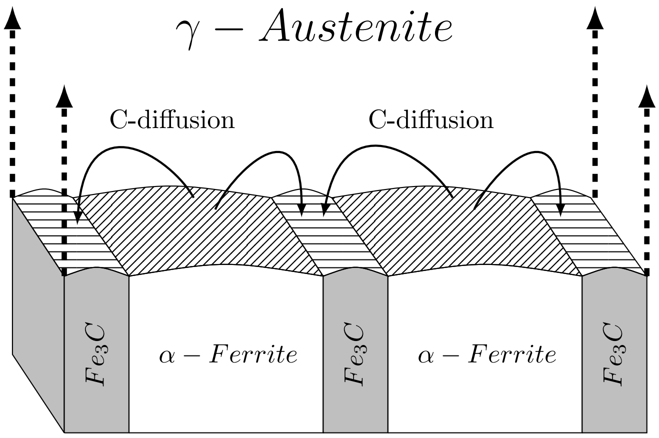


Figure 4.11: In pearlite formation, carbon diffuses from 0.8% C region (austenite) to 6.67% region (carbide). Carbon has much lower chemical potential in carbide.

Summary

1. By combining the first and the second law, we get $\delta w_{max} = \delta Q_{rev} - dU = TdS - dU$
2. Maximum work available from the system which leads to the concept of Free energy is $\delta W_{max} = -(dU – TdS) = -dA$
3. We are interested in properties of the system only, not the surrounding.
4. Internal Energy criterion for spontaneity $(dU)_{S,V} < 0$

5. Enthalpy criterion for spontaneity $(dH)_{S,P} < 0$
6. Entropy criterion for spontaneity $(dS)_{U,V} > 0$ or $(dS)_{H,P} > 0$
7. Free Energy criterion for spontaneity $(dA)_{V,T} < 0$ or $(dG)_{P,T} < 0$
8. Useful criteria involve keeping T and V (or P) constant which are easy to handle. Other criteria may require U, H or S to be constant which is impractical.
9. Most suitable criterion is $(dG)_{P,T} \leq 0$ as temperature is easy to control and most of the processes occur at constant pressure of one atmosphere.
10. Way Forward is to calculate change in free energy and find the equilibrium conditions or the direction of spontaneous process. Calculate ΔG using

$$\Delta G = G_{products} - G_{reactants}$$
$$\Delta G = \Delta H - T\Delta S$$
$$\Delta G = -nFE$$

11. Keeping the relation in mind, $\Delta G = \Delta H - T\Delta S$, four possibilities exist depending of signs of ΔH and ΔS.
12. Entropy change in reversible isothermal expansion of an ideal gas is $nR\ ln\frac{V_1}{V_2}$
13. Entropy change in a system in reversible adiabatic process is zero and such process is called isentropic process.
14. Change in entropy can be easily calculated when heat is given(or taken out) to a system which may increase its temperature or cause structural changes.
15. Entropy of melting (Richard's rule), entropy change in boiling (Trouton's rthe ule), entropy change in chemical reactions involving change in moles of gases, all provide useful estimates and point towards the concept of entropy as a measure of disorder.
16. Statistical Thermodynamics deals with particles. Using Boltzman equation ($S = k\ ln\ \Omega$), we can calculate entropy change from the number of ways in which energy is distributed among the particles (thermal) or number of possible arrangements (configurational). Since factorial of large numbers may be involved, we use Stirling's approximation.
17. Every field has a different kind of potential controlling the movement of species. Chemical Potential of a component is the driving force for the movement of chemical species. Chemical species move from higher chemical potential region to lower chemical potential region.

18. When interactions are not significant, chemical potential is represented by concentration. Therefore, species move from higher concentration region to lower concentration region. However, if interactions are significant, region having repulsion represents higher chemical potential and the region having attraction represents lower chemical potential. In such situation, species may move from low concentration region to high concentration region, a phenomenon termed as uphill diffusion.

Practice Problems

1. Evaluate the following statements:
    i. Entropy change can tell us about spontaneity of a process.
    ii. Entropy and enthalpy changes occur only when temperature changes.
    iii. An endothermic process can never be spontaneous.
    iv. We have a criterion of spontaneity for a process occurring adiabatically at constant pressure.
    v. There is a suitable spontaneity criterion for a process carried out in a closed container from which no heat gets in or comes out.
    vi. There is a suitable spontaneity criterion for a process carried out in a closed container whose temperature is kept constant.
    vii. First Law of Thermodynamics is not obeyed in case of spontaneous processes.
    viii. There are many spontaneity criteria but most of them are impractical.
    ix. Chemical species cannot move from region of low concentration to region of high concentration.
    x. Since nature is taking care of spontaneous processes, we are not interested in them.
    xi. Free energy of a pure element at room temperature can be taken as zero.
    xii. There are some chemical reactions which can go in nature in both directions.
    xiii. In a reversible process, entropy of a system cannot decrease.
    xiv. Enthalpy change could be useful in deciding whether a process is spontaneous or not.
    xv. Entropy of a system may decrease in an irreversible process.
    xvi. Change in internal energy may help us in deciding whether a process is spontaneous or not.
    xvii. We cannot carry out a reaction if Free Energy change is positive.
    xviii. Entropy change is an indicator of the reversibility of a process.

xix. Chemical species can move from low chemical potential to high chemical potential regions.

xx. In some situations, Helmholtz free energy should be used instead of Gibbs free energy criterion.

xxi. A process metallurgist is more interested in nonspontaneous processes.

2. Calculate ΔH° and ΔS° and find temperature for spontaneity of the following reactions when all the species are in their standard states. Justify the value of entropy change in each case.

I.	$H_2(g) + Cl_2(g) = 2HCl(g)$	$\Delta G^\circ = -182,200 - 43.68T$
II.	$CO(g) + \frac{1}{2}O_2(g) = CO_2(g)$	$\Delta G^\circ = -282,400 + 86.81T$
III.	$FeO(s) = Fe(s) + \frac{1}{2}O_2(g)$	$\Delta G^\circ = 263,700 - 64.35T$
IV.	$B(g) + C(g) = A(g)$	$\Delta G^\circ = 200,700 + 140T$
V.	$CaCO_3(s) = CaO(s) + CO_2(g)$	$\Delta G^\circ = +126,400 - 144T$
VI.	$C(s) + \frac{1}{2}O_2(g) = CO(g)$	$\Delta G^\circ = -111,700 - 87.65T$
VII.	$C(s) + CO_2(g) = 2CO(g)$	$\Delta G^\circ = 170,700\text{–}174.46T$
VIII.	$Na_2SiO_3(s) = Na_2O(s) + SiO_2(s)$	$\Delta G^\circ = 250,000 + 17T$
IX.	$Cu_2O(s) = 2Cu(s) + \frac{1}{2}O_2(g)$	$\Delta G^\circ = 162200\text{–}69.24T$
X.	$Mg(l) + Cl_2(g) = MgCl_2(l)$	$\Delta G^\circ = -603200 + 121.43T$
XI.	$MgO.Al_2O_3(s) = MgO(s) + Al_2O_3(s)$	$\Delta G^\circ = 35560 + 2.09T$

3. Following information about pure iron is available. Low temperature phase α transforms to γ at 910°C, γ transforms to δ at 1410 °C and δ melts at 1539 °C. Normal boiling point is 2862 °C. Write an expression for entropy of Fe vapors at a temperature 'T' above the boiling point. How will you find Gibbs free energy of Fe vapors at 'T'.

4. Entropy is a measure of disorder. Give at least 5 examples supported with numerical values to explain this statement.

5. Write down ΔG°, as a function of T, for hypothetical reactions with following thermodynamic properties.

   i. A reaction spontaneous at low temperature
   ii. A reaction spontaneous at high temperature
   iii. A reaction spontaneous at any temperature
   iv. A reaction non-spontaneous at any temperature
   In case of (i) and (ii) calculate temperatures for spontaneous reactions.

6. One mole of a monoatomic ideal gas undergoes an isothermal reversible expansion to double the volume. Entropy increases by 5.763 J/K and gas performs 1729 J of work. Calculate the temperature at which expansion is done.

7. Calculate the change in enthalpy and entropy when one mole of SiC is heated from 25 °C to 1000 °C.

$$C_p = 50.79 + 1.97 \times 10^{-3}T - 4.92 \times 10^{6}T^{-2} + 8.2 \times 10^{8}T^{-3} J/mole.K$$

8. Calculate entropy produced when molten aluminum solidifies at 800 K.
9. One mole of a monoatomic ideal gas undergoes a constant pressure reversible expansion. Entropy increases by 22.86 J/K and gas absorbs 12471 J of heat. Calculate initial and final temperature.
10. Describe four processes which are spontaneous in normal conditions and we don't like them. How do we control them?
11. Describe four processes which are of interest to us but are nonspontaneous in normal conditions. How do we solve our problem?
12. Compare and contrast from thermodynamic point of view
    i. Enthalpy and entropy
    ii. Gibbs Free Energy and Helmholtz Free Energy
    iii. Internal energy and Helmholtz free energy
    iv. Entropy of melting and boiling of BCC and FCC metal
13. Compare the entropy change using microscopic consideration with that using macroscopic consideration when 3 moles of an ideal gas A are mixed with 4 moles of another ideal gas B. Also find the enthalpy change and the free energy change on mixing.
14. According to one definition, entropy is a measure of disorder. Analyze the following situations with numerical *molar* values.
    i. A gaseous reaction in which moles of reactants are not equal to moles of products.
    ii. Mixing of two molten metals in equimolar ratio to form a regular solution.
    iii. Melting of a crystalline metal
    iv. Boiling of a liquid metal
    v. Sublimation of a crystalline metal
15. i. Write down assumed value of ΔG°, as a function of T, for a hypothetical reaction which is endothermic but spontaneous at room temperature.
    ii. Write down assumed value of ΔG°, as a function of T, for a hypothetical reaction which is exothermic but non-spontaneous at room temperature.
16. Give the estimates for entropy change in the following cases along with thermodynamic reasoning.

   i. Melting of one mole Chromium
   ii. Boiling of one mole Tungsten
   iii. Sublimation of one mole Lithium
   iv. Oxidation of one mole iron to form FeO
   v. Oxidation of Al to form one mole of aluminum oxide
   vi. Complete combustion of one mole ethane.
   vii. Mixing of one mole A and one mole of B ideal gases
   viii. Spontaneous freezing of an undercooled molten metal

17. Write down hypothetical values of $\Delta G^\circ(T)$ for two reactions, one spontaneous at lower temperatures and other spontaneous at higher temperatures. Indicate the values of ΔH° and ΔS°. Then calculate temperature for spontaneity of both reactions.

18. Following information about pure Zr is available. Low temperature phase α transforms to β at 863 °C and β melts at 1854 °C. Normal boiling point is 4406 °C.

   i. Write an expression for enthalpy of Zr vapors at temperature T above the boiling point.
   ii. Write an expression for entropy of Zr vapors at temperature T above the boiling point.

19. Calculate the change in entropy when two moles of an ideal gas are compressed isothermally reversibly from 2 atmosphere pressure to 6 atmosphere pressure. Calculate the change in entropy when the same compression is done using a reversible adiabatic process.

20. What is the thermodynamic driving force for diffusion? Explain the thermodynamic term used to define this behavior. Under what conditions there will be no net movement of any component between the two phases in contact? Under what conditions, a component will move from a region of low concentration to a region of high concentration.

21. ΔH°_{298} for the reaction

$$2Ag + \frac{1}{2}O_2 = Ag_2O$$

   is -30,540 J/mole. Calculate the heat of formation of Ag_2O. Estimate the entropy change on oxidation

22. Stating assumptions and rules you are using, write expressions for entropy and enthalpy of O_2 and H_2O at 1000 °C.

Chapter 5

Thermodynamic Treatment of Solutions

Learning Outcomes:

Student should be able to explain

- Effect of pressure on free energy of a gas
- Change in free energy on mixing of gases
- What is a solution, importance of solutions
- Laws governing behavior of ideal and non-ideal solutions
- Activity and activity coefficient
- Change in free energy on mixing in ideal and real solutions
- Effect of temperature and interactions on Free energy of Mixing
- Chemical potentials of components in a solution
- Calculating activity using Gibbs Duhem Equation

After deciding that the change in Gibbs free energy is the best criterion for spontaneity, we embark on calculations of change in free energy in various processes. The simplest is mixing of gases. Then we go for free energy change when we make a solution. This will lead us to the principles of phase equilibria.

5.1 Introduction

A solution is formed when two or more components mix homogeneously to form a single phase. A solution could be a gas phase, a liquid phase or a solid phase. The requirement is that we have uniform distribution of two or more components at atomic or molecular level. Remember, a phase may contain single element, single compound or a combination of elements or compounds. A solution requires more than one component.

In Materials Science, solutions are encountered everywhere in processing and applications. This includes extraction, refining, corrosion, alloy making, processing in controlled environment, etc. Hence, understanding of the behavior of solutions is very important. Solid solutions are important in metals and alloys. A solid solution will give only one set of peaks in X-ray diffraction corresponding to a single phase.

A phase diagram either represents a solution, intermetallic compound or a mixture of solutions and intermetallic compounds. Free energy of mixing leads to equilibrium phase diagrams.

We start with the behavior of gases as they are relatively easier to handle. After developing basic ideas, we move to various types of solutions.

5.2 Behavior of Gases

The behavior of ideal gases helps us in understanding the nature of changes in the thermodynamic state of the system. The concepts of mole fraction, partial pressure and partial molar quantities are necessary for understanding the thermodynamic properties of mixtures and solutions.

5.2.1 Mole Fraction

When a system has more than one component (variable composition), we express composition of the system in terms of concentration of various species. In thermodynamics, mole fraction is taken as the measure of concentration. Let us take an example of a three component system having components A, B and C with n_A, n_B, and n_C moles of each, respectively. The mole fraction of each component is obtained by dividing its moles by the total number of moles (sum of the moles of all components).

$$\begin{aligned}
&\text{mole fraction of A,} && X_A = \frac{n_A}{n_A + n_B + n_C} \\
&\text{mole fraction of B,} && X_B = \frac{n_B}{n_A + n_B + n_C} \\
&\text{mole fraction of C,} && X_C = \frac{n_C}{n_A + n_B + n_C}
\end{aligned}$$

The use of mole fraction is very convenient as the sum of mole fractions of all components in a system is unity. For example, for a system of three components,

$$X_A + X_B + X_C = 1$$

Similarly, for a system of two components:

$$X_A + X_B = 1$$

$$X_B = 1 - X_A$$

For a binary system, we need to know only one mole fraction X_A, the other X_B is then fixed. So, only one composition appears as a variable in a 2-component system.

5.2.2 Dalton's Law of Partial Pressures

Pressure 'P' exerted by a mixture of ideal gases is equal to the sum of the pressures exerted by individual component gases. The contribution of each gas is called the partial pressure of that gas.

$$P = p_A + p_B + p_C \tag{5.1}$$

Total pressure in the system is given by

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

As moles of the individual components contribute to the total pressure of the system, we have

$$P = (n_A + n_B + n_C)\left(\frac{RT}{V}\right)$$

$$P = \frac{n_A RT}{V} + \frac{n_B RT}{V} + \frac{n_C RT}{V} \tag{5.2}$$

The three terms represent the partial pressures of the components A, B and C, respectively.

Using equation Equation 5.2, we have

$$p_A = \frac{n_A RT}{V}$$

Since $\frac{P}{n} = \frac{RT}{V}$, we get

$$p_A = \frac{n_A P}{n}$$

As $\frac{n_A}{n}$ is mole fraction of A, termed as X_A, so

$$p_A = X_A P \tag{5.3}$$

Similarly

$$p_B = X_B P \quad \text{and} \quad p_C = X_C P$$

Thus, in a mixture of ideal gases, the partial pressure of a component gas is the product of its mole fraction and the total pressure. Total pressure of the gas mixture is the sum of all partial pressures. This is called the Dalton's law of partial pressures.

5.2.3 The Effect of Pressure on Gibbs Free Energy of a Gas

The pressure dependence of free energy of any thermodynamic component is governed by the following relationship:

$$G = f(P, T)$$

$$dG = -SdT + VdP$$

For isothermal process, dT would be zero,

$$dG = VdP$$

For one mole of ideal gas, on integration

$$\int dG = \int \frac{RT}{P} dP$$

$$G = RTlnP + K$$

For $P = 1\ atm$

$$G^{\circ} = K$$

Therefore, for each component gas, before mixing

$$G = G^{\circ} + RTlnP \tag{5.4}$$

Or

$$G(P, T) = G^{\circ}(T) + RTlnP$$

$G^{\circ}(T)$ represents standard free energy of the gas at the given temperature 'T'. The standard state for a gas is one mole of pure gas at one atmospheric pressure. We can get value of $G^{\circ}(T)$ for any gas from the handbook.

For example, for N_2,

$$G^{\circ}(298) = H^{\circ}(298) - TS^{\circ}(298) = 0\text{–}298(191.5) = -57,067 J/mol$$

Now we want to calculate G(298) for N_2 at 2 atm pressure

$$\begin{aligned} G(298, P_2) &= -57067 + RTln2 = -57067 + 8.314 \times 298ln2 \\ &= -57067 + 1717 = -55350 J/mol \end{aligned}$$

As shown in Figure 5.1, the effect of pressure on free energy of solid and liquid is not significant as compared to gas. For isothermal process, since $dG = VdP$, and the volume of gases is changed by huge amount with increasing pressure, gases show huge increase in Gibbs free energy as compared to liquids and solids.. The change in volume of liquids and solids is minimal but change in the volume of liquid is little more than that for solids.

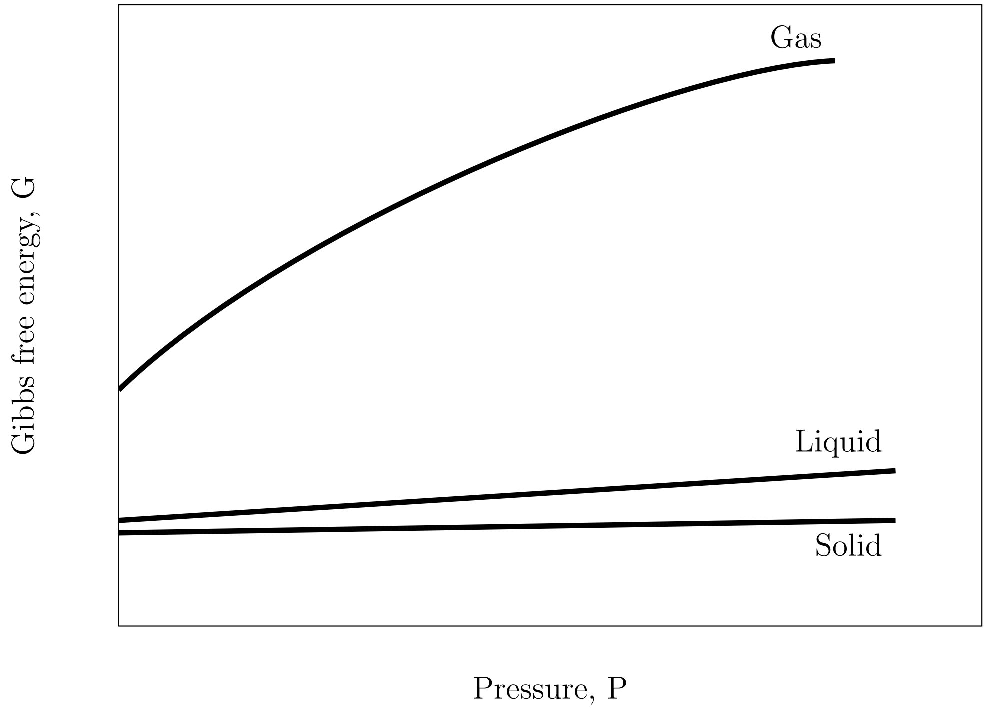


Figure 5.1: Effect of pressure on Gibbs free energy of gases, liquids and solids

5.2.4 Free Energy Change on Mixing of Gases

We have seen that the partial molar free energy of a component A is given by

$$\overline{G}_A = \mu_A = \left(\frac{\partial G}{\partial n_A}\right)_{T,P,n_B,n_C}$$

The total Gibbs free energy of a two-component system is given by

$$G = n_A\overline{G}_A + n_B\overline{G}_B$$

$\overline{G}_A$ is the partial molar free energy of gas 'A' in the mixture of two gases A and B.

Partial means pertaining to a certain component in a given mixture (solution). Molar means the value for one mole of that component.

Partial Molar Free Energy of a component 'A' in a gas mixture would be

$$\overline{G}_A = G^\circ_A + RT\ ln\ p_A \tag{5.5}$$

But

$$p_A = X_A P$$

Therefore

$$\overline{G}_A = G^\circ_A + RTln(X_A P)$$

$$\overline{G}_A = G^\circ_A + RTlnX_A + RTlnP$$

On rearranging

$$\overline{G}_A = (G^\circ_A + RTlnP) + RTlnX_A$$

As

$$G_A = G_A^\circ + RTlnP$$

$$\overline{G}_A = G_A + RTlnX_A \tag{5.6}$$

$\overline{G}_A$ = Molar free energy of A in mixture or partial molar free energy of A
G_A = Molar free energy of A when it is kept separated as pure
The difference is the change in free energy on mixing

$$\overline{G}_A - G_A = RTlnX_A$$

In case of mixing of various components
$\Delta G'$ = free energy of mixture - free energy of separate components

$$\begin{aligned}
\Delta G' &= \sum n_i\overline{G}_i - \sum n_i G_i \\
\Delta G' &= \sum n_i(\overline{G}_i - G_i) \\
\Delta G' &= \sum n_i(RTlnX_i) \\
\Delta G' &= RT\sum n_i lnX_i \\
\frac{\Delta G'}{n} &= RT\sum \frac{n_i}{n} lnX_i
\end{aligned}$$

The above equation gives free energy change per mole of mixture and is written as

$$\Delta G^M = RT\sum X_i lnX_i \tag{5.7}$$

for one mole of the gas mixture. Note that the free energy of mixing of gases is always negative as $X_i < 1$. So, in case of ideal gases, mixing is always spontaneous.

For two components A & B

$$\Delta G'^M = RT\left[n_A lnX_A + n_B lnX_B\right]$$

And

$$\Delta G^M = RT\left[X_A lnX_A + X_B lnX_B\right] \tag{5.8}$$

5.2.5 Enthalpy of Mixing of Ideal Gases

Due to the absence of interactions among ideal gas molecules, there is no enthalpy change on mixing ideal gases.

$$\Delta H^M = \sum n_i\overline{H}_i - \sum n_i H_i = 0$$

5.2.6 Entropy of Mixing of Ideal Gases

Using the relation

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

And the fact that there is no change in enthalpy on mixing of ideal gases, i.e.,

$$\Delta H^M = 0$$

We get

$$\Delta G^M = -T\Delta S^M$$

$$\Delta S^M = -\frac{\Delta G^M}{T}$$

$$\Delta S^M = -R\sum X_i ln X_i \tag{5.9}$$

This relation gives entropy change per mole of mixture.

For total moles in the system

$$\Delta S_T = -R\sum n_i ln X_i$$

Entropy always increases (positive) on mixing of gases as mixing of gases is a spontaneous process.

5.2.7 The Thermodynamics of Nonideal Gases

In an ideal gas, Gibbs free energy is a linear function of logarithm of the pressure of the gas. If the gas is not ideal, this relationship is not linear. However, a function is defined which, when used instead of pressure, makes this relationship linear. This function is known as fugacity, f.

For ideal gases

$$G = G^\circ + RT ln P$$

For non-ideal gases

$$G = G^\circ + RT ln f \tag{5.10}$$

Fugacity may be regarded as the effective pressure when there are interactions among the particles in the system.

In case of repulsions

$$f > P$$

And in case of attractions

$$f < P$$

Fugacity approaches pressure as the pressure approaches zero, i.e.,

$$\frac{f}{P} \to 1$$

As

$$P \to 0$$

Thus, standard state for non-ideal gases is determined where fugacity is unity at any temperature of interest and if there are deviations from ideality, the pressure of gas is explained in terms of fugacity.

The idea is similar to the activity used in solutions. Activity is the effective concentration of a component in a solution while fugacity is the effective pressure of a non-ideal gas.

5.3 Behavior of Solutions

If we study the behavior of vapors in equilibrium with solution, the principle of equilibrium can be used to understand the behavior of solutions.

5.3.1 Raoult's Law

Vapor Pressure of a solid or liquid is a function of temperature. When we make a solution, the total vapor pressure is determined by the vapor pressures of individual components. Ideal behavior is the one having no interactions among solute and solvent atoms/molecules. The solute and solvent behave indifferently. In an ideal solution, it is, therefore, expected that partial pressure of each component will be proportional to its mole fraction (concentration). This is called Raoult's Law.

According to Raoult's Law, for a solution of two components A and B

$$p_A \propto X_A$$

Where p_A is the vapor pressure of A whose mole fraction in solution is X_A.

For $X_A = 1$

$$p_A = p_A^\circ$$

where p_A° is the vapor pressure of pure A. Therefore, we may write

$$p_A = p_A^\circ X_A \tag{5.11}$$

and

$$p_B = p_B^\circ X_B$$

The total pressure would then be

$$p = p_A + p_B$$

$$p = p_A^\circ X_A + p_B^\circ X_B$$

In general, for a multicomponent system,

$$p = \sum p_i^\circ X_i \tag{5.12}$$

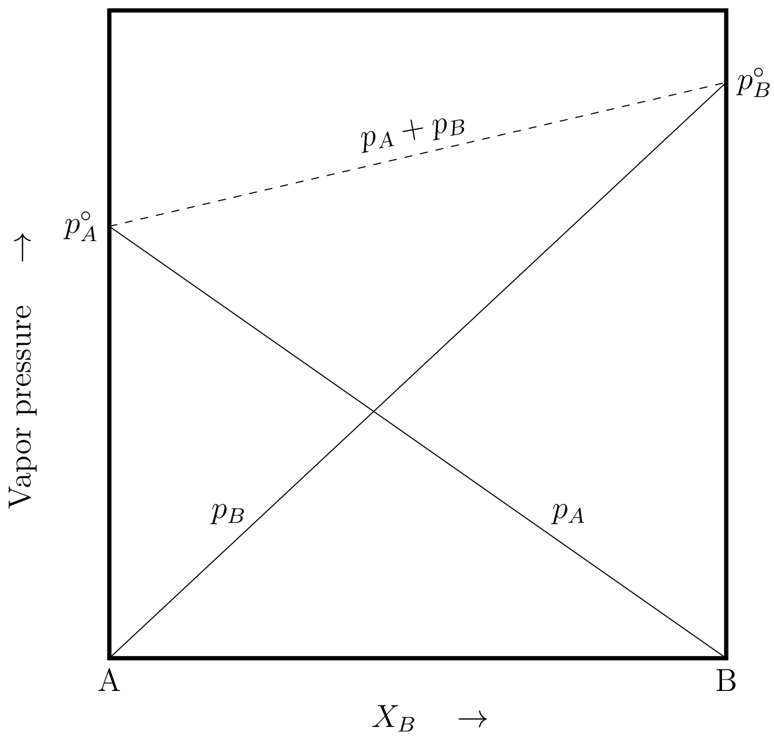


Figure 5.2: Variation of vapor pressure as a function of composition in an ideal solution of two components

For example, for a solution having 3 components, we would write

$$p = p_A^\circ X_A + p_B^\circ X_B + p_C^\circ X_C$$

Remember $\sum X_i = 1$ and for a two component system, only one composition need to be known as $X_B = 1 - X_A$.

Raoult's law in terms of p is,

$$p_i = X_i p_i^\circ$$

And the graphical representation for a two component solution is given in Figure 5.2

5.3.2 Henry's Law

In case of interactions, the actual vapor pressure will differ from the ideal values. In case of attractions (termed as negative interactions), the actual vapor pressure would be less than expected as the tendency to escape into vapor phase will decrease. In case of repulsions (termed as positive interactions), the actual vapor pressure would be more than expected as the tendency to escape into vapor phase will increase. In such cases, it becomes difficult to express vapor pressure as a function of mole fraction. Fortunately, the behavior in dilute solutions is simple. According to *Henry's Law*, the vapor pressure of solute in a dilute solution varies linearly with its concentration. These behaviors are shown in Figure 5.3.

Henry's Law says, for dilute solutions

$$p_B \propto X_B$$

Or

$$p_B = k_B X_B \tag{5.13}$$

Note that

- $k_B = p_B^\circ$ in case of ideal solution
- $k_B < p_B^\circ$ in case of attractions
- $k_B > p_B^\circ$ in case of repulsions

Remember, Raoult's law makes mathematical manipulation very simple. In case of interactions, Henry's law helps us in using simple mathematics to describe the behavior of dilute solutions. Both laws predict linear behavior but the proportionately constants are different.

5.3.3 Activities of Components in a Solution

Activity of a component represents its effective concentration in a given environment. It is defined in terms of vapor pressure of the component.

$$a_i = \frac{p_i}{p_i^\circ} = \frac{\text{partial pressure of 'i' in solution}}{\text{vapor pressure of pure component 'i'}}$$

Remember, we are using the idea of equilibrium between liquid and its vapors – the behavior of solution is depicted by its vapors. The activity of pure component is 1 while it is 0 when there is zero concentration of the particular component. So, the activity scale ranges from 0 to 1.

It is obvious that

For a pure component	$a_i = \frac{p_i}{p_i^\circ} = 1$
For a component in ideal solution	$a_i = \frac{p_i}{p_i^\circ} = X_i$
In case of attractions	$a_i < X_i$
In case of repulsions	$a_i > X_i$

Raoult's law in terms of activities is expressed as

$$a_i = \frac{p_i}{p_i^\circ} = X_i$$

Figure 5.4 shows behaviour in an ideal solution. Figure 5.5 shows a case of attractions in solution while Figure 5.6 shows a case of repulsions in solution.

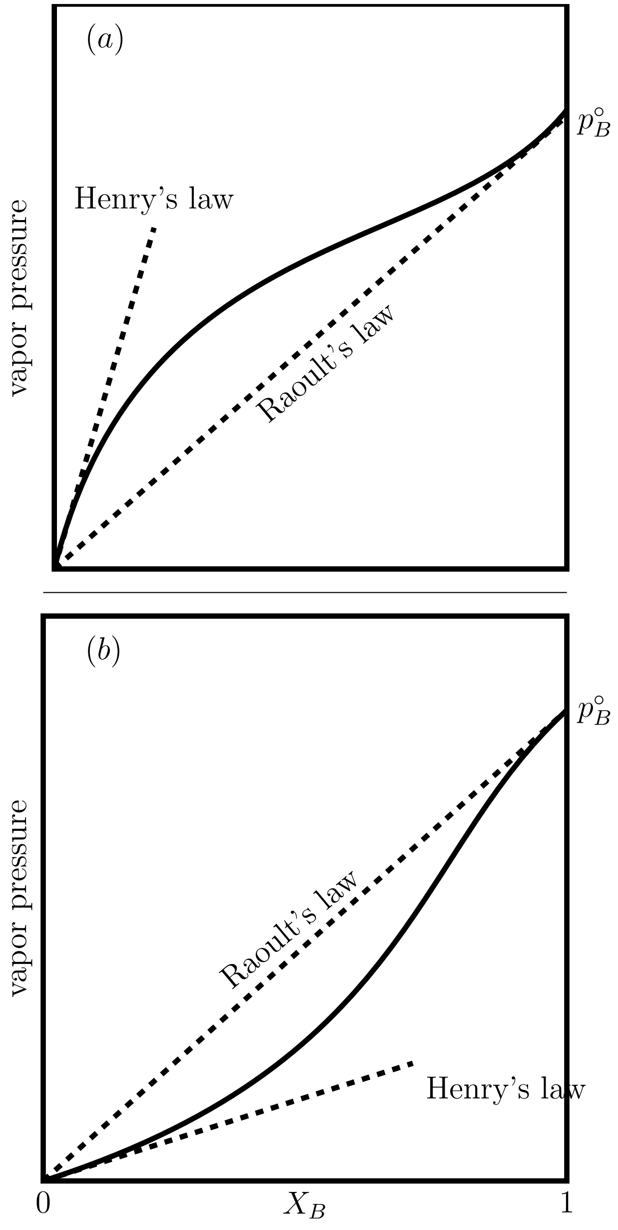


Figure 5.3: Real solutions showing applicability of Henry's law in dilute regime

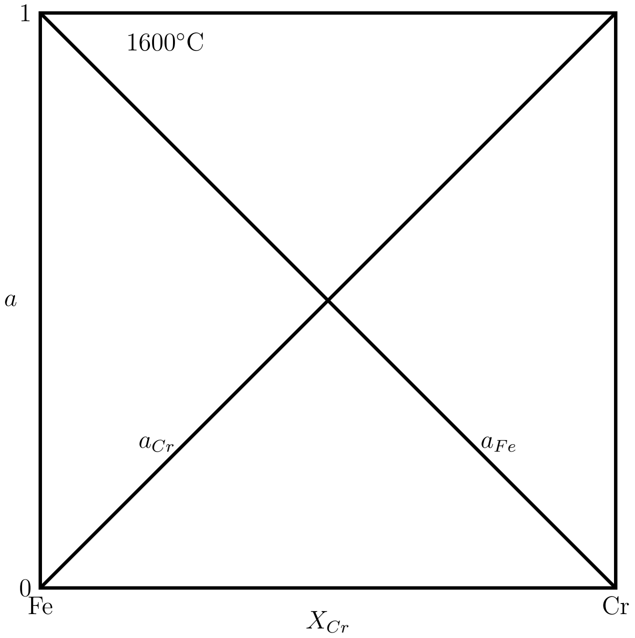


Figure 5.4: Chromium in molten iron at the steel making temperature showing ideal behaviour

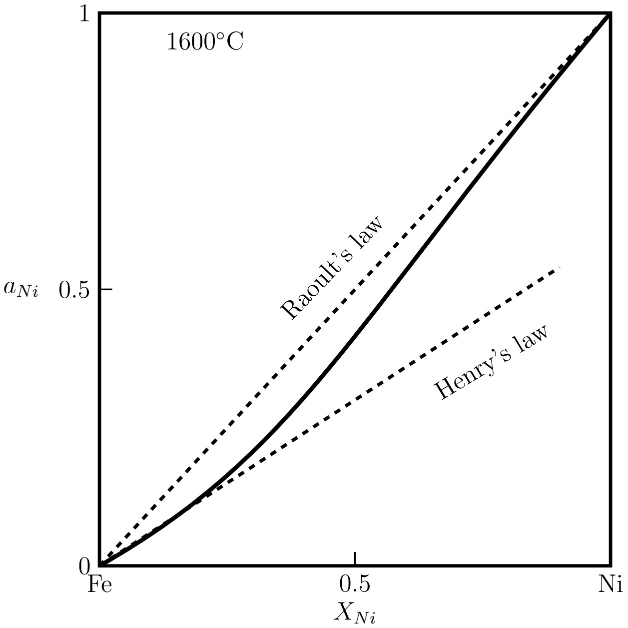


Figure 5.5: Nickel in molten iron at the steel making temperature showing negative interactions

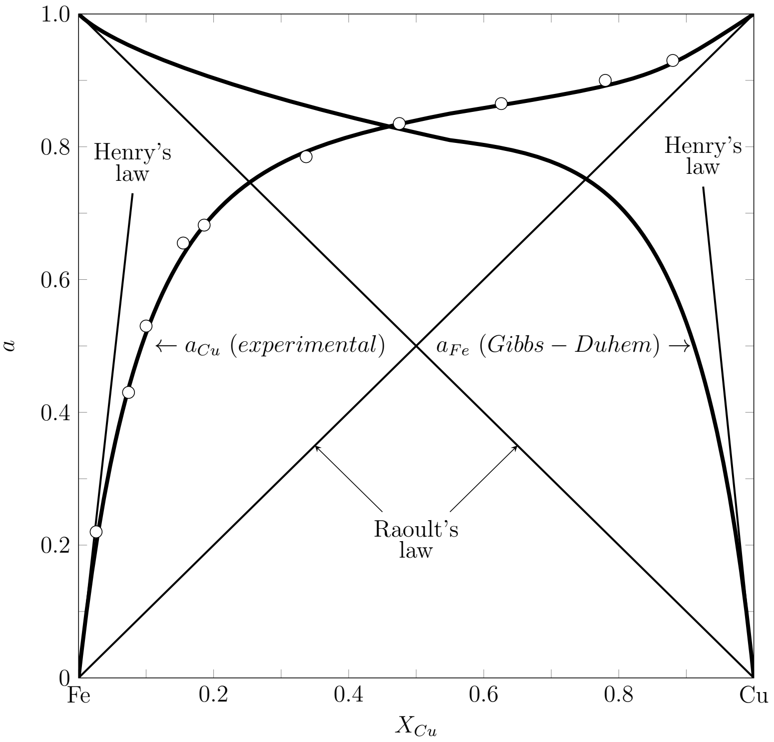


Figure 5.6: Copper in molten iron showing strong positive interactions

Henry's law in terms of activities is

$$a_i = \gamma_i X_i \tag{5.14}$$

γ_i is called the activity coefficient. It provides information about the interactions among the components.

For ideal solution	$\gamma_i = 1$
In case of attractions (negative interactions)	$\gamma_i < 1$ (*activity < mole fraction*)
In case of repulsions (positive interactions)	$\gamma_i > 1$ (*activity > mole fraction*)

As noted above, chromium behaves ideally in molten iron. Nickel shows attraction while copper shows repulsion in molten iron. Ni likes Fe and may lead to ordering at lower temperatures. Fe does not like Cu in solution. In fact, we get two immiscible liquids, one rich in Fe, other rich in Cu. A similar situation exists in Cu-Pb system, shown in Figure 5.7 where a monotectic isothermal reaction is evident. This leads to globules of lead which result in good machinability of Brass (Free Cutting Brass). Same is the case with Fe-Pb system.

Remember, for application of mathematics we need to know variation of activity as a function of composition, i.e.,

$$a_i = f(X_i)$$

For Ideal behaviour

$$a_i = X_i$$

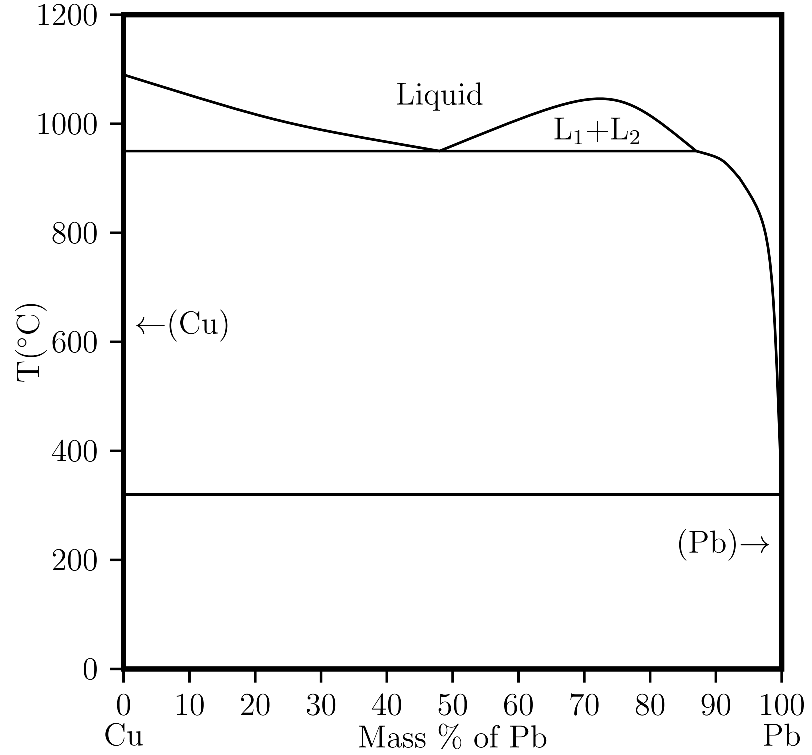


Figure 5.7: Cu-Pb phase diagram showing monotectic phase reaction due to repulsive behavior

For non-ideal behavior, we need some relation. Though activity coefficienct varies with concentration, Henry's Law helps us by saying that γ_i is a constant for dilute solutions.

$$a_i = \gamma_i X_i$$

In a dilute solution, when solute obeys Henry's law, the solvent obeys Raoult's Law, Figure 5.8.

In a dilute solution, solvent obeys Raoult's law (ideal behavior) as it experiences no significant effect due to solute. Solute obeys Henry's law (linear line) as solvent is much higher in quantity and thus solute experiences significant effects due to solvent. Think about the environment around solute atoms and environment around solvent atoms in a dilute solution.

5.3.4 Change in Free Energy on Formulation of a Solution (Free Energy of Mixing)

For a component i

$$\Delta\overline{G_i^M} = G_i(in\ solution) - G_i(pure)$$

The 'M' represent mixing in a solution, overhead bar represents partial quantity, while i represents component 'i'.

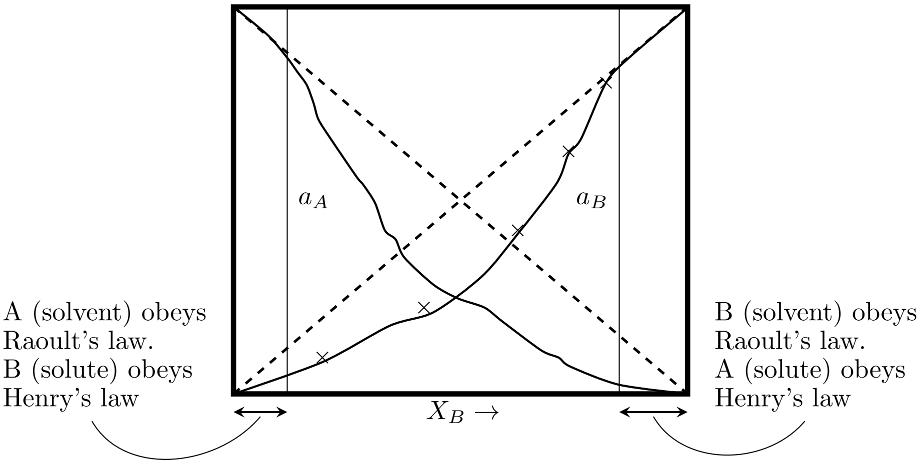


Figure 5.8: In a dilute solution where solute obeys Henry's law, solvent obeys Raoult's law.

Remember, we are using the idea of equilibrium between liquid and its vapors – the behavior of solution is depicted by its vapors.

$$\Delta\overline{G_i^M} = RTlnp_i - RTlnp_i^\circ$$

$$\Delta\overline{G_i^M} = RTln\frac{p_i}{p_i^\circ}$$

But

$$\frac{p_i}{p_i^\circ} = a_i$$

Thus

$$\Delta\overline{G_i^M} = RTlna_i$$

It can be represented properly as

$$\Delta\overline{G_i^M} = \overline{G}_i - G_i^\circ = RTlna_i \tag{5.15}$$

Recall that the change in free energy on mixing of an ideal gas is given by

$$\Delta\overline{G_A^M} = RTlnX_A$$

For an ideal solution,

$$a_i = X_i$$

and we get the same expression

$$\Delta\overline{G_i^M} = \overline{G}_i - G_i^\circ = RTlnX_i$$

When we make a solution by mixing n_A moles of A and n_B moles of B, we note that

$$\begin{aligned} &\text{Free energy before mixing} &=& \quad n_A G_A^\circ + n_B G_B^\circ \\ &\text{Free energy after mixing} &=& \quad n_A \overline{G_A} + n_B \overline{G_B} \end{aligned}$$

The Gibbs free energy of mixing is then given by

$$\Delta \overline{G'^M} = \left(n_A \overline{G_A} + n_B \overline{G_B}\right) - \left(n_A G_A^\circ + n_B G_B^\circ\right)$$

Rearranging the above equation, we get

$$\begin{aligned} \Delta \overline{G'^M} &= n_A \left(\overline{G_A} - G_A^\circ\right) + n_B \left(\overline{G_B} - G_B^\circ\right) \\ &= n_A(\text{partial molar free energy of mixing of A}) \\ &\quad + n_B(\text{partial molar free energy of mixing of B}) \\ &= n_A(RTlna_A) + n_B(RTlna_B) \end{aligned}$$

Now divide by $(n_A + n_B)$

$$\frac{\Delta \overline{G'^M}}{n_A + n_B} = \frac{n_A}{n_A + n_B} RTlna_A + \frac{n_B}{n_A + n_B} RTlna_B$$

$$\Delta G^M = X_A(RTlna_A) + X_B(RTlna_B)$$

This is the change in free energy on mixing per mole of the solution. In general,

$$\Delta G^M = RT\left[\sum X_i lna_i\right] \tag{5.16}$$

This is the free energy of mixing per mole of solution. For a ternary solution,

$$\Delta G^M = RT\left[(X_A lna_A) + (X_B lna_B) + (X_c lna_c)\right]$$

For ideal binary solution, $a_i = X_i$

$$\Delta G^M = RT\left[X_A ln(X_A) + X_B ln(X_B)\right]$$

Recall, we had the same expression for free energy of mixing of ideal gases per mole of mixture, i.e., $\Delta G^M = RT\left(\sum X_i lnX_i\right)$

In case of an ideal solution, the enthalpy change would be zero, i.e., $\Delta H^M = 0$ (No interactions)

From $\Delta G^M = \Delta H^M - T\left(\Delta S^M\right)$

We get

$$\Delta S^M = -R\left[X_A ln(X_A) + X_B ln(X_B)\right]$$

Note that entropy of mixing is always positive, same as that for ideal gas mixture and free energy of mixing is negative. Also it is clear that

$$\Delta G^M \propto T$$

As T increases, so does the magnitude of ΔG^M which becomes more negative and the graph shifts downward as shown in Figure 5.9

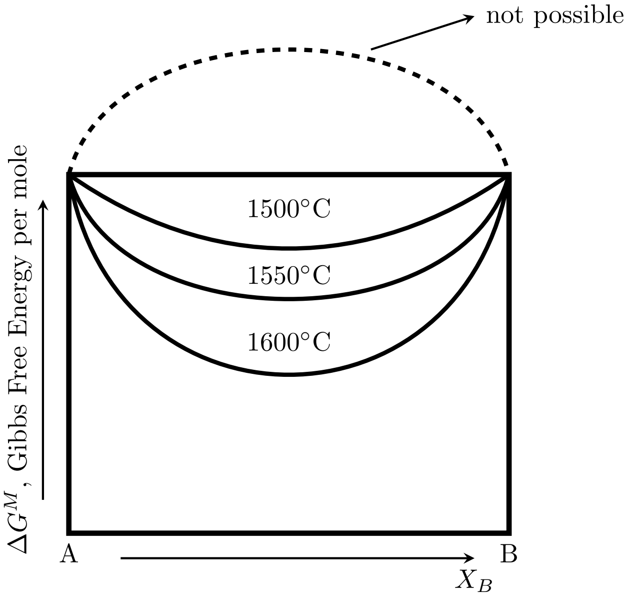


Figure 5.9: Free energy of mixing as a function of composition in a binary system and the effect of temperature.

5.3.5 Enthalpy of Mixing in a Regular Binary Solution

As

$$a_i = \gamma_i X_i$$

We can write

$$\Delta G^M = RT\left[\sum X_i ln \gamma_i X_i\right]$$

For a two components system,

$$\Delta G^M = RT\left[X_A ln\gamma_A X_A + X_B ln\gamma_B X_B\right]$$

$$\Delta G^M = RT\left[X_A ln\gamma_A + X_B ln\gamma_B\right] + RT\left[X_A lnX_A + X_B lnX_B\right]$$

Also

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

Comparing the above two equations

$$\Delta H^M = RT\left[X_A ln\gamma_A + X_B ln\gamma_B\right] \tag{5.17}$$

and

$$\Delta S^M = -R\left[X_A lnX_A + X_B lnX_B\right]$$

A regular solution is the one in which entropy change is same as that of ideal solution.

$$\Delta S = -R\left[X_A ln(X_A) + X_B ln(X_B)\right]$$

Table 5.1: Characteristics of non-ideal solutions

$\gamma > 1$	$\gamma < 1$
+ interactions	- interactions
repulsion	attraction
(Tendency for Clustering)	(Tendency for Ordering)
$\Delta H > 0$	$\Delta H < 0$
Endothermic	Exothermic

The effect of interactions can be clearly seen now. For ideal solution $\gamma = 1$, which leads to

$$\Delta H^M = 0$$

When there are attractions, i.e., $\gamma < 1$, we get exothermic mixing, i.e.,

$$\Delta H^M < 0$$

When repulsions are dominant, i.e., $\gamma > 1$, we get endothermic mixing, i.e.,

$$\Delta H^M > 0$$

Attraction will lead to the ordering whereby all ‘A’ particles tend to be surrounded by ‘B’ particles and all ‘B’ particles tend to be surrounded by ‘A’ particles.

Repulsion is the tendency of segregation. ‘A’ particle will tend to have ‘A’ type of particles around it while ‘B’ will tend to have ‘B’ around it.

If ΔH^M is highly positive, ΔG may become non-negative. In such case, solution mixing will not be possible.

It should be noted that, in the equation

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

The role of entropy is to randomize the particle distribution. ΔS^M is always positive in mixing and its role increases as temperature increases.

The characteristics of non-ideal solutions are shown in Table 5.1.

The role of interactions on the free energy of mixing may be represented graphically as shown in Figure 5.10.

Example. *For a dilute solution of Pb in molten Cu,*

$$a_{Pb} = 4X_{Pb}$$

i) What type of interactions are there ? Do you expect clustering or ordering?

ii) When we add 1 mole % of Pb into liquid Cu , calculate enthalpy change and entropy change using regular solution assumption.

Solution.

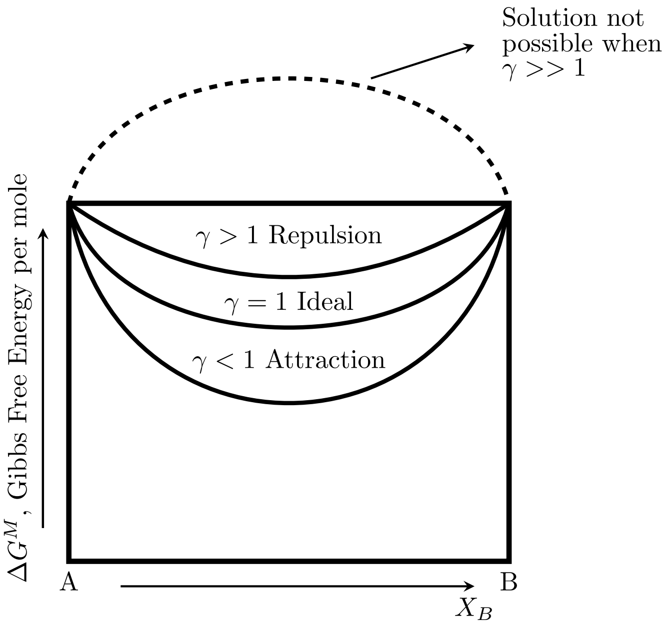


Figure 5.10: Effect of interactions on the free energy of mixing

i) $\gamma > 1$ This indicates positive interactions, i.e., repulsions which shows tendency for clustering

ii)

$$\begin{aligned} X_{Pb} &= 0.01, & X_{Cu} &= 1 - 0.01 = 0.99 \\ \gamma_{Pb} &= 4, & \gamma_{Cu} &= 1 (\text{Solution is dilute and Cu is solvent}) \end{aligned}$$

(Note: In a very dilute solution, solute obeys Henry's Law and solvent obeys Raoult's law)

Also we need to take temperature well above the melting point of Cu, say 1400 K

$$\begin{aligned} \Delta S^M &= -R\left[X_{Pb} ln(X_{Pb}) + X_{Cu} ln(X_{Cu)}\right] \\ &= -8.314 \times [0.01 ln(0.01) + 0.99 ln(0.99)] \\ &= 0.466 J/K/mol \end{aligned}$$

$$\begin{aligned} \Delta H^M &= RT\left[X_{Pb} ln(\gamma_{Pb}) + X_{Cu} ln(\gamma_{Cu})\right] \\ &= 8.314 \times 1400 * [0.01 ln(4) + 0.99 ln(1)] \\ &= +161.36 J/mol \end{aligned}$$

$$\begin{aligned} \Delta G^M &= \Delta H^M – T(\Delta S^M) \\ &= 161.36 – 1400 \times 0.465 = -489 J/mole\ of\ solution \end{aligned}$$

Though enthalpy of mixing is positive, the free energy of mixing is negative because of entropy contribution. And because of entropy role, free energy of mixing becomes more negative as temperature increases.

□

5.3.6 Gibbs-Duhem Equation

Determining activities is not easy especially at high temperatures. Thanks to mathematics, in a binary system, we need to find the activity of one component only. The activity of second component can be easily calculated using Gibbs-Duhem Equation.

Consider a solution of two components. The Gibbs free energy is a function of T, P, and n_1, n_2

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1} dn_2 \tag{5.18}$$

At constant T and P ...

$$dG = \mu_1 dn_1 + \mu_2 dn_2 \tag{5.19}$$

By definition, total energy of the solution would be

$$G = \mu_1 n_1 + \mu_2 n_2$$

Differentiating this equation, we get

$$dG = \mu_1 dn_1 + \mu_2 dn_2 + n_1 d\mu_1 + n_2 d\mu_2$$

But, from equation Equation 5.19,

$$dG = \mu_1 dn_1 + \mu_2 dn_2$$

Therefore

$$n_1 d\mu_1 + n_2 d\mu_2 = 0$$

This is one expression for Gibbs-Duhem Equation. In general

$$\sum n_i d\mu_i = 0 \tag{5.20}$$

If we divide everything by n (total number of moles)

$$X_1 d\mu_1 + X_2 d\mu_2 = 0$$

Though here we have used partial molar free energies, Gibbs-Duhem equation applies to all partial molar quantities and we write

$$\sum_j X_j dQ_j = 0 \tag{5.21}$$

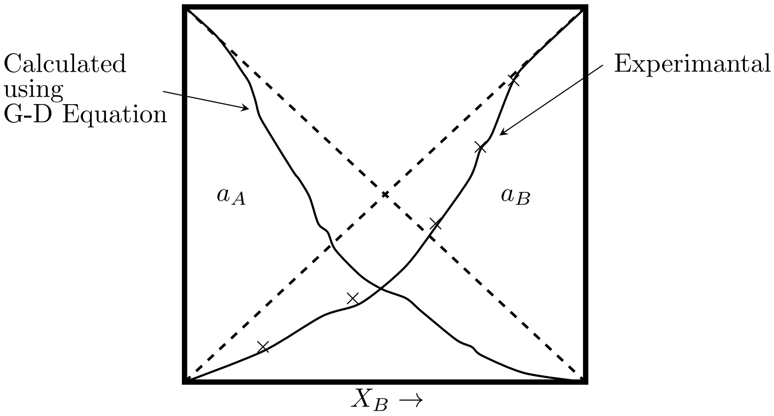


Figure 5.11: Using Gibbs-Duhem equation, we can calculate activity of second component after establishing activity of one component experimentally.

Where Q = V, U, H, A, G ,S, etc.

The Gibbs-Duhem equation signifies that the chemical potential of a component in a mixture cannot change independently of the chemical potential of the other components. For example, in a binary mixture we have:

$$d\mu_B = -\frac{X_A}{X_B} d\mu_A \tag{5.22}$$

i.e., if one chemical potential increases, the other must decrease.

$$\int d\mu_B = -\int \frac{X_A}{X_B} d\mu_A$$

Since $\mu_i = RTlna_i$

We can also write

$$\int dlna_B = -\int \frac{X_A}{X_B} dlna_A$$

Summary

1. We first study behavior of gases to understand the basic properties of solutions, in particular free energy of mixing.
2. Solutions are very important in materials science from processing and applications point of view.
3. Vapor pressure indicates the behavior of components in a solution.
4. Raoult's law applies to ideal solutions and indicates that vapor pressure varies linearly with mole fraction and proportionality constant is vapor pressure of pure component.

5. In case of non-ideal solution, Henry's Law makes things simple by pointing that, in a dilute solution, vapor pressure of solute varies linearly with its mole fraction.

6. In a dilute solution, when solute obeys Henry's law, solvent obeys Raoult's law.

7. The effective concentration, activity, of a component is defined as the ratio of its vapor pressure in solution to the vapor pressure of pure component.

8. In general, $a_i = \gamma_i X_i$ where $\gamma_i = 1$ for ideal solution, $\gamma_i > 1$ in case of repulsions and $\gamma_i < 1$ in case of attractions.

9. Extreme repulsive behavior may lead to immiscibility in liquid state. Monotectic isothermal reaction may appear in such situation in binary systems.

10. Free energy of mixing of solution per mole is $\Delta G^M = RT\left[\sum X_i ln a_i\right]$

11. Free energy of mixing for a regular solution may be split into two parts, enthalpy showing effects of interactions and entropy showing randomness as in ideal solution.

12. Free energy of mixing becomes more negative as temperature increases.

13. Free energy of mixing becomes more negative in case of attractions and less negative in case of repulsions.

14. Gibbs-Duhem Equation gives relation among partial molar properties of various components in a solution. For example, in case of binary solution, if we determine $a_B = f(X_B)$ experimentally, we can calculate $a_A = f(X_A)$ mathematically using Gibbs-Duhem Equation.

Practice Problems

1. Evaluate the following statements:

   i. Immiscibility of Pb in liquid state in brass can help us in machining of the alloy.
   ii. Even if A and B tend to repel each other, we can make their solution.
   iii. If uniform mixing at atomic or molecular level does occur, the free energy must decrease even if the mixing is endothermic.
   iv. Vapor pressure of components over a solution is a good indication of interactions happening within the solution.
   v. Enthalpy of mixing can explain the nature of interactions in a solution.
   vi. If uniform mixing at atomic or molecular level does occur, the solution making must be exothermic.

vii. A hump in a binary phase diagram could be important for industrial applications.

viii. In some binary phase diagrams we can clearly see that two liquid phases may coexist.

ix. A solution and a phase are synonyms.

x. In a region of dilute solution, when solute obeys Henry's law, solvent obeys Raoult's law.

2. When we add 0.3 mol% of C in A, the enthalpy of mixing at 800 K is found to be – 29.37 J per mole of solution. Find activity coefficient of C in this solution.

3. When we add 0.3 mol% of D in A, the enthalpy of mixing at 800 K is found to be +31.32 J per mole of solution. Find activity coefficient of D in this solution.

4. A very dilute solution is made by adding 1 mole% of Cu in Fe at steel making temperature. $\gamma_{Cu} = 5$. Calculate ΔG^M , ΔS^M and ΔH^M.

5. Assume that A is a solvent. B is a solute showing strong positive interactions. C is a solute showing strong negative interactions.

   i. We make a very dilute solution containing 1 mol% B.

   ii. We make a very dilute solution containing 0.5 mol% C.

   Calculate enthalpy and entropy of mixing per mole of solution in each case. Assume any required value.

6. Discuss the nature of interactions in the following cases indicating the tendency for ordering or clustering:

   i. When Pb is added in small amounts into molten Cu,
   $a_{Pb} = 8X_{Pb}$.

   ii. When Cr is added in small amounts into molten Fe,
   $a_{Cr} = X_{Cr}$.

   iii. When Ni is added in small amounts into molten Fe,
   $a_{Ni} = 0.8X_{Ni}$.

7. With the help of some hypothetical thermodynamic data, explain why a component which is not soluble at room temperature, may dissolve at 200 °C.

8. A very dilute solution is made by adding 1 mole% of Ni in Fe at steel making temperature. γNi = 0.8. Calculate ΔG^M , ΔS^M and ΔH^M.

9. Mn shows slight negative interaction with Fe. Suppose we make a 80/20 Fe-Ni alloy at the steel making temperature. Calculate the enthalpy, entropy and free energy of mixing. State proper assumptions you make in these calculations.

10. When Pb is added molten Cu, $a_{Pb} = 9X_{Pb}$. What types of interactions are there? How can we utilize such material? Discuss the feature of a binary phase diagram which may result from such interactions. Give one more example of such behavior.

11. i. Assume values for a very dilute regular solution showing strong positive interactions. Calculate Calculate ΔH^M , ΔS^M and ΔG^M.
    ii. Below what temperature, solution making will not be possible?
    iii. Draw a diagram showing activity of both components as a function of mole fraction.

Chapter 6

Phase Equilibria

Learning Outcomes:

Student should be able to explain

- One component phase diagram using free energy of various phases
- Chemical potential (activity) of each component in a binary solution
- Principle of equilibrium of phases
- How to get binary phase diagrams from free energy of mixing
- Phase rule

We are now in a position to use Gibbs free energy as a tool to understand the behavior of materials. Since material science is basically the understanding of processing-structure-property relationship, it is essential to know what phases exist in a material under the given conditions.

6.1 Phase Equilibria in One-component System

In a one-component system, since the composition is not a variable, the state of the system is described by two state variables, i.e., temperature and pressure. A one-component phase diagram represents phases and phase equilibria as a function of T and P. The component may undergo transformations like allotropic transformation (change within solid state), melting of solid to form liquid, boiling of liquid to form vapors and sublimation of solid to form vapors. Therefore, we have the following two-phase equilibria:

i) Solid – Solid (Allotropic change)

ii) Solid – Liquid (melting / freezing)

iii) Liquid – Vapor (boiling / condensation)

iv) Solid – Vapor (sublimation / condensation)

In addition, triple points may exist at which three phases are in equilibrium.

We know that a solid may melt spontaneously if it is at a temperature above the melting point and a liquid may freeze spontaneously when it is kept at a temperature below its freezing point. How do we explain this using the most suitable spontaneity criterion, i.e., decrease in Gibbs free energy?

Gibbs free energy for the liquid phase and the solid phase may be written as

$$G_l = H_l - TS_l$$

$$G_s = H_s - TS_s$$

Comparing with the equation of a straight line,

$$Y = A + BX$$

We note that enthalpy is represented by the intercept ‘A’ and entropy is represented by negative of the slope ‘-B’. Both enthalpy and entropy values for liquid are higher as compared to solid since liquid molecules are loosely bound as compared to solid and they have more randomness in the system. Therefore, on a G versus T plot, the liquid line will have larger intercept and higher slope, as shown in Figure 6.1. It is obvious that,

- At the melting point, the free energy of solid and liquid is same (S and L are in equilibrium)
- At lower temperature, solid, having lower G, is more stable. Freezing is spontaneous since free energy decreases in going from liquid to solid.
- At higher temperature, liquid is more stable. Melting is spontaneous since free energy decreases in going from solid to liquid.

One component phase diagram would then define various phase regions as a function of pressure and temperature,

$$\text{Phase region} = f(P, T)$$

While the equilibrium between two phases will be defined by

$$P = f(T)$$

The 3-phase equilibrium is represented by a point, i.e., fixed P and T.

A typical one component phase diagram is shown in Figure 6.2.

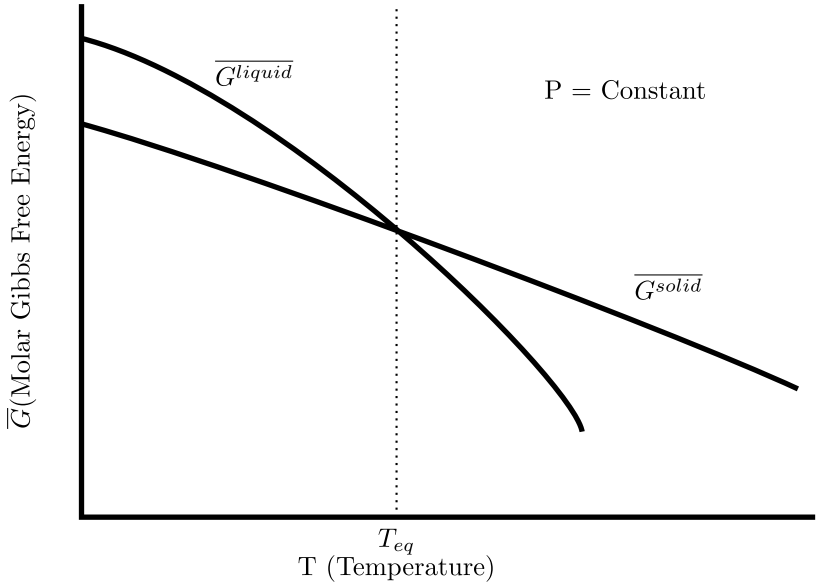


Figure 6.1: Change in Gibbs free energy of liquid and solid phase with temperature, explaining the stability of liquid and solid with respect to temperature

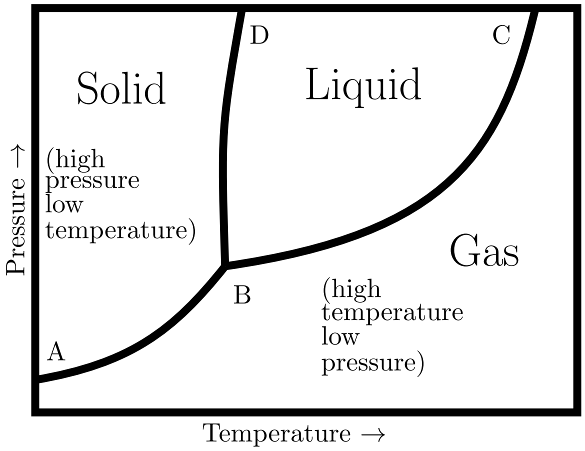


Figure 6.2: Phase equilibrium of solid, liquid and vapors in one component system

6.1.1 Differential Form of the Phase Diagram

To draw such a diagram, we need to find variation of pressure P with temperature T for various equilibria of solid, liquid and vapour phases (S/S, S/L, L/V, S/V). For this we proceed as follows:

We have seen that a closed system is described by the relation

$$dG = -SdT + VdP$$

Let us first consider equilibrium between solid and liquid phase.

For the liquid phase

$$dG_l = -S_l dT + V_l dP$$

And for the solid phase

$$dG_s = -S_s dT + V_s dP$$

At equilibrium, both solid and liquid have the same free energy

$$G_l = G_s$$

Or

$$dG_l = dG_s$$

$$-S_l dT + V_l dP = -S_s dT + V_s dP$$

On melting, we go from solid to liquid,

$$(V_l - V_s)dP = (S_l - S_s)dT$$

$$\frac{dP}{dT} = \frac{S_l - S_s}{V_l - V_s} = \frac{\Delta S_{s\to l}}{\Delta V_{s\to l}} = \frac{\text{Entropy Change on Melting}}{\text{Volume change on Melting}} \tag{6.1}$$

This is the *Differential Form* of the line BD in the diagram (Figure 6.2, line representing S/L equilibrium).

This relation gives us the effect of pressure on transformation temperature. In this case, we can find how the change in pressure affects melting or freezing temperature.

On boiling, we go from liquid to vapor. With the same considerations, we get

$$\frac{dP}{dT} = \frac{S_v - S_l}{V_v - V_l} = \frac{\Delta S_{l\to v}}{\Delta V_{l\to v}} \quad \text{(for boiling)} \tag{6.2}$$

This is the *Differential Form* of the line BC in the diagram (line representing L/V equilibrium).

On sublimation, we go from solid to vapor. Using the same approach, we get

$$\frac{dP}{dT} = \frac{S_v - S_s}{V_v - V_s} = \frac{\Delta S_{s\to v}}{\Delta V_{s\to v}} \quad \text{(for sublimation)} \tag{6.3}$$

This is the *Differential Form* of the line AB in the diagram (line representing S/V equilibrium).

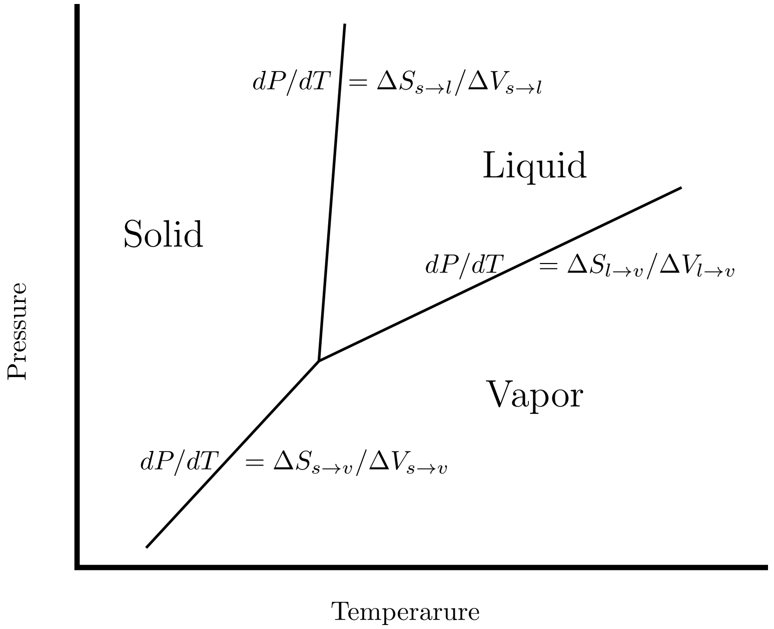


Figure 6.3: Phase equilibria in one component system expressed in differential form

The differential equations corresponding to these phase equilibria are shown in Figure 6.3.

For H_2O (also Bismuth, Gallium, Indium, Thalium), freezing results in expansion, i.e., ΔV on melting is negative. So, the slope of S/L line is negative as shown in Figure 6.4. This means that water expands on freezing and the melting point decreases as the pressure increases.

Referring back to Figure 6.2, we note that

- The region on left of ABD shows the region in which the solid phase is stable. This region has two degrees of freedom as we can select both P and T within this region.

- The region enclosed by DBC shows the region in which the liquid phase is stable. This region also has two degrees of freedom as we can select both P and T within this region.

- The region on right of ABC shows the region in which vapor phase is stable. This region also has two degrees of freedom as we can select both P and T within this region.

- The line BD represents equilibrium between solid and liquid. Along this line, we have one degree of freedom. If we choose T, pressure is fixed and if we select any P, temperature is fixed. This represents change in melting point with pressure. Generally melting temperature increases with increase in pressure. In some unusual cases like water, this line has negative slope. This is because change in volume on melting $\Delta V_{s\to l}$ is negative, i.e., water contracts on melting.

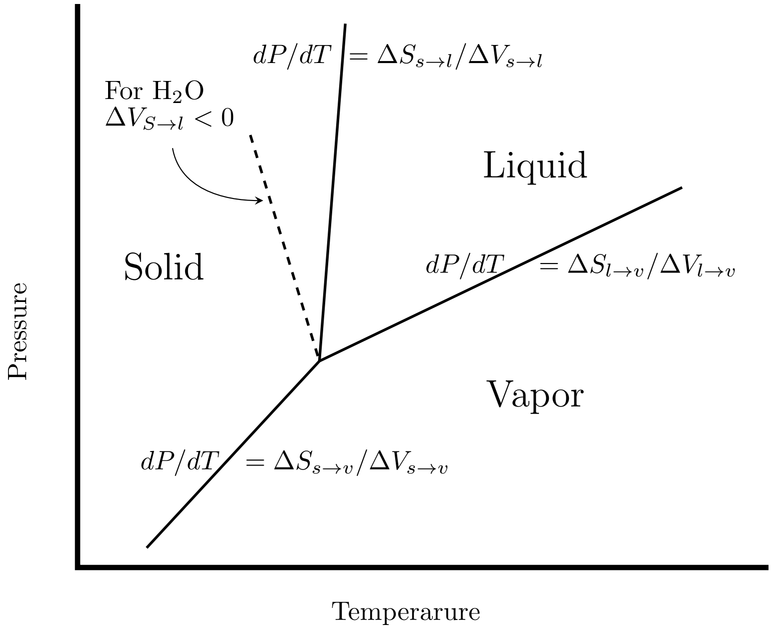


Figure 6.4: Phase equilibrium in one component system showing anomalous behavior of water

Density of ice is less than water. The phenomenon that melting point of water decreases as pressure increases has some useful applications like cutting of ice using a wire, ice skating, and compacting an ice slush. This anomalous behavior of water helps in the survival of marine life in extremely cold regions.

- The line BC represents equilibrium between liquid and vapor. Along this line, we have one degree of freedom. If we choose T, pressure is fixed and if we select any P, temperature is fixed. This line represents change in boiling point with pressure. Boiling temperature increases with increase in pressure. At high altitudes, where pressure is lower, boiling occurs at lower temperature. This is why cooking becomes difficult at high altitudes and pressure cookers are required for proper cooking.
- The line AB represents equilibrium between solid and vapor. This line also shows one degree of freedom. If we choose T, pressure is fixed and if we select any P, temperature is fixed. This line represents change in vapor pressure of solid with temperature.
- At point B we have three phase equilibrium. This is an invariant point having zero degree of freedom. At the *Triple Point* three phases co-exist. The triple point is specified by fixed values of T and P for any given system.

Keeping in view the relation

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$

We note that

- For line BD, ΔV is negligible so slope is high and line is almost vertical.
- When we compare slopes of lines AB and BD, we note that, while ΔV is almost same in both the cases, ΔS is larger for AB so slope is high in comparison with line BC.

In summary, each line in a one component phase diagram gives effect of pressure on equilibrium temperature.

1. S/L line gives the effect of pressure on melting point of solid (or freezing point of liquid).
2. L/V line gives the effect of pressure on the boiling point of liquid.
3. S/V line represents sublimation and gives vapor pressure of solid as a function of temperature.

6.1.2 Integral Form of the One-component Phase Diagram

The integral forms of the lines representing 2-phase equilibria can be found as follows:

In case of boiling

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$

The entropy change on transformation is

$$\Delta S = \frac{\Delta H}{T}$$

The change in volume on boiling is

$$\Delta V = V_v – V_l \approx V_v$$

as the volume of liquid can be neglected in comparison with the volume of vapors.

Therefore,

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

Assuming vapors to be ideal gas, we may write $V_v = \frac{RT}{P}$

Therefore,

$$\frac{dP}{dT} = \frac{\Delta HP}{RT^2}$$

$$\frac{dP}{PdT} = \frac{\Delta H}{RT^2}$$

$$\frac{dlnP}{dT} = \frac{\Delta H}{RT^2} \tag{6.4}$$

This equation is generally known as Clausius-Clapeyron equation.

Now we integrate this equation,

$$\int \frac{dP}{P} = \int \frac{\Delta H}{RT^2} dT$$

Assuming that ΔH does not change with temperature

$$lnP = \frac{\Delta H}{R}\left[-\frac{1}{T}\right] + C$$

$$lnP = \frac{A}{T} + C \tag{6.5}$$

This equation represents vapor pressure of a liquid as a function of temperature. In a similar manner, equation for vapor pressure of a solid can be derived.

Generally, variation of ΔH with temperature can be neglected. However, if we assume that ΔH varies linearly with temperature i.e.,

$$\Delta H = a + bT$$

We can integrate

$$\int \frac{dP}{P} = \int \left(\frac{a + bT}{R}\right) \frac{1}{T^2} dT$$

And we get

$$lnP = \frac{A}{T} + BlnT + C \tag{6.6}$$

This is the general form of equation for vapor pressure of solids and liquids and is one of the most tabulated property in a thermodynamic data book.

If vapor pressure equations for the solid phase and the liquid phase of a substance are given as

$$lnP_l = \frac{A_l}{T} + B_l$$

$$lnP_s = \frac{A_s}{T} + B_s$$

We can find

1. Normal boiling point by putting P = 1atm in vapor pressure equation for liquid
2. Triple point by equating the two equations
3. Enthalpies of boiling and sublimation, i.e., ΔH_b and ΔH_s by multiplying respective 'A' by (-R)
4. Enthalpy of melting ΔH_m may be estimated as $\Delta H_m \approx \Delta H_s - \Delta H_b$

Note that for one component system, in case of reversible processes,

$$\begin{aligned}
T_{melting} &= T_{freezing} \\
T_{boiling} &= T_{condensation} \\
\Delta H_{boiling} &= -\Delta H_{condensation} \\
\Delta H_{melting} &= -\Delta H_{freezing}
\end{aligned}$$

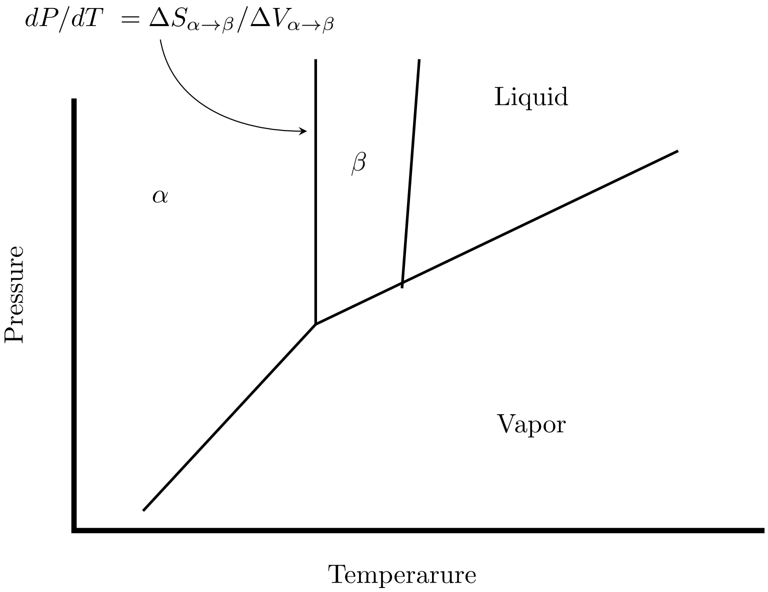


Figure 6.5: One component system showing allotropic transformation

When the component shows allotropy, the phase diagram will show two solid regions and hence two triple points as shown in Figure 6.5. The line for α/β equilibrium will be almost vertical as volume changes in allotropic transformations are very small.

When the triple point is above the atmospheric pressure, the solid does not melt on heating but sublimes directly to vapors as shown in Figure 6.6. In case of carbon dioxide, as shown in Figure 6.7, the triple point pressure is *5.11 atm.*. Below this pressure, liquid CO_2 cannot exist and the solid will *sublime* directly to vapor. Gaseous carbon dioxide at a pressure of 1 atm is in equilibrium with the solid at $-78.5°C$; this is the *normal sublimation temperature* of CO_2.

In contrast, when we observe a sample of solid iodine in the bottom of an open glass flask, at room temperature and 1 atm pressure, we see a faint colour of iodine vapour. As shown in Figure 6.8, although the vapour pressure of iodine is very low (about 0.03 atm), the vapour is coloured intensely enough that we can see it. Most of the 1 atm pressure is due to the air. If the flask is open, the iodine vapour can escape and eventually the iodine sublimes away.

Example. *Find out normal boiling point, ΔH_b, ΔH_s and triple point temperature and pressure for the given system.*

$$lnP = -\frac{5400}{T} + 9 \quad \textit{(for liquid phase)}$$

$$lnP = -\frac{7500}{T} + 14 \quad \textit{(for solid phase)}$$

Solution. The normal boiling point can be calculated by putting P = 1 atm in the

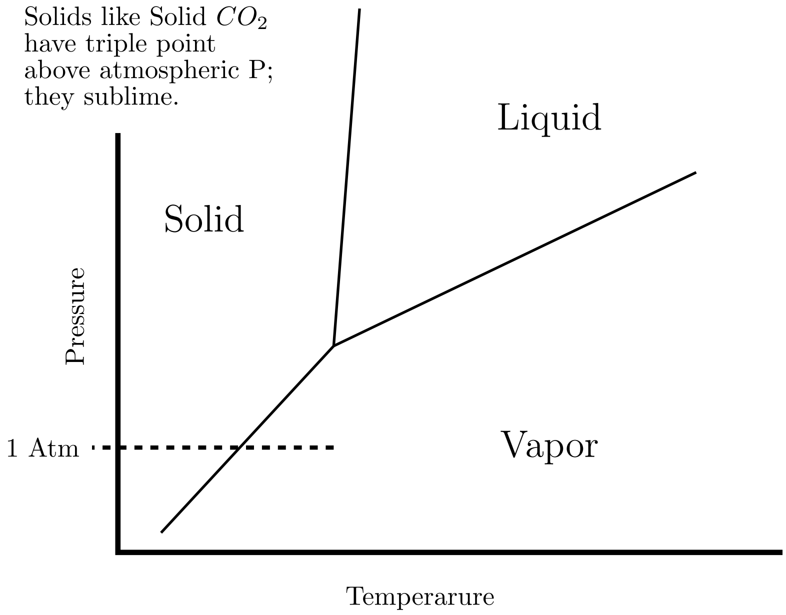


Figure 6.6: One component system, like CO_2, showing sublimation under normal conditions

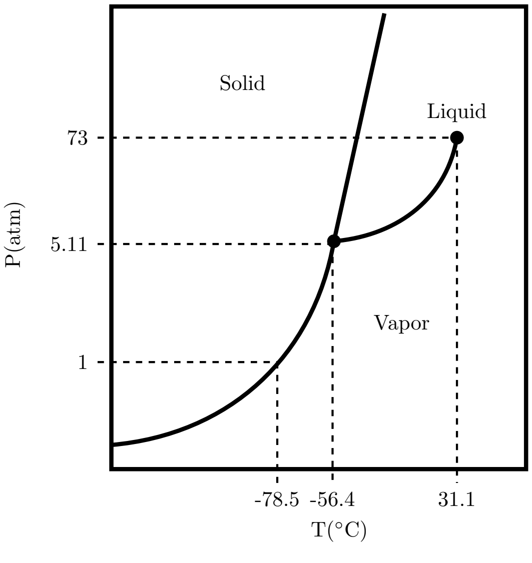


Figure 6.7: Phase diagram of CO_2

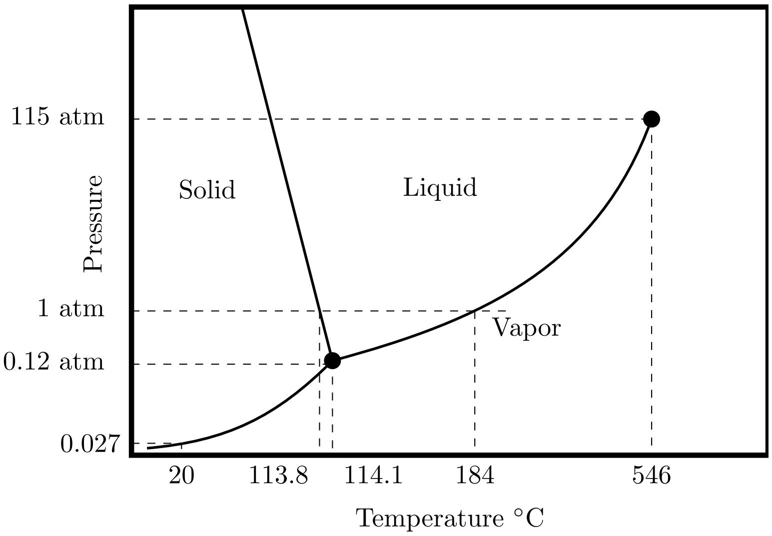


Figure 6.8: Phase diagram of Iodine

equation for liquid,

$$lnP = -\frac{5400}{T} + 9$$

$$\frac{5400}{T} = 9$$

$$T = 600K$$

For ΔH_b,

$$\frac{\Delta H_b}{R} = 5400$$

$$\Delta H_b = 5400 \times 8.314 \quad J/mol$$

$$\Delta H_b = 44.89 \quad kJ/mol$$

For ΔH_s,

$$\Delta H_s = 7500 \times R \quad J/mol$$

$$\Delta H_s = 62.35 \quad kJ/mol$$

At triple point

$$P_l = P_s$$

$$-\frac{5400}{T} + 9 = -\frac{7500}{T} + 14$$

Solving for T, we get:

$$T_{tr} = 420 \ K$$

T_{tr} is the triple point temperature and P_{tr} is the triple point pressure,

$$lnP_{tr} = -\frac{5400}{T_{tr}} + 9$$

Putting value of T_{tr}

$$lnP_{tr} = -\frac{5400}{420} + 9$$

$$lnP_{tr} = -\frac{27}{7}$$

$$P_{tr} = e^{-\frac{27}{7}}$$

$$P_{tr} = 0.021\ atm$$

□

Example. *Vapor pressure equation for a liquid is given below, find the enthalpy change on boiling.*

$$lnP = -\frac{10000}{T} + 10lnT + 14$$

Solution. Taking differential we get,

$$\frac{dlnP}{dT} = \frac{10000}{T^2} + \frac{10}{T}$$

But

$$\frac{dlnP}{dT} = \frac{\Delta H}{RT^2}$$

On comparing,

$$\frac{10000}{T^2} + \frac{10}{T} = \frac{\Delta H}{RT^2}$$

$$\Delta H = (10000 + 10T)R = 83140 + 83.14T$$

□

6.2 Phase Equilibria in Binary Systems

In a two component system, composition of the system becomes a variable and it is sufficient to define one composition as the other will be fixed. Now we have to consider chemical potentials of the two components and we need to know the variation of these potentials in each phase present in the system. This can be understood using free energy of mixing curves corresponding to various phases present in the system. This discussion then leads to the construction of binary phase diagram using the principle of equilibrium of phases.

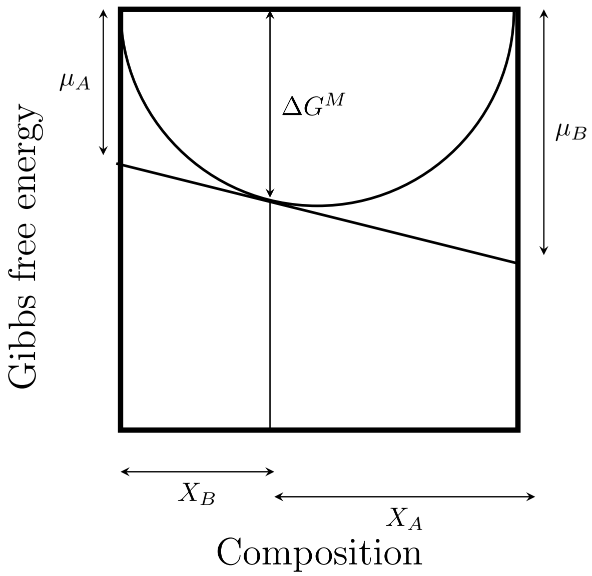


Figure 6.9: Free energy of mixing and chemical potentials of the two components in a binary alloy

6.2.1 Free Energy of Mixing and Chemical Potential

The free energy of mixing can also be represented in terms of chemical potentials of individual components.

$$\begin{aligned}\Delta G^M &= RT\left[X_A ln(a_A) + X_B ln(a_B)\right]\\ &= X_A\left[RT ln(a_A)\right] + X_B\left[RT ln(a_B)\right]\\ &= X_A\mu_A + X_B\mu_B\end{aligned}$$

This is graphically shown in Figure 6.9. As shown, when an alloy is made by mixing two components A and B with respective mole fractions of X_A and X_B, the free energy decreases by an amount ΔG^M per mole of alloy. The chemical potentials μ_A and μ_B in this alloy are obtained by the intercepts on the respective axes made by the tangent drawn at the alloy composition. The equation for this tangent line is

$$\Delta G^M = X_A\mu_A + X_B\mu_B \tag{6.7}$$

6.2.2 Principle of Phase Equilibria

Recall Free energy of mixing curves.

Next two figures show free energy of mixing for two alloys.

- In Figure 6.10, the composition of alloy is X_B and X_A

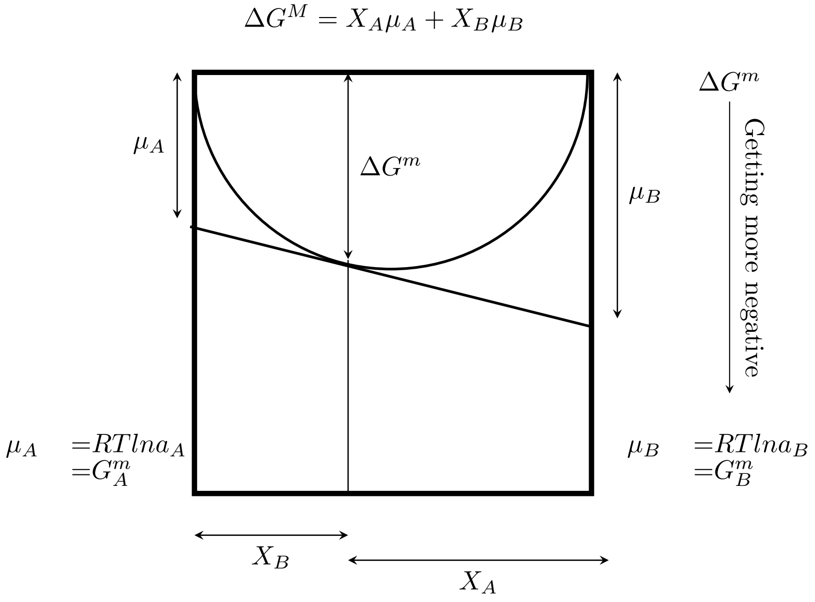


Figure 6.10: The free energy of mixing for an alloy having X_B mole fraction of B. The chemical potentials of both the components are also shown.

- In Figure 6.11, the composition of alloy is X'_B and X'_A
- Total free energy of mixing is given and then chemical potential of each component, A and B, is shown for both the alloys.

Note that we have to draw a tangent at the given composition and get respective chemical potentials as the intercepts. Also remember, chemical potential (Partial Molar Free Energy of Mixing) is related to activity.

At equilibrium, chemical potentials of each component in different phases must be equal.

When we add alcohol in a system containing two liquid phases, oil and water, the alcohol moves from aqueous phase to oily phase until the chemical potential of alcohol is equal in both the phases and then there is no net movement of alcohol molecules from one phase to the other.

$$(\mu_{alcohol})_{water} = (\mu_{alcohol})_{oil}$$

If chemical potential is equal, it means activity is also equal as

$$\mu_i = \Delta\overline{G_i} = RTlna_i$$

If a solid phase and a liquid phase are in equilibrium then

$$\Delta\overline{G}_A^M(\text{in the solid phase}) = \Delta\overline{G}_A^M(\text{in the liquid phase})$$

$$\Delta\overline{G}_B^M(\text{in the solid phase}) = \Delta\overline{G}_B^M(\text{in the liquid phase})$$

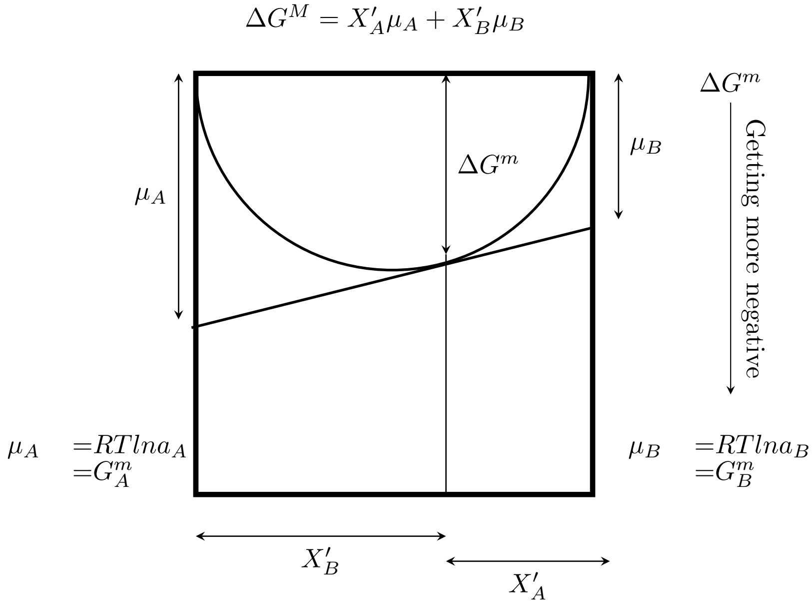


Figure 6.11: The free energy of mixing for an alloy having X'_B mole fraction of B. The chemical potentials of both the components are also shown.

For components 'A' and 'B'

$$\Delta G^M = X'_A(\Delta\overline{G}_A) + X'_B(\Delta\overline{G}_B)$$

$$\mu_A = \Delta\overline{G}_A = RTlna_A$$

If not equal, a component will move from higher chemical potential region to the lower chemical potential region. This diffusion will continue until equilibrium is established.

Now assume that we have an alloy of two elements 'A' and 'B'. This alloy has two phases 'α' and 'β'. The 'α' solid solution is based on 'A' with some 'B' dissolved in it. The structure of 'α' is same as the structure of 'A'. The 'β' solid solution is based on 'B' with some 'A' dissolved in 'B'. The structure of 'β' is same as the structure of B.

According to the principle of equilibrium, when equilibrium is established,

$$(\mu_A)_\alpha = (\mu_A)_\beta$$

$$(\mu_B)_\alpha = (\mu_B)_\beta$$

Now consider two alloys (all compositions in atom% or mol%) at a certain temperature.

1. A – 40% B

    a) α has 90% A and 10% B

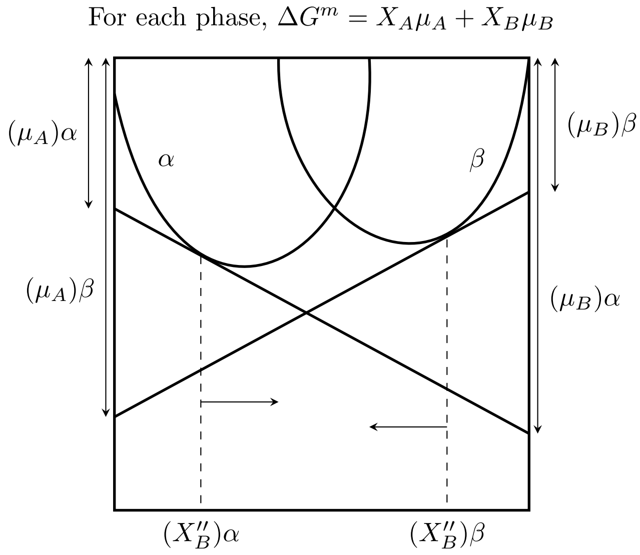


Figure 6.12: Two phases in contact with each other under non-equilibrium conditions. Composition of α is $(X''_B)_\alpha$ and composition of β is $(X''_B)_\beta$. As chemical potentials are not equal, diffusion occurs.

   b) β has 10% A and 90% B

2. A – 30% B
   a) α has 90% A and 10% B
   b) β has 10% A and 90% B

Alloy 1 has more B as compared to alloy 2. Alloy 1 has less α and more β as compared to alloy 2. At a given temperature, the composition of phases will be the same while the amount of phases will be different.

If the compositions of the phases are such that the chemical potentials of A and B are not equal in α and β, the components A and B will move from higher chemical potential region to lower chemical potential region. This diffusion will continue until equilibrium is established.

In Figure 6.12, composition of α is $(X''_B)_\alpha$ and composition of β is $(X''_B)_\beta$. As chemical potentials are not equal, diffusion occurs. The chemical potentials try to decrease their respective differences.

In Figure 6.13, composition of α is $(X'_B)_\alpha$ and composition of β is $(X'_B)_\beta$. The chemical potentials are getting closer but they are not yet equal, diffusion continues.

In Figure 6.14, composition of α is $(X_B)_\alpha$ and composition of β is $(X_B)_\beta$. As chemical potentials are now equal, diffusion stops. Now the equilibrium compositions of α phase and β phase have been achieved.

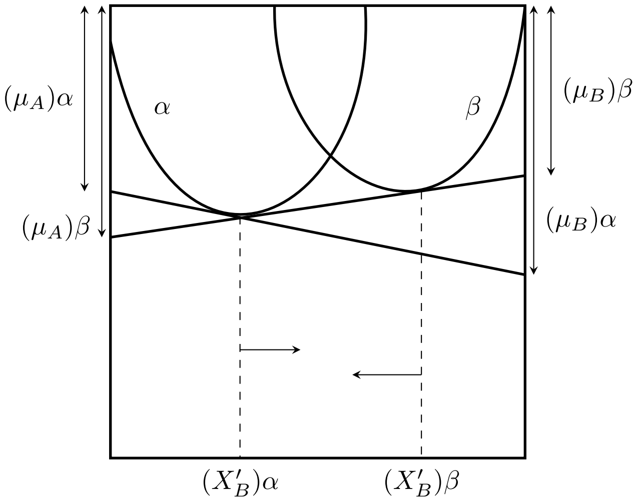


Figure 6.13: Two phases in contact with each other under non-equilibrium conditions. Composition of α is $(X'_B)_\alpha$ and composition of β is $(X'_B)_\beta$. Even now, the chemical potentials are not equal, diffusion continues.

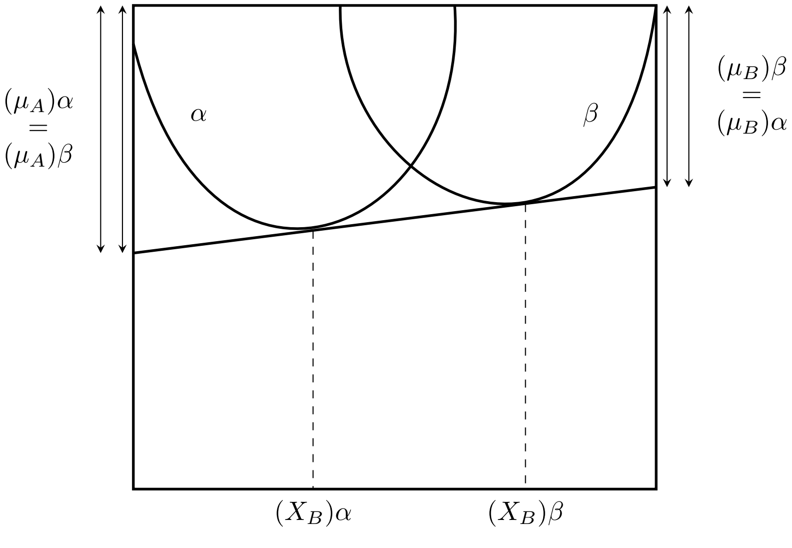


Figure 6.14: Two phases in contact with each other under equilibrium conditions. Composition of α is $(X_B)_\alpha$ and composition of β is $(X_B)_\beta$. As, the chemical potentials are now equal, diffusion stops.

6.2.3 Gibbs Free Energy Composition and Binary Phase Diagram

An alloy will be stable when its Gibbs free energy is minimum. According to the principle of equilibrium, when two or more phases are in equilibrium, the chemical potentials of each component in all the phases are equal. For example, when two phases α and β are in equilibrium in a binary alloy of A and B,

$$(\mu_A)_\alpha = (\mu_A)_\beta$$

$$(\mu_B)_\alpha = (\mu_B)_\beta$$

or

$$(a_A)_\alpha = (a_A)_\beta$$

$$(a_B)_\alpha = (a_B)_\beta$$

The principle of equilibrium is based on equality of activities rather than on the equalities of concentrations. This principle can be used to construct equilibrium phase diagrams.

Binary isomorphous phase diagram

A binary isomorphous system shows complete solubility in both the liquid phase and the solid phase, Figure 6.15. This means that both the components have same crystal structure. There are 3 phase fields; Liquid (L), Solid and Liquid (S + L), Solid (S).

Liquidus line separates liquid from (Solid + Liquid) region. Solidus line separates solid from (Solid + Liquid) region.

In a two-phase region (S+L), the compositions of two phases are fixed by temperature.

- At T_a, composition of L is given by point 3 and composition of S is point 4
- At T_b, composition of L is given by point 5 and composition of S is point 6

This is governed by thermodynamics. If we change composition of alloy, the amounts of S and L will change (Lever Rule) but compositions of S and L are fixed at a given temperature by Thermodynamics. So, if we know melting points of A and B and we can establish points 1, 2, 3, 4, 5, 6, we get the phase diagram. Here we have two phases S and L. When we have two solid phases, we generally say α and β phases.

The number of phases decides the number of curves of free energy of mixing. Hence, for an isomorphous system, we have 2 free energy of mixing curves designated by S and L.

As shown in Figure 6.16, we select temperature T_1 (say 1000 °C). At this temperature, only liquid is stable for all the compositions. This means free energy of liquid phase is less than free energy of solid phase for all the compositions.

Note that the difference in free energies for S and L is the lowest for Pure B and highest for pure A.

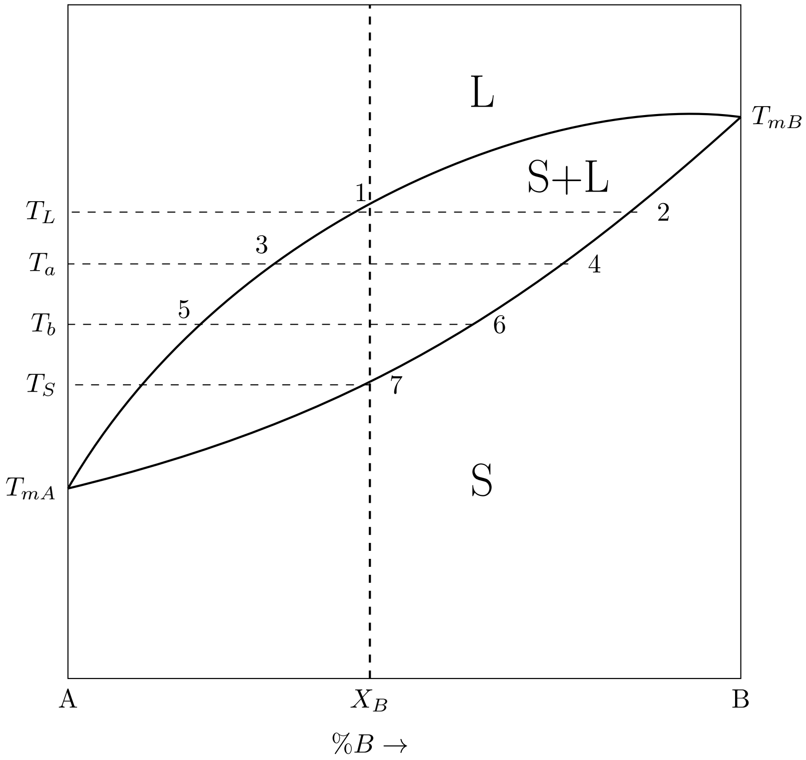


Figure 6.15: A binary isomorphous system of two components A and B showing complete solubility in solid state.

Now as we decrease the temperature, stability of solid starts increasing, i.e., its free energy decreases with respect to liquid. At the freezing point of B (say 900 °C), pure solid B and pure liquid B will have the same free energy, Figure 6.17. For any other composition, only liquid is stable (having free energy lower than solid alloys).

As we decrease the temperature further, S curve continues downward and we enter into two phase region.

At a temperature, say 850 °C, we are in a two phase region (S+L). Now compositions of two phases in equilibrium will be obtained by the common tangent, Figure 6.18.

As shown in Figure 6.19, again at this temperature (say 800 °C) we are in a two phase region (S+L). Compositions of two phases in equilibrium will be obtained by the common tangent.

When we reach the freezing point of pure A (say 700 °C), Figure 6.20, the free energy of pure A solid is equal to free energy of pure A liquid.

Below this temperature, Figure 6.21, only solid is stable for all the compositions.

Remember each diagram is at a FIXED temperature.

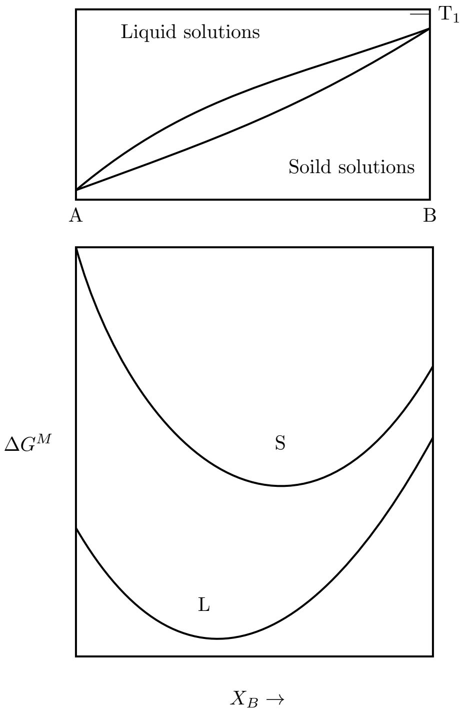


Figure 6.16: Free energy of mixing curves at T$_1$ (say 1000 °C)

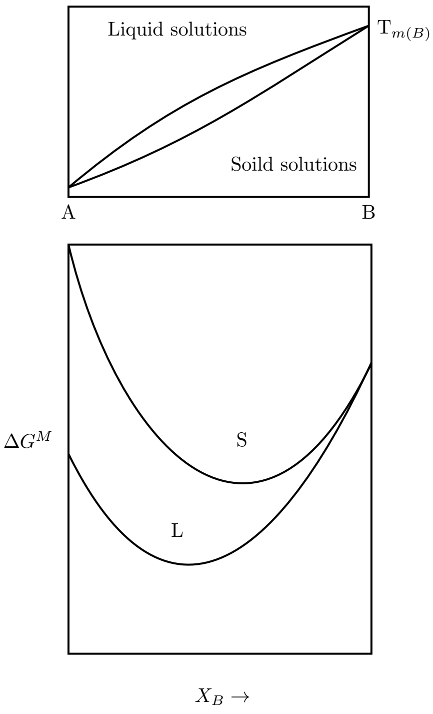


Figure 6.17: Free energy of mixing curves at 900 °C, the freezing point of pure B

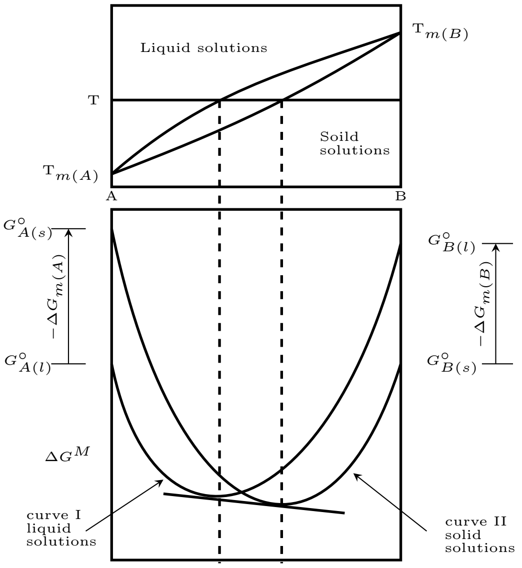


Figure 6.18: Free energy of mixing curves at 850 °C, showing the composition of solid and liquid phase in equilibrium

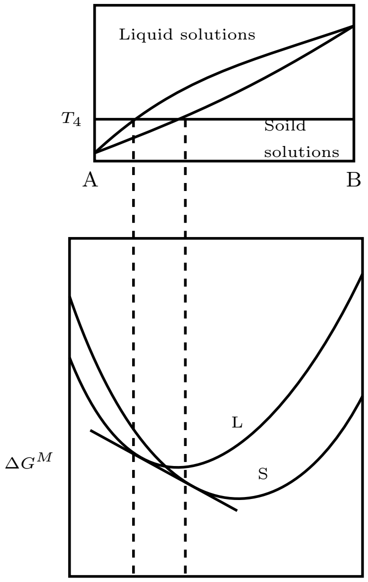


Figure 6.19: Free energy of mixing curves at 800 °C, showing the composition of solid and liquid phase in equilibrium

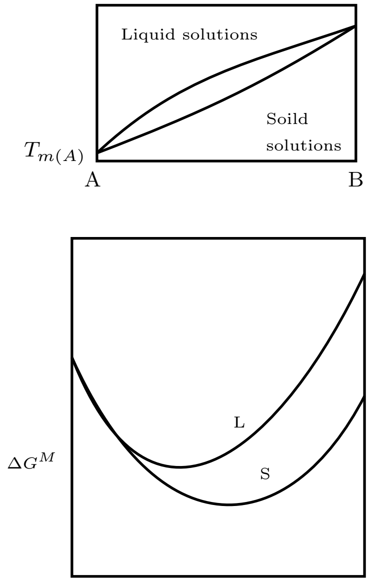


Figure 6.20: Free energy of mixing curves at 700 °C, the freezing point of pure B.

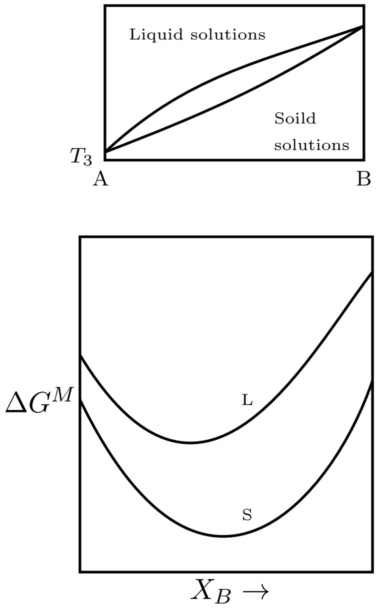


Figure 6.21: Free energy of mixing curves at 600 °C, only solid phase is stable now at any composition.

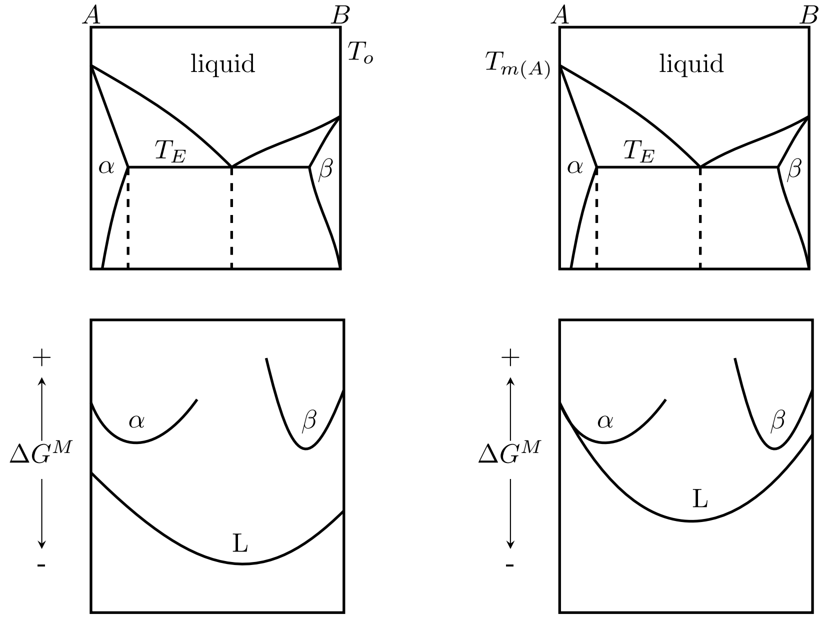


Figure 6.22: Free energy of mixing curves in a eutectic system at temperatures T_o and T_{mA}

Binary eutectic phase diagram

Eutectic reaction is the one in which one liquid transforms isothermally into two solids

$$L \leftrightarrow \alpha + \beta$$

Horizontal line in a binary phase diagram, known as an isotherm, represents a three phase equilibrium. The word 'Eutectic' means low melting, hence these alloys are easy to melt and cast. Eutectic alloys generally have lamellar microstructure.

Proeutectic α is the solid which forms when the content of alloying element is less than the eutectic composition. These alloys are also known as hypo-eutectic alloys. Proeutectic β is the solid which forms when the content of alloying element is more than the eutectic composition. These alloys are also known as hyper-eutectic alloys.

Free Energy curves at various temperatures for eutectic binary system are now presented. Since three phases (α, β and L) are involved, we start with three free energy curves.

As shown in Figure 6.22, at T_o only liquid is stable as it has the lowest free energy among all the three phases. Free energy of mixing curve for liquid is lower than that of α and β. When temperature is lowered to the freezing point of pure A, T_{mA}, pure solid A and pure liquid A will have the same free energy. For any other composition, only liquid is stable (having free energy lower than the solid phases).

Free energy of mixing curves at T_1 (Figure 6.23) show that there is one 2-phase region, (α + L) and then L region. We get equilibrium compositions of α and L using the common tangent.

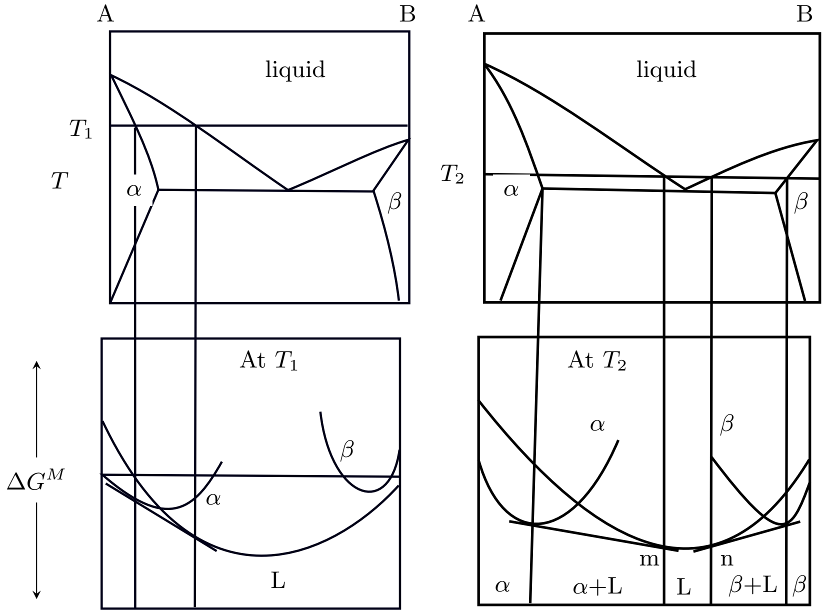


Figure 6.23: Free energy of mixing curves in a eutectic system at temperatures T_1 and T_2

Free energy of mixing curves at T_2 show that there are two 2-phase regions, (α + L) and (L + β). We have two common tangents which provide composition of α and equilibrium L and composition of β and equilibrium L.

Free energy of mixing curves at the eutectic temperature T_E, Figure 6.24, show that we have 3-phase equilibrium. So, we have a tangent common to all three curves (α, β, L) which provides equilibrium compositions of all 3 phases at the eutectic temperature.

At any temperature below the eutectic temperature, such as T_3, the liquid is not stable. α , β are the stable phases and their equilibrium compositions are obtained using the common tangent.

Here we have given two examples where free energy of mixing curves have been drawn at various temperatures when binary phase diagrams are given. It will be more useful if phase diagrams are developed when free energy of mixing curves are available at various temperature. Computational Materials Science attempts to generate free energy of mixing curves at various temperatures from interatomic interactions by computing the electron density of the material. This would require use of interatomic pseudo-potentials with strong database. From a series of such curves, a computed binary phase diagram can be generated.

6.3 Gibbs Phase Rule

So far we have discussed three types of potentials, T (thermal potential), P (mechanical potential) and the chemical potential μ of each component. Therefore, in a

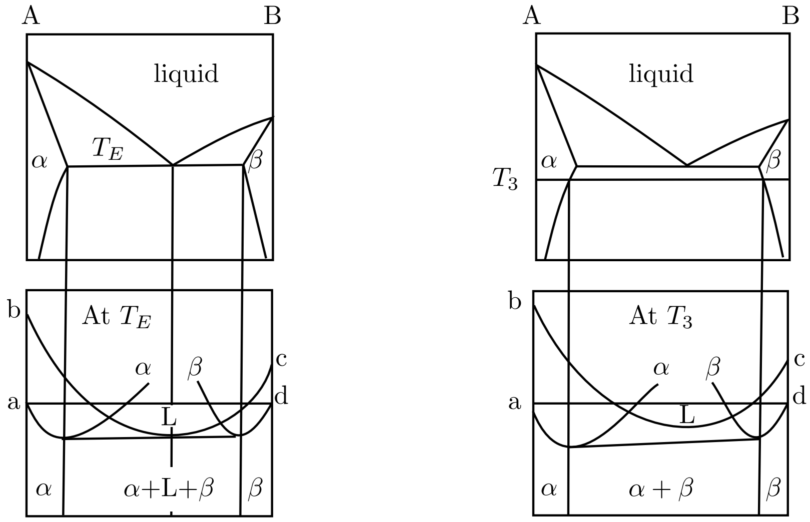


Figure 6.24: Free energy of mixing curves in a eutectic system at temperatures T_E and T_3

system containing C components, we need to know (C + 2) potentials. In a system, the potentials are related through two equations, the Gibbs–Duhem equation and the Gibbs phase rule:

$$-SdT + VdP + \sum n_i d\mu_i = 0$$

$$F + \mathcal{P} = C + 2 \tag{6.8}$$

The phase rule determines the number of degrees of freedom, F, i.e., the number of potentials that can be varied independently without changing the number of phases in equilibrium. In other words, this rule lets us know the degrees of freedom 'F' when the system contains 'C' components and '$\mathcal{P}$' phases. In the following, we develop the expression for phase rule. Here,

C = Number of chemically distinct species (components) present such as C_i, C_{ii}, C_{iii}, etc.

$\mathcal{P}$ = Number of phases present such as L, S, α, β, γ, etc.

Each phase has associated potentials, pressure, temperature and composition. When number of components is 'C', we require (C − 1) compositions. The total number of variables for each phase would be [(C -1) + 2] or (C + 1). When there are '$\mathcal{P}$' phases, number of variables would be $\mathcal{P}$×(C + 1).

The principle of equilibrium requires that each phase should have same values of all potentials, i.e., T, P and activity of each component (Recall $\mu_i = RTlna_i$).

$$T_1 = T_2 = T_3 = \dots \qquad (\mathcal{P}-1) \text{ equations}$$
$$P_1 = P_2 = P_3 = \dots \qquad (\mathcal{P}-1) \text{ equations}$$

$$a_i(1) = a_i(2) = a_i(3) = \dots \qquad (\mathcal{P}-1) \text{ equations}$$
$$a_{ii}(1) = a_{ii}(2) = a_{ii}(3) = \dots \qquad (\mathcal{P}-1) \text{ equations}$$
$$a_{iii}(1) = a_{iii}(2) = a_{iii}(3) = \dots \qquad (\mathcal{P}-1) \text{ equations}$$

Here $a_i(1)$ means activity of component 'i' in phase '1' and $a_{iii}(2)$ means activity of component 'iii' in phase '2'.

Regarding activity, we will have $C \times (\mathcal{P}-1)$ equations as there are 'C' components

Total number of equations will be

$$(\mathcal{P}-1) + (\mathcal{P}-1) + C \times (\mathcal{P}-1) = (C+2) \times (\mathcal{P}-1)$$

Total number of variables will be

$$\mathcal{P} \times (C+1)$$

Therefore, the number of degrees of freedom is

$$F = (C+2) \times (\mathcal{P}-1) - \mathcal{P} \times (C+1) = C + 2 – \mathcal{P}$$

Or

$$F + \mathcal{P} = C + 2$$

For a one-component system, the Gibbs phase rule says

$$F + \mathcal{P} = C + 2 = 3$$

and we can easily construct a P-T phase diagram in two dimensions, as shown in Figure 6.2.

It can be easily seen that the single phase regions have two degrees of freedom, F = 2, The lines representing 2-phase equilibrium have one degree of freedom and the points representing 3-phase equilibrium have zero degree of freedom.

For a binary system (C = 2), the Gibbs phase rule gives

$$F + \mathcal{P} = C + 2 = 4$$

It is usually convenient to fix the pressure as atmospheric pressure and decrease the degrees of freedom. Gibbs phase rule then becomes

$$F = C – \mathcal{P} + 1$$

At constant pressure the phase rule gives

$$F = 3 – \mathcal{P}$$

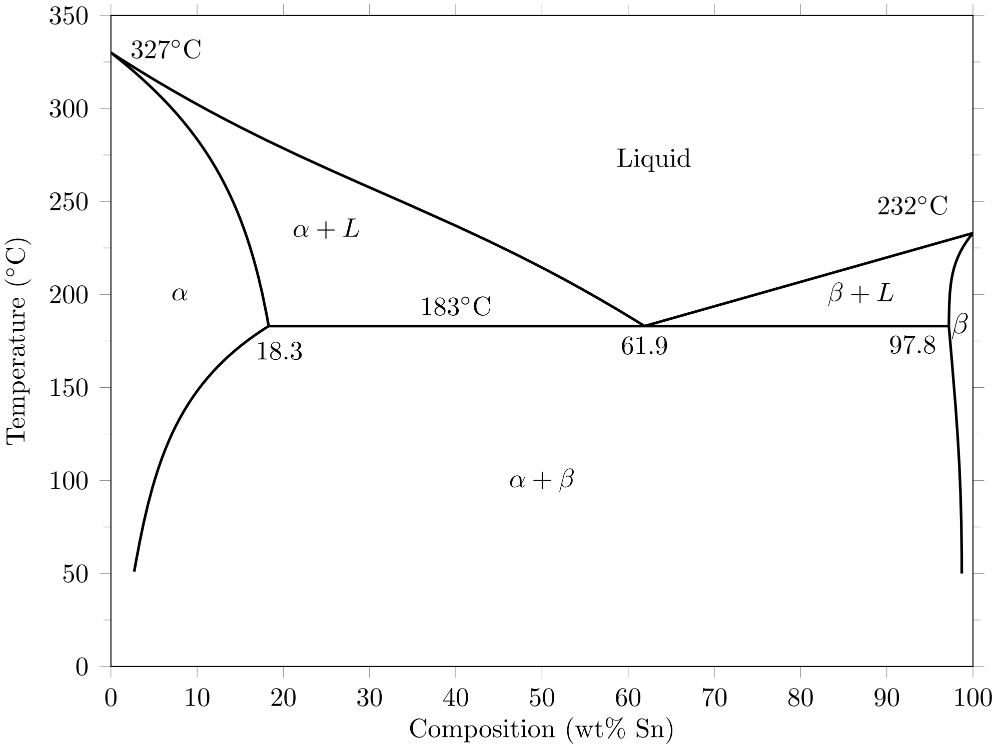


Figure 6.25: Pb-Sn phase diagram

for a binary system and we require only two independent variables to express the phase equilibria. We generally select temperature and composition as these variables. Let us look at Pb-Sn phase diagram, Figure 6.25.

There are only three phases in the system: the solid solutions α and β and the liquid solution containing Pb and Sn. α and β denote solid solutions with Pb and Sn as solvents and Sn and Pb as solutes, respectively. In a single phase region, for example liquid, F = 2. Both composition and temperature may be varied independently. The stability fields for the liquid and the two solid solutions α and β are therefore two-dimensional regions. When two phases are in equilibrium, the temperature and composition are not independent of each other. The compositions of two phases in equilibrium at a given temperature are fixed by thermodynamics. The compositions of the coexisting phases are defined by the bounding lines. In the case of a solid–liquid equilibrium, solidus and liquidus lines define the equilibrium compositions. This is called a univariant equilibrium since F = 1.

When three phases are present at equilibrium, F = 0 and the temperature and compositions of all three phases are fixed. Thus the isothermal phase reactions in a binary system are called invariant equilibrium. The temperature of the phase reaction is shown as a horizontal line, called the isotherm. Here, we have considered the system at constant pressure. If isobaric conditions are not considered, the invariant equilibrium becomes univariant, and a univariant equilibrium becomes divariant, etc. This means that the eutectic temperature in a binary system will vary with pressure. However, as noted earlier, small variations in pressure result in minor variations in the Gibbs energy of condensed phases. Thus minor variations in pressure do not have any significant effect on the phase reaction temperatures.

Summary

1. Phase changes occur to lower the free energy of the system.
2. One component phase diagram is drawn as P-T diagram and provides regions of stability of various phases, lines representing 2-phase equilibrium and points (triple points) representing 3-phase equilibrium. 2-phase equilibrium lines determine the effect of pressure on transformation temperature. Differential forms of these lines are obtained by equating free energies of the two phases involved and can be easily integrated using some assumptions.
3. Vapor pressures of solid and liquid phases are tabulated showing lnP as a function of temperature. Such data can be used to calculate various properties of solid and liquid phases.
4. Water shows anomalous behavior on freezing as its volume increases on solidification.
5. Chemical potential (activity) of each component in a binary solution can be obtained by intercepts of the tangent line on the free energy of mixing curves.
6. Principle of equilibrium of phases states that the chemical potential (activity) of a component is same in all the phases in equilibrium.
7. Free energy of mixing curves along with the principle of equilibrium can be used to generate binary phase diagrams.
8. Phase rule is a logical expression describing the number of degrees of freedom 'F' in a system of 'C' components when the number of phases present is '$\mathcal{P}$'.

Practice Problems

1. Evaluate the following statements:
    i. Slope of S/L equilibrium line is much higher than slope of L/V line.
    ii. Slope of S/V equilibrium line is higher than slope of L/V line.
    iii. The line separating liquid and vapor in a unary phase diagram cannot have negative slope.
    iv. We do not find a 3-phase region in a binary phase diagram.
    v. The lines separating two allotropes in a unary phase diagram is almost vertical.

vi. Phase diagrams are based on the concept of Chemical potential.

vii. We can pass a thin wire through a slab of ice without cutting it into two pieces.

viii. Ice skating is made possible due to the anomalous behavior of water.

ix. In some binary phase diagrams, we can clearly see that two liquid phases may coexist.

x. A component may sublime at STP.

xi. The line separating two allotropes in a unary phase diagram may have positive or negative slope.

xii. Iodine sublimes under normal conditions.

xiii. Information about vapor pressure of a component can give us an estimated value of the enthalpy of melting.

xiv. If composition of a binary alloy (in an isomorphous system) is 45/55, further addition of solute will not significantly decrease free energy of mixing.

xv. Phase rule can explain why, at atmospheric pressure, eutectic reaction in a binary system occurs at fixed temperature.

2. i. Draw a hypothetical binary phase diagram showing a eutectic isothermal phase reaction.

   ii. Label the diagram completely.

   iii. Now draw free energy of mixing curves at 4 different temperatures, one in completely liquid region, second through two phase regions, third at eutectic temperature and fourth below eutectic temperature.

3. Discuss the differential and integral forms of $P = f(T)$ lines in a one component phase diagram.

4. A pure element undergoes 3 allotropic transformations on heating. Draw a representative Pressure-Temperature diagram exhibiting regions of various phases. What do lines and points represent in this diagram?

5. i. Use free energy of mixing curves to explain that, at fixed pressure, if 3 phases are in equilibrium, the temperature and compositions of 3 phases are fixed by thermodynamics.

   ii. Use free energy of mixing curves to explain that, at fixed pressure and fixed temperature, if 2 phases are in equilibrium, the compositions of these 2 phases are fixed by thermodynamics.

6. Draw a set of free energy of mixing curves at various temperatures for a simple binary eutectic system.
   Use these curves to obtain the phase diagram.

7. Compare a typical standard unary and a binary (simple eutectic) phase diagram in terms of the following:
    i. Axes used
    ii. What do regions indicate? Discuss degrees of freedom.
    iii. What do lines indicate? Discuss degrees of freedom.
    iv. What do points/horizontal lines indicate? Discuss degrees of freedom.
8. Following information about pure Ti is available.
   Low temperature phase α (hcp) transforms to β(bcc) at 882°C. Normal melting point is 1668°C and normal boiling point is 3287°C.
    i. Write an expression for enthalpy and entropy of Ti vapors at T.
    ii. Estimate the enthalpy of melting of pure Ti.
    iii. Give an estimate for entropy change when α (hcp) transforms to β(bcc).
    iv. Draw the phase diagram of pure Ti.
    v. Briefly describe the extraction of Ti from its ore.
9. Draw hypothetical phase diagram of a component which shows an allotropic transformation and undergoes expansion on freezing. Properly label the diagram. Identify various regions w.r.t. degrees of freedom.
10. Use some hypothetical values to write vapor pressure equations for solid and liquid phase of a component. Use these equations to find
    i. Normal boiling point
    ii. ΔH (boiling)
    iii. ΔH (sublimation)
    iv. Triple point
    v. Estimate the ΔH (melting)
11. The vapor pressures of two states of a material are given below:

$$\begin{aligned} lnP &= (-32000/T) - 1.5lnT + 35 \quad (liquid) \\ lnP &= (-36000/T) - 2.9lnT + 34 \quad (solid) \end{aligned}$$

   Find
    i. ΔH (boiling)
    ii. Δ H (sublimation)

12. Carefully examine the phase diagrams of Iodine and CO_2. Comment on the behavior of vapors in these two unary phase diagrams.

13. The solid Pb and liquid Pb, at the normal MP, have molar volumes of 18.92 and 19.47 cm^3, respectively. Find the pressure required to increase the MP by 15 °C.

14. Two elements C and D have limited solubility and have the following properties:

    i. MP of C = 1200 °C, MP of B = 1300 °C
    ii. An isothermal phase reaction at 900 °C $L(45\%D) \leftrightarrow \alpha + \beta$
    iii. Max solubility α (15%D) β (20%C)
    iv. Negligible solubility at room temperature

    Draw a binary phase diagram.

    Then draw the free energy of mixing curves at 1250 °C, 1000°C, 900°C and Room temperature.

15. Data for a one-component system is given below:

    i. Normal Melting Point 100 °C, Normal Boiling Point 300 °C
    ii. ΔH (Boiling) = 16,628 J/mol
    iii. T(tr) = 120 °C, P(tr) = 0.7 atm
    iv. Vapor Pressure of solid at room temperature = 0.1 atm
        a. Draw phase diagram.
        b. Write down equation for vapor pressure of liquid as a function of temperature assuming ΔH to be independent of temperature.
        c. Comment on the density of solid and liquid.
        d. Do you observe sublimation of solid under normal conditions?

16. Find out normal boiling point, ΔH_b, ΔH_s and triple point from the given data. Give an estimate for the enthalpy change on freezing of the liquid.

    Given data:

$$
\begin{aligned}
lnP &= -\frac{14000}{T} + 14 \quad \text{for liquid state} \\
lnP &= -\frac{21000}{T} + 28 \quad \text{for solid state}
\end{aligned}
$$

17. Use various rules you have studied in thermodynamics and basics from physical chemistry to answer the following questions:

    i. A metal 'X' has normal MP 500 °C, normal BP 1000 °C, Triple point at 400 °C and 0.1 atm.
    Draw the phase diagram

ii. For this metal, give an estimate for ΔH_m , ΔH_b and ΔH_{sub}.

iii. Estimate the value of dP/dT for L/V and S/V equilibrium.

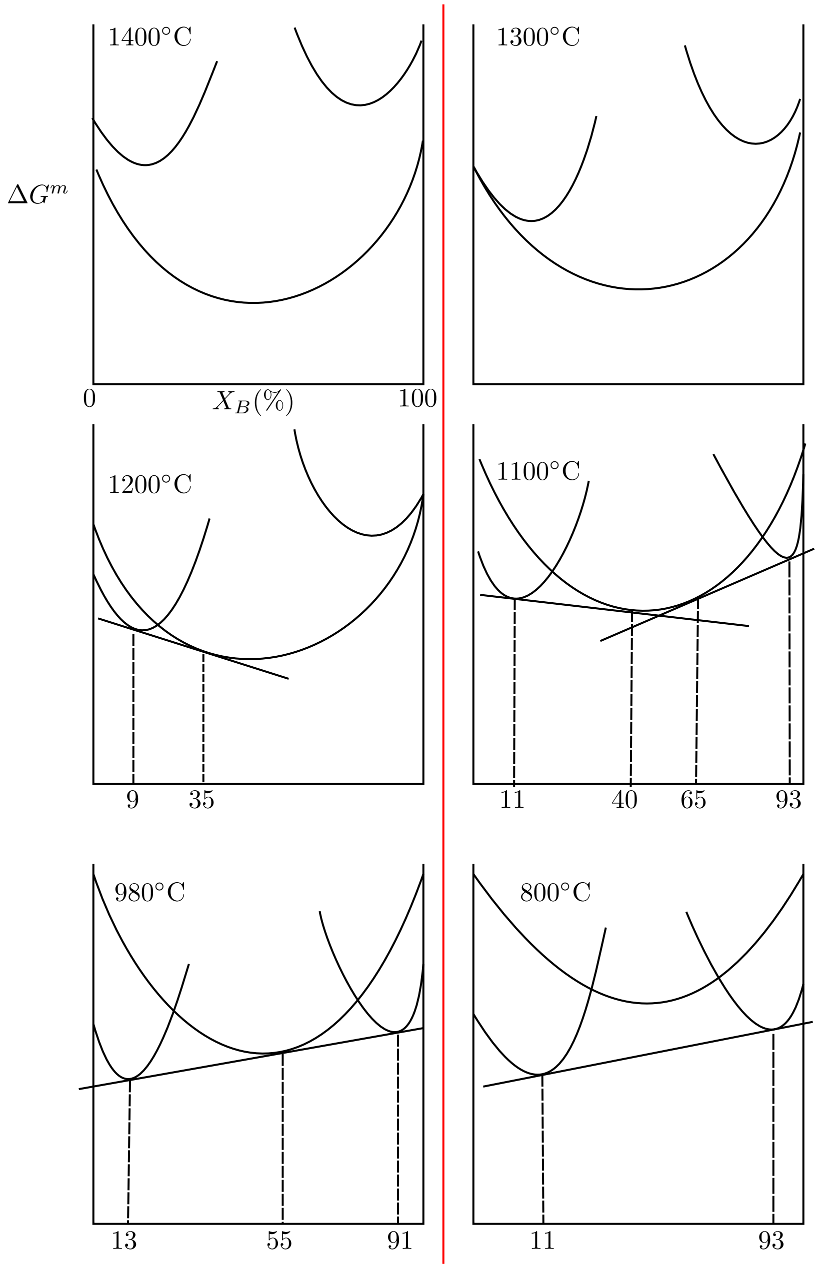
18. A set of free energy of mixing curves at various temperatures is provided.

    i. Draw the phase diagram

    ii. Identify any isothermal phase reaction and describe it completely.

    iii. Identify solubility limits for α and β.

    iv. Differentiate a triple point and a 3-phase isotherm.



Chapter 7

Thermodynamics Applied to Reaction Equilibria

Learning Outcomes:

Student should be able to explain

- How thermodynamic data can be used to get knowledge about equilibrium state in any reactive system.
- How can we express activity of a gas, activity of a pure condensed phase and activities of components in solutions
- How equilibrium constant 'K' is affected by change in temperature
- Equilibrium in a system involving gas only
- Cheap method to avoid oxidation in a furnace
- Application of thermodynamics to study equilibrium in system involving one gas phase
- Ellingham diagram and its uses
- Why carbon is regarded as a universal reducing agent
- Reaction equilibria involving condensed phases and the applications

While discussing the spontaneity criteria, we concluded that the most suitable criterion is the Gibbs free energy and we write,

$$\Delta G \leq 0$$

Here

$\Delta G < 0$ defines the condition for spontaneity while

$\Delta G = 0$ depicts that the system has no tendency to change, i.e., it is in the equilibrium state.

Now we use this conclusion to our benefit in order to analyze systems at equilibrium. Determining the composition of a system in equilibrium using free energy data is a success story of Materials Thermodynamics from applications point of view.

7.1 Free Energy and Equilibrium

Recall that in a given system, the free energies of individual components are given by

$$G_i = G_i^o + RTlna_i$$

The values of activities depend on the state of the component in the system.

For ideal gases	$a_i = p_i$	
For ideal solution	$a_i = X_i$	
For non-ideal solution	$a_i = \gamma_i X_i$	
For pure condensed phase	$a_i = 1$	(pure solid or pure liquid)

Now we look at the situation when a reaction system attains equilibrium.
For any reversible reaction

$$A + B \leftrightarrow C + D$$

The forward reaction is

$$A + B \rightarrow C + D$$

While the backward reaction is

$$C + D \rightarrow A + B$$

The equilibrium is attained when

Rate of forward reaction = Rate of backward reaction

At this stage, there is no net change in the composition. At equilibrium, the mixture has no tendency to change. The total free energy of the reactants is equal to the total free energy of the products.

$$\overline{G_A} + \overline{G_B} = \overline{G_C} + \overline{G_D}$$

So at equilibrium,

$$(G_A^\circ + RTlna_A) + (G_B^\circ + RTlna_B) = (G_C^\circ + RTlna_C) + (G_D^\circ + RTlna_D)$$

Simplifying the equation, we get

$$(G_C^\circ + G_D^\circ) - (G_A^\circ + G_B^\circ) = -RT\ ln\left[\frac{a_C.a_D}{a_A.a_B}\right]$$

The left side of the above equation is the difference between the standard free energies of products and the standard free energies of reactants.

$$\Delta G^{\circ} = -RT\ ln \left[\frac{a_C.a_D}{a_A.a_B} \right]$$

The expression in bracket is termed as the equilibrium constant 'K'.

$$\Delta G^{\circ} = -RTlnK \tag{7.1}$$

Equilibrium constant 'K' is the ratio of the activities of products over the activities of reactants.

This is a very powerful relation where standard free energy data can be used to give equilibrium composition in any reactive system. Also remember,

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

These two relations are among those thermodynamic relations which have very wide applications.

To reiterate, ΔG° is the standard Gibbs free energy change.

$$\Delta G^{\circ} = G^{\circ}(\text{products}) - G^{\circ}(\text{reactants})$$

which can now be related to the equilibrium constant 'K' which is the ratio of the activities of products over the activities of reactants.

7.1.1 Variation of Equilibrium Constant with Temperature

We use the following two equations to drive relation between 'K' and 'T'

$$G = H - TS$$

$$dG = VdP\text{–}SdT$$

From second relation, we get, at constant P	$(\partial G/\partial T)_P = -S$
Putting this in the first relation, we get	$G = H + T\,(\partial G/\partial T)_P$
At constant P, we may write	$GdT = HdT + TdG$
On rearrangement	$TdG - GdT = -HdT$
Dividing byT^2, we get	$(TdG - GdT)/T^2 = -(H/T^2)dT$
Or	$d(G/T) = -(H/T^2)dT$
Or	$d(G/T)/dT = -(H/T^2)$

For a process (change occurring in the system), we can write

$$d(\Delta G/T)/dT = -(\Delta H/T^2)$$

Using the relation

$$\Delta G^\circ = -RTlnK$$

or

$$\frac{\Delta G^\circ}{T} = -RlnK$$

We write

$$d(RlnK)/dT = (\Delta H^\circ/T^2)$$

Or

$$d(lnK)/dT = (\Delta H^\circ/RT^2) \tag{7.2}$$

Another way to look at it is as follows:

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ \frac{\Delta G^\circ}{T} &= \frac{\Delta H^\circ}{T} - \Delta S^\circ \\ \frac{-RTlnK}{T} &= \frac{\Delta H^\circ}{T} - \Delta S^\circ \\ lnK &= -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \end{aligned}$$

Now differentiating with respect to T

$$\frac{dlnK}{dT} = \frac{\Delta H^\circ}{RT^2}$$

In this procedure, we have to assume that ΔS° is independent of temperature which is not a very bad assumption. The above equation is known as Van't Hoff Equation. We may term it as a mathematical expressions for Le Chatelier's principle that relates the rate of change of 'K' with temperature.

Le-Chatelier's principle states that, "A system in equilibrium will respond to a change by moving in the direction that reduces the change as it returns to equilibrium." In other words, 'When a settled system is disturbed, it will adjust to diminish the change that has been made to it.' The changes that may be applied are varying the processing parameters such as changing the pressure, volume, concentration or temperature.

Temperature is an important parameter while dealing with reactions and shifts the chemical equilibrium in accordance with Le-Chatelier's principle.

If $\Delta H^\circ < 0$, the reaction is exothermic meaning that

$$\frac{dlnK}{dT} = \frac{\Delta H^\circ}{RT^2} < 0$$

The equation indicates that equilibrium constant expression would become negative. Therefore, on increasing the temperature, 'K' decreases and vice versa.

If $\Delta H^\circ > 0$, the reaction would be endothermic and the expression would be

$$\frac{dlnK}{dT} = \frac{\Delta H^\circ}{RT^2} > 0$$

Now the variation of equilibrium constant with temperature is positive indicating the direct influence of temperature on ‘K’ i.e., on increasing the temperature, ‘K’ increases.

In other words, ‘K’ increases as temperature increases if ΔH° is positive (endothermic forward reaction) and reaction proceeds in the forward direction. ‘K’ decreases as temperature increases if ΔH° is negative (exothermic forward reaction) and the reaction proceeds in the backward direction.

Let’s consider a reaction in which the reactants A & B react to form 2 moles of product C. This is a reversible reaction.

$$A + B \leftrightarrow 2C$$

When

$$A + B \rightarrow 2C \qquad \Delta H > 0 \ (Positive)$$

The enthalpy change in the forward reaction is positive which suggests that if we increase the temperature the reaction will move in the direction of absorbing heat, i.e., forward direction in order to resist the changes caused in system by increase in temperature. Hence, A and B will react to form more C if we increase the temperature.

While in the backward reaction

$$2C \rightarrow A + B \qquad \Delta H < 0 \ (Negative)$$

the product would decompose into the reactants. The enthalpy change in this reaction is negative which means exothermic reaction. So, on increasing the temperature, the system will move in a direction in which heat could be absorbed so that it can nullify the changes produced in the system.

On increasing the temperature, the system will shift in a direction to counteract the change. Therefore, to absorb heat, the reaction will move forward producing more of C.

Example. . Let us consider the reaction

$$N_{2(g)} + 3H_{2(g)} \leftrightarrow 2NH_3 \qquad \Delta H = -92\ kJ/mol$$

This reaction is an industrial process for the production of ammonia. Now if we increase the temperature, the equilibrium will be shifted towards the left side meaning the production of ammonia will decrease. In order to make the yield maximum within economical range, the temperature is maintained on lower side. However, we need to have sufficient temperature to maintain a reasonable rate of reaction. ☐

If $\Delta H > 0$ (Positive), we would prefer higher temperatures to increase the yield. Examples include decomposition of various compounds and thermal cracking.

7.2 Reactions Involving Gases

If all the components in a reacting system are gases,

$$A(g) + B(g) \leftrightarrow C(g) + D(g)$$

we can write

$$\Delta G^\circ = -RTln\frac{p_C{\cdot}p_D}{p_A{\cdot}p_B}$$

ΔG° is the standard free energy difference between products and reactants and p_i is the partial pressure of component i. In such a case, the equilibrium constant is generally written as K_p

$$\frac{p_C{\cdot}p_D}{p_A{\cdot}p_B} = K_p$$

$$\Delta G^\circ = -RTlnK_p \tag{7.3}$$

The subscript p is used for gases. Let us see how thermodynamic data can be used to get an idea about equilibrium composition in a system.

Example. . For the reaction

$$A(g) + B(g) = 2C(g)$$

The value of ΔG° at 700 K is found from the data book to be -4900 J per mole (per mole of A or per mole of B).

Using the relation

$$\Delta G^\circ = -RTlnK_p$$

We get

$$lnK_p = -\frac{\Delta G^\circ}{RT}$$

Putting values and solving for K_p at 700 K, we get

$$K_p = 2.321$$

For this reaction

$$K_p = \frac{p_C^2}{p_A{\cdot}p_B}$$

Therefore, at equilibrium, we have

$$\frac{p_C^2}{p_A{\cdot}p_B} = 2.321$$

If initial conditions are given, we can find the individual values of respective partial pressures at equilibrium. □

Example. . In order to avoid oxidation of a metal during heating at high temperature, we need to have very low oxygen pressure. One way is to use vacuum pumps but we will require expensive set of vacuum pumps for low oxygen. For extremely low oxygen, say $p_{O_2} < 10^{-14}$, vacuum pumps are not available. Another possibility is to create an atmosphere which maintains very low p_{O_2}.

Let's consider the following reaction:

$$H_{2_{(g)}} + \frac{1}{2}O_{2_{(g)}} = H_2O_{(g)}$$

For this reaction

$$\Delta G^\circ = -247500 + 55.85T$$

Here

$$K_p = \frac{p_{H_2O}}{p_{H_2}.p_{O_2}^{1/2}}$$

Suppose we want to heat a metal at 1250 °C.

At T=1250 °C (1523 K)

$$-RTlnK_p = -247500 + 55.85T$$

$$lnK_p = 12.83$$

$$K_p = 3.7325 \times 10^5$$

$$\frac{p_{H_2O}}{p_{H_2}.p_{O_2}^{1/2}} = 3.7325 \times 10^5$$

Suppose we want to have an atmosphere with low oxygen, say $p_{O_2} = 10^{-14}$

$$p_{O_2}^{1/2} = 10^{-7}$$

Putting this value, we get

$$\frac{p_{H_2O}}{p_{H_2}} = 0.037325$$

So we should introduce a mixture in the chamber (furnace) having $p_{H_2O}/p_{H_2} = 0.037325$

If we take

$$p_{H_2} = 1\ atm$$

Then

$$p_{H_2O} = 0.037325\ atm$$

This is the vapor pressure of water at 28 °C. So, if we pass hydrogen gas at one atmospheric pressure through water at 28 °C, this gas will get water vapors with

$$p_{H_2O} = 0.037325$$

Introduce this mixture of water vapors and hydrogen gas into the furnace. This mixture will give p_{H_2O}/p_{H_2} required to maintain the desired p_{O_2}. This method is an inexpensive way to avoid oxidation of metals during heating in a furnace.

If we want to have much lower oxygen pressure, say $p_{O_2} = 10^{-20}$, some other equilibrium such as

$$CO + \frac{1}{2}O_2 = CO_2$$

may be used whereby we will maintain a certain $\frac{p_{CO_2}}{p_{CO}}$ in order to get the required low value of p_{O_2}. ☐

7.3 Reactions Involving Only One Gaseous Phase

We get simplified and interesting results when all the components involved in a reaction are pure condensed phases except one component which is in gaseous state. Condensed phase means either liquid or solid phase.

The equilibrium constant is related to the standard free energy change as

$$\Delta G^\circ = -RTlnK$$

where equilibrium constant 'K' is the ratio of activities of products and activities of reactants.

$$K = \frac{\prod a_{products}}{\prod a_{reactants}}$$

Remember $\sum$ represents summation, $\prod$ represents product.

For gases, activities can be replaced with partial pressures assuming the ideal behavior.

Let us consider the oxidation of a pure metal:

$$M_{(s)} + O_{2_{(g)}} \leftrightarrow MO_{2_{(s)}}$$

For this reaction,

$$K = \frac{a_{MO_2}}{a_M . a_{O_2}}$$

Since the reaction involves pure solid metal and pure solid oxide, for both of which activities can be taken as unity,

$$K = \frac{a_{MO_2}}{a_M . a_{O_2}} = \frac{1}{1.p_{O_2}}$$

$$\Delta G^\circ = -RTlnK = -RTln\,(1/p_{O_2})$$

$$\Delta G^\circ = RTln\,(p_{O_2}) \tag{7.4}$$

Now suppose the metal M is in equilibrium with its oxide at $p_{O_2} = 10^{-11}$, then we say that:

- If $p_{O_2} = 10^{-11}$, the oxidation reaction is at equilibrium.
- If $p_{O_2} > 10^{-11}$, the reaction proceeds forward, i.e., oxidation of 'M' will be spontaneous.
- If $p_{O_2} < 10^{-11}$, the reaction proceeds backwards, i.e., decomposition of metal oxide will be spontaneous.

Let's consider another example involving metal carbonates,

$$MO_{(s)} + CO_{2_{(g)}} \leftrightarrow MCO_{3_{(s)}}$$

Here,

$$\Delta G^\circ = G^\circ_{MCO_3} - \left(G^\circ_{MO} + G^\circ_{CO_2}\right)$$

And similar considerations lead to

$$\Delta G^\circ = -RTln\left(a_{MCO_3}/a_{MO}.p_{CO_2}\right)$$

Since we have carbonate and oxide as pure solids,

$$\Delta G^\circ = RTlnp_{CO_2}$$

This p_{CO_2} is the pressure of CO_2 in equilibrium with pure MO and pure MCO_3

So, in case of calcination of $CaCO_3$ in an enclosed container at a given temperature T',

$$CaCO_{3_{(s)}} \leftrightarrow CaO_{(s)} + CO_{2_{(g)}}$$

the decomposition will continue until a pressure p_{CO_2} is reached as given by

$$\Delta G^\circ = RT'lnp_{CO_2}$$

Where

$$\Delta G^\circ(T') = G^\circ_{CaCO_3} - \left(G^\circ_{CaO} + G^\circ_{CO_2}\right)$$

In another example, where hydration of a metal oxide occurs to give hydroxide of the metal,

$$H_2O_{(g)} + MO_{(s)} \leftrightarrow M(OH)_{2_{(s)}}$$
$$\Delta G^\circ = RTlnp_{H_2O}$$

Now let us concentrate on oxidation of metals. First we consider oxidation of pure copper.

$$4Cu_{(s)} + O_{2_{(g)}} \leftrightarrow 2Cu_2O_{(s)}, \qquad \Delta G^\circ = -324,400 + 138.5T$$

In this case,

$$\Delta S^\circ = -138.5\ J/K.mol$$
$$\Delta H^\circ = -324,400 J/mol$$
$$\Delta G^\circ = RTlnp_{O_2}$$

Now consider oxidation of Ni

$$2Ni_{(s)} + O_{2_{(g)}} \leftrightarrow 2NiO_{(s)}, \qquad \Delta G^\circ = -471,200 + 172T$$

$$K = \frac{a_{NiO}}{a_{Ni}.a_{O_2}} = \frac{1}{1.p_{O_2}}$$

$$\Delta G^\circ = -RTlnK = RTlnp_{O_2}$$

At 1500 K

$$\begin{aligned}\Delta G^\circ &= -213200\ J\ per\ mole\\ \Delta G^\circ &= RTlnp_{O_2}\\ -213200 &= (8.314)(1500)lnp_{O_2}\\ p_{O_2} &= 4.09 \times 10^{-8}\ atm\end{aligned}$$

- If $p_{O_2} = 4.09 \times 10^{-8}$, the reaction is at equilibrium.
- If $p_{O_2} > 4.09 \times 10^{-8}$, the reaction proceeds forward i.e., oxidation of Ni starts.
- If $p_{O_2} < 4.09 \times 10^{-8}$, the reaction proceeds backwards i.e., metal oxide NiO reduces or starts to decompose.

Now consider example of Cr,

$$\frac{4}{3}Cr_{(s)} + O_{2(g)} \leftrightarrow \frac{3}{2}Cr_2O_{3(s)}, \qquad \Delta G^\circ = -740,067 + 165T$$

$$\begin{aligned}K &= \frac{a^{3/2}_{Cr_2O_3}}{a^{4/3}_{Cr}.a_{O_2}} = \frac{1}{1.p_{O_2}}\\ \Delta G^\circ &= -RTlnK = RTlnp_{O_2}\\ \Delta S^\circ &= -165\ J/mol.K\\ \Delta H^\circ &= -740,067\ J/mol\end{aligned}$$

In all these cases, reactions are written in such a way that one mole oxygen is utilized.

7.3.1 Ellingham Diagram

Ellingham Diagram is a graph between ΔG° and T, i.e., ΔG° as a function of T for the oxidation of various elements, mostly metals. ΔG° is the standard Gibbs free energy change on oxidation of various elements per mole of oxygen. It represents the standard free energy of formation of various oxides, using one mole of oxygen, as a function of temperature.

If we compare the equation for ΔG° ,

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

with the equation of straight line $y = c + mx$ and look at the variation of ΔG° with T, we see that

$$\begin{aligned}\Delta G^\circ &= y\\ T &= x\\ \Delta H^\circ &= c\\ -\Delta S^\circ &= m\end{aligned}$$

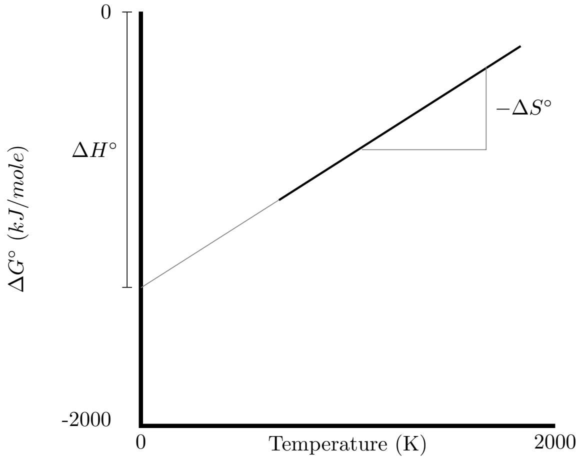


Figure 7.1: When the standard free energy of formation of various oxides, using one mole of oxygen, is plotted as a function of temperature, we get straight lines with enthalpy change as intercept and negative of entropy change as slope.

So, if we plot ΔG° as a function of T, Figure 7.1, we get a straight line having slope of $-\Delta S^\circ$ and intercept of ΔH°.

When ΔG° is plotted versus temperature, a series of straight lines will be obtained having $-\Delta S^\circ$ as slope and ΔH° as intercept. All the lines are almost parallel as entropy of 1 mole of $O_{2(g)}$ is under consideration. For example, in the case of copper oxide 1 mole of oxygen reacts with four mole of copper to form 2 moles of copper oxide. During this reaction one mole of gas will be disappearing. Entropy change will be negative as a gas reacts with a condensed phase and produces a condensed phase. So there is decrease in entropy and the line will be sloping upward.

$$4Cu_{(s)} + O_{2_{(g)}} \leftrightarrow 2Cu_2O_{(s)}$$

Now in case of Cr, we will write the equation such that one mole of oxygen is consumed.

$$\frac{4}{3}Cr_{(s)} + O_{2_{(g)}} \leftrightarrow \frac{3}{2}Cr_2O_{3(s)} \qquad \Delta G^\circ = -740,067 + 165T$$

Therefore, for the slopes in Ellingham Diagram, Figure 7.4 we note that

1. Most of the lines slope upwards since both the metal and the oxide are present as condensed phases (solid or liquid).

2. In all the cases, one mole O_2 is consumed, $\Delta S^\circ \approx -150J/K$. Hence, all the lines are almost parallel.

3. Slope changes when there is any phase change (melting, boiling or sublimation of element or oxide).

7.3.2 Uses of Ellingham Diagram

Ellingham diagram can be used to

1. Determine the relative ease of reducing a given oxide to metal.
2. Determine the partial pressure of oxygen that is in equilibrium with an element and its oxide at a given temperature.
3. This equilibrium partial pressure of oxygen, p_{O_2} (eq) is also given by (p_{CO}/p_{CO_2}) as well as (p_{H_2}/p_{H_2O}) as nomographic scales.

It should be noted that

- Oxidation tendency increases from top to bottom. Lower the oxides, more is its stability. Bottom part has more stable oxides, like CaO, MgO.
- Stability of oxide decreases as we move upwards. Compare CaO with CuO.
- Lower elements can reduce upper oxides by oxidizing themselves. For example, if we consider two elements calcium and silicon, calcium can reduce the silicon oxide as its line lies below the line of silicon.

$$2Ca_{(s)} + SiO_{2_{(s)}} \leftrightarrow Si_{(s)} + 2CaO_{(s)}$$

- With increase in temperature, reducing power of carbon increases.

Ellingham diagram provides information about the stability of oxide as a function of temperature. The lower metals can reduce the upper oxides. Metals present on the top are stable and their oxides are unstable, so the reduction of their oxides is easy. On the other hand, metals at the bottom are less stable and their oxides are more stable, so these metals get oxidized easily.

The stability of oxides depends upon the ΔG° values. The metals which are at bottom have more negative ΔG° value compared to oxides lying above so their oxides are more stable and such elements can reduce the oxides lying above.

Aluminum oxide is very stable so aluminum can reduce iron oxide (the so called Thermit welding process) and this reaction releases enough heat to melt the reduced iron.

$$2Al_{(s)} + Fe_2O_{3_{(s)}} \leftrightarrow Al_2O_{3_{(s)}} + 2Fe_{(l)}$$

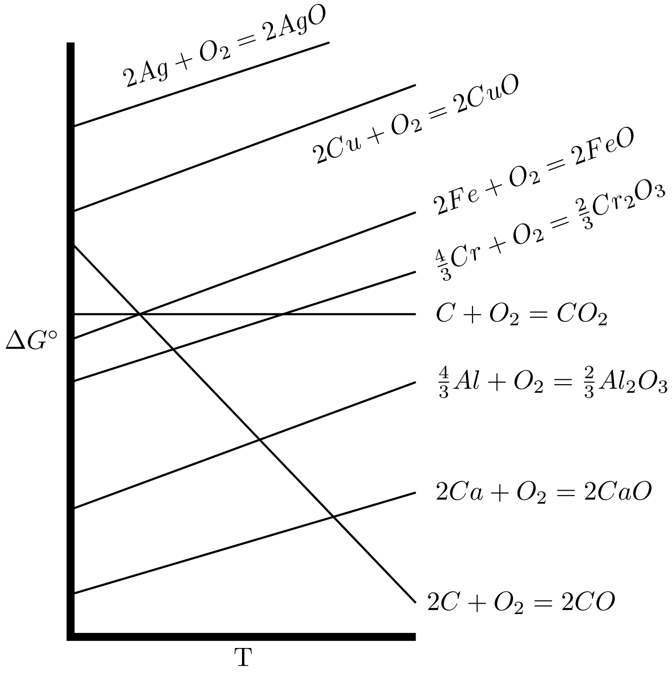


Figure 7.2: The lines representing oxidation of carbon in Ellingham diagram. Few other oxidation lines are shown for reference.

7.3.3 Carbon as a Reducing Agent

The oxidation of carbon can give two types of oxides

1. In the reaction
$$C_{(s)} + O_{2_{(g)}} \leftrightarrow CO_{2_{(g)}}$$
a solid (C) is reacting with a mole of gas (O_2) to produce a mole of gas (CO_2), and so there is little change in entropy and the line is almost horizontal having zero slope.

2. For the reaction
$$2C_{(s)} + O_{2_{(g)}} \leftrightarrow 2CO_{(g)}$$
we have a solid (C) reacting with a mole of gas (O_2) to produce two moles of gas (CO_2), so there is a substantial increase in entropy and the line slopes downward sharply.

As shown in Figure 7.2, this line crosses all the lines as temperature is increased. Therefore, carbon can reduce any oxide depending on the temperature. Due to this fact, carbon is regarded as a universal reducing agent. However, the temperature required to reduce stable oxides like CaO, MgO and Al_2O_3 would be very high making this process impractical.

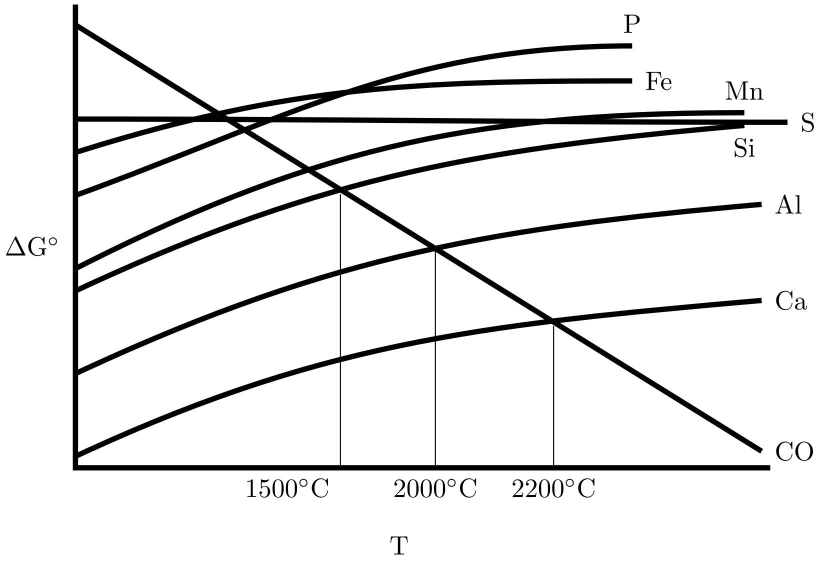


Figure 7.3: Position of oxidation lines for various elements relative to iron.

7.3.4 Composition of Pig Iron

In the blast furnace where iron is extracted from its oxide ore, the conditions are maintained so that iron oxide is reduced. The components which reduce iron oxide also reduce the oxides of phosphorous and sulphur as their lines are close to each other as shown in Figure 7.3. Therefore, phosphorous and sulphur also get incorporated in iron metal and removal of these elements becomes difficult. Remember, oxides go to slag and elements go into metal phase.

The composition of pig iron obtained from the blast furnace, Figure 7.4, can be explained as follows:

- Phosphorus line is very close to Iron. It is mostly reduced and goes to metal.
- Manganese line is close to iron. It is partly reduced, reduced form goes to metal, oxide goes to slag.
- Silicon line is relatively close to Iron. It is partly reduced, reduced form goes to metal, oxide goes to slag.
- Oxides of Al, Ca, Mg are not reduced. They go to slag.
- Molten iron absorbs carbon from coke. (Pig iron is sometimes referred to as carbon saturated iron)
- Sulphur is also present in coke. Its oxide is reduced and sulphur goes into metal.

One of the uses of Ellingham diagram is that we can calculate, or read directly, the equilibrium partial pressure of the oxygen. If the partial pressure of oxygen is

		Elements in Molten Metal	Oxides in Molten Slag
Fe:	92%	Fe	Fe_2O_3
C:	3.5-4%	C	Al_2O_3
Mn:	0.4-2.0%	Si	SiO_2
Si:	0.5-1.5%	Mn	CaO
P:	0.5%	P	P_2O_5
S:	0.5%	S	SO_4^-
			MnO_2

Figure 7.4: A typical composition of pig iron and slag obtained from blast furnace

higher compared to equilibrium partial pressure then the metal will be oxidized and if it is lower then the oxide will be reduced. On the right side of Ellingham diagram we have p_{O_2}. First we select the temperature and mark the point on the oxidation line corresponding to that temperature. There is a point on the upper left corner of the diagram marked as "0". Now, we draw a straight line through the point "0" and that marked point. We read the point where it will cross p_{O_2} scale. This is the equilibrium partial pressure of oxygen.

Similarly we can find the equilibrium ratio of (p_{CO}/p_{CO_2}) and (p_{H_2}/p_{H_2O}), using points 'C' and 'H', respectively on the left side of the Ellingham diagram as shown in Figure 7.5.

7.3.5 Richardson Ellingham Diagrams

We have similar diagrams for carbides, nitrides, chlorides, etc., and the principles discussed for oxides are applicable to these diagrams as well.

7.4 Reactions Equilibria Involving Condensed Phases

Consider a reaction in which 'a' moles of A react with 'b' moles of B to produce 'c' moles of C and 'd' moles of D. The equation for the reaction is:

$$aA + bB \leftrightarrow cC + dD$$

In the relation between the standard free energy change and equilibrium constant

$$\Delta G^\circ = -RTlnK$$

the equilibrium constant is

$$K = \frac{a_D^d . a_C^c}{a_A^a . a_B^b} \tag{7.5}$$

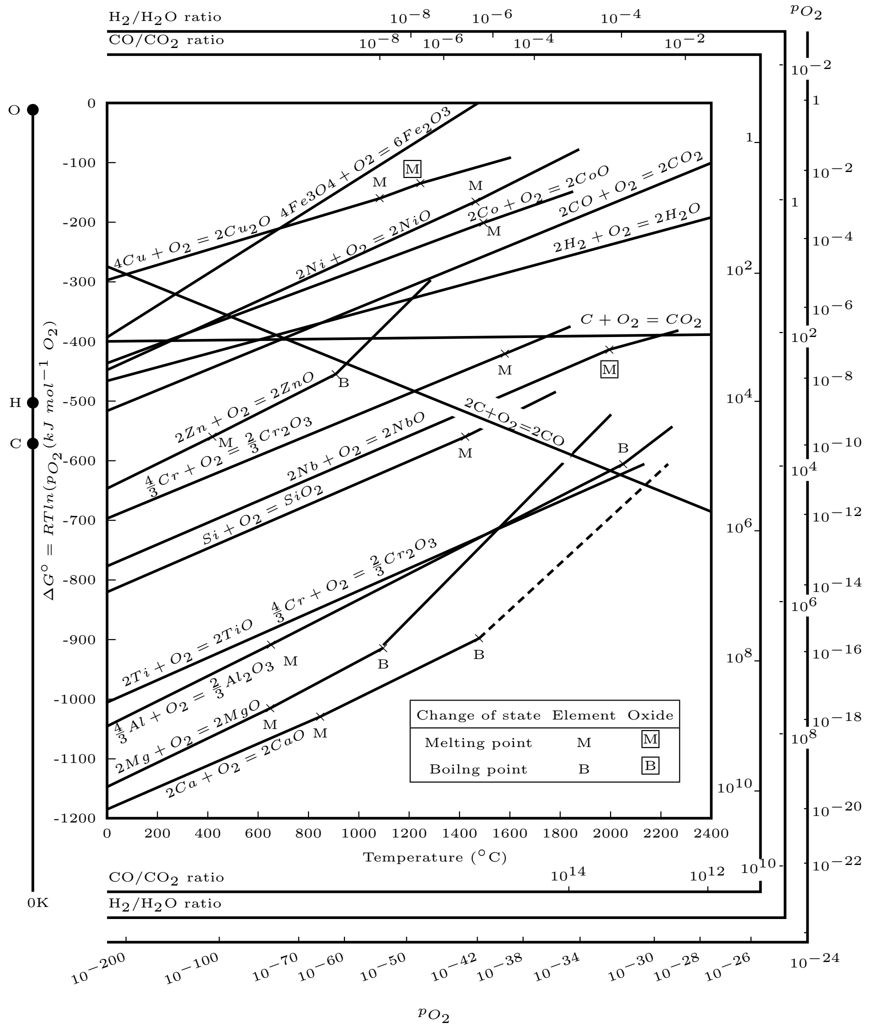


Figure 7.5: Ellingham Diagram showing nomographic scales for p_{O_2}, p_{CO}/p_{CO_2} and p_{H_2}/p_{H_2O}

Recall,

For pure condensed phases (pure liquid or pure solid), $a_i = 1$
For ideal solution, $a_i = X_i$ (X is mole fraction)
For non-ideal solution, $a_i = \gamma_i X_i$ (γ is the activity coefficient)
For gases, $a_i = p_i$ (p is partial pressure)

7.4.1 Examples – Equilibria Involving Condensed Phases

Let us see how we handle equilibria when different types of phases are involved.

These considerations are important in extraction, refining, corrosion protection, etc.

Remember, a lot of thermodynamics data is available. We need to establish proper relations and apply the principles learnt.

Example 1: Fe-Mn equilibrium in the presence of oxygen

Imagine we have a molten alloy of Fe and Mn. In the presence of oxygen, we will have an oxide solution (slag having MnO and FeO) on top of the liquid metal.

We start with separate oxidation equations for molten Mn and molten Fe.

$$Mn_{(l)} + \frac{1}{2}O_{2_{(g)}} = MnO_{(l)} \quad \Delta G^\circ = -344,800 + 55.90T \quad \text{(Data Given)}$$

$$Fe_{(l)} + \frac{1}{2}O_{2_{(g)}} = FeO_{(l)} \quad \Delta G^\circ = -232,700 + 45.15T \quad \text{(Data Given)}$$

Equilibrium is established under the same partial pressure of $O_{2_{(g)}}$, hence we eliminate it by subtracting the second equation from the first equation. Remember, equations for ΔG° are also handled using algebraic principles.

$$Mn_{(l)} + FeO_{(l)} = Fe_{(l)} + MnO_{((l)} \quad \Delta G^\circ = -112,100 + 10.75T$$

At 1873 K (steel making temperature),

$$\Delta G^\circ = -91928 J/mol$$

Using the relation

$$\Delta G^\circ = -RTlnK$$

We find that K = 365

Here, the equilibrium constant is

$$K = \frac{(a_{MnO})[a_{Fe}]}{(a_{FeO})[a_{Mn}]}$$

Conventionally, the square bracket [ ] is used for metal solution and round bracket ( ) is used for oxide solution.

Assuming that both solutions are ideal.

$$K = \frac{(X_{MnO})[X_{Fe}]}{(X_{FeO})[X_{Mn}]}$$

For 2% Mn

$$K = \frac{(X_{MnO})[0.98]}{(X_{FeO})[0.02]}$$

$$\frac{(X_{MnO})}{(X_{FeO})} = 7.5$$

Since

$$X_{MnO} + X_{FeO} = 1$$

We can write

$$\frac{(1 - X_{FeO})}{(X_{FeO})} = 7.5$$

Solving for (X_{FeO}), we get

$$X_{FeO} = 0.12$$

And

$$X_{MnO} = 0.88$$

The values show that MnO is much more stable oxide, Mn has higher tendency for oxidation that is why it is found in slag in higher amount. If we know that solutions are not ideal, we will use the relation $a = \gamma X$

Now, suppose our sample shows that we have more than 2% Mn and we want to reduce it to 2%. If we increase FeO in slag, Mn in metal will be oxidized, thus decreasing Mn content of metal. This is the principle used in refining.

Another important thing to remember is that a component moves from higher chemical potential region to lower chemical potential region. A region having attracting environment has low potential. Suppose we want to decrease phosphorous in molten steel. We increase the content of CaO in the slag. CaO is a basic oxide which has attraction for P_2O_5 which is an acidic oxide. Now if phosphorous in molten steel is oxidized, it will be attracted by CaO rich slag thus reducing P in the metal.

Example 2

Silicon reacts with oxygen to form silicon dioxide at a temperature $1600°C$. Find

a) Partial pressure of oxygen for oxidation of pure silicon

b) Partial pressure of oxygen for oxidation of silicon in iron with 1 wt% silicon (having $X_{Si} = 0.02$) assuming ideal solution

c) Partial pressure of oxygen for oxidation of silicon in iron with 1 wt% silicon (having $X_{Si} = 0.02$) assuming non ideal solution with activity coefficient of $\gamma_{Si} = 0.001$

d) Partial pressure of oxygen for oxidation of silicon in iron with 1 wt% silicon having $X_{Si} = 0.02$ assuming non ideal solution with activity coefficient of $\gamma_{Si} = 10$ (hypothetical).

e) Activity of SiO_2 (a_{SiO_2}) if $X_{SiO_2} = 0.5$ and $\gamma_{SiO_2} = 0.1$

f) Using value of activity of SiO_2 from part (e), find partial pressure of oxygen for oxidation of pure silicon in equilibrium with this silicon dioxide.

g) Comment on the change in oxidation tendency in each case.

$$Si_{(l)} + O_{2_{(g)}} \leftrightarrow SiO_{2_{(s)}} \quad \Delta G^\circ = -952,700 + 204T \ J/mol$$

At T = 1600°C = 1873 K, ΔG°= -570608 J

a)

$$K = \frac{a_{SiO_2}}{a_{Si}.p_{O_2}}$$

For pure Si and pure SiO_2

$$\begin{aligned} K &= \frac{1}{p_{O_2}} \\ \Delta G^\circ &= -RTlnK \\ \Delta G^\circ &= RTlnp_{O_2} \\ (-570608) &= (8.314)(1873)lnp_{O_2} \\ p_{O_2} &= 1.22 \times 10^{-16}\ atm \end{aligned}$$

b) For ideal solution with $X_{Si} = 0.02$ and pure SiO_2

$$\begin{aligned} K &= \frac{a_{SiO_2}}{a_{Si}.p_{O_2}} \\ K &= \frac{1}{(0.02)p_{O_2}} \\ p_{O_2} &= \frac{1}{0.02K} = 6.1 \times 10^{-15}\ atm \end{aligned}$$

Note that oxidation tendency of Si has decreased as the equilibrium oxygen pressure has increased. Now Si can afford more oxygen.

c) $X_{Si} = 0.02$ and $\gamma_{Si} = 0.001$ and pure SiO_2

$$\begin{aligned} K &= \frac{a_{SiO_2}}{a_{Si}.p_{O_2}} \\ K &= \frac{1}{(0.001)(0.2)p_{O_2}} \\ p_{O_2} &= 6.1 \times 10^{-12}\ atm \end{aligned}$$

Note that oxidation tendency of Si has further decreased due to attractions in molten metal.

d) $X_{Si} = 0.02$ and $\gamma_{Si} = 10$ and pure SiO_2

$$\begin{aligned} K &= \frac{a_{SiO_2}}{a_{Si}.p_{O_2}} \\ K &= \frac{1}{(10)(0.2)p_{O_2}} \\ p_{O_2} &= 6.1 \times 10^{-16}\ atm \end{aligned}$$

Note that oxidation tendency of Si has now increased due to repulsions in molten metal. This is a hypothetical case as silicon actually shows negative interaction (attraction) in molten iron.

e) $X_{SiO_2} = 0.5$ and $\gamma_{SiO_2} = 0.1$ and pure Si

$$\begin{aligned} a_{SiO_2} &= \gamma X \\ a_{SiO_2} &= (0.1)(0.5) = 0.05 \end{aligned}$$

f) $a_{SiO_2} = 0.05$

$$\begin{aligned} K &= \frac{a_{SiO_2}}{a_{Si}.p_{O_2}} \\ K &= \frac{0.05}{p_{O_2}} \\ p_{O_2} &= 0.24 \times 10^{-18}\ atm \end{aligned}$$

In this case a_{SiO_2} is less than 1 and oxidation tendency will increase as there is attraction for Si as oxide in slag.

Remember, as the equilibrium pressure of O_2 increases, the tendency of oxidation becomes low. The greater the tendency of the oxidation of a metal, the lower will be the partial pressure of O_2 at equilibrium.

For a reactive metal, we may have $p_{O_2} = 10^{-35}\ atm$ which is very low and, therefore, it has greater tendency of forming oxide as compared to a metal for which $p_{O_2} = 10^{-5}\ atm$ which is quite high and hence this metal has much lower tendency of forming oxide.

Example (3). *Given that*

1. $H_{2(g)} + 1/2O_{2(g)} = H_2O_{(g)} \quad \Delta G^\circ = -247,500 + 55.85T\ Joules$
2. $2Ag_{(s)} + 1/2O_{2(g)} = Ag_2O_{(s)} \quad \Delta G^\circ = -30,540 + 66.11T\ J/mol$

a) *Write formula for equilibrium constant corresponding to reaction (1) and (2).*

b) *Find* $\frac{P_{H_2O}}{p_{H_2}}$ *in equilibrium with pure silver and pure silver oxide at 1000 K.*

c) *Find* $\frac{P_{H_2O}}{p_{H_2}}$ *in equilibrium with ideal solution with 0.5 mole fraction of Ag and pure* Ag_2O *at 1000 K. Evaluate oxidation tendency in comparison to pure Ag.*

d) *Find* $\frac{P_{H_2O}}{p_{H_2}}$ *in equilibrium with pure silver and with silver oxide solution having 0.5 mole fraction of* Ag_2O *and activity coefficient of 0.4 at 1000 K. Evaluate oxidation tendency in comparison to pure* Ag_2O*.*

Solution.

a) Equilibrium constants

- $K_1 = \frac{a_{H_2O}}{a_{H_2}.a_{O_2}^{1/2}} = \frac{p_{H_2O}}{p_{H_2}.p_{O_2}^{1/2}}$

- $K_2 = \frac{a_{Ag_2O}}{a_{Ag}^2.a_{O_2}^{1/2}} = \frac{a_{Ag_2O}}{a_{Ag}^2.p_{O_2}^{1/2}}$

b) At 1000K

$$H_{2_{(g)}} + \frac{1}{2}O_{2_{(g)}} = H_2O_{(g)} \quad \Delta G^\circ = -247,500 + 55.85T\ Joules \tag{i}$$

$$2Ag_{(s)} + \frac{1}{2}O_{2_{(g)}} = Ag_2O_{(s)} \quad \Delta G^\circ = -30,540 + 66.11T\ Joules \tag{ii}$$

After subtracting Equation ii from Equation i

$$H_{2(g)} + Ag_2O_{(s)} = H_2O_{(g)} + 2Ag_{((s)} \quad \Delta G^\circ = -216,960 - 10.26T\ Joules$$

$$\Delta G^\circ = -227,220\ J$$

$$\begin{aligned}
\Delta G^\circ &= -RTlnK \\
-\frac{\Delta G^\circ}{RT} &= lnK \\
-\frac{-227,220}{(8.314)(1000)} &= ln\frac{a_{Ag}^2.a_{H_2O}}{a_{Ag_2O}.a_{H_2}} \\
27.33 &= ln\frac{p_{H_2O}}{p_{H_2}} \\
\frac{p_{H_2O}}{p_{H_2}} &= 7.4 \times 10^{11}\ atm
\end{aligned}$$

c) At 1000K and $X_{Ag} = 0.5$ (ideal solution)

$$\begin{aligned}
27.33 &= ln\frac{(0.5)^2.p_{H_2O}}{p_{H_2}} \\
e^{27.33} &= \frac{(0.25).p_{H_2O}}{p_{H_2}} \\
\frac{p_{H_2O}}{p_{H_2}} &= \frac{e^{27.33}}{0.25} \\
\frac{p_{H_2O}}{p_{H_2}} &= 3 \times 10^{12}\ atm
\end{aligned}$$

d) At 1000 K $X_{Ag_2O} = 0.5,\ \gamma = 0.4$

$$\begin{aligned}
27.33 &= ln\frac{a_{Ag}^2.a_{H_2O}}{a_{Ag_2O}.a_{H_2}} \\
27.33 &= ln\frac{p_{H_2O}}{X_{Ag_2O}\gamma_{Ag_2O}.a_{H_2}} \\
27.33 &= ln\frac{p_{H_2O}}{(0.5)(0.4).p_{H_2}} \\
\frac{p_{H_2O}}{p_{H_2}} &= (e^{27.33})(0.4)(0.5) \\
\frac{p_{H_2O}}{p_{H_2}} &= 1.5 \times 10^{10}\ atm
\end{aligned}$$

As $\frac{p_{H_2O}}{p_{H_2}} = 1.5 \times 10^{10}$ is lower, there is greater tendency of forming oxide as compared to 7.4×10^{11} and 3×10^{12} where the tendency of forming oxide is lower.

□

Summary

- Thermodynamic data can be used to get knowledge about equilibrium state in any reactive system, the governing relation is $\Delta G^\circ = -RTlnK$ where ΔG° is the standard Gibbs free energy change and 'K' is the equilibrium constant.
- Equilibrium constant for generalized reaction

$$aA + bB \leftrightarrow cC + dD$$

$$K = \frac{a_C^c.a_D^d}{a_A^a.a_B^b}$$

  - For condensed phases(pure liquid and pure solid), $a = 1$
  - For ideal solution, $a = X$ (mole fraction)
  - For non-ideal solution, $a = \gamma X$
  - For gases, $a = p$ (partial pressure)
- Gas equilibria can be used to calculate a gas mixture as a cheap method to avoid oxidation of a component in a furnace.
- Equilibrium constant 'K' varies with temperature depending on the sign of ΔH° in conformity with Le Chatelier's principle.
- Ellingham Diagram can be conveniently used to compare oxidation behavior of various elements. The diagram is the graphical representation of temperature variation of the standard free energy of oxidation per mole of oxygen.

- Carbon can be regarded as a universal reducing agent as carbon oxidation line goes down with temperature and crosses all other lines. However, for very stable oxides, temperature required for reduction is impractically high.

- Reaction equilibria involving condensed phases can be conveniently used to study slag/metal reactions, oxidation of metals under various environments, etc.

- We started with all gas phases, then one gas phase and then condensed phases and combinations. In all cases, we write suitable reaction and use $\Delta G^\circ = -RTlnK$ where K is the ratio of activities of products and activities of reactants.

Practice Problems

1. Evaluate the following statements using thermodynamic reasoning.

    i. If we want to remove an impurity from molten metal, its activity in slag should be reduced.
    ii. Almost all the phosphorous present in the blast furnace charge comes into pig iron.
    iii. Thermodynamics can explain why platinum does not oxidize in air.
    iv. If we heat $CaCO_3$ in an enclosed container, its decomposition will stop after some time.
    v. Oxidation tendency of a pure element is higher in comparison to when it is in solution.
    vi. Mg and Al are difficult to extract by carbon reduction; hence they are extracted using electrochemical methods.
    vii. Temperature effect on chemical equilibrium can be easily explained mathematically. This explanation is consistent with Le Chatelier's principle.

2. A Fe-Cr solid solution contains 0.1 mole fraction of Cr which behaves ideally. Upon reaction with a H_2O/H_2 gas mixture, pure solid Cr_2O_3 forms. Calculate the H_2O/H_2 ratio in the gas mixture in equilibrium with the Fe-Cr solid solution and pure solid Cr_2O_3 at 800°C.

$$2Cr_{(s)} + 3/2O_{2(g)} = Cr_2O_{3(s)} \qquad \Delta G^\circ = -1120,800 + 260.0T$$

$$3H_{2(g)} + 3/2O_{2(g)} = 3H_2O_{(g)} \qquad \Delta G^\circ = -738,000 + 164.4T$$

3. Describe the extraction of Fe from its ore from thermodynamic point of view.

4. Draw a graph of standard free energy of oxidation per mole of oxygen as a function of temperature for the following elements:

   i. $D_{(s)} + O_{2(g)} = DO_{2(s)}$ ΔH° = -1100 J/mol
   ii. $E_{(s)} + O_{2(g)} = EO_{2(s)}$ ΔH° = -1400 J/mol
   iii. $G_{(s)} + O_{2(g)} = GO_{2(s)}$ ΔH° = -1800 J/mol
   iv. $F_{(s)} + O_{2(g)} = FO_{2(g)}$ ΔH° = -1000 J/mol
   v. $2F_{(s)} + O_{2(g)} = 2FO_{(g)}$ ΔH° = -900 J/mol

   Why the element F may be regarded as a universal reducing agent?

5. Using the following data, find the equilibrium ratio pH_2/pH_2O at 450 °C.

   i. $2B_{(s)} + (3/2)O_{2(g)} = B_2O_{3(s)}$, ΔG° = -776,000 + 208 T J
   ii. $3H_{2(g)} + (3/2)O_{2(g)} = 3H_2O_{(g)}$, ΔG° = -740,000 + 167 T J

   Propose a cheap method of avoiding oxidation of metal B during heating at 450 °C.

6. Consider the oxidation of Pb:

$$Pb_{(l)} + (1/2)O_{2(g)} = PbO_{(l)}, \quad \Delta G^\circ = -181,200 - 68TJ$$

   i. Find equilibrium pressure of oxygen 1200 °C.
   ii. Find equilibrium pressure of oxygen when 1 mole% Pb is dissolved in copper assuming ideal solution.
   iii. We know that Pb has strong positive interaction with copper. How does it affect the equilibrium pressure of oxygen.
   iv. If oxides of Cu and Pb have negative interaction, how will it affect the equilibrium pressure of oxygen.

7. Using the reaction

$$Mn_{(l)} + 1/2O_{2(g)} = MnO_{(l)}, \quad \Delta G^\circ = -344,800 + 55.90T$$

   Find the equilibrium partial pressure of O_2 ,

   i. When Mn and MnO are pure liquids.
   ii. When 3 mole% Mn is in liquid solution with iron and behaves ideally.
   iii. When 3 mole% Mn is in liquid solution with iron and $\gamma_{Mn} = 0.7$
   iv. When 3 mole% Mn is in liquid solution with iron, $\gamma_{Mn} = 0.7$ and $\gamma_{MnO} = 0.5$

   Discuss the options a steel smelter has when he finds that the molten steel does not have the desired Mn content.

8. Use the following reactions and the corresponding data to answer:

$$\begin{aligned} CO_{(g)} + \tfrac{1}{2}O_{2(g)} = CO_{2(g)} & \quad \Delta G^\circ = -282,400 + 86.81T \\ Fe_{(s)} + \tfrac{1}{2}O_{2(g)} = FeO_{(s)} & \quad \Delta G^\circ = -263,700 + 64.35T \end{aligned}$$

   i. Find p_{CO}/p_{CO_2} in equilibrium with pure Fe and pure FeO.
   ii. What happens to oxidation tendency of Fe if Fe is in solution? Explain
   iii. What happens to oxidation tendency of Fe if FeO is in solution? Explain

9. Similar to oxidation, we have Ellingham- Richardson diagram for the sulfidation of elements.

$$M_{(s)} + S_{2(g)} = MS_{2(s)}$$

   Use the following information to draw the lines in a properly labeled diagram.

$$\begin{array}{lll} a. & 2C_{(s)} + S_{2(g)} = 2CS_{(g)} & \Delta H^\circ = +400kJ \\ b. & C_{(s)} + S_{2(g)} = CS_{2(g)} & \Delta H^\circ = -20kJ \\ c. & 2Fe_{(s)} + S_{2(g)} = FeS_{(s)} & \Delta H^\circ = -300kJ \\ d. & 2Mn_{(s)} + S_{2(g)} = 2MnS_{(s)} & \Delta H^\circ = -600kJ \\ e. & 2Ca_{(s)} + S_{2(g)} = 2CaS_{(s)} & \Delta H^\circ = -1200kJ \end{array}$$

   Comment on the metallothermic reduction of sulphides.

10. Using the standard Gibbs free energies of formation of NiO from solid Ni and liquid Ni, calculate the melting temperature, molar heat of melting and molar entropy of melting of Ni.

11. The partial pressure of oxygen in equilibrium with pure liquid lead and pure liquid lead oxide at 1200 K is $2.16\times10^{(-9)}$ atm. When SiO_2 is added to liquid PbO to form a lead silicate melt, the pO_2(eq) decreases to $5.41\times10^{(-10)}$ atm. Calculate a_{PbO} in the lead silicate melt.

Chapter 8

Thermodynamics in Electrochemistry

Learning Outcomes:

Student should be able to explain

- Importance of electrochemistry in materials science
- Free energy change in an electrochemical reaction
- How to determine ΔG, ΔH and ΔS through electrochemical method
- How to determine activities using electrochemical method
- Pourbaix diagram and its use

8.1 Introduction

Electrochemistry is the branch of physical chemistry which deals with the interaction between the chemical change and electrical energy. Electrochemistry has its applications in energy storage devices, metal refining, corrosion protection, electroplating, etc. In addition, it is a tool for thermodynamic measurements and is a very useful technique for the generation of thermodynamic data.

An electrochemical reaction is the one which involves a chemical reaction accompanied with transfer of electrons. It involves a redox reaction which can be represented as

$$YO + X \leftrightarrow XO + Y \tag{8.1}$$

In this reaction, X is getting oxidized by giving up electrons to Y which is getting reduced.

$$\begin{array}{ll} X \rightarrow X^{++} + 2e^{-} & \text{oxidation (half cell reaction)} \\ Y^{++} + 2e^{-} \rightarrow Y & \text{reduction (half cell reaction)} \end{array}$$

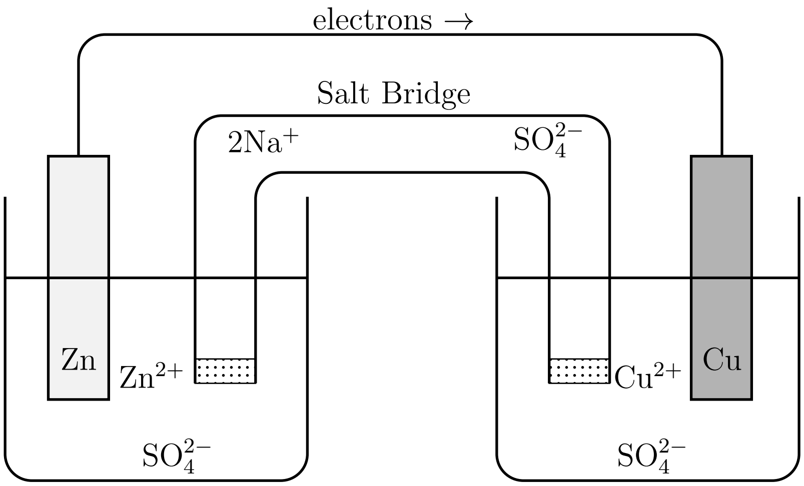


Figure 8.1: Arrangement in a Daniel Cell

An electrochemical cell may be utilizing a spontaneous chemical reaction to generate electricity whereby it is referred to as a galvanic cell. On the other hand, it may be using electrical energy to carry out a chemical reaction in which case it is known as an electrolytic cell.

8.1.1 Galvanic Cell

Galvanic cell, also termed as voltaic cell, utilizes a spontaneous redox chemical reaction to produce electricity as in batteries.

Let us consider the Daniel cell, i.e., Zn-Cu cell as shown in Figure 8.1. It consists of a Zn anode submerged in $ZnSO_4$ solution and a Cu cathode in $CuSO_4$ solution under standard conditions. Both electrodes are connected externally through wire for the electron flow and through salt bridge for ionic flow.

The overall redox reaction in Cu-Zn Daniel cell is given as

$$Zn_{(s)} + CuSO_{4_{(aq)}} \leftrightarrow ZnSO_{4_{(aq)}} + Cu_{(s)} \qquad \Delta G^\circ = -213,040\ J/mol \text{ at } 298\text{K}$$

$$EMF(E^\circ) = 1.10\ V$$

The cell potential corresponding to the above mentioned reaction is simply the difference in the half cell potentials of Zn and Cu electrodes and is also termed as EMF (Electro Motive Force) of the cell. It depends on electrodes as well as on the nature of electrolytes.

8.1.2 Electrolytic Cell

In an electrolytic cell, the electrical energy is used to carry out a chemical reaction. This reaction would otherwise be non-spontaneous and work has to be done on the system to carry out this change. This cell can be utilized in electroplating, electro refining, hydrogen production, electrolysis of different salts, etc.

8.2 Thermodynamics of a Reversible Electrochemical Cell

Let us consider that the electrodes as well as the electrolytes in an electrochemical cell are in their respective standard states. If we attach a high resistance volt meter across the electrochemical cell, the standard EMF across the cell can be measured. Recall, EMF is the voltage measured when no current is flowing. The voltage measured when current is flowing will be less than the EMF as there will be some potential drop within the cell.

Let us consider the example of Zn-Cu Daniel cell. For this cell, the high resistance volt meter measures a value of 1.10 V across the cell.

To understand the concept of reversibility, we attach an external battery source across the cell to oppose the EMF generated by the cell as shown in Figure 8.2. As the applied voltage is increased, current decreases. Now we increase the external applied voltage up to 1.0 V. As the opposing voltage is less the standard EMF of the cell, current will flow in the forward direction but it will be much less as compared to the case without the opposing battery source. If the opposing voltage is further increased, say to 1.09V, infinitesimally small current will still flow across the cell. But, when the opposing voltage is increased above 1.10 V, the direction of flow will be reversed and anode will become cathode and cathode will become anode. So, by changing the externally applied voltage, we can reverse the direction of current and hence control the reaction in both, forward as well as backward direction, just by adjusting the value of external driving force, i.e., the opposing voltage of the battery.

Let us again consider the reaction

$$YO + X = Y + XO$$

Chemically, X reduces YO, while electrically X gives two e^- to form X^{++} and Y^{++} gains two e^- to form Y. In the external circuit, electrons flow from X to YO; in internal circuit, O^{--} move from YO to X. Thermodynamically, X has tendency to get oxidized and Y has tendency to get reduced. This is the thermodynamic driving force and a current will spontaneously flow when the circuit is closed. Now we oppose this tendency by applying voltage in the opposite direction. On increasing the opposing voltage, current will decrease. At one stage, current will stop. A balance occurs between the electromotive force and the applied opposing voltage. Now, if we decrease applied voltage by δV, current starts again. If applied voltage is increased by δV, current goes in the opposite direction.

Recall the definition of a 'Reversible Process',

> 'A reversible process occurs under infinitesimally small driving force, the direction of process can be changed by changing the direction of the

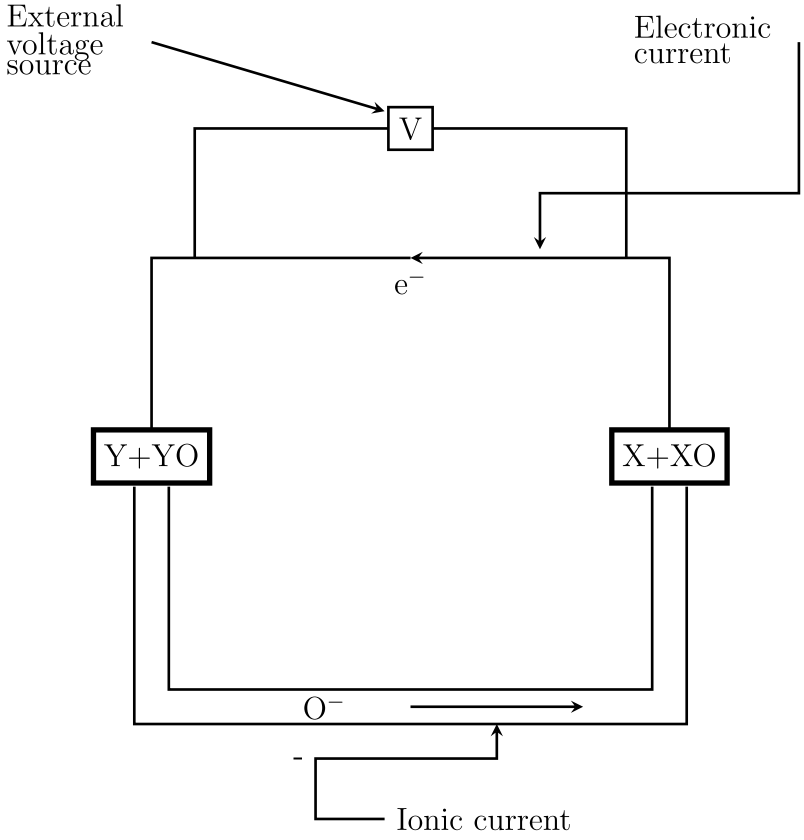


Figure 8.2: Schematic diagram to explain reversibility in an electrochemical cell

> driving force. The system passes through a series of equilibrium stages and is never away from equilibrium.'

The present process is, as per definition, a reversible process. In fact, only in electrochemical processes we approach reversibility. This is a very important concept in thermodynamics. Also, recall that a reversible process corresponds to the maximum work available from a system. If we have to do work on the system, it will be the minimum if the process is reversible.

When we increase the driving force δV (by decreasing the applied voltage), current increases and available work becomes less than the maximum. In the limiting case, when we short circuit (applied voltage zero), very high current passes; all the useful work is converted into heat, the process becomes completely irreversible.

For the thermodynamic measurements, the process should be reversible in nature. Due to this reason, electrochemical methods are very useful for thermodynamic studies as they can be operated in almost a reversible manner.

8.2.1 Relation between EMF and ΔG

During an electrochemical reaction, free energy difference between products and reactants is the driving force for the reaction. As noted above, the electrochemical reactions are the processes in which the reversibility can be approached. Recall that the change in free energy during a process is given by

$$dG = VdP - SdT - \delta w'$$

This is a general expression for change in Gibbs free energy and the last term can be any type of work; in case of an electrochemical cell, it is the electrical work.

If we consider that the process is taking place at constant pressure and temperature, this equation reduces to

$$dG = -\delta w'$$

Or

$$\delta w' = -dG$$

The above equation shows that the work done by a system, at constant T and P, is equal to the decrease in its free energy.

The above relation represents very small changes. For a finite change, we may write

$$(\Delta G)_{T,P} = -w' \tag{8.2}$$

Now, recall that the electrical work is mathematically given as,

$$\text{Electrical Work} = \text{Potential} \times \text{charge transferred across this potential}$$

$$\delta w' = E\delta q$$

For the charge transferred, we have

$$\delta q = zFdn$$

Where z is the valency involved and dn is the number of moles reacted. 'F' is Faraday's constant which represents charge of one mole of electrons (96487 Coulombs/mole).

For one mole reacted,

$$\Delta q = zF$$

$$w' = zFE \tag{8.3}$$

Combining the above equation with Equation 8.2, we get,

$$\Delta G = -zFE \tag{8.4}$$

For standard states,

$$\Delta G^\circ = -zFE^\circ \tag{8.5}$$

The negative sign indicates that a positive cell potential corresponds to a negative free energy change, and thus the cell reaction will spontaneously proceed to the right. Oxidation will occur on the left side, reduction on the right side.

The value of ΔG expresses the maximum useful work that a system can do. Useful work is the work which can be extracted from the cell by electrical means in order to operate any device.

Let us consider the following reactions in Cu-Zn cell:
At anode, oxidation of zinc is taking place which can be written as,

$$Zn \rightarrow Zn^{++} + 2e^-$$

For cathode, reduction of Cu can be written as,

$$Cu^{++} + 2e^- \rightarrow Cu$$

The overall redox reaction is shown as,

$$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$$

The standard free energy change for this reaction is

$$\Delta G^\circ = -213,040\ J/mol \text{ at 298K}$$

Using the Equation 8.5,

$$\begin{aligned} \Delta G^\circ &= -zFE^\circ \\ -213,140 &= -2 \times 96487 \times E^\circ \\ E^\circ &= 1.104V \end{aligned}$$

This is the EMF of the standard Zn-Cu electrochemical cell.

Example: Decomposition of H_2O by electric energy

Let us consider decomposition of water to give hydrogen and oxygen gas.

$$H_2O_{(l)} \rightarrow H_{2_{(g)}} + \frac{1}{2}O_{2_{(g)}}$$

For this reaction,

$$\begin{aligned} \Delta H^\circ_{298} &= +285.5\ kJ/mol \\ \Delta S^\circ_{298} &= +163\ J/K/mol \\ \Delta G^\circ &= 285.5 - 298(0.163) = +237\ kJ/mole \end{aligned}$$

As ΔG° is positive, in order to make the reaction go, we must supply at least 237 kJ of useful work to the system from surroundings (e.g. a battery) to give the reaction system the required amount of energy. If we wish, we may supply 250 or 280 kJ but in no case we can electrolyze a mole of water by furnishing less than 237 kJ/mol.

Now look at this reaction from electrochemical point of view. The respective half-cell reactions with the half-cell potentials are

$$\frac{1}{2}O_{2_{(g)}} + 2H^{+}_{(aq)} + 2e^{-} \rightarrow H_2O_{(l)} \quad (E = 1.23V)$$

$$2H^{+} + 2e^{-} \rightarrow H_{2(g)} \qquad (E = 0)$$

On subtraction, we get

$$H_2O_{(l)} \rightarrow \frac{1}{2}O_{2_{(g)}} + H_{2_{(g)}} \quad (\Delta E^{\circ} = -1.23V)$$

Now, if we use cell potential to find the free energy change, we obtain

$$\begin{aligned} \Delta G^{\circ} &= -zFE^{\circ} \\ &= -2 \times (96487\ J/V/mol) \times (-1.23V) \\ &= 237\ kJ/moles \end{aligned}$$

If we use it as a fuel cell, the reaction would be

$$\frac{1}{2}O_{2_{(g)}} + H_{2_{(g)}} \rightarrow H_2O_{(l)} \qquad (\Delta E = 1.23V)$$

And if we supply electricity for electrolysis, the reaction is

$$H_{2O_{(l)}} \rightarrow \frac{1}{2}O_{2_{(g)}} + H_{2_{(g)}} \qquad (\Delta E = -1.23V)$$

8.2.2 Effect of Concentrations on EMF of electrochemical cell

To understand the effect of concentration, let us consider a simple reaction at equilibrium

$$A + B = 2C$$

The standard free energy of the reaction can be given as the difference between the standard free energy of the product minus the reactant, i.e.,

$$\Delta G^{\circ} = 2G^{\circ}_{C} - (G^{\circ}_{A} + G^{\circ}_{B})$$

$$\Delta G^{\circ} = -RTlnK$$

The above equation provides the value of equilibrium constant K, which can be calculated on the basis of standard free energy change.

Now, let us consider the general equation for free energy change when the components are not in their standard states:

$$\Delta G = \Delta G^{\circ} + RTlnQ$$

Here, ΔG represents the driving force for the reaction, the higher its value, the more spontaneous it will be. Here Q is the ratio of activities of products over reactants in non-standard conditions. For an electrolyte, the standard condition corresponding to unit activity is that of saturated solution.

Again, considering the Zn-Cu Daniel cell under non-standard condition, we get

$$\Delta G = \Delta G^{\circ} + RTln\frac{a_{Cu}.a_{ZnSO_4}}{a_{Zn}.a_{CuSO_4}} \tag{8.6}$$

The above equation represents the effect of concentrations on free energy change under non-standard condition.

Note that when all the components are in their standard states, Q = 1 and $\Delta G = \Delta G^{\circ}$.

When Q = K, the equilibrium is reached and hence the driving force of the reaction, ΔG, becomes zero and the rate of forward reaction becomes equal to the rate of backward reaction.

As, at equilibrium, the change in free energy, ΔG, is zero, we get

$$\Delta G^{\circ} = -RTlnK$$

In order to calculate the EMF across the cell under non-standard conditions, again consider the general equation for free energy change for Zn-Cu cell,

$$\Delta G = \Delta G^{\circ} + RTln\frac{a_{Cu}.a_{ZnSO_4}}{a_{Zn}.a_{CuSO_4}}$$

Using the relation

$$\Delta G = -zFE$$

the above equation becomes

$$-zFE = -zFE^{\circ} + RTln\frac{a_{Cu}.a_{ZnSO_4}}{a_{Zn}.a_{CuSO_4}}$$

If we assume the electrodes to be pure Zn and pure Cu, their activities can be taken as unity

$$-zFE = -zFE^{\circ} + RTln\frac{a_{ZnSO_4}}{a_{CuSO_4}}$$

$$E = E^{\circ} - \frac{RT}{zF}ln\frac{a_{Red}}{a_{ox}} \tag{8.7}$$

The above equation is known as the Nernst Equation where E represents the EMF across the cell under non-standard conditions and E° represents EMF in the standard conditions.

8.2.3 Entropy Change – Temperature Coefficient of EMF

Electrochemical measurements, in many cases, provide easy and quick way to obtain thermodynamic data experimentally. Whereas the free energy change can be directly found from EMF value, entropy change can be determined by measuring EMF over a range of temperature values. Once free energy change and entropy change is known, the enthalpy change can be easily calculated.

From the basic equation

$$dG = -SdT + VdP$$

we get

$$d(\Delta G) = -(\Delta S)dT + (\Delta V)dP$$

On rearranging, at constant 'P', we get

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

Using the relation between ΔG and E, we can write

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

$$\Delta S = zF\left(\frac{\partial E}{\partial T}\right)_P \tag{8.8}$$

The above equation uses the rate of change of EMF with temperature. Thus, by measuring EMF at various temperatures, we could determine temperature coefficient of EMF from which we can calculate the entropy change.

For ΔH, we put Equation 8.8 in the general mathematical form of Gibbs free energy and get

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

$$\Delta H = -zFE + zF\left(\frac{\partial E}{\partial T}\right)_P T \tag{8.9}$$

Example. *Consider the following reaction and calculate the Gibbs free energy of formation of* $MgCl_2$.

$$Mg_{(l)} + Cl_{2_{(g)}} \leftrightarrow MgCl_{2(l)}$$

Solution. The corresponding cell is shown in Figure 8.3.

The standard emf of the cell with respect to temperature is given as

$$E^\circ = 3.135 - 6.5 \times 10^{-4}T$$

$$\frac{\partial E^\circ}{\partial T} = -6.5 \times 10^{-4}$$

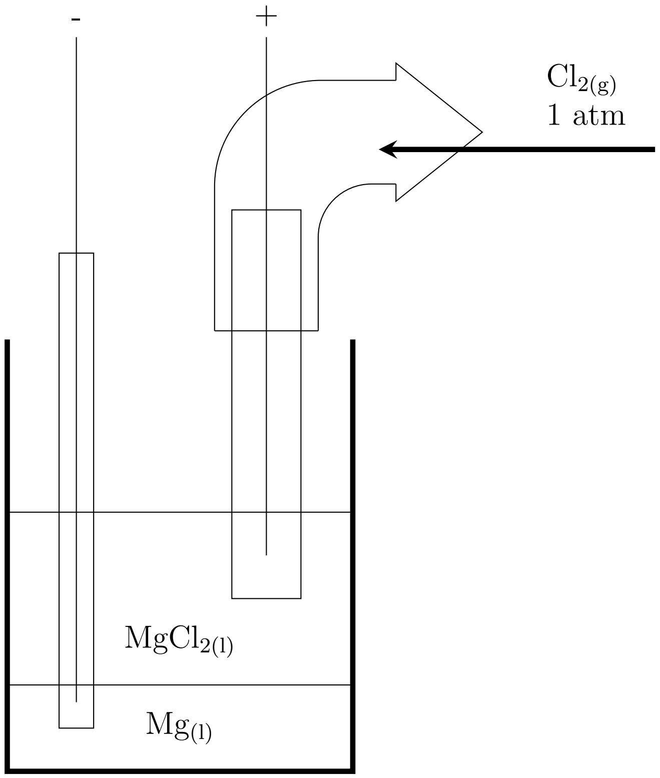


Figure 8.3: Electrochemical setup for the formation of $MgCl_2$

For z=2

$$\begin{aligned}\Delta G^\circ &= -zFE^\circ \\ &= -2 \times 96487 \times (3.135 - 6.5 \times 10^{-4}T) \\ &= -604,973 + 125.4T\end{aligned}$$

Comparing the above equation with

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

we get

$$\Delta H^\circ = -604,973\ J/mol \text{ of Mg}$$
$$\Delta S^\circ = -125.4 J/K/mol \text{ of Mg}$$

□

Example. *EMF of the galvanic cell*

$$Pb(s)|PbCl_2(s)||HCl(aq)||AgCl(s)|Ag(s)$$

is 0.490 V at 25°C and temperature coefficient of EMF is -1.84×10^{-4} *volts/deg. Write cell reaction and find* $\Delta G^\circ, \Delta H^\circ, \Delta S^\circ$.

Solution.
The cell reaction would be

$$Pb(s) + 2AgCl(s) \rightarrow PbCl_2(s) + 2Ag(s)$$

Here z = 2 , F = 96487 C/mol

$$\Delta G^\circ = -zFE^\circ = -2 \times (96487) \times (0.490) = -94557\ J/mol$$

$$\Delta S^\circ = zF\,(\partial E^\circ/\partial T) = 2 \times 96487 \times [-1.84 \times 10^{-4}] = -35.5\ J/K/mol$$

$$\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ = -94557 + (-35.5) \times (298) = -105136\ J/mol$$

To find the value of ΔH°, we could also use $\Delta H^\circ = -zFE^\circ + zFT\left(\frac{\partial E^\circ}{\partial T}\right)$ □

8.2.4 Determination of Activity of a Component in an Alloy

Electrochemical technique provides a simple method to determine activities of components in solution.

Example. *The following electrochemical cell is established to find the activity of Cd in Cd-Pb alloy at 800 K. The cell EMF is found to be 0.1 V.*

W | Cd (pure liquid) || $CdCl_2$ *dissolved in molten LiCl–KCl || [Cd–Pb] (liquid alloy) | W*

Solution. It is a concentration cell. In the left electrode, activity of Cd (pure liquid) is 1 and in the alloy (right electrode), the activity of Cd is a_{Cd}.

$$\mu(\text{Cd in alloy}) - \mu^\circ(\text{Cd pure}) = -zFE$$

$$RTlna_{Cd} - RTln(1) = -zFE \rightarrow E = -(RT/2F)lna_{Cd}, \qquad a_{Cd} = 0.055$$

To understand this we can also look at it from another point of view.

Suppose we have one cell in which pure Cd is one electrode and second is SHE (Standard Hydrogen Electrode with E = 0), then EMF of this cell is $E_1 = E^\circ$

Now we have second cell in which Cd-Pb alloy is one electrode and second is SHE (Standard Hydrogen Electrode with E = 0), Then EMF of this cell is $E_2 = E^\circ - (RT/2F)lna_{Cd}$.

$$E_2 - E_1 = -(RT/2F)lna_{Cd}$$

This example shows how we can determine activity of one component in a solution. We can make a series of alloys and determine activity of one component as a function of its mole fraction. Then use Gibbs-Duhem equation to determine activity of the second component as a function of its mole fraction. This was illustrated in Figure 5.11

□

8.2.5 Driving Force for an Electrochemical Reaction

In the above discussion, we have seen that dissimilar metals could make an electrochemical cell. In fact, minute differences in the microstructures of the materials or the environment may result in the electromotive force. Some situations are given below:

- Dissimilar metals
- Different cold work states in different regions of a metal
- Different grain sizes in different regions
- Difference in local chemistry such as segregation in an alloy
- Differential aeration regions
- Difference in the availability of species for a reaction (concentration cells)

Such situations could be used for our benefit like in galvanic cells. However, in most of the cases, these situations create problem especially in the case of corrosion of materials.

8.3 Solid State Electrolytes

A solid state electrolyte is a solid medium which conducts through movement of ions. The conduction of ions in solid state electrolytes can be through vacancy or interstitial diffusion depending on the size of ion, the number of available vacant sites and the activation energy required. Since the movement of ions is through the mechanism of diffusion, ion conduction or diffusivity is temperature dependent. Solid state electrolytes are utilized in a number of applications such as solid state batteries, measurement of thermodynamic properties, atmospheric controller in reaction chambers, etc.

The diffusion in solid state electrolytes is mainly due to the difference in ionic concentration across the electrolyte. Hence, they are concentration cells in nature. Some of the common examples of solid state electrolytes are ZrO_2-CaO, ZrO_2-Y_2O_3, ThO_2-Y_2O_3, CaF_2 doped YF_3, etc.

8.3.1 Stabilized zirconia as a solid state electrolyte

ZrO_2 is a high temperature ceramic material and is used as a refractory material. During heating and cooling, pure ZrO_2 undergoes phase transformation which may result in cracking. In order to prevent failure, some oxide such as CaO, MgO or Y_2O_3 is added as stabilizer which suppresses the transformation. In case of calcia stabilized zirconia, CaO forms solid solution with ZrO_2 and the divalent Ca^{2+} occupies some cationic sites in place of tetravalent Zr^{4+}. In order to maintain local electrical neutrality, oxygen ions get removed from some of the anionic sites resulting in anion vacancies. In this way, O^{2-} ion movement by vacancy mechanism occurs and, therefore, the stabilized zirconia acts as a solid electrolyte.

Since solid state electrolytes are concentration cells, emf of the cell is due to the difference in chemical potential of the two electrodes. To calculate emf of the cell, we consider the emf across the cell due to the difference in the chemical potential of oxygen partial pressure. General representation of these cells with ZrO_2-CaO electrolyte is,

O_2(g, at $P^1_{O_2}$), Pt | ZrO_2-CaO | Pt, O_2(g, at $P^2_{O_2}$)

(Electrode 1) Electrolyte (O^{2-}) (Electrode 2)

On the basis of chemical potential difference

$$\mu O_2^2 - \mu O_2^1 = -zFE \tag{8.10}$$

As

$$\mu O_2 = RT ln p_{O_2}$$

Taking z = 4, we can write

$$E = \left(\mu^1_{O_2} - \mu^2_{O_2}\right)/4F$$

And thus, we get the relation of emf across the concentration cell.

$$E = (RT/4F) ln\left(p^1_{O_2}/p^2_{O_2}\right) \tag{8.11}$$

The above relation can be utilized in a number of applications. In one application it is used to calculate the percentage of dissolved oxygen in molten steel by simply dipping the solid electrolyte in the molten steel and measuring the emf due to the difference in partial pressure of oxygen across the cell. In a similar manner we may carry out thermodynamic measurement of activities of components in a solid solution. The activity of the component in the alloy is found by making a concentration cell between pure component and the alloy of that component. Such data obtained for series of alloys is used in Gibbs-Duhem equation to calculate the thermodynamic properties of the second component mathematically.

8.4 EMF Series

An electrochemical cell requires two electrodes and the cell potential is the difference in potential of these electrodes. In order to assign potential to a single electrode, a reference electrode is required. Hydrogen reduction has been taken as reference and potential assigned to it is zero. It is known as Standard Hydrogen Electrode (SHE):

$$2H^+ + 2e^- \rightarrow H_2$$

All metals have been arranged in a series according to their standard reduction potential (ϕ°) values. Metals are ranked in accordance with their potential in 1 N solution of their salts. Such ranking is called Electrochemical Series and is shown in Figure 8.4. Such series has the following characteristics:

- The more positive values correspond to noble metals and the more negative values correspond to reactive metals (when arranged according to reduction potential).
- If two metals make up a cell, the more active metal acts as the anode and the more noble metal will act as cathode.
- If metal has positive value (Au, Ag, Pt), it is called noble metal or semi-noble (Cu).
- If metal has negative value (Fe, Al, Mg, Zn), it is called active metal.

Such a series has some limitations:

- In real situations, activities of metal ions in equilibrium with the respective metals usually do not equal unity.
- The position of a metal in EMF series may change because of complex formation as is the case with tin (Sn) and iron (Fe).
- Alloys are not included in the EMF series.
- In oxidizing environment, some metals undergo passivation. Transition metals usually show passive behavior in aerated aqueous environment. The dual position of some metals is not reflected in EMF series.

Some of these limitations are removed in another series, known as Galvanic Series, which has more practical applications.

8.5 Pourbaix Diagrams

Pourbaix diagrams show conditions of potential and pH under which a metal will either

- be immune (No corrosion)
- be passive (protection by formation of a passive layer)
- corrode (by forming ions M^{++}, M^{+++}, MO^{2-}, etc.)

A simplified Pourbaix diagram for iron is shown in Figure 8.5. We make such diagrams using concepts of thermodynamic equilibria. The following basic principles are used in Pourbaix diagrams:

- The value of either ΔG° or E° is generally available for the equilibria of interest.
- If H^+ ions are involved we get pH since $pH = -log[H^+]$

EMF Series

Electrode Reaction	Standard Potential $\phi^\circ(V)$ at 25°C
$Au^{3+} + 3e^- = Au$	1.50
$Pt^{2+} + 2e^- = Pt$	1.2
$Pd^{2+} + 2e^- = Pd$	0.987
$Hg^{2+} + 2e^- = Hg$	0.854
$Ag^+ + e^- = Ag$	0.800
$Hg_2^{2+} + 2e^- = 2Hg$	0.789
$Cu^+ + e^- = Cu$	0.521
$Cu^{2+} + 2e^- = Cu$	0.342
$2H^+ + 2e^- = H_2$	0.000
$Pb^{2+} + 2e^- = Pb$	−0.126
$Sn^{2+} + 2e^- = Sn$	−0.136
$Mo^{3+} + 3e^- = Mo$	−0.2
$Ni^{2+} + 2e^- = Ni$	−0.250
$Co^{2+} + 2e^- = Co$	−0.277
$Tl^+ + e^- = Tl$	−0.336
$In^{3+} + 3e^- = In$	−0.342
$Cd^{2+} + 2e^- = Cd$	−0.403
$Fe^{2+} + 2e^- = Fe$	−0.440
$Ga^{3+} + 3e^- = Ga$	−0.53
$Cr^{3+} + 3e^- = Cr$	−0.74
$Zn^{2+} + 2e^- = Zn$	−0.763
$Cr^{2+} + 2e^- = Cr$	−0.91
$Nb^{3+} + 3e^- = Nb$	−1.1
$Mn^{2+} + 2e^- = Mn$	−1.18
$Zr^{4+} + 4e^- = Zr$	−1.53
$Ti^{2+} + 2e^- = Ti$	−1.63
$Al^{3+} + 3e^- = Al$	−1.66
$Hf^{4+} + 4e^- = Hf$	−1.70
$U^{3+} + 3e^- = U$	−1.80
$Be^{2+} + 2e^- = Be$	−1.85
$Mg^{2+} + 2e^- = Mg$	−2.37
$Na^+ + e^- = Na$	−2.71
$Ca^{2+} + 2e^- = Ca$	−2.87
$K^+ + e^- = K$	−2.93
$Li^+ + e^- = Li$	−3.05

Figure 8.4: EMF Series

- If electrons (e^-) are involved, we get potential.
- Horizontal lines mean constant potential, e.g., lines ed and ab in Figure 8.5.
- Vertical lines mean constant pH, e.g., lines fd, nb.
- Inclined lines will have both pH and potential, e.g., gf, fh, dc, ci, np, bj, cn.

It should be noted that potential and pH conditions may correspond to the existing environment and the condition of the metal or these conditions may be imposed by us as in the case of cathodic and anodic protection of metals.

8.5.1 Use of Thermodynamic Data to Draw Pourbaix Diagram

Let us see how we can draw Pourbaix diagram for aluminum. First of all, we find all the species involved. In this case, these are Al, $Al^{(+3)}$, Al_2O_3 and $AlO_2^{(-)}$. Then we look at possible equilibria among these species. Thermodynamic data is generally available in the form of ΔG°. We make use of the following relations

$$\Delta G^\circ = -zFE^\circ$$

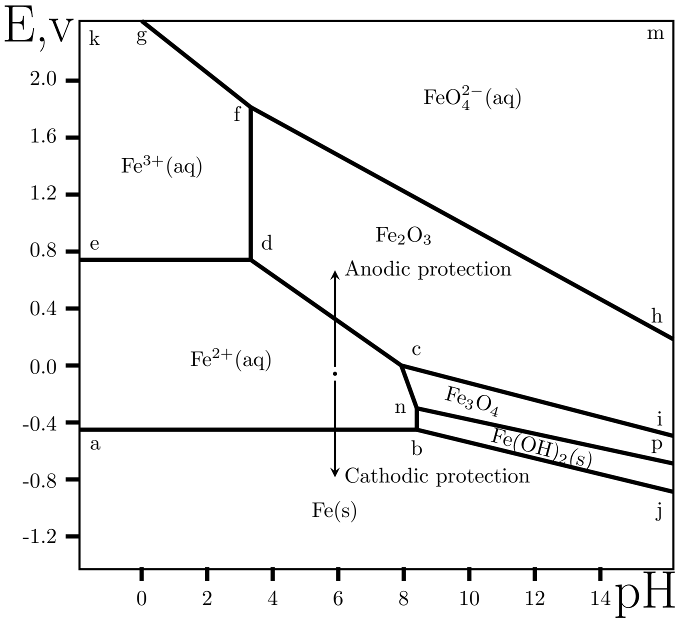


Figure 8.5: Simplified Pourbaix diagram for iron at room temperature

$$\Delta G^{\circ} = -RTlnK$$

$$E = E^{\circ} - (RT/zF)ln[a(red)/a(ox)]$$

And find the relation between E and pH. The procedure is outlined here keeping in view various lines shown in the Figure 8.6.

Line 1: Al and $Al^{(+3)}$ Equilibrium

$$Al^{(+3)} + 3e^- = Al$$

$$\begin{aligned}
\Delta G^{\circ} &= 481200\ J \\
E^{\circ} &= -\Delta G^{\circ}/3F = -1.66V \\
E &= E^{\circ} - (RT/3F)ln1/[Al_{(+3)}] \\
E &= -1.66 + 0.0198log[Al^{(+3)}]
\end{aligned}$$

For various values of [$Al^{(+3)}$], we will get different horizontal lines. In figure, one line is shown as line 1 corresponding to [$Al^{(+3)}$] = 0.01

Line 2: Al and Al_2O_3 Equilibrium

$$6H^+ + Al_2O_3 + 6e^- = 2Al + 3H_2O$$

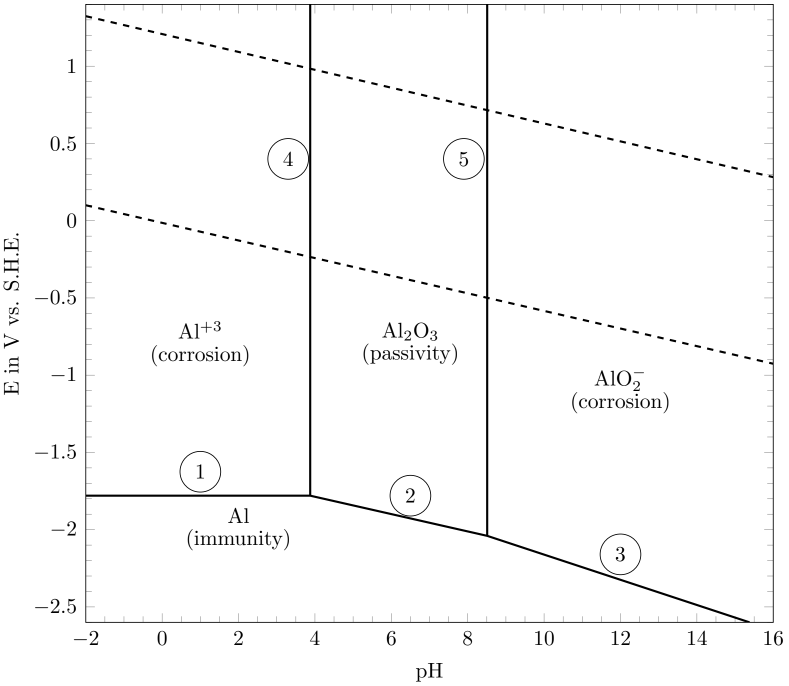


Figure 8.6: Simplified Pourbaix diagram for aluminum

$$\Delta G^\circ \ = 897300\ J$$

$$E^\circ \ = -\Delta G^\circ/6F = -1.55V$$

$$K \ = 1/[H^+]^{(6)}$$

$$E \ = E^\circ - (RT/6F)ln1/[H^+]^{(6)}$$

$$E \ = -1.55 - 0.0591pH$$

Here we get an inclined line, shown as Line 2, involving both E and pH.

Line 3: Al and $AlO_2^{(-)}$ Equilibrium

$$AlO_2^{(-)} + 4H^+ + 3e^- = 2H_2O + Al$$

$$\begin{aligned}
\Delta G^\circ &= 365400\ J \\
E^\circ &= -\Delta G^\circ/3F = -1.26V \\
K &= 1/[H^+]^{(4)}[AlO_2^{(-)}] \\
E &= E^\circ - (RT/3F)ln1/[H^+]^{(4)}[AlO_2^{(-)}] \\
E &= -1.26 + 0.0198log[AlO_2^{(-)}]–0.0789pH
\end{aligned}$$

Here we get various inclined lines, for different values of [$AlO_2^{(-)}$], involving both E and pH. One line is shown as Line 3.

Line 4: $Al^{(+3)}$ and Al_2O_3 Equilibrium

$$6H^+ + Al_2O_3 = 2Al^{(+3)} + 3H_2O$$

$$\begin{aligned}
\Delta G^\circ &= -65100\ J \\
\Delta G^\circ &= -RTlnK \\
K &= [Al^{(+3)}]^{(2)}/[H^+]^{(6)} \\
log[Al^{(+3)}] &= 5.70–3pH
\end{aligned}$$

For various values of [$Al^{(+3)}$], we will get different vertical lines. In figure, one line is shown as Line 4.

Line 5: Al_2O_3 and $AlO_2^{(-)}$ Equilibrium

$$H_2O + Al_2O_3 = 2AlO_2^{(-)} + 2H^+$$

$$\begin{aligned}
\Delta G^\circ &= 166500\ J \\
\Delta G^\circ &= -RTlnK \\
K &= 1/[H^+]^{(2)}[AlO_2^{(-)}]^{(2)} \\
log[AlO_2^{(-)}] &= pH - 14.59
\end{aligned}$$

For various values of [$AlO_2^{(-)}$] , we will get different vertical lines. In figure, one line is shown as Line 5.

Pourbaix diagrams represent a simple way to show the corrosion processes for a given material. The approach is useful for visualization of material's behavior in corrosive environments. The diagrams conveniently summarize thermodynamics of the corrosion processes and propose the remedy (cathodic/anodic protection options). However, the approach is limited to aqueous corrosion where varying pH is involved. Pourbaix diagrams provide only general prediction for uniform corrosion and do not apply in case of localized corrosion.

Summary

- Electrochemistry plays important role in various metallurgical processes such as extraction, refining, electroplating, etc.
- Electrochemical processes may approach thermodynamic reversibility in limiting cases.
- Electrochemistry provides a very powerful and convenient tool for the determination of thermodynamics properties. Free energy change can be calculated by arranging a relevant set up and measuring EMF ($\Delta G = -zFE$). Entropy change can be determined from the rate of change of EMF with temperature ($\Delta S = zF\frac{\partial E}{\partial T}$).

  So, in order to find ΔG, ΔS and ΔH for any process, just set up an appropriate electrochemical cell and measure EMF at various temperatures (3 or 4 temperatures).
- Nernst equation can be used to find the effect of concentration of various species on the EMF of an electrochemical cell.
- A convenient set up may be used to determine activity of a component in alloys. Gibbs-Duhem equation can then be used to calculate activity of the other component as a function of composition.
- Elements have been arranged, according to their reduction potentials, in EMF series. The reference here is the hydrogen reduction, the corresponding half-cell has been assigned zero potential.
- Pourbaix diagrams are convenient presentations of Potential–pH diagrams for various metals showing regions of immunity, passivation and corrosion in aqueous medium.

Practice Problems

1. Evaluate the following statements using thermodynamic reasoning.

   i. Ca and Al are extracted using electrochemical methods.
   ii. Entropy and energy changes in a reaction can only be determined using thermal methods.

   iii. Pourbaix diagram may guide us for the use of a certain metal in a given environment.
   iv. From thermodynamic data you can tell about the conditions in which a metal may passivate.
   v. In electrochemical processes, the conditions for reversibility may be approached.
   vi. Electrochemical reduction may be more useful than carbon reduction in some situations.
   vii. The combination of Gibbs Duhem equation and electrochemical measurements can completely describe activity relations in a binary alloy system.

2. $MgCl_2$ is decomposed by electrolysis, for the production of Magnesium, according to the following reaction:

$$MgCl_{2(l)} = Mg_{(l)} + Cl_{2(g)}, \quad \Delta G^\circ = 603200 - 121.43T$$

   Calculate minimum voltage required for the decomposition at 775 °C.

3. For the reaction

$$H_{2(g)} + Cl_{2(g)} = 2HCl_{(g)}, \quad \Delta G^\circ = -182,200 + 3.60TlnT - 43.68T$$

   An appropriate electrochemical cell was established.

   i. Calculate the expression for E°.
   ii. Calculate expression for ΔS°
   iii. Calculate expression for ΔH°
   iv. Calculate the values of ΔG° , ΔS° , ΔH° all at 298 K.

4. For the reaction $E_{2(g)} + F_{2(g)} = 2EF_{(l)}$

   An appropriate electrochemical cell was established. ΔG was found to vary with temperature as follows:

$$\Delta G = -315,200 + 285T$$

   Calculate the values of E, ΔS and ΔH, all at 298 K.
   How does EMF vary with temperature?

5. A hypothetical chemical reaction is spontaneous at room temperature and becomes nonspontaneous at high temperature.

   i. Write expression for the standard free energy change as a function of temperature using assumed values.
   ii. Calculate the temperature above which this reaction would be nonspontaneous.

   iii. Now calculate the voltage required to carry out the reverse reaction at room temperature which is normally nonspontaneous.
   iv. From your assumed values, evaluate the rate of change of electrochemical potential with temperature.

6. For an electrochemical cell, E° has been found to vary with T as

$$E^\circ = 1.58 - 20.5 T ln T - 1.4 \times 10^{(-3)} T.$$

   Find ΔG° , ΔS° and ΔH°

7. Describe a procedure for finding activities of both the components as a function of composition in a binary system at a given temperature.

8. In an electrochemical cell, one electrode is pure Al and the other electrode is Al-Mn alloy with 0.1 mole fraction of Mn. The electrolyte is molten salt. The measured EMF is 7.9 mV at 450 °C. Find the activity and activity coefficient of Al in the alloy.

9. For the reaction

$$Zn_{(s)} + CuSO_{4(saturated)} = Cu_{(s)} + ZnSO_{4(saturated)}$$

   The standard free energy change at room temperature is -213000 J/mol. Find the EMF of the cell. Give an estimate of EMF if the concentration of the following is reduced to half.

   i. $CuSO_4$ ($ZnSO_4$ remains saturated)

   ii. $ZnSO_4$ ($CuSO_4$ remains saturated)

10. Get Pourbaix diagram of Zn
    i. Describe regions of immunity, passivation and corrosion.
    ii. Describe equilibria corresponding to various lines.
    iii. Describe the general mathematical form of each line.

11. In order to calculate activity of Al in an Al-Zn alloy, the following cell was established.

$$Al_{(s)}|AlCl_3\text{–}NaCl(molten)|Al - Zn_{(s)}$$

    EMF was found to be 8 mV at 400 °C. Calculate activity of Al in the alloy.

12. Keeping in view the following data,

$$2Al + 3/2O_2 = Al_2O_3, \quad \Delta G^\circ = -1,687,200 + 326.8T$$

  i. Calculate the minimum voltage required to extract Al metal electrochemically.
  ii. Determine the ΔH° and ΔS° per mole of alumina.
  iii. The MP of pure alumina is 2072 °C making it impractical to use molten alumina as electrolyte. Propose a scheme to overcome this problem.

13. Compare and contrast Ellingham diagram and Pourbaix diagram considering the following points.
  i. Simple schematic representation of both diagrams
  ii. The axes used to draw the diagrams with appropriate units.
  iii. Mathematical forms of various lines occurring in the diagrams
  iv. Usefulness
  v. Limitations

Chapter 9

Few Applications of Materials Thermodynamics

Learning Outcomes:

Student should be able to explain

- Thermodynamic explanation of positive and negative adsorption
- How a certain concentration of point defects can stabilize a solid
- Thermodynamic barrier in nucleation of a new phase
- How heterogeneities may help in nucleation

As already mentioned, thermodynamics helps us to understand natural processes and guides us how can we carry out otherwise non-spontaneous processes. We have an energy function, Gibbs free energy, which can be used to determine when a system is in equilibrium and what is the direction of change if a system is not in equilibrium. Now we see few examples where we apply thermodynamic principles to understand natural processes.

9.1 Thermodynamics Applied to Surfaces

A surface of a material is the free surface which separates a condensed phase from surrounding gas or vacuum. A surface possesses some extra energy as the work has to be done to create it. From an atomistic view, work is required to create free bonds on the surface.

Surface energy is generally defined as Energy/Area with units of Joules per square meter. It is also known as the Surface Tension (Force/Length) with units of Newton per meter. Both surface energy and surface tension have same numerical values in the consistent units.

An interface is a surface separating two condensed phases. This may include interface between two immiscible liquids like oil and water, interface between a solid and a liquid such as ice cubes in water, interface between two solids such as ferrite and carbide or grain boundaries.

When a solute is dissolved in a solvent, we may notice higher or lower concentration of solute in the surface region as compared to the bulk. This is due to the difference in bonding in the surface region and the bulk. The phenomenon is termed as adsorption. Let us have a look at how thermodynamics handles adsorption in the light of what we have discussed so far. It should be noted that the discussion could be applied to any kind of interface.

Recall, at constant T and P, the free energy of a phase in terms of moles and chemical potentials of the components is given by

$$dG' = \mu_1 dn_1 + \mu_2 dn_2 + \cdots = \sum \mu_i dn_i \tag{9.1}$$

If the surface area of the phase becomes a variable, we may write

$$dG' = \sum \mu_i dn_i - \delta w \tag{9.2}$$

where

$$\delta w = -\sigma d\mathcal{A}$$

σ is the surface energy and the work is done on the system in increasing its area by $d\mathcal{A}$.

So, we write

$$dG' = \sum \mu_i dn_i + \sigma d\mathcal{A} \tag{9.3}$$

Note that the work done on the system has increased its energy. The integral form of this equation would be

$$G' = \sum \mu_i n_i + \sigma \mathcal{A}$$

This equation is the basis of Gibbs Adsorption Isotherm. As we have done in case of Gibbs-Duhem equation, we now differentiate this equation.

$$dG' = \sum \mu_i dn_i + \sum n_i d\mu_i + A d\sigma + \sigma d\mathcal{A}$$

On re-arranging,

$$dG' = \sum \mu_i dn_i + \sigma dA + \sum n_i d\mu_i + \mathcal{A} d\sigma$$

Now, we recognize that a portion of this equation is the same as Equation 9.3. Therefore, the remaining part becomes trivial, i.e.,

$$\sum n_i d\mu_i + \mathcal{A} d\sigma = 0 \tag{9.4}$$

If we consider adsorption of one component only,

$$n_i d\mu_i + \mathcal{A} d\sigma = 0$$

$$\frac{n_i}{\mathcal{A}} = -\frac{d\sigma}{d\mu_i} \tag{9.5}$$

For a surface active component, the surface concentration will be significantly different from the bulk. Thus $\frac{n_i}{\mathcal{A}}$ represents surface concentration of i. This relation states that the moles of i on the surface depend on the rate of decrease of surface energy with the chemical potential of component 'i'. Chemical potential in turn depends on the concentration and interactions. Recall the relation between chemical potential and activity, $d\mu_i = RTdlna_i$, where $a_i = \gamma_i X_i$.

Points to note:

- Surface Segregation $= -\frac{d\sigma}{d\mu_i}$
- Segregation is positive if, by increasing the concentration, the surface tension decreases. In other words, if the component decreases the surface tension, it will go to the surface (Positive segregation).
- Segregation is negative if increase in concentration increases the surface tension. Thus, if the component increases the surface tension, it will remain below the surface (Negative segregation).

This behavior basically describes the tendency of a system to decrease its free energy by readjusting the distribution of solute. The entropy factor tends to make the distribution uniform while the interactions (enthalpy term) tend to have non-uniform distribution. The resultant distribution is defined by the free energy ($\Delta G = \Delta H – T\Delta S$).

9.2 Thermodynamics of Defects

Thermodynamics principles can be used to get idea about equilibrium concentration of various types of defects in otherwise perfect crystalline solids. Here we present how to find equilibrium concentration of vacancies. The approach is to balance the energy required to create the vacancies and increase in entropy of the crystal due to distribution of these vacancies. Again it is the free energy which controls the situation.

Suppose there are N atoms in a perfect crystal. n_v atoms are removed from the lattice points and moved to the surface. This is now the number of vacancies.

Hence, the number of moles of vacancies = n_v/N_a

where N_a is the Avogadro number. Total free energy change of the crystal would be

$$\begin{aligned} \Delta G &= \text{Free energy of formation of vacancies} + \text{Free energy of mixing} \\ &= (n_v/N_a) \times \Delta G_v + \Delta G^M \end{aligned} \tag{9.6}$$

Where ΔG_v is the free energy of formation of vacancies per mole.

If we assume ideal solution, the free energy of mixing would be

$$\Delta G^M = -T\Delta S^M$$

Therefore,

$$\Delta G = (n_v/N_a) \times \Delta G_v - T\Delta S^M \tag{9.7}$$

Now we use Boltzman equation to find entropy of mixing,

$$\Delta S^M = kln\Omega$$

where $k = R/N_a$
Here $\Omega = [(N + n_v)!/(N!) \times (n_v!)]$
Using Stirling's approximation

$$\begin{aligned} ln\Omega &= ln\left[(N + n_v)!/(N!) \times (n_v!)\right] \\ &= [(N + n_v)ln(N + n_v) - (N + n_v)] - [NlnN – N] - [n_v lnn_v - n_v] \\ &= (N + n_v)ln(N + n_v) - NlnN - n_v lnn_v \end{aligned}$$

Since

$$\Delta G = (n_v/N_a) \times \Delta G_v - T(R/N_a)ln\Omega \tag{9.8}$$

$$\begin{aligned} N_a \times \Delta G &= n_v \times \Delta G_v - RTln\Omega \\ &= n_v \times \Delta G_v - RT\left[(N + n_v)ln(N + n_v) - NlnN - n_v lnn_v\right] \end{aligned}$$

Now we want to find the minima of ΔG. So we differentiate w.r.t. n_v

$$\begin{aligned} N_a \times \partial(\Delta G)/\partial n_v &= \Delta G_v - RT\left[(N + n_v)/(N + n_v) + ln(N + n_v)\right. \\ &\quad \left. - n_v/n_v - lnn_v\right] \\ &= \Delta G_v - RT\left[ln(N + n_v) – lnn_v\right] \\ &= \Delta G_v + RTln\left[n_v/(N + n_v)\right] \end{aligned}$$

$$\begin{aligned} \text{Putting} \quad \partial(\Delta G)/\partial n_v &= 0 \\ \text{We get} \quad RTln\left[n_v/(N + n_v)\right] &= -\Delta G_v \end{aligned}$$

Since the mole fraction of vacancies is $X_v = [n_v/(N + n_v)]$
We get

$$RTlnX_v = -\Delta G_v$$

On rearranging,

$$X_v = e^{\frac{-\Delta G_v}{RT}} \tag{9.9}$$

Thus, using the free energy of vacancy formation and free energy of mixing, we get expression for equilibrium concentration of vacancies.

As we know

$$\Delta G_v = \Delta H_v - T\Delta S_v$$

where ΔH_v is the molar enthalpy of vacancy formation and ΔS_v is the molar entropy of vacancy formation. Since entropy change on vacancy formation is negligible, we generally write

$$X_v = e^{\frac{-\Delta H_v}{RT}} \tag{9.10}$$

This is the expression generally found in the books of solid state physics for the equilibrium concentration of vacancies as a function of temperature. At low temperature, this fraction would be very low. However, it increases with temperature and close to the melting point, it could reach around 1%. Samples quenched from high temperature will have higher concentration of vacancies termed as quenched-in vacancies. Because of the quenched-in vacancies, the diffusion rates in quenched samples are significantly higher.

The concentration of other point defects, such as interstitials, could also be treated in a similar way.

9.3 Thermodynamics of Phase Transformations

The simplest type of phase transformation is the one that does not involve any change in composition. Such transformations occur in a single-component system and may include condensation of vapors, freezing of liquid, allotropic transformations, etc. All these have been discussed under the title ‘Phase equilibria in one component system’.

Let us consider solidification of a pure component.

Above the freezing temperature (which would be same as the melting temperature, T_m, under the equilibrium conditions), any fluctuation of atomic arrangement in the liquid phase resembling that of the solid would increase the free energy of the system. Hence, these fluctuations are unstable and dissolve back into the liquid. As seen in Figure 9.1, at the freezing point, both phases are equilibrium phases and have same Gibbs free energy. There is no decrease in Gibbs free energy and hence no driving force for the formation of the solid. If a fluctuation in the liquid produces a small region of the solid phase (embryo), such a fluctuation would also be stable since there is no increase in the volume free energy.

However, now we have to consider the interface between the liquid phase and the new solid phase. This interface has a surface energy associated with it. Due to this surface energy, the change in Gibbs free energy of a volume of liquid into a volume of solid is positive at the freezing point. Therefore, we require undercooling of the liquid before the solid phase could form.

For calculation purposes, we assume that a small, spherical solid particle forms in the under-cooled liquid. Due to the undercooling, the volume free energy change,

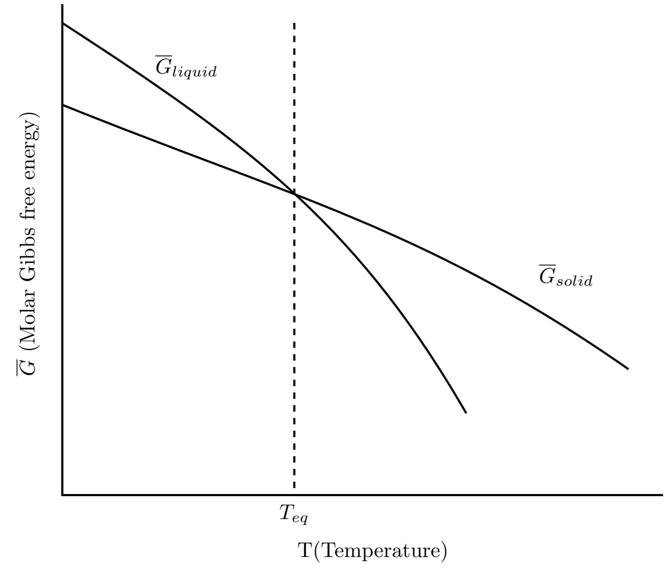


Figure 9.1: Free energy of solid and liquid phase of a pure component as a function of temperature at constant pressure.

ΔG_f, is negative, but the new surface created increases energy. ΔG_f is the volume free energy (per unit volume) and γ_S is the surface energy (per unit area).

The total change in Gibbs free energy, ΔG, when a solid sphere of radius 'r' forms:

$$\Delta G = (4\pi/3)r^3(\Delta G_f) + (4\pi)r^2\gamma_S \tag{9.11}$$

The change in the Gibbs free energy, ΔG, as a function of 'r' is shown in Figure 9.2. There are two terms, one is volume term (involving r^3) which is negative and the other is area term (involving r^2) which is positive. When 'r' is very small, the surface term dominates and the sign of the free energy change is positive.

If the solid region is large enough, the decrease in the free energy due to the volume of the new phase will exceed the increase in the free energy due to the creation of new surface. In such a case, the change in free energy will be negative and the nucleus of the solid phase will be stable.

Differentiating with respect to radius and setting the result equal to zero, the critical radius for the initiation of the transformation is obtained.

$$r_c = -2(\gamma_S)/(\Delta G_f) \tag{9.12}$$

This is the size of a fluctuation where the Gibbs free energy accompanying the formation of the solid begins to decrease. Substituting the value of this critical radius into Equation 9.11, we get the critical activation energy which must be overcome in order that the fluctuation can grow.

$$\Delta G_c = (16\pi)\gamma_S^3/(3)(\Delta G_f)^2 \tag{9.13}$$

For the estimation of the value of ΔG_f, we use the following approach.

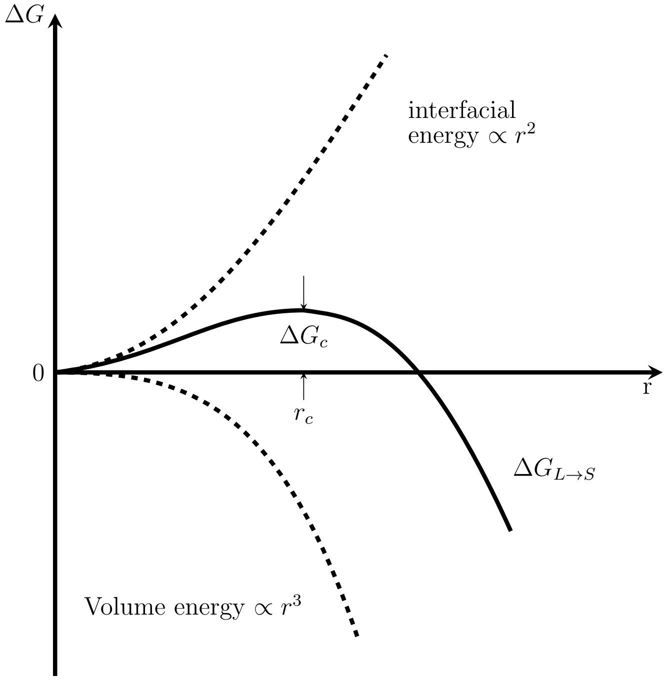


Figure 9.2: Change in volume free energy and surface energy as a function of radius of the embryo

The free energy of liquid and solid phase can be written as

$$\begin{aligned} G_l &= H_l - TS_l \\ G_s &= H_s - TS_s \end{aligned}$$

At equilibrium temperature, T_m , The difference in the free energies of solid and liquid is zero

$$\begin{aligned} \Delta G_f &= G_s - G_l = (H_s - H_l) - T_m(S_s - S_l) \\ &= \Delta H_f - T_m \Delta S_f = 0 \end{aligned}$$

Which means $\Delta S_f = \Delta H_f / T_m$
Putting this value,

$$\begin{aligned} \Delta G_f &= \Delta H_f - T(\Delta H_f / T_m) \\ &= \Delta H_f (1 - T/T_m) \end{aligned}$$

$$\Delta G_f = (\Delta H_f / T_m)\Delta T \tag{9.14}$$

Or

$$\Delta G_f \propto \Delta T$$

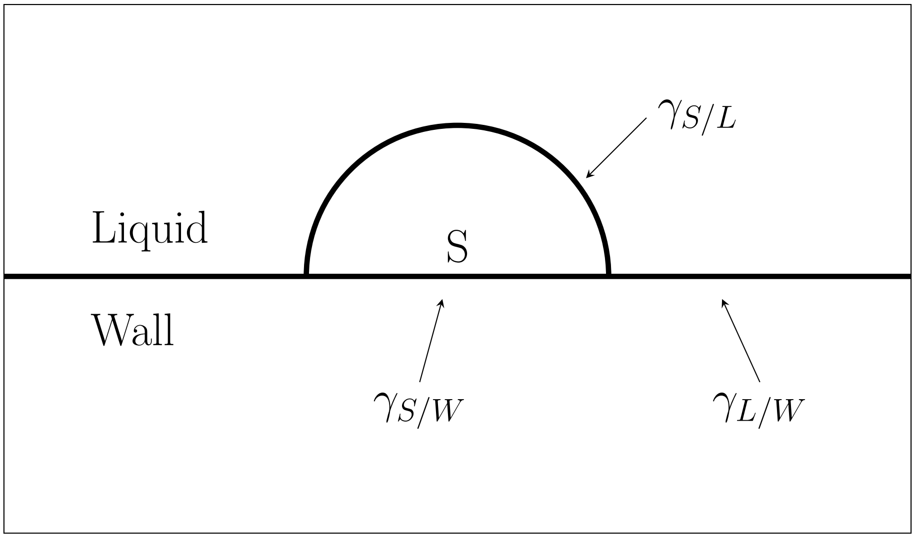


Figure 9.3: The nucleation of solid on the wall of the mold containing liquid

This means that the larger the undercooling (ΔT), the larger is the magnitude of the value of ΔG_f, and hence, the smaller is the size of the new solid phase that can grow into a stable particle.

Note the cubic dependence of critical activation energy on the surface free energy in Equation 9.13.

9.3.1 Homogeneous nucleation

In case of homogeneous nucleation, the solid phase may form at any of the sites within the liquid. However, due to surface energy, a large undercooling will be required before stable nuclei form in case of homogeneous nucleation.

9.3.2 Heterogeneous nucleation

The most common nucleation method is by heterogeneous nucleation, which means that the initiation of the solid occurs at specific sites. While dispersed solid particles may provide such sites, it is highly likely that the nucleation of the solid phase starts on the walls of the container of the liquid.

Heterogeneous nucleation is much more frequent because the energy barrier to the formation of the solid is reduced at such sites. For example, consider the nucleation of a solid on the wall of the vessel containing the liquid phase as shown in Figure 9.3.

There are now two variations. First is the shape of the nucleus as constrained by the wall; it will be a part of sphere, such as hemisphere. Secondly, and more importantly, the wall has its surface in contact with the liquid having its own surface energy. When the solid phase nucleates on the wall, the wall– liquid surface is replaced with the wall - solid surface. The wall– solid surface energy is usually less than that of the wall– liquid, and therefore, there is an energetic advantage for the 'S' phase to form there. This effectively reduces the free energy barrier to nucleation, ΔG_c, allowing for the formation of the new phase at substantially less undercooling. Let us calculate this effect.

If a hemisphere nucleated heterogeneously is formed on the wall of the vessel which contains the liquid, we write the following for the energy changes:

$$\Delta G = (2\pi/3)r^3(\Delta G_f) + (2\pi)r^2\gamma_{S/L} + \pi r^2(\gamma_{S/W} - \gamma_{L/W}) \tag{9.15}$$

From this, we get the critical radius in heterogeneous nucleation as

$$r_c = -(2\gamma_{S/L} + \gamma_{S/W} - \gamma_{L/W})/(\Delta G_f) \tag{9.16}$$

and the energy barrier as

$$\Delta G_c = (\pi)(2\gamma_{S/L} + \gamma_{S/W} - \gamma_{L/W})^3/(3)(\Delta G_f)^2 \tag{9.17}$$

These values may be compared with the critical radius and energy barrier in homogeneous case:

$$r_c = -2(\gamma_{S/L})/(\Delta G_f)$$

$$\Delta G_c = (16\pi)\gamma_{S/L}^3/(3)(\Delta G_f)^2$$

If the surface energy '$\gamma_{S/W}$' equals that of the surface energy '$\gamma_{S/L}$' , there is no particular advantage to form on the wall. If, however, $\gamma_{L/W} > \gamma_{S/W}$, there is a smaller barrier for the heterogeneous formation of the solid phase on the wall of the vessel.

The role of heterogeneous nucleation lies in the value of the energy barrier which appears in exponential expression for the rate of nucleation.

$$N_c = fexp(-\Delta G_c/RT)$$

Hence, small changes in the magnitude of the barrier to nucleation result in large effect on the rate of transformation. If the solid phase and 'W' have similar structures, $\gamma_{S/W}$ will be very low. This happens when we make Spheroidal Graphitic (SG) Iron or Nodular Cast Iron where Mg or Ce is added in molten iron to help in nucleation of graphite.

A common technique in growing crystals is seeding which helps in growth of crystals where spontaneous homogeneous nucleation is difficult to occur.

Epitaxial growth refers to growth of crystals on a pre-existing surface whereby growth will occur in a particular crystal direction.

Artificial rain is caused by cloud seeding, where substances are introduced into the clouds to help in precipitation. A common substance used is silver iodide since it has crystal structure similar to ice.

A similar effect can be noted for other interfacial defects such as grain boundaries in solid– solid phase transformations as well as defects that have strain energies associated with them (e.g., dislocations). In the case of dislocations, the new phase decreases the local strain energy, thereby effectively lowering the barrier to nucleation.

Summary

- Adsorption is the tendency of the system to decrease its free energy by readjusting the distribution of solute. The entropy factor tends to make the distribution uniform while the enthalpy factor tends to have non-uniform distribution. The resultant distribution is defined by the change in free energy. If a component decreases the surface energy, it will go to the surface. If the component increases the surface energy, it will remain below the surface.

- Using the free energy of vacancy formation and the free energy of mixing, we get expression for the equilibrium concentration of vacancies.

- The beginning of a new phase is opposed by the energy of the newly created surface. In case of homogeneous nucleation, this hurdle is overcome by large undercooling. In case of heterogeneous nucleation, the surface energy requirement may be reduced as, instead of creating a new surface, we are now replacing an existing surface with a new surface. The effect could be dramatic if the structure of the nucleating surface is similar to the existing surface.

Practice Problems

1. Evaluate the following statements using thermodynamic reasoning.

    i. Vacancies are defects and we cannot have them in a solid in equilibrium state.
    ii. A solution may have difference in the concentration of solute in various regions.
    iii. The phenomenon of adsorption is a manifestation of system's tendency to decrease its free energy.
    iv. The structure of surface available for nucleation of a solid in a melt is important.
    v. Very small embryos cannot act as nuclei for growth of a solid from the melt.
    vi. A smooth wall mold kept in vacuum will result in large grains of solid.
    vii. A solute may avoid surface region to decrease free energy of the solution.
    viii. A certain number of point defects may increase the stability of a solid.
    ix. Statistically there are many regions resembling solid in a liquid (just below freezing temperature) but most of them cannot grow.
    x. A chilled carbonated drink starts rapid bubbling when we add salt in it.
    xi. Heterogeneous nucleation could be more effective if the crystal structure of available surface matches the structure of solid being solidified.

xii. In a solution we may have solute depleted surface layer.

xiii. In a given solid, vacancy concentration increases very rapidly and we may get 20% close to the melting point.

xiv. We could attain a high degree of under-cooling if a melt is kept in a polished container under vacuum.

xv. Entropy favors random mixing. Yet we may observe that surface has more solute than the bulk. This effect diminishes as temperature increases.

xvi. Mg or Ce is added in molten cast iron to make SG Iron.

xvii. In a given metal sample, you may find much higher concentration of vacancies.

2. Write down 5 most common mathematical relations in Materials Thermodynamics briefly describing their uses.

3. Following information about pure Fe is available.

   Low temperature phase α (bcc) transforms to γ(fcc) at 910 °C. γ(fcc) transforms to δ(bcc) at 1490 °C. Normal melting point is 1540 °C.

   i. Write an expression for enthalpy and entropy of Fe vapors at T.
   ii. Estimate the enthalpy of melting of pure Fe.
   iii. Estimate entropy change when α (bcc) transforms to γ(fcc).
   iv. Draw the phase diagram of pure Fe.
   v. Describe the extraction of Fe from its ore.

4. Given that variation of vacancy concentration with temperature is given by

$$X_v = e^{\frac{-\Delta H_v}{RT}}$$

   i. Propose a method to find ΔH_v
   ii. Use some reasonable value of ΔH_v for any metal
   iii. Calculate X_v at 0.1T$_m$ and 0.9T$_m$ where T$_m$ is the melting point

   Comment on the rate of phase transformation in a quenched metal and a slowly cooled metal.

5. Calculate the size of the critical radius and the activation energy barrier when solid nickel forms by homogeneous nucleation of the super cooled liquid at 1000 °C.

   ΔH for freezing is 2756 J/cm^3

   T_m for Ni is 1453 °C

   $\gamma_{S/L} = 255 \times 10^{(-7)}$ J/cm^2

i. Ni is FCC with lattice parameter 3.5167 °A . Calculate number of atoms in the critical nucleus.

ii. We have some surface (W) available for heterogeneous nucleation. Calculate the critical radius and the activation energy barrier if

$$\begin{aligned}\gamma_{W/L} &= 250 \times 10^{(-7)} \quad J/cm^2 \\ \gamma_{W/S} &= 50 \times 10^{(-7)} \quad J/cm^2\end{aligned}$$

Bibliography

[1] D. R. Askeland, P. P. Fulay, and W. J. Wright, *The Science and Engineering of Materials*. Stamford: Cengage Learning, 6 ed., 2010.

[2] P. W. Atkins and J. de Paula, *Physical Chemistry*. Oxford University Press, 7 ed., 2001.

[3] S. K. Bose and S. K. Roy, *Principles of Metallurgical Thermodynamics*. IIM Series in Metallurgy and Materials Science, India: Universities Press, 2014.

[4] L. S. Darken and R. W. Gurry, *Physical Chemistry of Metals*. New York: McGrawHill, 1953.

[5] *Thermodynamics in Materials Science*. New York: McGrawHill, 1993.

[6] O. F. Devereux, *Topics in Metallurgical Thermodynamics*. New York: John Wiley, 1983.

[7] S. M. Eugen, *An Introduction to Aspects of Thermodynamics and Kinetics Relevant to Materials Science*. Elsevier, 3 ed., 2007.

[8] G. R. Fitterer, ed., *Applications of Fundamental Thermodynamics to Metallurgical Processes*. Gordon and Breach, 1967.

[9] D. Gaskell and D. E. Laughlin, *Introduction to the Thermodynamics of Materials*. Boca Raton, FL: Taylor & Francis, CRC Press, 6 ed., 2018.

[10] A. Ghosh, *Textbook of Materials and Metallurgical Thermodynamics*. Prentice Hall of India, 2002.

[11] J. W. Gibbs, *The Collected Work, Volume I Thermodynamics*. Yale University Press, 1948.

[12] A. R. H. Goodwin, K. N. Marsh, and W. A. Wakeham, eds., *Measurement of the Thermodynamic Properties of Single Phases*. Amsterdam: Elsevier Science, 2003.

[13] E. A. Guggenheim, *Thermodynamics: An Advanced Treatment for Chemists and Physicists*. Amsterdam: North-Holland, 7 ed., 1985.

[14] T. L. Hill, *Introduction to Statistical Thermodynamics.* New York: Dover Publications, 1986.

[15] M. Hillert, *Phase Equilibria, Phase Diagrams and Phase Transformations.* Cambridge: Cambridge University Press, 1998.

[16] M. Hillert and M. Selleby, *Computerized Thermodynamics for Materials Scientists and Engineers.* Stockholm: KTH, 2013.

[17] J. M. Howe, *Interfaces in Materials.* New York: John Wiley & Sons, 1997.

[18] R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelly, *Selected Values of Thermodynamic Properties of Metals and Alloys.* New York: John Wiley, 1963.

[19] Q. Jiang and Z. Wen, *Thermodynamics of Materials.* Springer-Verlag, 2011.

[20] O. Kubaschewski, C. B. Alcock, and P. J. Spencer, *Materials Thermochemistry.* Oxford: Pergamon Press, 6 ed., 1993.

[21] G. N. Lewis and M. Randall, *Thermodynamics and the free energy of chemical substances.* New York: McGraw-Hill, 1923.

[22] C. H. P. Lupis, *Chemical Thermodynamics of Materials.* New York: North-Holland, 1983.

[23] R. W. Cahn and P. Haasen, eds., *Physical Metallurgy*, vol. 1. Amsterdam: Elsevier Science BV., 4 ed., 1996.

[24] A. D. Pelton, *Phase diagrams.* Vol. 1 of Cahn and Haasen [23], 4 ed., 1996.

[25] D. V. Ragone, *Thermodynamics of Materials.* Wiley, 1995.

[26] F. D. Rossini, *Chemical Thermodynamics.* Chichester: John Wiley & Sons, 1950.

[27] S. Stolen and T. Grande, *Chemical Thermodynamics of Materials.* Sussex: John Wiley, 2004.

[28] D. Surovtseva and K. Kannoorpatti, *Benefits and drawbacks of pourbaix diagram, Annual Conference of the Australasian Corrosion Association (ACA 2014).* September 2014.

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