Problems in Metallurgical Thermodynamics and Kinetics
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Publisher at Pergamon Press
Problems in Metallurgical Thermodynamics and Kinetics

BY

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DEDICATED TO

Professor Baldeva Upadhyaya
Thermodynamics and kinetics are important core subjects in metallurgy, and they invariably involve calculations. The standard texts dealing with the above lean heavily on the theoretical concepts; the practical applications of these are left to the individual. The present book is intended to mitigate the above handicap, and the authors' aim has been to provide an illustration of the calculations encountered in the study of metallurgical thermodynamics and kinetics. It is divided into nine chapters, and each contains solved numerical examples - both basic and applied - preceded by a comprehensive account of the theory. In presenting the theory, the aim has not been to elaborate it but to present the same in a lucid and instructive style. A set of unsolved numerical examples (with answers) are given at the end of each chapter. The numerical problems have been drawn from a wide range of metallurgical processes. This is intentional, so that students may accept thermodynamics and kinetics as essential core subjects, and not as peripheral academic additions. Moreover, the exercises have been graded in such a manner that both undergraduate and postgraduate students at universities, polytechnics and technical colleges can derive advantage.

It has been necessary to limit the section illustrative of reaction kinetics for reasons of ultimate size, and cost, of what is essentially a text for students. The choice has been made to examine chemically-controlled reaction kinetics in detail and to deal briefly with the kinetics of reactions controlled by transport phenomena.

In framing the problems, the authors have made use of publications by various research workers in the field of metallurgical thermodynamics and kinetics. The extensive bibliographies could not be incorporated in this book, but grateful acknowledgement is made of the assistance derived from them.

As at present, the change-over from traditional units to SI units is in an early stage, the numerical data of the examples and exercises have been given both in the traditional and SI units. However, only traditional units have
been used for solving the examples, and a similar procedure may be used for solving them, using SI units. Answers to the exercises are given in traditional units, and the conversion factors given in Appendix 2 may be used to calculate the answers in SI units.

The authors are grateful to Mr. D. W. Hopkins, M.Sc., F.I.M. for reading the manuscript and making valuable suggestions.

AUTHORS
### LIST OF SYMBOLS AND ABBREVIATIONS

#### 1. Symbols

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<th>Meaning</th>
<th>Traditional Units</th>
<th>SI Units</th>
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<tr>
<td>A</td>
<td>Arrhenius frequency factor; Molar Helmholtz free energy</td>
<td>cal/mole</td>
<td>J/mol</td>
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<tr>
<td>a</td>
<td>Activity (Raoultian)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>Concentration; Heat capacity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C_P</td>
<td>Molar heat capacity at constant pressure</td>
<td>cal/deg/mole</td>
<td>J/K/mol</td>
</tr>
<tr>
<td>ΔC_P</td>
<td>Change in heat capacity at constant pressure</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C_V</td>
<td>Molar heat capacity at constant volume</td>
<td>cal/deg/mole</td>
<td>J/K/mol</td>
</tr>
<tr>
<td>D</td>
<td>Diffusion coefficient</td>
<td>cm²/sec</td>
<td>m²/s</td>
</tr>
<tr>
<td>E</td>
<td>Activation energy; Electromotive force</td>
<td>cal/mole</td>
<td>J/mol</td>
</tr>
<tr>
<td></td>
<td></td>
<td>V</td>
<td>V</td>
</tr>
<tr>
<td>e_B</td>
<td>Interaction parameter of C on B, in which activity coefficient is relative to infinitely dilute, wt% standard state</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>Faraday's constant; Partition function</td>
<td></td>
<td></td>
</tr>
<tr>
<td>f</td>
<td>Fugacity; Activity coefficient (Henrian)</td>
<td>atm</td>
<td>N/m²</td>
</tr>
<tr>
<td>G</td>
<td>Molar Gibbs free energy</td>
<td>cal/mole</td>
<td>J/mol</td>
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<tr>
<td>ΔG</td>
<td>Free energy change</td>
<td></td>
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<tr>
<td>H</td>
<td>Molar enthalpy or heat content</td>
<td>cal/mole</td>
<td>J/mol</td>
</tr>
<tr>
<td>ΔH</td>
<td>Enthalpy change</td>
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<tr>
<td>h</td>
<td>Activity (Henrian); Planck's constant</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
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<tr>
<td>--------</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>Equilibrium constant; Henry's law constant</td>
<td></td>
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<tr>
<td>k</td>
<td>Rate constant</td>
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<tr>
<td>k</td>
<td>Boltzmann's constant</td>
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<td></td>
</tr>
<tr>
<td>M</td>
<td>Molecular weight</td>
<td></td>
<td></td>
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<tr>
<td>N</td>
<td>Avagadro's number</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n</td>
<td>Number of g-atoms or g-moles; Order of reaction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>Pressure; Probability or steric factor</td>
<td></td>
<td></td>
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<tr>
<td>p</td>
<td>Partial pressure</td>
<td></td>
<td></td>
</tr>
<tr>
<td>q</td>
<td>Heat absorbed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R</td>
<td>Gas constant</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>Molar entropy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ΔS</td>
<td>Entropy change</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S_A</td>
<td>Solubility of gas A in a metal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t</td>
<td>Time</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t_0.5</td>
<td>Half-life period</td>
<td></td>
<td></td>
</tr>
<tr>
<td>U</td>
<td>Internal energy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>Volume</td>
<td></td>
<td></td>
</tr>
<tr>
<td>v</td>
<td>Rate or velocity of a reaction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>w</td>
<td>Work done</td>
<td></td>
<td></td>
</tr>
<tr>
<td>x</td>
<td>Mole fraction or atom fraction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Z</td>
<td>Extensive molar thermodynamic property (e.g. H, S, G, etc.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Z_i</td>
<td>Partial molar thermodynamic property of component i</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ΔZ_M</td>
<td>Integral molar thermodynamic property of mixing</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
List of Symbols and Abbreviations

\( \bar{z}_M^i \) Partial molar thermodynamic property of mixing (or relative partial molar thermodynamic property) of component \( i \)

\( x_s^E \) Excess integral molar thermodynamic property of solution

\( x_s^E \) Excess partial molar thermodynamic property of component \( i \)

\( z \) Electrochemical valency

\( z_{AB} \) Number of collisions per sec between \( A \) and \( B \)

**Greek Letters**

\( \gamma \) Activity coefficient (Raoultian)

\( \gamma^0 \) Raoultian activity coefficient at infinite dilution

\( \epsilon \) Interaction parameter of \( C \) on \( B \), in which activity coefficient is relative to infinitely dilute, atom fraction standard state

\( \kappa \) Transmission coefficient

\( \mu \) Chemical potential cal/mole \( j/mol \)

\( \Sigma \) Summation operator

**Superscripts**

\( ^0 \) Standard value of the thermodynamic property (e.g. \( H^0, S^0, G^0 \), etc.)

\( ^\dagger \) Thermodynamic property associated with the formation of the activated complex of a reaction (e.g. \( \Delta H^\dagger, \Delta S^\dagger, \Delta G^\dagger \), etc.)

**Subscripts**

\( A \) of \( A \) (e.g. \( x_A \) = mole fraction of component \( A \))

\( f \) of fusion (e.g. \( \Delta H_f \) = heat of fusion)

\( s \) of sublimation (e.g. \( \Delta H_s \) = heat of sublimation)

\( T \) at temperature \( T \) kelvin (e.g. \( \Delta H_T^0 \) = standard enthalpy change at \( T \) kelvin)

\( v \) of vaporization (e.g. \( \Delta H_v \) = heat of vaporization)
List of Symbols and Abbreviations

Miscellaneous

< > Solid
{ } Liquid
( ) Gas

\((X)_{\text{slag}}\) X dissolved in the slag phase.

\([X]_{\text{metal}}\) X dissolved in the metal phase, the standard state of X being the pure substance

\([X]_{\text{metal, wt\%}}\) X dissolved in the metal phase, the standard state of X being the infinitely dilute, 1 wt\% solution of X in the specified metal

2. Abbreviations

\begin{align*}
\text{atm} & \quad \text{Atmosphere(s)} & \ln x & \quad \text{Natural logarithm of } x, \log_e x \\
\text{cal} & \quad \text{Calorie(s)} & \log x & \quad \text{Logarithm to the base 10 of } x, \log_{10} x \\
\text{c.c.} & \quad \text{Cubic centimetre(s)} & m & \quad \text{Metre(s)} \\
\degree C & \quad \text{Degree centigrade} & \min & \quad \text{Minute(s)} \\
\text{C} & \quad \text{Coulomb(s)} & \text{mV} & \quad \text{Millivolt(s)} \\
\text{dil} & \quad \text{Dilute} & N & \quad \text{Newton(s)} \\
\text{e.m.f.} & \quad \text{Electromotive force} & s & \quad \text{Second(s)} \\
\text{g} & \quad \text{Gramme(s)} & \sec & \quad " \\
\text{hr} & \quad \text{Hour(s)} & \text{s.s.} & \quad \text{Standard state} \\
J & \quad \text{Joule(s)} & V & \quad \text{Volt(s)} \\
kcal & \quad \text{Kilocalorie(s)} & \text{wt\%} & \quad \text{Weight percent} \\
kg & \quad \text{Kilogramme(s)} & \text{K} & \quad \text{Kelvin}
\end{align*}
CHAPTER 1

THE FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics has been expressed in many ways. Most of the definitions consist of a statement about 'energy' and its conservation, and the law could be stated as:

Energy can neither be created nor destroyed in a system of constant mass, although it may be converted from one form to another.

Consider a mass of gas contained in a cylinder fitted with a frictionless piston, and let the internal energy of this gaseous system be denoted by $U$. Suppose some external energy, $q$, in the form of heat or other energy is supplied to the system which, while absorbing this energy, performs the amount of work $w$. Then

$$\Delta U = q - w, \quad (1.1)$$

where $\Delta U$ is the increase in the internal energy of the system. The above equation can be regarded as the mathematical expression of the first law of thermodynamics.

The internal energy is a state function or state property. Therefore the change in the internal energy is characteristic of the initial and final states of the system, and does not depend on the path taken to bring about the change.

1.1 Heat Content or Enthalpy

If the volume of the system is maintained constant, then the system does no work, and Eq. (1.1) becomes

$$\Delta U = q. \quad (1.2)$$

For an infinitesimal change of state, Eq. (1.2) can be written as

$$dU = dq. \quad (1.3)$$
If the pressure, \( P \), is maintained constant, Eq. (1.1) becomes

\[
\Delta U = q - P \Delta V, \tag{1.4}
\]

where \( \Delta V \) is the volume change in the system. If the initial and final states of the above gaseous system are denoted by \( A \) and \( B \) respectively, Eq. (1.4) can be written as

\[
U_B - U_A = q - P(V_B - V_A),
\]

or

\[
q = (U_B + PV_B) - (U_A + PV_A). \tag{1.5}
\]

The term \( (U + PV) \) is called 'heat content' or 'enthalpy', \( H \), so that

\[
(U_B + PV_B) = H_B,
\]

and

\[
(U_A + PV_A) = H_A.
\]

Hence, from Eq. (1.5), we have

\[
q = H_B - H_A,
\]

or

\[
q = \Delta H. \tag{1.6}
\]

For an infinitesimal change of state, Eq. (1.6) becomes

\[
\delta q = dH^*. \tag{1.7}
\]

From Eq. (1.4) and (1.6) we have

\[
\Delta H = \Delta U + P \Delta V \tag{1.8}
\]

at a constant pressure.

* 'd' indicates the differential element of a state function, while 'δ' indicates the differential element of some quantity which is not a state function.
Enthalpy is an extensive property of the system, depending upon the amount of substances present in the system. If the reaction is exothermic $\Delta H$ is negative, and if the reaction is endothermic $\Delta H$ is positive. This sign convention has been used in this book. Also, like internal energy, enthalpy is a state function.

1.2 Heat Capacity

The heat capacity, $C$, of a system may be expressed as

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

where $q$ is the amount of heat added to or withdrawn from the system resulting in a temperature change of $\Delta T$. If the temperature change is infinitesimally small, then

$$C = \frac{\delta q}{\delta T}.$$  \hspace{1cm} (1.9)

At constant volume, Eq. (1.9) becomes

$$C_V = \left(\frac{\delta q}{\delta T}\right)_V.$$  \hspace{1cm} (1.10)

From Eq. (1.3) and (1.10) we have

$$C_V = \left(\frac{dU}{dT}\right)_V = \left(\frac{\delta q}{\delta T}\right)_V.$$  \hspace{1cm} (1.11)

At constant pressure, Eq. (1.9) becomes

$$C_p = \frac{\delta q}{\delta T}_p.$$  \hspace{1cm} (1.12)

From Eq. (1.7) and (1.12) we have

$$C_p = \left(\frac{\delta q}{\delta T}\right)_p = \left(\frac{dH}{dT}\right)_p.$$  \hspace{1cm} (1.13)

The above equation is called Kirchhoff's equation.

At this point we must differentiate between the extensive property of the
entire system and per mole of the system. For a system containing \( n \) moles, the value of the extensive property \( Z \) (such as \( H, C, \) etc.) for the entire system will be denoted as \( Z' \), and for one mole as \( Z \). Thus

\[
Z' = nZ
\]

and the Eq. (1.11) and (1.13) can be rewritten as

\[
C_V' = \left( \frac{dU'}{dT} \right)_V,
\]

or

\[
C_V = \left( \frac{dU}{dT} \right)_V.
\]

and

\[
C_P' = \left( \frac{dH'}{dT} \right)_P,
\]

or

\[
C_P = \left( \frac{dH}{dT} \right)_P.
\]

The heat capacity is also an extensive property of the system, depending on the amount of the substances present in the system. Usually, it is more convenient to use molar heat capacity.

1.3 Thermochemistry and its Application in Metallurgy

Thermochemistry is the study of heat effects accompanying chemical reactions, the formation of solutions and changes in the state of matter such as melting or vaporization, and other physico-chemical processes.

(1) Heat of Reaction

The heat of reaction is the heat evolved or absorbed when the reactants react completely to produce products. It could be expressed in terms of either per mole of any reactant or any product.

(2) Heat of Formation

The heat of formation per mole of a compound is the heat evolved or
absorbed (i.e. change in enthalpy) when one mole of the compound is formed from its constituent elements. Its value depends upon the temperature, pressure, and the chemical state of the reactants and products; and for this reason it is generally expressed in terms of 'standard heat of formation'.

The heat of formation of a compound from its elements in their standard states is called 'standard heat of formation'. The standard state of an element is the most stable form under the chosen standard conditions of temperature and pressure. Thus, the most commonly used standard state for a solid, liquid, and gas at a particular temperature is as follows:

- **solid**: the most stable form at 1 atmosphere pressure (101325 N/m²).
- **liquid**: the most stable form at 1 atmosphere pressure (101325 N/m²).
- **gas**: at 1 atmosphere pressure (101,325 N/m²).

The standard heat of formation of compounds is generally tabulated at 25°C (298 K). For a compound, say MO at 25°C (298 K) it is denoted by \( \Delta H^0_{298, \text{MO}} \). In the case of an element, say M, the standard heat of formation at 25°C, \( \Delta H^0_{298, \text{M}} \) could be regarded as the standard enthalpy or standard heat content of the element M at 25°C, \( H^0_{298, \text{M}} \). As a convention, a value of zero is assigned to the standard heat content of an element at 25°C. In the case of a compound, say NiO, the standard heat of formation at 25°C is -57,500 cal/mole. It means that 57,500 cal of heat is evolved when 1 mole of Ni at 25°C and 1 atm pressure reacts with \( \frac{1}{2} \) mole of O₂ at 25°C and 1 atm pressure to form 1 mole of NiO at 25°C and 1 atm pressure, according to the following reaction:

\[
\text{<Ni> + } \frac{1}{2}(\text{O}_2) = \text{<NiO>}. \tag{1.16}
\]

The standard enthalpy change of reaction (1.16) could be written as

\[
\Delta H^0_{298,(1.16)} = H^0_{298,\text{NiO}} - H^0_{298,\text{Ni}} - \frac{1}{2}H^0_{298,(\text{O}_2)}.
\]

Since \( H^0_{298,\text{Ni}} \) and \( H^0_{298,(\text{O}_2)} \) are equal to zero, we have

\[
\Delta H^0_{298,(1.16)} = H^0_{298,\text{NiO}}.
\]
Since the enthalpy change of reaction (1.16) is also equal to the heat of formation of one mole of \( \text{NiO} \), we have

\[
\Delta H_{298}^{\circ}, \text{NiO} = H_{298}^{\circ}, \text{NiO}
\]

Thus, the heat content of a compound or alloy in the standard state is equal to its standard heat of formation.

(3) **Heat of Combustion**

Heat of combustion of a substance is the enthalpy change when one mole of the substance is completely burnt in oxygen.

(4) **Heat of Solution**

When one substance dissolves in another, there will be a change in enthalpy. This is called the heat of solution, and depends on the concentration of the solution.

**Example 1.A**

Calculate the standard heat of reaction at 25\(^\circ\)C (298 K) and 1 atm pressure of

\[
3\text{FeO} + 2\text{Al} = \text{Al}_2\text{O}_3 + 3\text{Fe}
\]

in terms of per mole of \( \text{Al}_2\text{O}_3 \) formed, per mole of Fe formed, per mole of FeO reacted, per mole of Al reacted and per g of Fe formed.

Given:

\[
\Delta H_{298}^{\circ}, \text{FeO} = -63.3 \text{ kcal/mole ( } -264.84 \text{ kJ/mol) }.
\]

\[
\Delta H_{298}^{\circ}, \text{Al}_2\text{O}_3 = -400.0 \text{ kcal/mole ( } -1673.6 \text{ kJ/mol) }.
\]

Atomic weight of Fe = 56.

**Solution:**

\[
3\text{FeO} + 2\text{Al} = \text{Al}_2\text{O}_3 + 3\text{Fe}.
\]  

(1.A.1)
The standard heat of reaction of (I.A.1) at 25°C and 1 atm pressure, 
\[ \Delta H_{298}^{\circ}(\text{I.A.1}) \], can be written as

\[ \Delta H_{298}^{\circ}(\text{I.A.1}) = \sum H_{298}^{\circ}\text{product} - \sum H_{298}^{\circ}\text{reactant} \]

\[ = H_{298}^{\circ}\langle \text{Al}_2\text{O}_3\rangle + 3H_{298}^{\circ}\langle \text{Fe}\rangle - 3H_{298}^{\circ}\langle \text{FeO}\rangle - 2H_{298}^{\circ}\langle \text{Al}\rangle. \]

Since the standard heat content of a pure element is zero and the standard heat content of a compound is equal to its standard heat of formation, we have

\[ \Delta H_{298}^{\circ}(\text{I.A.1}) = \Delta H_{298}^{\circ}\langle \text{Al}_2\text{O}_3\rangle - 3\Delta H_{298}^{\circ}\langle \text{FeO}\rangle \]

\[ = -400.0 - (3x - 63.3) \]

\[ = -210.1 \text{ kcal.} \]

Thus, the standard heat of reaction of (I.A.1) is -210.1 kcal. In other words, when 3 moles of solid FeO react with 2 moles of solid Al at 25°C and 1 atm pressure, to form 1 mole of solid Al\(_2\)O\(_3\) and 3 moles of solid Fe at 25°C and 1 atm pressure, the heat of reaction is -210.1 kcal/mole of Al\(_2\)O\(_3\) formed. Since 3 moles of Fe are formed, the heat of reaction is 
\[ -210.1/3 = -70.03 \text{ kcal/mole of Fe formed.} \]

Similarly, the heat of reaction is -70.03 kcal/mole of FeO reacted and -105.05 kcal/mole of Al reacted. In order to calculate the heat of reaction per g of Fe formed, the heat of reaction per mole of Fe formed should be divided by its atomic weight. Hence, the heat of reaction is 
\[ -70.03/56 = -1.255 \text{ kcal/g of Fe formed.} \]

1.4 Hess's Law

The law states that the heat content change in a chemical reaction is the same whether it takes place in one or several stages, provided the temperature and either pressure or volume remain constant. The subsequent example illustrates the application of Hess's law in calculating the standard heat of formation of WO\(_3\).
Example 1.B

Calculate the standard heat of formation of solid \( \text{WO}_3 \) from solid \( \text{W} \) and \( \text{O}_2 \) gas at 25°C (298 K) and 1 atm pressure from the following data at 25°C (298 K) and 1 atm pressure:

\[
\begin{align*}
\text{\<W> + \(0_2\) = \<\text{WO}_2\> ; \Delta H^\circ_{298} = -134 \text{ kcal} \ (-560.66 \text{ kJ}).} \\
3\text{\<WO}_2\> + \(0_2\) = \<\text{W}_3\text{O}_8\> ; \Delta H^\circ_{298} = -131.5 \text{ kcal} \ (-550.20 \text{ kJ}).} \\
\text{\<W}_3\text{O}_8\> + \frac{1}{2}(0_2) = 3\text{\<WO}_3\> ; \Delta H^\circ_{298} = -66.5 \text{ kcal} \ (-278.24 \text{ kJ}).}
\end{align*}
\]

Solution: The problem consists of calculating the standard heat of the following reaction at 25°C and 1 atm pressure:

\[
\text{\<W> + \(\frac{3}{2}(0_2) = \<\text{WO}_3\>.} \quad (1. B.1)
\]

The Eq. (1. B.1) could be regarded as being made up of the following reactions:

\[
\begin{align*}
3\text{\<W> + 3}(0_2) & = 3\text{\<WO}_2>, \quad (1. B.2) \\
3\text{\<WO}_2> + (0_2) & = \text{\<W}_3\text{O}_8>, \quad (1. B.3) \\
\text{\<W}_3\text{O}_8> + \frac{1}{2}(0_2) & = 3\text{\<WO}_3>, \quad (1. B.4)
\end{align*}
\]

Adding (1.B.2), (1.B.3) and (1.B.4), we get the following:

\[
\text{3\<W> + \(\frac{9}{2}(0_2) = 3\text{\<WO}_3>.} \quad (1. B.5)
\]

According to Hess's law,

\[
\Delta H^\circ_{298, (1. B.5)} = \Delta H^\circ_{298, (1. B.2)} + \Delta H^\circ_{298, (1. B.3)} + \Delta H^\circ_{298, (1. B.4)}
\]

\[
= (3\times-134.0) + (-131.5) + (-66.5)
\]

\[
= -600.0 \text{ kcal.}
\]
Dividing the heat of reaction of Eq. (1.8.5) by 3, we get the heat of reaction of Eq. (1.8.1). Thus

\[ \Delta H_{298}^0 \text{(1.8.1)} = -200.0 \text{ kcal}. \]

Therefore, the standard heat of formation of solid WO₃ at 25°C and 1 atm pressure is -200.0 kcal/mole.

### 1.5 Variation of Enthalpy Change with Temperature

The standard enthalpy change of a reaction can be easily calculated at 25°C from the available data; but the kinetics of many reactions are not fast enough at 25°C for the changes to be complete in a measurable period of time. Therefore it often becomes necessary to find out the enthalpy change of the reactions at a higher temperature. Applying Eq. (1.5) for a chemical reaction occurring at a constant pressure, we have

\[ \frac{d(\Delta H^0)}{dT} = \Delta C_p. \] (1.18)

On integrating the Eq. (1.18) between the values of \( \Delta H^0_{T_1} \) and \( \Delta H^0_{T_2} \) at \( T_1 \) and \( T_2 \) K, we have

\[ \int_{\Delta H^0_{T_1}}^{\Delta H^0_{T_2}} d(\Delta H^0) = \int_{T_1}^{T_2} \Delta C_p \, dT, \]

or

\[ \Delta H^0_{T_2} - \Delta H^0_{T_1} = \int_{T_1}^{T_2} \Delta C_p \, dT, \]

or

\[ \Delta H^0_{T_2} = \Delta H^0_{T_1} + \int_{T_1}^{T_2} \Delta C_p \, dT, \] (1.19)
or \[ \Delta H^0_{T_2} = \Delta H^0_{T_1} + \int_{T_1}^{T_2} \left[ \Sigma C_P, \text{product} - \Sigma C_P, \text{reactant} \right] dT. \] (1.20)

Thus, if the standard enthalpy change of a reaction at a temperature is known, Eq. (1.20) could be applied to calculate the standard enthalpy change at some other temperature, as illustrated in the Example (1.C). If any transformation, e.g. melting, evaporation, etc. is taking place either in reactants or products, their enthalpy changes must be introduced into Eq. (1.20), as illustrated in the Example (1.D).

Example 1.C

Calculate the standard heat of formation of PbO from Pb and O2 at 227°C (500 K) from the following data:

\[ \Delta H^0_{298, \text{PbO}} = -52.4 \text{ kcal/mole (}-219.24 \text{ kJ/mol}). \]

\[ C_P, \text{PbO} = 10.6 + 4.0 \times 10^{-3} T \text{ cal/deg/mole } (44.35 + 16.74 \times 10^{-3} T \text{ J/K/mol}). \]

\[ C_P, \text{Pb} = 5.63 + 2.33 \times 10^{-3} T \text{ cal/deg/mole } (23.56 + 9.75 \times 10^{-3} T \text{ J/K/mol}). \]

\[ C_P, \text{O}_2 = 7.16 + 1.0 \times 10^{-3} T - 0.4 \times 10^5 T^{-2} \text{ cal/deg/mole } (29.96 + 4.184 \times 10^{-3} T - 1.67 \times 10^5 T^{-2} \text{ J/K/mol}). \]

Solution: For the reaction

\[ \text{Pb} + \frac{1}{2} \text{O}_2 = \text{PbO}, \]

we have \[ \Delta H^0_{298, (1.C.1)} = -52,400 \text{ cal}. \]

Applying Eq. (1.20), we have

\[ \Delta H^0_{500, (1.C.1)} = \Delta H^0_{298, (1.C.1)} + \int_{298}^{500} \left[ \Sigma C_P, \text{product} - \Sigma C_P, \text{reactant} \right] dT. \]
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\[ \Delta H_{298}^0(\text{C.I.1}) + \int_{298}^{500} \left[ C_p,\text{PbO} - C_p,\text{Pb} - \frac{1}{2} C_p,\text{O}_2 \right] dT \]

\[ = -52,400 + \int_{298}^{500} \left[ (10.6 + 4.0 \times 10^{-3} T) - (5.63 + 2.33 \times 10^{-3} T) \right. \]

\[ - \frac{1}{2} (7.16 + 1.0 \times 10^{-3} T - 0.4 \times 10^5 T^{-2}) \left. \right] dT \]

\[ = -52,400 + \int_{298}^{500} \left[ 1.39 + 1.17 \times 10^{-3} T + 0.2 \times 10^5 T^{-2} \right] dT \]

\[ = -52,400 + 1.39(500 - 298) + \frac{1.17 \times 10^{-3}}{2} (500^2 - 298^2) \]

\[ - 0.2 \times 10^5 \left( \frac{1}{500} - \frac{1}{298} \right) \]

\[ = -51,998 \text{ cal.} \]

The standard enthalpy change of reaction (1.C.1) at 227°C is -51,998 cal. In other words, the standard heat of formation of PbO at 227°C is -51,998 cal/mole.

Example 1.D

Calculate the standard heat of formation of solid PbO from liquid Pb and \( \text{O}_2 \) gas at 527°C (800 K). The melting point of lead is 327°C (600 K) and its latent heat of fusion is 1.15 kcal/mole (4.81 kJ/mol). The molar heat capacity at constant pressure of liquid Pb, \( C_p,\text{Pb} \), is 7.75 - 0.74 \( \times \) 10\(^{-3}\) T cal/deg/mole (32.43 - 3.10 \( \times \) 10\(^{-3}\) T J/K/mol). Use other data as given in the previous example.

Solution: The problem basically consists of calculating the standard enthalpy change of the reaction

\[ \{\text{Pb}\} + \frac{1}{2}(\text{O}_2) = \text{PbO} \] (1.D.1)
at 527°C from the standard enthalpy change of the reaction

\[ \text{<Pb>} + \frac{1}{2}(O_2) = \text{<PbO>} \quad (1.0.2) \]

at 25°C and heat capacity data. The present problem differs from the previous one in the sense that Pb is in liquid form at 527°C, in contrast to solid form at 25°C, and therefore enthalpy change of this transformation must be taken into account. The scheme of calculation would be somewhat as follows:

1. Calculate the standard enthalpy change of the reaction (1.0.2) at 25°C, \( \Delta H_{298}^{\circ},(1.0.2) \), which is the same as the standard heat of formation of PbO at 25°C.

2. Calculate the standard enthalpy change of the reaction (1.0.2) at 327°C, \( \Delta H_{500}^{\circ},(1.0.2) \), from \( \Delta H_{298}^{\circ},(1.0.2) \) and \( \Delta C_p,(1.0.2) \) values, using Eq. (1.20).

3. Calculate the standard enthalpy change of the reaction (1.0.1) at 327°C, \( \Delta H_{600}^{\circ},(1.0.1) \), with the help of the \( \Delta H^0 \) of the reaction

\[ \text{(Pb)} = \text{<Pb>} \quad (1.0.3) \]

at 327°C, i.e. the melting point of Pb, and that of the reaction (1.0.2) as calculated in step (2).

The addition and subtraction of the standard enthalpies of the reactions can only be done at the same temperature. Therefore the \( \Delta H^0 \) of the reaction (1.0.2) at 327°C should be added to that of the reaction (1.0.3) which takes place at 327°C. This explains the necessity of step (2).

4. Calculate the \( \Delta H^0 \) of the reaction (1.0.1) at 527°C, \( \Delta H_{800}^{\circ},(1.0.1) \), from the \( \Delta H_{600}^{\circ},(1.0.1) \) and \( \Delta C_p,(1.0.1) \) values, using Eq. (1.20). Care should be taken to consider \( C_p \) of liquid Pb while calculating \( \Delta C_p,(1.0.1) \) value.

Thus:

\[ \Delta H_{800}^{\circ},(1.0.1) = \Delta H_{298}^{\circ},(1.0.2) + \int_{298}^{800} \Delta C_p,(1.0.2) \, dT \]

\[ + \Delta H_{600}^{\circ},(1.0.3) + \int_{600}^{800} \Delta C_p,(1.0.1) \, dT \quad (1.0.4) \]
Now:

\[
\int_{298}^{600} \Delta C_{P,s}(1.0.2) \, dT = \int_{298}^{600} \left[ C_{P,s,<\text{PbO}>} - C_{P,s,<\text{Pb}>} - \frac{1}{2} C_{P,s,(O_2)} \right] \, dT
\]

\[
= \int_{298}^{600} \left[ (10.6 + 4.0 \times 10^{-3}T) - (5.63 + 2.33 \times 10^{-3}T) - \frac{1}{2}(7.16 + 1.0 \times 10^{-3}T - 0.4 \times 10^5 T^{-2}) \right] \, dT
\]

\[
= 1.39(600 - 298) + \frac{1.17 \times 10^{-3}}{2} (600^2 - 298^2)
\]

\[
-0.2 \times 10^5 \left[ \frac{1}{600} - \frac{1}{298} \right]
\]

\[
= 612.2.
\]

It is given that the latent heat of fusion of Pb is 1,150 cal/mole, i.e. the standard enthalpy change of the reaction <\text{Pb}> = {\text{Pb}} at 327°C is 1,150 cal/mole. In other words, the standard enthalpy change of the reaction (1.0.3) at 327°C, \( \Delta H^\circ_{600,(1.0.3)} \), is -1,150 cal.

Similarly,

\[
\int_{600}^{800} \Delta C_{P,s}(1.0.1) \, dT = \int_{600}^{800} \left[ C_{P,s,<\text{PbO}>} - C_{P,s,<\text{Pb}>} - \frac{1}{2} C_{P,s,(O_2)} \right] \, dT
\]

\[
= \int_{600}^{800} \left[ (10.6 + 4.0 \times 10^{-3}T) - (7.75 - 0.74 \times 10^5 T^{-2}) - \frac{1}{2}(7.16 + 1.0 \times 10^{-3}T - 0.4 \times 10^5 T^{-2}) \right] \, dT
\]

\[
= \int_{600}^{800} \left[ -0.73 + 4.24 \times 10^{-3}T + 0.2 \times 10^5 T^{-2} \right] \, dT
\]
Putting the appropriate values in Eq. (1.D.4), we have

\[ \Delta H^0_{600, (1.D.1)} = -52,400 + 612.20 - 1150 + 455.93 \]

\[ = -52,482 \text{ cal.} \]

1.6 Maximum Reaction Temperature: Flame Temperature

It is possible to consider a reaction taking place under adiabatic conditions so that no heat enters or leaves the system. For a constant pressure, this means that the enthalpy change will be zero. In such a reaction, the temperature of the system will change, so that the products will be at a different temperature from that of the reactants. If the enthalpy change is positive, i.e. heat is absorbed, the temperature of the adiabatic system will fall. In case the enthalpy change is negative, the temperature will rise during the course of the reaction. From a knowledge of heat of reaction and the variation of the heat capacities of the reactants and products with temperature, it is possible to calculate the final temperature of the system.

Such a type of treatment is useful in calculating the maximum flame temperature in connection with the combustion of fuels. Assuming that the process is adiabatic, the combustion of a fuel can be represented as

Fuel + Oxidant (at 298 K) \rightarrow\text{Combustion products (at a very high temperature, say } T_m)\]

However, the above reaction may be performed in two imaginary steps, i.e.
(1) Fuel + Oxidant (at 298 K) → Combustion products (at 298 K).

(2) Combustion products (at 298 K) → Combustion products (at $T_m$).

The reaction represented in step (1) will be always exothermic. The available thermal energy is then used to heat up the combustion products from 298 K to their final temperature $T_m$. Using Eq. (1.13), we have

$$ q = \int_{298}^{T_m} \Sigma C_p,_{product} \, dT, \quad (1.21) $$

where $q$ is the heat evolved in step (1) which can be found out from the standard enthalpy change value, and $\Sigma C_p,_{product}$ is the sum of the heat capacity at constant pressure of the combustion products. However, the actual flame temperature will be somewhat lower than that obtained by Eq. (1.21), because of heat losses.

**Example 1.6**

The combustion of acetylene fuel with nitrous oxide as oxidant at 25°C (298 K) is widely performed in flame emission spectrophotometry. Calculate the maximum temperature attained if the best mixture corresponds to the reaction

$$(\text{C}_2\text{H}_2) + 3(\text{N}_2\text{O}) = 2(\text{CO}) + (\text{H}_2\text{O}) + 3(\text{N}_2).$$

Assume that water is undissociated.

Given:

$$\Delta H^{0}_{298, (\text{C}_2\text{H}_2)} = 54.23 \text{ kcal/mole} (226.30 \text{ kJ/mol}).$$

$$\Delta H^{0}_{298, (\text{N}_2\text{O})} = 19.70 \text{ kcal/mole} (82.42 \text{ kJ/mol}).$$

$$\Delta H^{0}_{298, (\text{CO})} = -26.42 \text{ kcal/mole} (-110.64 \text{ kJ/mol}).$$

$$\Delta H^{0}_{298, (\text{H}_2\text{O})} = -57.80 \text{ kcal/mole} (-241.84 \text{ kJ/mol}).$$
\[ C_{P}(\text{CO}) = 6.8 + 1.0 \times 10^{-3} T - 0.11 \times 10^{5} T^{-2} \text{ cal/deg/mole} \\
(28.45 + 4.184 \times 10^{-3} T - 0.46 \times 10^{5} T^{-2} \text{ J/K/mol}). \]

\[ C_{P}(\text{H}_2\text{O}) = 7.17 + 2.56 \times 10^{-3} T + 0.08 \times 10^{5} T^{-2} \text{ cal/deg/mole} \\
(30.0 + 10.71 \times 10^{-3} T + 0.33 \times 10^{5} T^{-2} \text{ J/K/mol}). \]

\[ C_{P}(\text{N}_2) = 6.5 + 1.0 \times 10^{-3} T \text{ cal/deg/mole} \\
(27.20 + 4.184 \times 10^{-3} T \text{ J/K/mol}). \]

**Solution:**

The first step is to calculate the standard enthalpy change of the reaction

\[
(C_2\text{H}_2) + 3(\text{N}_2\text{O}) = 2(\text{CO}) + (\text{H}_2\text{O}) + 3(\text{N}_2) \tag{1.E.1}
\]

at 25°C. Thus, we have

\[
\Delta H_{298}^0 (\text{1.E.1}) = 2\Delta H_{298}^0 (\text{CO}) + \Delta H_{298}^0 (\text{H}_2\text{O}) - \Delta H_{298}^0 (C_2\text{H}_2) - 3\Delta H_{298}^0 (\text{N}_2\text{O})
\]

\[
= (2 \times -26.42) + (-57.80) - (54.23) - (3 \times 19.70)
\]

\[ = -223.97 \text{ kcal}. \]

In other words, 223.97 kcal of heat is evolved during the reaction (1.E.1), which is used to heat up 2 moles of CO, 1 mole of H\text{\textsubscript{2}}\text{O} and 3 moles of N\text{\textsubscript{2}} from 25°C to the final maximum temperature, say \(T_m\). Applying Eq. (1.21), we have

\[
\text{Heat evolved} = \int_{298}^{T_m} \sum C_{P,\text{product}} dT,
\]

or

\[
223970 = \int_{298}^{T_m} \left[ 2C_{P}(\text{CO}) + C_{P}(\text{H}_2\text{O}) + 3C_{P}(\text{N}_2) \right] dT
\]
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\[ \int_{298}^{T_m} \left[ (13.6 + 2.0 \times 10^{-3}T - 0.22 \times 10^6T^{-2}) + (7.17 + 2.56 \times 10^{-3}T + 0.08 \times 10^{5}T^{-2}) + (19.5 + 3.0 \times 10^{-3}T) \right] dT \]

\[ = \int_{298}^{T_m} \left[ 40.27 + 7.56 \times 10^{-3}T - 0.14 \times 10^5T^{-2} \right] dT \]

\[ = \left[ 40.27 T + 3.78 \times 10^{-3}T^2 + 0.14 \times 10^5T^{-1} \right]_{298}^{T_m} \]

\[ = 40.27 (T_m - 298) + 3.78 \times 10^{-3} (T_m^2 - 298^2) + 0.14 \times 10^5 \left( \frac{1}{T_m} - \frac{1}{298} \right) \]

\[ = 3.78 \times 10^{-3} T_m^2 + 40.27 T_m + 0.14 \times 10^5 T_m^{-1} - 12383. \]

Neglecting the \( T_m^{-1} \) term, we have

\[ 223970 = 3.78 \times 10^{-3} T_m^2 + 40.27 T_m - 12383, \]

or \[ 3.78 \times 10^{-3} T_m^2 + 40.27 T_m - 236353 = 0. \]

On solving the above equation in \( T_m \) and neglecting the negative value, it follows

\[ T_m = 4207 \text{ K}, \]

or \[ T_m = (4207 - 273)^{\circ}\text{C} \]

\[ = 3934^{\circ}\text{C}. \]

Thus, the maximum temperature attained is \( 3934^{\circ}\text{C}. \)
Exercises

1.1 The enthalpy changes for the following reactions are as follows:

\[
2B + 3H_2 + 3O_2 + \text{aq.} = 2H_3BO_3(\text{dil.sol}); \\
\Delta H^\circ_{298} = -512.8 \text{ kcal} (-2,146.6 \text{ kJ}).
\]

\[
B_2O_3 + 3H_2O(\lambda) + \text{aq.} = 2H_3BO_3(\text{dil.sol}) \\
\Delta H^\circ_{298} = -4.12 \text{ kcal} (-17.24 \text{ kJ}).
\]

\[
H_2 + \frac{1}{2}O_2 = H_2O(\lambda); \\
\Delta H^\circ_{298} = -68.73 \text{ kcal} (-287.57 \text{ kJ}).
\]

Calculate the standard heat of formation of \(B_2O_3\) in terms of per mole of \(B_2O_3\) and per g of \(B_2O_3\). Atomic weights of B and O are 10.82 and 16.0 respectively.

1.2 Calcium carbide is considered to be a potential fuel in a basic oxygen converter and would be expected to burn into CaO and CO or CO\(_2\), depending upon the conditions. If the heat required to raise steel scrap to 1600°C (1873 K) is 333 kcal/kg (1,393.27 kJ/kg) of scrap, calculate how many kg of steel scrap can be charged per 1000 kg of CaC\(_2\) when

(i) all CaC\(_2\) is consumed to form CO,

(ii) all CaC\(_2\) is consumed to form CO\(_2\), and

(iii) 60% of CaC\(_2\) is utilized to produce CO\(_2\) and rest for CO.

Assume that reaction takes place at 25°C (298 K).
Given:  

(i)  \[ \Delta H_{298}^{\circ} \text{CaC}_2 = -14.1 \text{ kcal/mole (-58.99 kJ/mol)} \].  

(ii)  \[ \Delta H_{298}^{\circ} \text{CaO} = -151.8 \text{ kcal/mole (-635.13 kJ/mol)} \].  

(iii)  \[ \Delta H_{298}^{\circ} \text{CO} = -26.42 \text{ kcal/mole (-110.54 kJ/mol)} \].  

(iv)  \[ \Delta H_{298}^{\circ} \text{CO}_2 = -94.05 \text{ kcal/mole (-393.50 kJ/mol)} \].  

(v)  Atomic weights of Ca and C are 40 and 12 respectively.

1.3  \( \text{Fe}_2\text{O}_3, \text{PbO} \) and \( \text{Cu}_2\text{O} \) present in a dead roasted tin ore react according to the following equations, during leaching with 1.11 M \( \text{HCl} (= \text{HCl}(50 \text{H}_2\text{O})) \) at \( 25^\circ\text{C (298 K)} \)

\[
\text{Fe}_2\text{O}_3 + 6\text{HCl}(50 \text{H}_2\text{O}) = 2\text{FeCl}_3(150 \text{H}_2\text{O}) + 3\text{H}_2\text{O},
\]

\[
\text{PbO} + 2\text{HCl}(50 \text{H}_2\text{O}) = \text{PbCl}_2(100 \text{H}_2\text{O}) + \text{H}_2\text{O},
\]

\[
\text{Cu}_2\text{O} + 2\text{HCl}(50 \text{H}_2\text{O}) = 2\text{CuCl}(50 \text{H}_2\text{O}) + \text{H}_2\text{O}.
\]

Calculate the heat of the leaching process at \( 25^\circ\text{C (298 K)} \) per 100 kg of ore, assuming that the \( \text{SiO}_2 \) and \( \text{SnO}_2 \) present in the ore are unaffected during leaching.

Given: (i)  Composition of dead roasted tin ore is 10\% \( \text{Fe}_2\text{O}_3 \), 5\% \( \text{PbO} \), 5\% \( \text{Cu}_2\text{O} \), 15\% \( \text{SiO}_2 \) and rest \( \text{SnO}_2 \).

(ii)  Standard heats of formation of \( \text{Fe}_2\text{O}_3, \text{Cu}_2\text{O}, \text{PbO}, \text{FeCl}_3(150 \text{H}_2\text{O}), \text{CuCl}(50 \text{H}_2\text{O}), \text{PbCl}_2(100 \text{H}_2\text{O}), \text{HCl}(50 \text{H}_2\text{O}) \) at \( 25^\circ\text{C} \) are -196.3, -40.0, -52.4, -92.0, -30.9, -83.2, -68.32 and -17.4 kcal/mole \((-821.3, -167.4, -218.2, -394.9, -129.3, -348.1, -285.8 \) and -72.8 kJ/mol) respectively.
1.4 The reduction of iron oxide in the blast furnace proceeds according to the following reactions:

\[ 3\text{Fe}_2\text{O}_3 + \text{CO} = 2\text{Fe}_3\text{O}_4 + \text{CO}_2; \]
\[ \Delta H^0_{298} = -12.7 \text{ kcal} \ (\sim -53.1 \text{ kJ}). \]

\[ \text{Fe}_3\text{O}_4 + \text{CO} = 3\text{FeO} + \text{CO}_2; \]
\[ \Delta H^0_{298} = +9.8 \text{ kcal} \ (\sim +41.0 \text{ kJ}). \]

\[ \text{FeO} + \text{CO} = \text{Fe} + \text{CO}_2; \]
\[ \Delta H^0_{298} = -4.4 \text{ kcal} \ (\sim -18.4 \text{ kJ}). \]

Calculate \( \Delta H^0_{298} \) for the reaction

\[ \text{Fe}_2\text{O}_3 + 3\text{CO} = 2\text{Fe} + 3\text{CO}_2. \]

1.5 Calculate the heat of reaction of the Hall-Heroult process, viz.

\[ \text{Al}_2\text{O}_3 + 3\text{C} = 3\text{CO} + 2\text{Al} \]
at 25°C (298 K) from the following data:

\[ 2\text{Al} + \frac{3}{2}\text{O}_2 = \text{Al}_2\text{O}_3; \]
\[ \Delta H^0_{298} = -7,400 \text{ cal} \ (\sim -30,962 \text{ J}) \text{ per g of Al reacted.} \]

\[ \text{C} + \frac{1}{2}\text{O}_2 = \text{CO}; \]
\[ \Delta H^0_{298} = -2,250 \text{ cal} \ (\sim -9,414 \text{ J}) \text{ per g of C reacted.} \]

Atomic weights of Al and C are 27 and 12 respectively.
1.6 Calculate (a) the enthalphy of NiO at 1707°C (1980 K), (b) the heat required to raise the temperature of 1 mole of NiO from 25°C (298 K) to 1707°C (1980 K).

Given: \( \Delta H_{298}^{0} \text{NiO} = -57.5 \text{ kcal/mole} \) (-240.6 kJ/mol).
\[ C_{p, \text{NiO}} = 12.91 \text{ cal/deg/mole} \) (54.01 J/K/mol).

1.7 Calculate the heat of reaction of chlorination of zirconium oxide at 25°C (298 K) and 777°C (1050 K), according to the following reaction:

\[ \text{ZrO}_2 + 2\text{Cl}_2 + \text{C} \rightarrow \text{ZrCl}_4 + \text{CO}_2. \]

Given: For \( \text{ZrCl}_4 \): \( \Delta H_{298}^{0} = -234.7 \text{ kcal/mole} \) (-931.98 kJ/mol).
\[ C_{p} = 31.92 - 2.91 \times 10^{-5} T^{-2} \text{ cal/deg/mole} \)
(133.55 - 12.18 \times 10^{-5} T^{-2} J/K/mol).

For \( \text{CO}_2 \): \( \Delta H_{298}^{0} = -94.05 \text{ kcal/mole} \) (-393.50 kJ/mol)
\[ C_{p} = 10.55 + 2.16 \times 10^{-3} T - 2.05 \times 10^{-5} T^{-2} \text{ cal/deg/mole} \)
(44.14 + 9.04 \times 10^{-3} T - 8.58 \times 10^{-5} T^{-2} J/K/mol).

For \( \text{ZrO}_2 \): \( \Delta H_{298}^{0} = -259.5 \text{ kcal/mole} \) (-1085.75 kJ/mol).
\[ C_{p} = 16.64 + 1.80 \times 10^{-3} T - 3.36 \times 10^{-5} T^{-2} \text{ cal/deg/mole} \)
(69.62 + 7.53 \times 10^{-3} T - 14.06 \times 10^{-5} T^{-2} J/K/mol).

For \( \text{Cl}_2 \): \[ C_{p} = 8.82 + 0.06 \times 10^{-3} T - 0.68 \times 10^{-5} T^{-2} \text{ cal/deg/mole} \)
(36.90 - 0.25 \times 10^{-3} T - 2.85 \times 10^{-5} T^{-2} J/K/mol).

For \( \text{C} \): \[ C_{p} = 4.10 + 1.02 \times 10^{-3} T - 2.10 \times 10^{-5} T^{-2} \text{ cal/deg/mole} \)
(17.15 + 4.27 \times 10^{-3} T - 8.79 \times 10^{-5} T^{-2} J/K/mol).
1.8 The mean molar heat capacities at constant pressure of hydrogen, oxygen and water vapour in the temperature range from 25°C (298 K) to 100°C (373 K) are 6.92, 7.04 and 8.03 cal/deg/mole (29.46 and 33.60 J/K/mol) respectively. Calculate the heat of formation of water vapour at 100°C (373 K), if ΔH°₂⁹⁸ for water is -57.80 kcal/mole (-241.84 kJ/mol).

1.9 In the dead roasting of zinc sulphide, the reaction occurs as

$$2\text{ZnS} + 3\text{O}_2 \rightarrow 2\text{ZnO} + 2\text{SO}_2.$$  

With the help of the following data, find the standard heat of reaction at 25°C (298 K) and 827°C (1100 K):

For ZnS: $\Delta H^0_{298} = -48.2$ kcal/mole ($-201.67$ kJ/mol).

$C_p = 12.16 + 1.24 \times 10^{-3} T - 1.36 \times 10^5 T^{-2}$ cal/deg/mole  
($50.88 + 5.19 \times 10^{-3} T - 5.69 \times 10^5 T^{-2}$ J/K/mol).

For O₂: $C_p = 7.16 + 1.0 \times 10^{-3} T - 0.4 \times 10^5 T^{-2}$ cal/deg/mole  
($29.96 + 4.184 \times 10^{-3} T - 1.67 \times 10^5 T^{-2}$ J/K/mol).

For ZnO: $\Delta H^0_{298} = -83.2$ kcal/mole ($-348.11$ kJ/mol).

$C_p = 11.71 + 1.22 \times 10^{-3} T - 2.18 \times 10^5 T^{-2}$ cal/deg/mole  
($48.99 + 5.10 \times 10^{-3} T - 9.12 \times 10^5 T^{-2}$ J/K/mol).

For SO₂: $\Delta H^0_{298} = -70.95$ kcal/mole ($-296.85$ kJ/mol).

$C_p = 10.38 + 2.54 \times 10^{-3} T - 1.42 \times 10^5 T^{-2}$ cal/deg/mole  
($43.43 + 10.83 \times 10^{-3} T - 5.94 \times 10^5 T^{-2}$ J/K/mol).

1.10 Find a general formula for the heat of the following reaction in terms of temperature:

$$\text{ZnO} + \text{C} \rightarrow \text{Zn} + \text{CO}.$$
The First Law of Thermodynamics

Given: For ZnO: $\Delta H^{\circ}_{298} = -83.2 \text{ kcal/mole} (-348.11 \text{ kJ/mol}).$

$$C_p = 11.71 + 1.22 \times 10^{-3} T - 2.18 \times 10^5 T^{-2} \text{ cal/deg/mole}$$

$$= (48.99 + 5.10 \times 10^{-3} T - 9.12 \times 10^5 T^{-2} \text{ J/K/mol}).$$

For C:

$$C_p = 4.10 + 1.02 \times 10^{-3} T - 2.10 \times 10^5 T^{-2} \text{ cal/deg/mole}$$

$$= (17.15 + 4.27 \times 10^{-3} T - 8.79 \times 10^5 T^{-2} \text{ J/K/mol}).$$

For Zn:

$$C_p = 5.35 + 2.40 \times 10^{-3} T \text{ cal/deg/mole}$$

$$= (22.38 + 10.04 \times 10^{-3} T \text{ J/K/mol}).$$

For CO: $\Delta H^{\circ}_{298} = -26.4 \text{ kcal/mole} (-110.46 \text{ kJ/mol}).$

$$C_p = 6.80 + 1.0 \times 10^{-3} T - 0.11 \times 10^5 T^{-2} \text{ cal/deg/mole}$$

$$= (28.45 + 4.184 \times 10^{-3} T - 0.46 \times 10^5 T^{-2} \text{ J/K/mol}).$$

1.11 In an investigation of the thermodynamic properties of $\alpha$-manganese, the following heat contents were determined:

$$H^{\circ}_{700} - H^{\circ}_{298} = 2,895 \text{ cal/g-atom} (12,113 \text{ J/g-atom}).$$

$$H^{\circ}_{1000} - H^{\circ}_{298} = 5,450 \text{ cal/g-atom} (22,803 \text{ J/g-atom}).$$

Find a suitable equation for $[H^o_T - H^o_{298}]$ and also for $C_p$ as a function of temperature in the form $(a + bT)$. Assume that no structural transformation takes place in the given temperature range.

1.12 Calculate the heat of vaporization of liquid silver at 1000°C (1273 K) and heat of fusion of solid silver at 900°C (1173 K).

Given:

$$C_{p, Ag} = 5 \text{ cal/deg/mole} (20.92 \text{ J/K/mol}).$$

$$C_{p, Ag} = 7.3 \text{ cal/deg/mole} (30.54 \text{ J/K/mol}).$$

$$C_{p, Ag} = 5 \text{ cal/deg/mole} (20.92 \text{ J/K/mol}).$$
Heat of fusion of Ag at 961°C (1234 K) = 2.69 kcal/mole (11.25 kJ/mol).

Heat of vaporization of Ag at 2200°C (2473 K) = 60 kcal/mole (251 kJ/mol).

Boiling point and melting point of Ag are 2200°C (2473 K) and 961°C (1234 K) respectively.

1.13 Pure ZnO is reduced by the stoichiometric amount of carbon in a retort at 25°C (298 K). The products leave the retort at 907°C (1180 K).

\[ \text{ZnO(s, 25°C) + C(graphite, 25°C) = Zn(g, 907°C, 1 atm) + CO(g, 907°C, 1 atm)} \]

Calculate the amount of heat per kg of zinc produced, which must be transmitted to the retort for complete reaction.

Given: (i) Standard heats of formation of ZnO and CO at 25°C (298 K) are -83.2 kcal/mole (-348.11 kJ/mol) and -26.42 kcal/mole (-110.54 kJ/mol) respectively.

(ii) Heat of fusion of zinc at M.P. (420°C) = 1.74 kcal/mole (7.28 kJ/mol).

(iii) Heat of evaporation of zinc at B.P. (907°C) = 27.3 kcal/mole (114.22 kJ/mol).

(iv) Molar heat capacity of zinc at constant pressure
    \[ = 5.35 + 2.40 \times 10^{-3} T \text{ cal/deg/mole} (22.38 + 10.04 \times 10^{-3} T \text{ J/K/mole}) \]
    in the temperature range 25°C - 420°C (298 - 693 K), and
    \[ = 7.75 \text{ cal/deg/mole} (32.43 \text{ J/K/mol}) \]
    in the temperature range 420°C - 927°C (693 - 1200 K).

(v) Molar heat capacity of CO at constant pressure
    \[ = 6.8 + 0.98 \times 10^{-3} T - 0.11 \times 10^5 T^{-2} \text{ cal/deg/mole} \]
The First Law of Thermodynamics

\[ (28.45 + 4.10 \times 10^{-3} T - 0.46 \times 10^6 T^{-2} \text{ J/K/mol} ) \text{ in the temperature range } 25^\circ \text{-} 2227^\circ C \ (298 - 2500 \text{ K}). \]

(vi) Atomic weight of zinc = 65.38.

1.14 Calculate the enthalpy change of the following reaction at 1097\(^\circ\)C (1370 K)

\[
\{\text{Cu}\} + \frac{1}{2}(\text{Cl}_2) = \{\text{CuCl}\}.
\]

Given: (i) Standard heat of formation of CuCl at 25\(^\circ\)C (298 K)
\[ = -32.2 \text{ kcal/mole} (-134.72 \text{ kJ/mol}). \]

(ii) Heats of fusion of Cu and CuCl are 3.1 kcal/mole (12.87 kJ/mol) and 2.45 kcal/mole (10.25 kJ/mol) respectively.

(iii) Melting points of Cu and CuCl are 1083\(^\circ\)C (1356 K) and 430\(^\circ\)C (703 K) respectively.

(iv) Molar heat capacity of Cu at constant pressure
\[ = 5.41 + 1.50 \times 10^{-3} T \text{ cal/deg/mole} (22.64 + 6.28 \times 10^{-3} T \text{ J/K/mol}) \text{ in the temperature range } 25^\circ \text{-} \text{M.P.}, \text{ and} \]
\[ = 7.50 \text{ cal/deg/mole} (31.38 \text{ J/K/mol}) \text{ in the temperature range M.P.} - 1327^\circ C. \]

(v) Molar heat capacity of CuCl at constant pressure
\[ = 5.87 + 19.20 \times 10^{-3} T \text{ cal/deg/mole} (24.56 + 80.33 \times 10^{-3} T \text{ J/K/mol}) \text{ in the temperature range } 25^\circ \text{C} - \text{M.P.}, \text{ and} \]
\[ = 15.80 \text{ cal/deg/mole} (66.10 \text{ J/K/mol}) \text{ in the temperature range M.P.} - 1097^\circ C. \]

(vi) Molar heat capacity of Cl\(_2\) at constant pressure
\[ = 8.82 + 0.06 \times 10^{-3} T - 0.68 \times 10^5 T^{-2} \text{ cal/deg/mole} (36.90 + 0.28 \times 10^{-3} T - 2.85 \times 10^5 T^{-2} \text{ J/K/mol}) \text{ in the temperature range } 25^\circ \text{C} - 2727^\circ C. \]
1.15 Calculate the heat required per kg to raise the temperature of steel scrap from 25°C (298 K) to 1600°C (1873 K) from the following data given for iron:

(i) Iron undergoes solid state transformation at 760°C, 910°C and 1400°C (1033, 1183 and 1673 K) with heat of formation of 326, 215 and 165 cal/mole (1,364, 900 and 690 J/mol) respectively.

(ii) Melting point of iron is 1537°C (1810 K) and heat of fusion is 3,670 cal/mole (15,355 J/mol).

(iii) Temperature range

<table>
<thead>
<tr>
<th>Temperature Range</th>
<th>Heat Capacity, $C_p,Fe$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C - 760°C (298 - 1033 K)</td>
<td>$3.0 + 7.58 \times 10^{-3} T + 0.6 \times 10^5 T^{-2}$ cal/deg/mole (12.55 + 31.71 \times 10^{-3} T + 2.51 \times 10^5 T^{-2}$ J/K/mol)</td>
</tr>
<tr>
<td>760°C - 910°C (1033 - 1183 K)</td>
<td>11.13 cal/deg/mole (46.57 J/K/mol)</td>
</tr>
<tr>
<td>910°C - 1400°C (1183 - 1673 K)</td>
<td>$5.80 + 2.0 \times 10^{-3} T$ cal/deg/mole (24.27 + 8.37 \times 10^{-3} T J/K/mol)</td>
</tr>
<tr>
<td>1400°C - 1537°C (1673 - 1810 K)</td>
<td>$6.74 + 1.64 \times 10^{-3} T$ cal/deg/mole (28.20 + 6.86 \times 10^{-3} T J/K/mol)</td>
</tr>
<tr>
<td>1537°C - 2700°C (1810 - 2973 K)</td>
<td>$9.77 + 0.40 \times 10^{-3} T$ cal/deg/mole (40.88 + 1.67 \times 10^{-3} T J/K/mol)</td>
</tr>
</tbody>
</table>

(iv) Atomic weight of iron = 55.85.

1.16 Ti($\alpha$) transforms to Ti($\beta$) at 882°C (1155 K), with a heat of transformation equal to 830 cal/mole (3,473 J/mol). Calculate the heat of reaction when Ti($\beta$) is oxidized by pure oxygen gas to form TiO$_2$ at 1400°C (1673 K).
The First Law of Thermodynamics

Given:

\[ \text{Ti}(\alpha) + O_2 = \text{TiO}_2; \]
\[ \Delta H^0_{298} = -225.5 \text{ kcal/mole } \left( -943.49 \text{ kJ/mol} \right). \]
\[ C_{p,Ti}(\alpha) = 5.28 + 2.4 \times 10^{-3} T \text{ cal/deg/mole} \]
\[ \left( 22.09 + 10.04 \times 10^{-3} T \text{ J/K/mol} \right). \]
\[ C_{p,Ti}(\beta) = 6.91 \text{ cal/deg/mole } \left( 28.91 \text{ J/K/mol} \right). \]
\[ C_{p,TiO_2} = 18.0 + 0.28 \times 10^{-3} T - 4.35 \times 10^5 T^{-2} \text{ cal/deg/mole} \]
\[ \left( 75.31 + 1.17 \times 10^{-3} T - 18.2 \times 10^5 T^{-2} \text{ J/K/mol} \right). \]
\[ C_{p,O_2} = 7.16 + 1.0 \times 10^{-3} T - 0.4 \times 10^5 T^{-2} \text{ cal/deg/mole} \]
\[ \left( 29.96 + 4.184 \times 10^{-3} T - 1.67 \times 10^5 T^{-2} \text{ J/K/mol} \right). \]

1.17 The transformation in manganese can be represented as:

\[ \text{Mn}(\alpha) \quad 720^\circ C \quad 1100^\circ C \quad 1136^\circ C \quad \text{Mn}(\delta). \]

Calculate the heat of reaction when Mn(δ) is oxidized by pure oxygen to form MnO at 1200°C (1473 K).

Given:

\[ \text{Mn}(\alpha) + \frac{1}{2}(O_2) = \text{MnO}; \]
\[ \Delta H^0_{298} = -92,000 \text{ cal/mole } \left( -384,928 \text{ J/mol} \right). \]
\[ \text{Mn}(\alpha) \rightarrow \text{Mn}(\beta); \]
\[ \Delta H_f = 0.48 \text{ kcal/mole } \left( 2.0 \text{ kJ/mol} \right). \]
\[ \text{Mn}(\beta) \rightarrow \text{Mn}(\gamma); \]
\[ \Delta H_f = 0.55 \text{ kcal/mole } \left( 2.30 \text{ kJ/mol} \right). \]
\[ \text{Mn}(\gamma) \rightarrow \text{Mn}(\delta); \]
\[ \Delta H_f = 0.43 \text{ kcal/mole } \left( 1.80 \text{ kJ/mol} \right). \]
\[ C_{P,Mn}(\alpha) = 5.16 + 3.81 \times 10^{-3} T \text{ cal/deg/mole} \]
\[ (21.59 + 15.94 \times 10^{-5} T \text{ J/K/mol}). \]

\[ C_{P,Mn}(\beta) = 8.33 + 0.66 \times 10^{-3} T \text{ cal/deg/mole} \]
\[ (34.85 + 2.76 \times 10^{-5} T \text{ J/K/mol}). \]

\[ C_{P,Mn}(\gamma) = 10.7 \text{ cal/deg/mole} \]
\[ (44.77 \text{ J/K/mol}). \]

\[ C_{P,Mn}(\delta) = 11.30 \text{ cal/deg/mole} \]
\[ (47.28 \text{ J/K/mol}). \]

\[ C_{P,MnO} = 11.1 + 1.94 \times 10^{-3} T - 0.88 \times 10^{-5} T^{-2} \text{ cal/deg/mole} \]
\[ (46.44 + 8.12 \times 10^{-5} T - 3.68 \times 10^{-5} T^{-2} \text{ J/K/mol}). \]

\[ C_{P,O_{2}} = 7.16 \times 10^{-3} T - 0.4 \times 10^{-5} T^{-2} \text{ cal/deg/mole} \]
\[ (29.96 + 4.184 \times 10^{-5} T - 1.67 \times 10^{-5} T^{-2} \text{ J/K/mol}). \]

1.18 A fuel gas containing 40% CO, 10% CO\(_2\) and rest N\(_2\) (by volume) is burnt completely with air in a furnace. The incoming and outgoing temperatures of the gases in the furnace are 500°C (773 K) and 977°C (1250 K) respectively. Calculate (a) the maximum flame temperature, and (b) heat supplied to the furnace per cu.ft of exhaust gas.

Given:
(i) \( \Delta H_{298,CO}^0 = -26,400 \text{ cal/mole} (-110,458 \text{ J/mol}). \)

(ii) \( \Delta H_{298,CO_2}^0 = -94,000 \text{ cal/mole} (-393,296 \text{ J/mol}). \)

(iii) \( C_{P,CO} = 6.8 + 0.95 \times 10^{-3} T - 0.1 \times 10^{-5} T^{-2} \text{ cal/deg/mole} \)
\[ (28.46 + 3.97 \times 10^{-5} T - 0.42 \times 10^{-5} T^{-2} \text{ J/K/mol}). \]

(iv) \( C_{P,CO_2} = 10.6 + 2.2 \times 10^{-3} T - 2.0 \times 10^{-5} T^{-2} \text{ cal/deg/mole} \)
\[ (44.35 + 9.20 \times 10^{-5} T - 8.37 \times 10^{-5} T^{-2} \text{ J/K/mol}). \]

(v) \( C_{P,O_2} = 7.15 \times 0.98 \times 10^{-3} T - 0.4 \times 10^{-5} T^{-2} \text{ cal/deg/mole} \)
\[ (29.92 + 4.10 \times 10^{-5} T - 1.67 \times 10^{-5} T^{-2} \text{ J/K/mol}). \]

(vi) \( C_{P,N_2} = 6.7 + 1.0 \times 10^{-3} T \text{ cal/deg/mole} \)
\[ (28.03 + 4.184 \times 10^{-5} T \text{ J/K/mol}). \]
CHAPTER 2
THE SECOND LAW OF THERMODYNAMICS: ENTROPY AND FREE ENERGY

The first law of thermodynamics provides no universally applicable criterion as to whether a particular reaction will occur or not. However, it could be deduced from it that a chemical reaction is feasible at constant temperature and pressure if the change in enthalpy is negative. Many spontaneous reactions satisfy the above criterion, but there are also many spontaneous reactions with positive values of $\Delta H$. For example, the enthalpy change for the reaction

$$\langle \text{Sn}\rangle_{\text{white}, 298 \, K} \rightarrow \langle \text{Sn}\rangle_{\text{grey}, 298 \, K}$$

is $-500 \text{ cal}(-2092 \, J)$. According to the first law of thermodynamics, grey tin should exist at 25°C ($298 \, K$). However, white tin is found to exist as the stable form at that temperature. Therefore there is a need for defining another thermodynamic property which can provide information regarding the spontaneity of a reaction. This can be obtained from the second law of thermodynamics.

There are several ways of defining the second law of thermodynamics, but a very useful statement, according to Kelvin and Planck, is as follows:

> It is impossible to construct a machine that, operating in a cycle, will take heat from a reservoir at constant temperature and convert it into work without accompanying changes in the reservoir or its surroundings.

2.1 Entropy

Consider a reversible process in which the system absorbs in a reversible manner an infinitesimal quantity of heat $\delta q$ at temperature $T$. The term $\delta q/\Gamma$ is called the entropy change. In spite of the fact that $\delta q$ is not a
state property, $\delta q/\gamma$ is a state property. Thus

$$dS = \frac{\delta q_{\text{rev}}}{T}. \quad (2.1)$$

Entropy ($S$) is an extensive property of the system as it depends on the mass of the system, and hence entropy values are additive in the same way as heat content. It is a thermodynamic property, depending only on the state of the system, and not on its history. The unit of molar entropy is cal/deg/mole (or J/deg/mol) which is also expressed as an entropy unit (e.u.). In entropy calculations, it is very important to distinguish between the 'system' and the 'surroundings'. The combination of a system and its surroundings constitutes an 'isolated system'.

### 2.2 Entropy Change for a Reversible Process

For a reversible process, the sum of the entropy change of the system and of the surroundings is always zero, i.e.

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0. \quad (2.2)$$

Since the combination of a system and its surroundings constitutes an isolated system, it can also be stated that the entropy change for a reversible process in an isolated system is always zero.

### 2.3 Entropy Change for an Irreversible Process

For an irreversible, i.e. spontaneous, process the sum of the entropy change of the system and its surroundings is a positive quantity, i.e.

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0. \quad (2.3)$$
Alternatively, an irreversible process in an isolated system will occur with an increase in entropy.

2.4 Entropy Change for a Chemical Reaction

The entropy change accompanying a chemical reaction is defined as the difference between the sum of the entropies of all products and the sum of the entropies of all reactants. Thus for a reaction

\[ aA + bB + \ldots = mM + nN + \ldots, \]

the entropy change, \( \Delta S \), is given by

\[ \Delta S = (m S_M + n S_N + \ldots) - (a S_A + b S_B + \ldots), \]

where \( S_M, S_N, \ldots \) are the entropies per mole of the various substances. If the reactants and products of a reaction are in their standard states, \( \Delta S \) will be written as \( \Delta S^0 \) - the standard entropy change of the reaction. Thus

\[ \Delta S^0 = (m S_M^0 + n S_N^0 + \ldots) - (a S_A^0 + b S_B^0 + \ldots), \]

where \( S_M^0, S_N^0, \ldots \) refer to the standard entropies per mole of the various substances. The entropy change of a reaction is generally evaluated at constant temperature and pressure. To obtain \( \Delta S \) for a reaction, the entropies of reactants and products at the desired temperature and pressure must be known. The entropy values of elements and compounds are calculated with the help of the third law of thermodynamics, and values at 25°C and 1 atm pressure are available in the literature. The entropy of substances, and therefore of a chemical reaction, at any other temperature can be calculated by the method described in (2.5) below.
Example 2.4

Calculate the standard entropy change for the reaction

\[ \text{Cr}_2\text{O}_3(g) + 3\text{C}(s) = 2\text{Cr}(l) + 3\text{CO}(g) \]

at 25°C (298 K).

Given:

\[ S^0_{298,\text{Cr}_2\text{O}_3} = 19.4 \text{ cal/deg/mole (81.17 J/K/mol).} \]
\[ S^0_{298,\text{C}} = 1.36 \text{ cal/deg/mole (5.69 J/K/mol).} \]
\[ S^0_{298,\text{Cr}} = 5.68 \text{ cal/deg/mole (23.76 J/K/mol).} \]
\[ S^0_{298,\text{CO}} = 47.3 \text{ cal/deg/mole (197.90 J/K/mol).} \]

Solution: The standard entropy change of the given reaction at 25°C can be written as

\[ \Delta S^0_{298} = 2S^0_{298,\text{Cr}} + 3S^0_{298,\text{CO}} - S^0_{298,\text{Cr}_2\text{O}_3} - 3S^0_{298,\text{C}}. \]

Putting the appropriate values in the above equation,

\[ \Delta S^0_{298} = (2 \times 5.68) + (3 \times 47.3) - 19.4 - (3 \times 1.36) \]

\[ = 129.78 \text{ cal/deg.} \]

2.5 Variation of Entropy Change with Temperature

To calculate the change in entropy accompanying a finite change in a system, Eq.(2.1) should be integrated between the limits of temperature involved in the change. It follows, therefore, that

\[ \int_{T_1}^{T_2} dS = \int_{T_1}^{T_2} \frac{\delta q_{rev}}{T} \]
The Second Law of Thermodynamics: Entropy and Free Energy

or \[ S_{T_2} - S_{T_1} = \int_{T_1}^{T_2} \frac{\delta q_{\text{rev}}}{T}, \]

where \( S_{T_2} \) and \( S_{T_1} \) are the entropies of the system at temperatures \( T_2 \) and \( T_1 \) respectively. Since

\[ C_p = \frac{\delta q_{\text{rev}}}{dT}, \]

it follows that

\[ S_{T_2} - S_{T_1} = \int_{T_1}^{T_2} \frac{C_p}{T} dT, \quad (2.4) \]

or

\[ S_{T_2} = S_{T_1} + \int_{T_1}^{T_2} \frac{C_p}{T} dT. \quad (2.5) \]

The above equation permits the calculation of entropy of a substance at a temperature from its value at another temperature. The entropy values are generally stated at \( 25^\circ\text{C} (298 \text{ K}) \), thus

\[ S_{T_2} = S_{298} + \int_{298}^{T_2} \frac{C_p}{T} dT. \quad (2.6) \]

For a substance in its standard state, Eq.(2.4) can be written as

\[ S_{T_2}^o - S_{T_1}^o = \int_{T_1}^{T_2} \frac{C_p}{T} dT. \quad (2.7) \]

In the case of a chemical reaction involving reactants and products in their standard states, the changes in the standard entropies and heat capacities must be considered, and Eq.(2.7) becomes
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\[
\Delta S_{T_2}^0 - \Delta S_{T_1}^0 = \int_{T_1}^{T_2} \frac{\Delta C_p}{T} \, dT,
\]

or

\[
\Delta S_{T_2}^0 = \Delta S_{T_1}^0 + \int_{T_1}^{T_2} \frac{\Delta C_p}{T} \, dT. \tag{2.8}
\]

Eq.(2.7) is true for the substances in which there is no phase transformation or change of state between \( T_1 \) and \( T_2 \). However, if there is a phase transformation such as melting, vaporization, etc., at a temperature \( T' \) in between \( T_1 \) and \( T_2 \), then an additional term must be introduced for the entropy change accompanying it. Thus

\[
S_{T_2}^0 = S_{T_1}^0 + \int_{T_1}^{T'} \frac{C_p'}{T} \, dT + \frac{H_t}{T'} + \int_{T'}^{T_2} \frac{C_p''}{T} \, dT, \tag{2.9}
\]

where \( C_p' \) and \( C_p'' \) are the heat capacities of the substance before and after the transformation, respectively, and \( \Delta H_t \) is the enthalpy change of the transformation. If there is more than one transformation, then entropy changes for all the transformations must be included. A similar equation can be derived for chemical reactions involving phase transformations either in reactants, products, or both.

2.6 Criterion of Spontaneity Based on Entropy

For a chemical reaction proceeding from the initial state \( A \) to the final state \( B \), the total entropy change, i.e. that of the system and its surroundings, can be written as

\[
\Delta S_{\text{total}} = S_{B, \text{total}} - S_{A, \text{total}}.
\]

Under the restricted conditions of constant \( E \) and \( V \), or constant \( H \) and \( P \), the following criteria can be utilized in assessing the probability of
spontaneous change in the system:

(i) If \( \Delta S_{\text{total}} = 0 \), the system is at equilibrium and no spontaneous change will occur.

(ii) If \( \Delta S_{\text{total}} > 0 \), the reaction will tend to occur spontaneously from state A to state B.

(iii) If \( \Delta S_{\text{total}} < 0 \), the reaction will tend to occur spontaneously in the reverse direction, i.e. from state B to state A.

It must be remembered that the above statements apply for the total entropy change, i.e. that of system and of its surroundings.

**Example 2.B**

Calculate the standard entropy of solid copper at 1073°C (1346 K) from the following data:

- \( S_{300, \text{Cu}}^0 = 8.0 \text{ cal/deg/mole} \) (33.47 J/K/mol).
- \( C_P, \text{Cu} = 5.41 + 1.50 \times 10^{-3} T \text{ cal/deg/mole} \) (22.63 + 6.27 \times 10^{-3} T J/K/mol).

**Solution:** Applying Eq.(2.7),

\[
S_{1346, \text{Cu}}^0 - S_{300, \text{Cu}}^0 = \int_{300}^{1346} \left( \frac{5.41 + 1.50 \times 10^{-3} T}{T} \right) dT,
\]

or

\[
S_{1346, \text{Cu}}^0 = 8.0 + 5.41 \left( 1346 - 300 \right) + 1.50 \times 10^{-3} \frac{1}{(1346 - 300)}
\]

\[
= 17.69 \text{ cal/deg/mole}.
\]
Example 2.C

Zinc melts at 420°C (693 K) and its standard entropy at 25°C (298 K) is 9.95 cal/deg/mole (41.63 J/K/mol). Calculate the standard entropy of zinc at 750°C (1023 K).

Given: Heat of fusion of Zn at the melting point, \( \Delta H_f = 1.74 \text{ kcal/mole (7.28 kJ/mol).} \)

\[ C_{p,\text{Zn}} = 5.35 + 2.40 \times 10^{-3} T \text{ cal/deg/mole} \]

\[ (22.38 + 10.04 \times 10^{-3} \text{ J/K/mol).} \]

\[ C_{P,\text{Zn}} = 7.50 \text{ cal/deg/mole (31.38 J/K/mol).} \]

Solution: There is a phase change at 420°C, and hence in order to calculate the standard entropy of zinc at 750°C, the entropy change of this phase change, i.e. melting, at 420°C must be considered. Applying Eq.(2.9),

\[ S_{1023,\text{Zn}}^0 = S_{298,\text{Zn}}^0 + \int_{298}^{693} \frac{C_{P,\text{Zn}}}{T} dT + \frac{\Delta H_f}{T} \]

Putting the appropriate values in the above,

\[ S_{1023,\text{Zn}}^0 = 9.95 + \int_{298}^{693} \left( \frac{5.35}{T} + 2.40 \times 10^{-3} \right) dT + \frac{1.740}{693} \]

\[ + \int_{693}^{1023} \frac{7.50}{T} dT \]

\[ = 9.95 + 5.35 \left( \ln 693 - \ln 298 \right) + 2.40 \times 10^{-3} \]

\[ (693 - 298) + 2.51 + 7.50 \left( \ln 1023 - \ln 693 \right) \]

\[ = 20.85 \text{ cal/deg/mole.} \]
Example 2.D

The phase transformation in pure iron may be represented as follows:

\[1033\text{K} \rightarrow 1183\text{K} \rightarrow 1673\text{K} \rightarrow 1812\text{K} \rightarrow \{\text{Fe}\} \]

Calculate the standard entropy of pure iron at 1627°C (1900 K) if its standard entropy at 25°C (298 K) is 6.50 cal/deg/mole (27.20 J/K/mol).

Given:

\[C_p,\alpha-\text{Fe} = 4.18 + 5.92 \times 10^{-3} T \text{ cal/deg/mole} \quad (17.49 + 24.77 \times 10^{-3} T \text{ J/K/mol}).\]

\[C_p,\beta-\text{Fe} = 9.0 \text{ cal/deg/mole} \quad (37.66 \text{ J/K/mol}).\]

\[C_p,\gamma-\text{Fe} = 1.84 + 4.66 \times 10^{-3} T \text{ cal/deg/mole} \quad (7.70 + 19.50 \times 10^{-3} T \text{ J/K/mol}).\]

\[C_p,\delta-\text{Fe} = 10.50 \text{ cal/deg/mole} \quad (43.93 \text{ J/K/mol}).\]

\[C_p,\{\text{Fe}\} = 10.0 \text{ cal/deg/mole} \quad (41.84 \text{ J/K/mol}).\]

\[\Delta H^0_{1033} = 660 \text{ cal/mole} \quad (2761.4 \text{ J/mol}).\]

\[\Delta H^0_{1183} = 215 \text{ cal/mole} \quad (899.6 \text{ J/mol}).\]

\[\Delta H^0_{1673} = 165 \text{ cal/mole} \quad (690.4 \text{ J/mol}).\]

\[\Delta H^0_{1812} = 3670 \text{ cal/mole} \quad (15,355 \text{ J/mol}).\]

Solution: In the present example, several phase transformations are taking place in iron between 25°C and 1627°C, and therefore the entropy change of these must be considered in order to calculate the standard entropy of iron at 1627°C. Thus,

\[S^0_{1900,\{\text{Fe}\}} = S^0_{298,\alpha-\text{Fe}} + \int_{298}^{1033} \frac{C_p,\alpha-\text{Fe}}{T} dT + \frac{\Delta H^0_{1033}}{1033} \frac{M_{\alpha-\beta}}{1033} \]
Putting the appropriate values in the above,

$$S^0_{1900, \{Fe\}} = 6.5 + \int_{298}^{1033} \left( \frac{4.18}{T} + 5.92 \times 10^{-3} \right) dT + \frac{660}{1033}$$

$$+ \int_{1033}^{1183} \frac{9.0}{T} dT + \int_{1183}^{1673} \left( \frac{1.84}{T} + 4.66 \times 10^{-3} \right) dT$$

$$+ \int_{1673}^{1812} \frac{10.5}{T} dT + \frac{3{,}670}{1812}$$

$$+ \int_{1812}^{1900} \frac{10.0}{T} dT$$

$$= 6.5 + 4.18 \left( \ln 1033 \right. - \ln 298\right) + 5.92 \times 10^{-3} \left( 1033 - 298 \right)$$

$$+ 0.63 + 9 \left( \ln 1183 \right. - \ln 1033\right) + 0.18 + 1.84$$

$$\left( \ln 1673 \right. - \ln 1183\right) + 4.66 \times 10^{-3} \left( 1673 - 1183 \right) + 0.10$$

$$+ 10.5 \left( \ln 1812 \right. - \ln 1673\right) + 2.02 + 10.0$$

$$\left( \ln 1900 \right. - \ln 1812\right)$$

$$= 24.41 \text{ cal/deg/mole.}$$
Example 2.E

Small droplets of gold have been observed to supercool by a maximum amount of approximately 230°C. What is the entropy change associated with the isothermal solidification of 1 g-atom of such supercooled gold? What is the entropy change of the surroundings if they are assumed to remain at the same temperature as the supercooled gold? Also, calculate the total entropy change.

Given:  \[ C_{p,<Au>} = 5.0 \text{ cal/deg/mole (20.92 J/K/mol).} \]
\[ C_{p,<Au> \text{ solid}} = 7.0 \text{ cal/deg/mole (29.29 J/K/mol).} \]
Melting point of gold = 1063°C (1336 K).
Heat of fusion of gold, \( \Delta H_f \) = 3,050 cal/mole (12,781 J/mol).

Solution: This is an example of irreversible process. The entropy change of the system can be calculated by considering a series of reversible steps leading from a supercooled gold at 1063 - 230 = 833°C. One such series might be as follows:

(1) Supercooled liquid gold is transformed reversibly from 833°C to 1063°C (melting point of gold).
\( \{<Au> \text{ at 833°C} \rightarrow<Au> \text{ at 1063°C}; \Delta S_1. \)

(2) At 1063°C, liquid gold is transformed reversibly to solid gold.
\( \{<Au> \text{ at 1063°C} \rightarrow<Au> \text{ at 1063°C}; \Delta S_2. \)

(3) The solid gold is brought from 1063°C to 833°C.
\( <Au> \text{ at 1063°C} \rightarrow< Au> \text{ at 833°C}; \Delta S_3. \)

On adding (1), (2) and (3), we get the required reaction, i.e.
\( \{<Au> \text{ at 833°C} \rightarrow< Au> \text{ at 833°C}; \)
\[ \Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3. \]
\[ \Delta S_1 = \int \frac{1336}{1106} \frac{C_{P,Au}}{T} dT \]
\[ = \int \frac{1336}{1106} \frac{7.0}{T} dT \]
\[ = 1.32 \text{ cal/deg.} \]

\[ \Delta S_2 = \frac{\text{Enthalpy change of the reaction (2)}}{(1,063 + 273)} \]
\[ = -\frac{(\text{Heat of fusion of gold})}{1,336} \]
\[ = -\frac{3,050}{1,336} \]
\[ = -2.28 \text{ cal/deg.} \]

\[ \Delta S_3 = \int \frac{1106}{1336} \frac{C_{P,Au}}{T} dT \]
\[ = \int \frac{1106}{1336} \frac{5.0}{T} dT \]
\[ = -0.94 \text{ cal/deg.} \]

\[ \therefore \Delta S_1 + \Delta S_2 + \Delta S_3 = 1.32 - 2.28 - 0.94 \]
\[ = -1.90 \text{ cal/deg.} \]

Now consider the surroundings. The irreversible process is able to transfer heat reversibly to the isothermal reservoir. The temperature of the surroundings is the same as that of the supercooled gold i.e. 833°C.

\[ \Delta S_{\text{surroundings}} = \frac{\text{Heat absorbed by the surroundings}}{\text{Temperature of the surroundings}} \]
Now, total heat evolved from the system = $\Delta H_1 + \Delta H_2 + \Delta H_3$, where $\Delta H_1$, $\Delta H_2$ and $\Delta H_3$ are the heats of reaction of (1), (2) and (3), and can be calculated as follows:

\[
\Delta H_1 = \int_{1336}^{1106} C_{P,\text{Au}} \, dT
\]
\[
= \int_{1336}^{1106} 7.0 \, dT
\]
\[
= 1,610 \text{ cal.}
\]
\[
\Delta H_2 = -3,050 \text{ cal.}
\]
\[
\Delta H_3 = \int_{1336}^{1106} C_{P,<\text{Au}>} \, dT
\]
\[
= \int_{1336}^{1106} 5.0 \, dT
\]
\[
= -1,150 \text{ cal.}
\]

\[\text{Total heat evolved from the system} = 1,610 - 3,050 - 1,150 = -2,590 \text{ cal.}\]

Hence, the heat absorbed by the surroundings is equal to 2,590 cal.

\[\Delta S_{\text{surroundings}} = \frac{2,590}{1,106} = 2.34 \text{ cal/deg.}\]

Total entropy change of the reaction (2.E.1)

\[= \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}
\]
\[= -1.90 + 2.34
\]
\[= 0.44 \text{ cal/deg.}\]
2.7 Free Energy

Chemical reactions are rarely studied under conditions of constant energy, and therefore the criterion of spontaneity based on the entropy change is not of much practical use. Most reactions of chemical and metallurgical interest are performed at constant pressure and temperature. Some reactions operating at constant volume and constant temperature are also studied. A system under these conditions, i.e. constant $P$ and $T$, or constant $V$ and $T$, is called a 'closed system' and is characterized by the fact that no mass can be transferred across the boundary of the system, but the transfer of energy is allowed. It is most desirable, therefore, to obtain a criterion for spontaneity based on a thermodynamic function which is applicable under the above conditions. Such a criterion can be established by the use of 'Free Energy' functions - Gibbs free energy and Helmholtz free energy.

The Gibbs free energy, $G$, and Helmholtz free energy, $A$, of a system are defined as

$$G = H - TS, \quad (2.10)$$

and

$$A = U - TS, \quad (2.11)$$

respectively. The free energy change for a reaction is the difference between the sum of the free energies of the products and of the reactants. Thus, for a reaction at temperature $T$, the Gibbs free energy change, $\Delta G$, is given as

$$\Delta G = \Sigma G_{\text{product}} - \Sigma G_{\text{reactant}}$$

$$= \left( \sum H_{\text{product}} - T \sum S_{\text{product}} \right) - \left( \sum H_{\text{reactant}} - T \sum S_{\text{reactant}} \right)$$

$$= \left( \sum H_{\text{product}} - \sum H_{\text{reactant}} \right) - T \left( \sum S_{\text{product}} - \sum S_{\text{reactant}} \right)$$

$$= \Delta H - T \Delta S, \quad (2.12)$$

where $\Delta H$ and $\Delta S$ are the enthalpy and entropy change of the reaction at temperature $T$. More precisely, the above equation should be written as
\[ \Delta G_T = \Delta H_T - T \Delta S_T. \]

But more frequently, the subscript is not written, and it generally follows that \( \Delta G, \Delta H \) and \( \Delta S \) refer to temperature, \( T \). Similarly, the Helmholtz free energy change, \( \Delta A \), can be written as

\[ \Delta A = \Delta U - T \Delta S. \]  \hspace{1cm} (2.13)

### 2.8 Criterion of Spontaneity Based on Free Energy

For a reaction at constant volume and constant temperature, the following criteria have been established:

(i) If \( \Delta A \) is zero, the system is in equilibrium.

(ii) If \( \Delta A \) is negative, the reaction tends to proceed spontaneously.

(iii) If \( \Delta A \) is positive, the reaction will occur spontaneously in the opposite direction.

Similarly, for a reaction at constant pressure and constant temperature, the following criteria have been established:

(i) If \( \Delta G \) is zero, the system is in equilibrium.

(ii) If \( \Delta G \) is negative, the reaction tends to proceed spontaneously.

(iii) If \( \Delta G \) is positive, the reaction will occur spontaneously in the opposite direction.

If the reactants and products are present in their standard states, \( \Delta G \) will be replaced by \( \Delta G^0 \) - the standard Gibbs free energy change.
It should be noticed that in the above statements the free energy change is that for the system, and the role of the surroundings need not be included. Since most reactions of chemical and metallurgical interest are performed under constant pressure and constant temperature conditions, the subsequent discussions will be concerned only with the Gibbs free energy, $G$, and will be described simply as free energy.

### 2.9 Calculation of Free Energy Change

In order to determine the spontaneity or otherwise of a reaction occurring at a constant pressure and temperature, it is necessary to know its free energy change. For simplicity, free energy change of reactions is generally calculated when the reactants and products are in their standard states, and this is called the standard free energy change, $\Delta G^\circ$. However, if the reactants and products are not in their standard states, corrections are made to take account of this, and this aspect is dealt with in Chapter 5. Thus, for the reaction

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

the standard free energy change $\Delta G^\circ$ at 25°C (298 K) is given by

$$\Delta G^\circ_{298} = \sum G^\circ_{298,\text{product}} - \sum G^\circ_{298,\text{reactant}}$$

$$= cG^\circ_{298,C} + dG^\circ_{298,D} - aG^\circ_{298,A} - bG^\circ_{298,B}.$$
The free energies of the stable form of the elements at 25°C and 1 atm pressure are arbitrarily assigned a zero value.

The free energies of formation of compounds are calculated on the basis of the above assumption and the value is described as the standard free energy of reaction or the standard free energy of formation. The standard free energy of formation of a compound is the free energy change accompanying the reaction by which it is formed from its elements when all reactants and products are in their standard states, and it is expressed in terms of cal/mole (or J/mol). This quantity is generally reported at 25°C, and for a compound, say MO, it would be written as $\Delta G^0_{298\text{K},MO}$. Thus, for example, the standard free energy of formation of solid NiO at 25°C is -50,786 cal/mole. It follows that the standard free energy change of the reaction

$$<\text{Ni}> + \frac{1}{2}(O_2) = <\text{NiO}>$$

at 25°C is -50,786 cal(-212,480 J).

In the same way as the enthalpy change, the free energy change of a system depends upon the initial and final states of the system, and does not depend on the path taken to bring about the change. Also, it is an extensive property of the system - depending upon the amount of substances present in the system. The free energy changes of reactions can be added or subtracted. Thus, for instance, the free energy changes of the two reactions at 25°C are given below.

$$<\text{NiO}> = <\text{Ni}> + \frac{1}{2}(O_2); \quad (2.14)$$

$$\Delta G^0_{298\text{K},(2.14)} = 50,786 \text{ cal.}$$

$$<\text{H}_2\text{O}> = <\text{H}_2> + \frac{1}{2}(O_2); \quad (2.15)$$

$$\Delta G^0_{298\text{K},(2.15)} = 54,996 \text{ cal.}$$

When (2.15) is subtracted from (2.14), the following equation is obtained:

$$<\text{NiO}> + (\text{H}_2) = <\text{Ni}> + (\text{H}_2\text{O}). \quad (2.16)$$
The free energy change of the above reaction can be obtained by subtracting the free energy change of reaction (2.15) from that of reaction (2.14), i.e.

$$\Delta G_{298, (2.16)} = \Delta G_{298, (2.14)} - \Delta G_{298, (2.15)}$$

$$= 50,786 - 54,996$$

$$= -210 \text{ cal.}$$

However, it must be remembered that the free energy change of a reaction can be added to, or subtracted from that of another reaction only when both free energy data are given for the same conditions of temperature and pressure.

The standard free energy of formation of the compound $\text{MO}$ at 25°C, $\Delta G_{298, \text{MO}}$, and the standard free energy of the compound $\text{MO}$ at 25°C, $G_{298, \text{MO}}$, are sometimes confusing, but as will be seen below, they are the same.

$$\text{M} + \frac{1}{2}\text{O}_2 = \text{MO} \quad (2.17)$$

$$\Delta G_{298, (2.17)} = G_{298, \text{MO}} - G_{298, \text{M}} - \frac{1}{2}G_{298, \text{O}_2}.$$ 

Since the standard free energy of elements at 25°C and 1 atm pressure is zero, we have

$$\Delta G_{298, (2.17)} = G_{298, \text{MO}}.$$ 

According to the definition of standard free energy of formation, the standard free energy change of reaction (2.17) is also equal to the standard free energy of formation of $\text{MO}$, and hence,

$$\Delta G_{298, \text{MO}} = G_{298, \text{MO}}.$$ 

The following examples illustrate the calculation of free energy change of reactions and the prediction relating to their spontaneity.
Example 2.F

Calculate the standard free energy change of the reaction

\[ \langle \text{MoO}_3 \rangle + 3(\text{H}_2) = \langle \text{Mo} \rangle + 3(\text{H}_2\text{O}) \]

at 727°C (1,000 K) and 1 atm pressure from the following data:

\[ \Delta G_{1000}^{0} \langle \text{MoO}_3 \rangle = -120,000 \text{ cal/mole} \ (-502,080 \text{ J/mole}). \]

\[ \Delta G_{1000}^{0} (\text{H}_2\text{O}) = -45,500 \text{ cal/mole} \ (-190,372 \text{ J/mole}). \]

Also, comment on the possibility of reducing MoO$_3$ by H$_2$ at 727°C and 1 atm pressure.

Solution: From the data \( \Delta G_{1000}^{0} \langle \text{MoO}_3 \rangle = -120,000 \text{ cal/mole} \), it follows that the standard free energy change of the reaction

\[ \langle \text{Mo} \rangle + \frac{3}{2}(\text{O}_2) = \langle \text{MoO}_3 \rangle \]  \hspace{1cm} (2.F.1)

at 727°C (1,000 K) and 1 atm pressure is -120,000 cal. Similarly, the standard free energy change of the reaction

\[ (\text{H}_2) + \frac{1}{2}(\text{O}_2) = (\text{H}_2\text{O}) \]  \hspace{1cm} (2.F.2)

at 727°C and 1 atm pressure is -45,500 cal.

\[ \therefore \Delta G_{1000}^{0},(2.F.1) = -120,000 \text{ cal}, \]

and \[ \Delta G_{1000}^{0},(2.F.2) = -45,500 \text{ cal}. \]

Since free energy change is an extensive property, for the reaction

\[ 3(\text{H}_2) + \frac{3}{2}(\text{O}_2) = 3(\text{H}_2\text{O}), \]  \hspace{1cm} (2.F.3)

\[ \Delta G_{1000}^{0},(2.F.3) = 3 \times \Delta G_{1000}^{0},(2.F.2) \]

\[ = 3 \times (-45,500) \]

\[ = -136,500 \text{ cal}. \]
On subtracting (2.F.1) from (2.F.3), we have
\[ <\text{MoO}_3> + 3(H_2) = <\text{Mo}> + 3(H_2O). \]  
(2.F.4)

Since the free energy changes of the reactions can be added or subtracted,
\[ \Delta G^0_{1000,(2.F.4)} = \Delta G^0_{1000,(2.F.3)} - \Delta G^0_{1000,(2.F.1)} \]
\[ = -136,500 - (-120,000) \]
\[ = 16,500 \text{ cal}. \]

Since the standard free energy change of (2.F.4) is negative at 727°C and 1 atm pressure, it follows that it is possible to reduce \( \text{MoO}_3 \) by \( H_2 \) at that temperature and pressure.

\textit{Example 2.G}

Given the following data, determine which metal has the greater probability of oxidation in steam at 827°C (1100 K) and 1 atm pressure
\[ <\text{NiO}> + (H_2) = <\text{Ni}> + (H_2O); \quad \Delta G^0 = -550 - 10.18 T \text{ cal} \]
\[ (-2,501 - 42.59 T \text{ J}). \]
\[ \frac{1}{3} <\text{Cr}_2\text{O}_3> + (H_2) = \frac{2}{3} <\text{Cr}> + (H_2O); \quad \Delta G^0 = 30,250 - 7.33 T \text{ cal} \]
\[ (126,566 - 30.67 T \text{ J}). \]

\textit{Solution:}
\[ <\text{NiO}> + (H_2) = <\text{Ni}> + (H_2O). \]  
(2.G.1)
\[ \frac{1}{3} <\text{Cr}_2\text{O}_3> + (H_2) = \frac{2}{3} <\text{Cr}> + (H_2O). \]  
(2.G.2)
\[ <\text{Ni}> + (H_2O) = <\text{NiO}> + (H_2). \]  
(2.G.3)
\[ 2<\text{Cr}> + 3(H_2O) = <\text{Cr}_2\text{O}_3> + 3(H_2). \]  
(2.G.4)
By observation,

$$\Delta G^0(2.G.3) = -\Delta G^0(2.G.1)$$

$$= 550 + 10.18 \text{T cal.}$$

At 827°C (1,100 K),

$$\Delta G^0_{1100}(2.G.3) = 550 + 10.18 \times 1,100$$

$$= 11,748 \text{ cal.}$$

Similarly,

$$\Delta G^0(2.G.4) = 3 \times (-\Delta G^0(2.G.2))$$

$$= 3 \times (-30,250 + 7.33 \text{T})$$

$$= -90,750 + 21.99 \text{T cal.}$$

At 827°C

$$\Delta G^0_{1100}(2.G.4) = -90,750 + 21.99 \times 1,100$$

$$= -66,561 \text{ cal.}$$

Since $\Delta G^0_{1100}(2.G.3)$ is positive, it follows that reaction (2.G.3) will not proceed in the forward direction at 827°C, i.e. nickel will not form nickel oxide in a steam atmosphere at 827°C. On the other hand, $\Delta G^0_{1100}(2.G.4)$ is negative, and it follows that reaction (2.G.4) will take place in the forward direction at 827°C, i.e. chromium will form chromic oxide in a steam atmosphere at 827°C. In other words, nickel will not oxidise in steam at 827°C, but chromium will. However, because of the physical and chemical characteristics of the film formed on the chromium surface, the reaction will cease in a very short time.
2.10 Calculation of $\Delta G^0$ at High Temperatures

Since the standard enthalpies of formation and standard entropies of compounds are usually reported in the literature at 25°C, the standard enthalpy and entropy change, and hence standard free energy change, of a reaction at 25°C can be easily calculated. However, metallurgists are generally interested in calculating $\Delta G^0$ and $\Delta G$ for reactions at high temperatures. It is possible to calculate $\Delta G^0$ of a reaction at a high temperature from the $\Delta H^0$ and $\Delta S^0$ values at 25°C in the following way:

The free energy equation can be written more precisely as

$$\Delta G^0_T = \Delta H^0_T - T \Delta S^0_T.$$  

The values of $\Delta H^0_T$ and $\Delta S^0_T$ can be obtained in terms of the $\Delta H^0_{298}$ and $\Delta S^0_{298}$ values from Eqs.(1.20) and (2.8) respectively, provided the $\Delta C_p$ for the reaction is known. Thus,

$$\Delta G^0_T = \left[ \Delta H^0_{298} + \int_{298}^{T} \Delta C_p \, dT \right] - T \Delta S^0_{298} + \int_{298}^{T} \frac{\Delta C_p}{T} \, dT. \quad (2.18)$$

This equation makes it possible to calculate $\Delta G^0$ for a reaction at any temperature $T$ from $\Delta H^0_{298}$, $\Delta S^0_{298}$ and $\Delta C_p$ values, as illustrated in Example 2.H. However, it must be remembered that if any transformation, e.g. melting, allotropic modification, etc., takes place between 25°C and $T$ in reactants or products, proper correction terms must be introduced into Eq.(2.18) while calculating $\Delta H^0_T$ and $\Delta S^0_T$, as illustrated in Example (2.1).

**Example 2.H.**

Calculate the standard free energy change of the reaction

$$\langle \text{Ni} \rangle + \frac{1}{2}(\text{O}_2) = \langle \text{NiO} \rangle$$

at 327°C (600 K) from the following data:
The Second Law of Thermodynamics: Entropy and Free Energy

$\Delta H^0_{298, <NiO>}$ = -57,500 cal/mole (-240,580 J/mol).

$S^0_{298, <Ni>}$ = 7.12 cal/deg/mole (29.79 J/K/mol).

$S^0_{298, (O_2)}$ = 49.02 cal/deg/mole (205.09 J/K/mol).

$S^0_{298, <NiO>}$ = 9.10 cal/deg/mole (38.07 J/K/mol).

$C_P, <Ni>$ = 6.03 + 10.44 x 10^{-6} T^2 - 2.5 x 10^{-3} T$ cal/deg/mole 
(25.23 + 43.68 x 10^{-6} T^2 - 10.46 x 10^{-3} T J/K/mol).

$C_P, (O_2)$ = 7.16 + 1.0 x 10^{-3} T - 0.4 x 10^5 T^{-2}$ cal/deg/mole 
(29.96 + 4.18 x 10^{-3} T - 1.67 x 10^5 T^{-2} J/K/mol).

$C_P, <NiO>$ = 12.91 cal/deg/mole (54.01 J/K/mol).

Solution: $<Ni> + \frac{1}{2}(O_2) = <NiO>$  (2.H.1)

$\Delta H^0_{298, (2.H.1)} = \Delta H^0_{298, <NiO>}$

= -57,500 cal.

$\Delta S^0_{298, (2.H.1)} = 9.10 - 7.12 - 24.51$

= -22.53 cal/deg.

$\Delta C_P = 12.91 - (6.03 + 10.44 x 10^{-6} T^2 - 2.50 x 10^{-3} T) - \frac{1}{2}(7.16 + 1.0 x 10^{-3} T - 0.4 x 10^5 T^{-2})$

= (3.30 - 10.44 x 10^{-6} T^2 + 2.0 x 10^{-3} T + 0.2 x 10^5 T^{-2})$ cal/deg.

The scheme of calculation would be as follows:

1. Calculate $\Delta H^0_{600, (2.H.1)}$ from $\Delta H^0_{298, (2.H.1)}$ and $\Delta C_P, (2.H.1)$ values.
(2) Calculate $\Delta S_{600,(2.H.1)}^0$ from $\Delta S_{298,(2.H.1)}^0$ and $\Delta C_p,(2.H.1)$ values.

(3) Calculate $\Delta G_{600,(2.H.1)}^0$ from (1) and (2) using Eq.(2.12).

\[
\Delta H_{600,(2.H.1)}^0 = \Delta H_{298,(2.H.1)}^0 + \int_{298}^{600} \frac{\Delta C_p,(2.H.1)}{T} dT
\]

\[
= -57,500 + \int_{298}^{600} \left( 3.30 - 10.44 \times 10^{-6} T^2 + 2.0 \times 10^{-3} T 
- 3 \frac{1}{2} \left( 600^2 - 298^2 \right) \right) dT
\]

\[
= -57,500 + 3.30 (600 - 298) - \frac{10.44}{3} \left( 600^3 - 298^3 \right)
+ 2.0 \times 10^{-3} \left( 600^2 - 298^2 \right) - 0.2 \times 10^5 \left( \frac{1}{600} - \frac{1}{298} \right)
\]

\[
= -56,858 \text{ cal.}
\]

Similarly,

\[
\Delta S_{600,(2.H.1)}^0 = \Delta S_{298,(2.H.1)}^0 + \int_{298}^{600} \frac{\Delta C_p,(2.H.1)}{T} dT
\]

\[
= -22.53 + \int_{298}^{600} \left( 3.30 T^{-1} - 10.44 \times 10^{-6} T
+ 2.0 \times 10^{-3} + 0.2 \times 10^5 T^{-3} \right) dT
\]

\[
= -22.53 + 3.30 \left( \ln 600 - \ln 298 \right) - \frac{10.44 \times 10^{-6}}{2}
\left( 600^2 - 298^2 \right) + 2.0 \times 10^{-3} \left( 600 - 298 \right)
- \frac{0.2 \times 10^5}{2} \left( \frac{1}{600^2} - \frac{1}{298^2} \right)
\]

\[
= -20.96 \text{ cal/deg.}
\]

Putting the appropriate values in the equation $\Delta G_T^0 = \Delta H_T^0 - T \Delta S_T^0$, 
\[ \Delta G^0_{600} = -56,858 + 600 \times 20.96 \]
\[ = -44,282 \text{ cal.} \]

**Example 2.1**

Calculate the standard free energy change of the reaction

\[ \{\text{Pb}\} + \frac{1}{2}(O_2) = \text{PbO} \]

at 527°C (800 K) from the following data:

\[ \Delta H_{298,\text{PbO}}^0 = -52,400 \text{ cal/mole} \] \((-219,242 J/K/mol).)\]

\[ S_{298,\text{PbO}}^0 = 16.20 \text{ cal/deg/mole} \] \((67.78 J/K/mol).)\]

\[ S_{298,\text{Pb}}^0 = 15.50 \text{ cal/deg/mole} \] \((64.85 J/K/mol).)\]

\[ S_{298,(O_2)}^0 = 49.02 \text{ cal/deg/mole} \] \((205.09 J/K/mol).)\]

\[ C_{P,\text{PbO}} = 10.60 + 4.0 \times 10^{-3} T \text{ cal/deg/mole} \] \((44.35 + 16.74 \times 10^{-3} T J/K/mol).)\]

\[ C_{P,\text{Pb}} = 5.63 + 2.33 \times 10^{-3} T \text{ cal/deg/mole} \] \((23.55 + 9.75 \times 10^{-3} T J/K/mol).)\]

\[ C_{P,(\text{Pb})} = 7.75 - 0.74 \times 10^{-3} T \text{ cal/deg/mole} \] \((32.43 - 3.09 \times 10^{-3} T J/K/mol).)\]

\[ C_{P,(O_2)} = 7.16 + 1.0 \times 10^{-3} T - 0.4 \times 10^5 T^{-2} \text{ cal/deg/mole} \]
\[ (29.86 + 4.184 \times 10^{-3} T - 1.67 \times 10^5 T^{-2} J/K/mol). \)
Melting point of Pb, $T_m = 327^\circ C$ (600 K).

Latent heat of fusion of Pb, $L_f = 1,150$ cal/mole (4,812 J/mol).

**Solution:** The problem basically consists of calculating the standard free energy change of the reaction

$$\text{(Pb)} + \frac{1}{2}(O_2) = \text{<PbO>} \quad (2.1.1)$$

at $527^\circ C$ from $\Delta H^0$, $\Delta S^0$ and $\Delta C_p$ values of the reaction

$$\text{<Pb>} + \frac{1}{2}(O_2) = \text{<PbO>} \quad (2.1.2)$$

at $25^\circ C$. This problem is similar to the previous one, except for the fact that a transformation, i.e. melting, is taking place in one of the reactants, i.e. Pb, at $327^\circ C$, and proper correction terms must be included. The scheme of calculation would be as follows:

1. Calculate $\Delta H^0_{800},(2.1.1)$.
2. Calculate $\Delta S^0_{800},(2.1.1)$.
3. Calculate $\Delta G^0_{800},(2.1.1)$ from (1) and (2), using Eq.(2.12).

$\Delta H^0_{800},(2.1.1)$ can be calculated similar to that illustrated in Example (2.H).

Thus,

$$\Delta H^0_{800},(2.1.1) = \Delta H^0_{298},(2.1.2) + \int_{298}^{600} \Delta C_p,(2.1.2) \, dT - L_f + \int_{298}^{600} \Delta C_p,(2.1.1) \, dT. \quad (2.1.3)$$
Now,
\[ \Delta C_p, (2.1.2) = (10.60 + 4.0 \times 10^{-3} T) - (5.63 + 2.33 \times 10^{-3} T) \]
\[ - \frac{1}{2}(7.16 + 1.0 \times 10^{-3} T - 0.4 \times 10^5 T^{-2}) \]
\[ = (1.39 + 1.17 \times 10^{-3} T + 0.2 \times 10^5 T^{-2}) \text{ cal/deg}, \]
and \[ \Delta C_p, (2.1.1) = (10.60 + 4.0 \times 10^{-3} T) - (7.75 - 0.74 \times 10^{-3} T) \]
\[ - \frac{1}{2}(7.16 + 1.0 \times 10^{-3} T - 0.4 \times 10^5 T^{-2}) \]
\[ = (-0.73 + 4.24 \times 10^{-3} T + 0.2 \times 10^5 T^{-2}) \text{ cal/deg}. \]

Putting the appropriate values in Eq. (2.1.3),
\[ \Delta H^0_{800, (2.1.1)} = -52,400 + \int_{298}^{800} \left( 1.39 + 1.17 \times 10^{-3} T + 0.2 \times 10^5 T^{-2} \right) dT \]
\[ - 1,150 + \int_{298}^{800} \left( -0.73 + 4.24 \times 10^{-3} T + 0.2 \times 10^5 T^{-2} \right) dT \]
\[ = -52,400 + 1.39(600 - 298) + \frac{1.17 \times 10^{-3}}{2}(600^2 - 298^2) \]
\[ - 0.2 \times 10^5 \left( \frac{1}{600} - \frac{1}{298} \right) - 1,150 - 0.73(800 - 600) \]
\[ + 4.24 \times 10^{-3} \left( 800^2 - 600^2 \right) - 0.2 \times 10^5 \left[ \frac{1}{800} - \frac{1}{600} \right] \]
\[ = -52,482 \text{ cal}. \]

Similarly, \[ \Delta S^0 \] can be calculated,
\[ \Delta S^0_{800, (2.1.1)} = \Delta S^0_{298, (2.1.2)} + \int_{298}^{800} \frac{\Delta C_p, (2.1.2) T}{T} \frac{dT}{T} - \int_{298}^{800} \frac{\Delta C_p, (2.1.1) T}{T} \frac{dT}{T}. \]

(2.1.4)
Now,

$$\Delta S^0_{298,(2.1.2)} = 16.2 - 15.5 - \frac{1}{4} (49.02)$$

$$= -23.81 \text{ cal/deg.}$$

Putting the appropriate values in the Eq.(2.1.4),

$$\Delta S^0_{800,(2.1.1)} = -23.81 + \int_{298}^{600} (1.39 \frac{1}{T} + 1.17 \times 10^{-3} + 0.2 \times 10^5 \frac{1}{T^3}) dT$$

$$- \int_{298}^{600} (0.73 \frac{1}{T} + 4.24 \times 10^{-3} + 0.2 \times 10^5 \frac{1}{T^3}) dT$$

$$-23.81 + 1.39 \left( \ln 600 - \ln 298 \right) + 1.17 \times 10^{-3} (600 - 298)$$

$$- 0.2 \times 10^5 \left( \frac{1}{600^2} - \frac{1}{298^2} \right) - \frac{1.150}{600}$$

$$- 0.73 \left( \ln 800 - \ln 600 \right) + 4.24 \times 10^{-3} (800 - 600)$$

$$- 0.2 \times 10^5 \left( \frac{1}{800^2} - \frac{1}{600^2} \right)$$

$$= -23.67 \text{ cal/deg.}$$

Putting the values of $\Delta H^0_{800,(2.1.1)}$ and $\Delta S^0_{800,(2.1.1)}$ in Eq.(2.12),

$$\Delta G^0_{800,(2.1.1)} = -52,482 - 800 \times (-23.67)$$

$$= -33,546 \text{ cal.}$$
2.11 Gibbs Free Energy and the Thermodynamic Functions

\[ G = H - TS, \]

or

\[ G = (U + PV) - TS. \]

Differentiating,\[ dG = dU + PdV + VdP - TdS - SdT. \] (2.19)

Since\[ dU = \delta q - PdV, \] (2.20)

and\[ dS = \frac{\delta Q}{T} \]

for a reversible change, Eq.(2.19) can be written as\[ dU = TdS - PdV. \]

Substituting the value of \( dU \) in Eq.(2.19),\[ dG = VdP - SdT. \] (2.21)

At constant pressure and variable temperature, (2.21) gives\[ \left( \frac{\partial G}{\partial T} \right)_p = -S. \] (2.22)

At constant temperature and variable pressure, (2.21) gives\[ \left( \frac{\partial G}{\partial P} \right)_T = V. \] (2.23)

Similarly, for any reaction\[ \left( \frac{\partial \Delta G}{\partial T} \right)_p = -\Delta S, \] (2.24)
and
\[ \left( \frac{\partial \Delta G}{\partial P} \right)_T = \Delta V. \tag{2.25} \]

Eq.(2.24) suggests that the slope of a plot of $\Delta G$ against $T$ gives the entropy change $\Delta S$ with the opposite sign. Eqs.(2.24) and (2.25) are also valid for $\Delta G^\circ$ provided the other thermodynamic properties are referred to the standard state. For example,
\[ \left( \frac{\partial \Delta G^\circ}{\partial T} \right)_P = -\Delta S^\circ. \tag{2.26} \]

2.12 Gibbs-Helmholtz Equation

\[ \Delta G = \Delta H - T \Delta S. \]

Substituting Eq.(2.24) in the above equation,
\[ \Delta G = \Delta H + T \left( \frac{\partial \Delta G}{\partial T} \right)_P. \tag{2.27} \]

This is known as the Gibbs-Helmholtz equation, and could also be written in the following form:
\[ \left[ \frac{\partial (\Delta G/T)}{\partial T} \right]_P = -\frac{\Delta H}{T^2}, \tag{2.28} \]

or
\[ \left[ \frac{\partial (\Delta G/T)}{\partial (1/T)} \right]_P = \Delta H. \tag{2.29} \]

The Gibbs-Helmholtz equation permits the calculation of $\Delta G^\circ$ for a reaction at any temperature from its value at another temperature. Similar equations can also be written for $\Delta G^\circ$. For example,
The Second Law of Thermodynamics: Entropy and Free Energy

\[ \Delta G^0 = \Delta H^0 + T \left( \frac{\partial \Delta G^0}{\partial T} \right)_p, \quad (2.30) \]

\[ - \frac{\partial (\Delta G^0 / T)}{\partial T} \bigg|_P = - \frac{\Delta H^0}{T^2}, \text{ etc.} \quad (2.31) \]

The application of the Gibbs-Helmholtz equation is illustrated in Examples (2.J) and (2.K).

**Example 2.J**

Calculate the standard enthalpy and entropy changes at 25°C (298 K) for the reaction

\[ 2\text{Cu} + \frac{1}{2}(O_2) = \text{Cu}_2O; \]

\[ \Delta G^0 = -40,500 - 3.92 \times 0.4343 T \ln T + 29.5 T \text{ cal} \]

\[ (-169,452 - 16.40 T \ln T + 123.43 T \text{ J}). \]

**Solution:** \[ \Delta G^0 = -40,500 - 3.92 \times 0.4343 T \ln T + 29.5 T \]

\[ = -40,500 - 1.702 T \ln T + 29.5 T, \quad (2.J.1) \]

or

\[ \frac{\Delta G^0}{T} = - \frac{40,500}{T} - 1.702 \ln T + 29.5. \]

Differentiating,

\[ \frac{\partial (\Delta G^0 / T)}{\partial T} = \frac{40,500}{T^2} - \frac{1.702}{T} \]

From Eq.(2.31),

\[ - \frac{\Delta H^0}{T^2} = \frac{40,500}{T^2} - \frac{1.702}{T}, \]
or \[ \Delta H^0 = -40,500 + 1.702 \, T. \]

At 25°C,
\[ \Delta H_{298}^0 = -40,500 + 1.702 \times 298 \]
\[ = -39,993 \, \text{cal} \]
\[ = -39.99 \, \text{kcal} \]

Differentiating (2.1.1),
\[ \frac{\partial \Delta G^0}{\partial T} = -1.702 - 1.702 \ln T + 29.5 \]
\[ = 27.798 - 1.702 \ln T. \]

From Eq.(2.26),
\[ - \Delta S^0 = 27.798 - 1.702 \ln T. \]

At 25°C,
\[ \Delta S_{298}^0 = -27.798 + 1.702 \ln 298 \]
\[ = -18.10 \, \text{cal/deg}. \]

**Example 2.K**

\[ \Delta G^0 \] for the reaction
\[ \langle \text{Ni} \rangle + \frac{1}{2} (\text{O}_2) = \langle \text{NiO} \rangle \]

at 25°C (298 K) is -50,786 cal (-212,489 J). Calculate \[ \Delta G^0 \] at 327°C (500 K) from the following data:
\[ \Delta H_{298}^{0, \langle \text{NiO} \rangle} = -57,500 \, \text{cal/mole} (-240,580 \, \text{J/mol}) \]
\[ C_P, \langle \text{Ni} \rangle = 6.03 + 10.44 \times 10^{-6} \, T^2 - 2.50 \times 10^{-3} \, T \, \text{cal/deg/mole} \]
\[ (25.23 + 43.08 \times 10^{-6} \, T^2 - 10.46 \times 10^{-3} \, T \, \text{J/K/mol}). \]
The Second Law of Thermodynamics: Entropy and Free Energy

\[
C_p,_{(O_2)} = 7.16 + 1.0 \times 10^{-3} T - 0.4 \times 10^5 T^{-2} \text{ cal/deg/mole}
\]
\[
(29.96 + 4.184 \times 10^{-3} T - 1.67 \times 10^5 T^{-2} \text{ J/K/mol}).
\]

\[
C_p,_{<NiO>} = 12.91 \text{ cal/deg/mole}
\]
\[
(54.01 \text{ J/K/mol}).
\]

**Solution:** Applying the Gibbs-Helmholtz equation to the reaction under question,

\[
\frac{\Delta G^0}{T} = -\int \frac{\Delta H^0}{T^2} \, dT,
\]

or

\[
\Delta G^0 = -T \int \frac{\Delta H^0}{T^2} \, dT. \tag{2.K.1}
\]

But

\[
\Delta H^0 = \int \Delta C_p \, dT
\]

\[
= \left( \frac{C_p,_{<NiO>} - C_p,_{<Ni>}}{2} - \frac{1}{2} C_p,_{(O_2)} \right) \, dT
\]

\[
= \int (12.91 - (6.03 + 10.44 \times 10^{-6}T^2 - 2.50 \times 10^{-3}T) - \frac{1}{2}(7.16 + 1.0 \times 10^{-3} T - 0.4 \times 10^5 T^{-2}) \, dT
\]

\[
= \int (3.30 - 10.44 \times 10^{-6}T^2 + 2.0 \times 10^{-3}T + 0.2 \times 10^5 T^{-2}) \, dT
\]

\[
= 3.30 T - \frac{10.44 \times 10^{-6}T^3}{3} + \frac{2.0 \times 10^{-3}T^2}{2} - 0.2 \times 10^5 T^{-1} + \Delta H_0, \tag{2.K.2}
\]

where \(\Delta H_0\) is an integration constant. At 25°C, the standard enthalpy change of the reaction is -57,500 cal/mole. Putting this value in (2.K.2),

\[
-57,500 = 3.30 \times 298 - \frac{10.44 \times 10^{-6} \times 298^3}{3} + 1.0 \times 10^{-3} \times 298^2
\]

\[
- \frac{0.2 \times 10^5}{298} + \Delta H_0
\]

\[
= 913 + \Delta H_0,
\]
or \[ \Delta H_0 = -57,500 - 913 \]

\[ = -58,413. \]

Putting the value of \( \Delta H_0 \) in (2.K.2),

\[ \Delta H^0 = 3.30 T - 3.48 \times 10^{-6} T^3 + 1.0 \times 10^{-3} T^2 - 0.2 \times 10^5 T^{-1} - 58,413, \]

or \[ \frac{\Delta H^0}{T^2} = 3.30 T^{-1} - 3.48 \times 10^{-6} T + 1.0 \times 10^{-3} - 0.2 \times 10^5 T^{-3} - 58,413 T^{-2}. \]

Substituting the value of \( \frac{\Delta H^0}{T^2} \) in (2.K.1),

\[ \Delta G^0 = -T \int (3.30 T^{-1} - 3.48 \times 10^{-6} T + 1.0 \times 10^{-3} - 0.2 \times 10^5 T^{-3} - 58,413 T^{-2}) \, dT \]

\[ = -T \left[ 3.30 \ln T - \frac{3.48 \times 10^{-6}}{2} T^2 + 1.0 \times 10^{-3} T + \frac{0.2 \times 10^5}{2} T^{-2} \right. \]

\[ + \frac{58,413}{1} T^{-1} + I \left. \right] \]

\[ = \left[ -3.30 \ln T + 1.74 \times 10^{-6} T^3 - 1.0 \times 10^{-3} T^2 - 0.1 \times 10^5 T^{-1} \right. \]

\[ - 58,413 - 298 I \left. \right], \]

(2.K.3)

where \( I \) is an integration constant. At 25°C, the standard free energy change of the reaction under question is -50,786 cal. Substituting this value in the above equation,

\[ -50,786 = -3.30 \times 298 \times \ln 298 + 1.74 \times 10^{-6} \times 298^3 - 1.0 \times 10^{-3} \times 298^2 \]

\[ - \frac{0.1 \times 10^5}{298} - 58,413 - 298 I \]

\[ = -64,091.85 - 298 I, \]
or \[ 298 \, I = - 64,091.85 + 50,786 \]
\[ = - 13,305.85, \]
or \[ I = - 44.65. \]

Putting the value of \( I \) in (2.K.3),

\[ \Delta G^0 = - 3.30 \, T \ln T + 1.74 \times 10^{-6} \, T^3 - 1.0 \times 10^{-3} \, T^2 - 0.1 \times 10^5 \, T^{-1} \]
\[- 58,413 + 44.65 \, T \]
\[ = - 58,413 + 1.74 \times 10^{-6} \, T^3 - 1.0 \times 10^{-3} \, T^2 - 3.30 \, T \ln T \]
\[ + 44.65 \, T - 0.1 \times 10^5 \, T^{-1}. \]

\[ \Delta G^0_{600} = - 58,413 + 1.74 \times 10^{-6} \times 600^3 - 1.0 \times 10^{-3} \times 600^2 - 3.30 \times 600 \]
\[ \times \ln 600 + 44.65 \times 600 - \frac{0.1 \times 10^5}{600} \]
\[ = - 44,290 \, \text{cal.} \]

**Exercises**

2.1 The reversible transformation of grey tin to white tin occurs at 13°C (286 K) and 1 atm, and the heat of transformation is 500 cal/mole (2092 J/mol). Calculate the entropy change.

2.2 Calculate the changes in heat content and entropy associated with the reduction of the oxides of iron and aluminium at 25°C, according to the following reactions:
Fe₂O₃ + 3C = 2Fe + 3CO.

Al₂O₃ + 3C = 2Al + 3CO.

Comment on the result.

Given:

2Fe + \frac{3}{2}O₂ = Fe₂O₃;

\Delta H°₂₉₈ = -200,000 cal (-836,800 J).

2Al + \frac{3}{2}O₂ = Al₂O₃;

\Delta H°₂₉₈ = -404,000 cal (-1,690,336 J).

C(graphite) + \frac{1}{2}O₂ = CO;

\Delta H°₂₉₈ = -25,000 cal (-104,600 J).

Entropies of CO, Al, Fe, Al₂O₃, Fe₂O₃ and C(graphite) at 25°C are 47.3, 6.7, 6.5, 12.8, 21.5, and 1.39 cal/deg/mole (197.9, 28.0, 27.2, 53.6, 89.9, and 5.8 J/K/mol), respectively.

2.3 The heat capacity of solid magnesium at 1 atm pressure in the temperature range from 0° to 560°C (273 to 833 K) is given by the expression

\[ C_p = 6.20 + 1.33 \times 10^{-3} T + 6.78 \times 10^4 T^{-2} \text{cal/deg/mole} \]

\[ (26.94 + 5.56 \times 10^{-3} T + 28.37 \times 10^4 T^{-2} \text{J/K/mol}). \]

Determine the increase of entropy per mole for an increase of temperature from 27° to 527°C (300 to 800 K) at 1 atm (101325 N/m²) pressure.

2.4 Two identical copper ingots, one at 500°C (773 K) and the other at 300°C (573 K) are placed in an insulated enclosure. Heat flows from the hot ingot to the cold ingot until the temperature of both ingots is the same (400°C). Calculate the total entropy change accompanying this process,
assuming that the transfer of heat from the ingots to the material of construction of the enclosure is negligible. Comment on whether the process is spontaneous or not.

Given: \[ C_p,_{Cu} = 5.41 + 1.50 \times 10^{-3} T \text{ cal/deg/mole} \]
\[ (22.84 + 6.28 \times 10^{-3} T \text{ J/K/mol}). \]

2.5 Calculate the standard entropy change of the following reaction at 727°C (1000 K)

\[ 2Al + \frac{3}{2}O_2 = Al_2O_3; \]
\[ \Delta S_{298}^0 = -74.87 \text{ cal/deg/mole} (-313.26 \text{ J/K/mol}). \]

Given: Melting point of aluminium = 659°C (932 K).
Heat of fusion of Al at the m.p. = 2,500 cal/mole (10,460 J/mol).
\[ C_p,_{Al} = 25.14 \text{ cal/deg/mole (105.19 J/K/mol).} \]
\[ C_p,_{O_2} = 7.57 \text{ cal/deg/mole (31.67 J/K/mol).} \]
\[ C_p,_{Al} = 6.76 \text{ cal/deg/mole (28.28 J/K/mol).} \]
\[ C_p,_{Al} = 7.00 \text{ cal/deg/mole (29.29 J/K/mol).} \]

2.6 Calculate the entropy change of the system and the surroundings for the isothermal freezing of one mole of supercooled liquid copper at 900°C (1,173 K) when the surroundings are also at the same temperature. Assume that \( C_p \) for liquid copper also holds good for supercooled liquid copper.

Given: Melting point of copper = 1,083°C (1,355 K).
Heat of fusion of copper at m.p. = 3,100 cal/mole (12,970 J/mol).
2.7 Calculate the entropy changes of the system and surroundings for the case of isothermal freezing of one mole of supercooled liquid silver at 850°C, when the surroundings are also at the same temperature.

Given: Melting point of silver = 961°C (1234 K).
Heat of fusion of silver at 961°C = 2,690 cal/mole (11,255 J/mol).

\[
\begin{align*}
C_p,_{\text{Ag}} &= 5.09 + 2.04 \times 10^{-3} T \text{ cal/deg/mole (21.30} + 8.54 \times 10^{-3} T \text{ J/K/mol).} \\
C_p,_{\text{Ag}} &= 7.30 \text{ cal/deg/mole (30.54 J/K/mol).}
\end{align*}
\]

2.8 Using the following values, calculate the standard free energy change per mole of the metal at 727°C (1,000 K) for the reduction of molybdenic oxide and chromic oxide by hydrogen:

\[
\begin{align*}
\Delta G_{1000, \text{Cr}_2O_3}^0 &= -205.5 \text{ kcal/mole (-859.8 kJ/mol).} \\
\Delta G_{1000, \text{MoO}_3}^0 &= -120.0 \text{ kcal/mole (-502.0 kJ/mol).} \\
\Delta G_{1000, \text{H}_2\text{O}}^0 &= -45.5 \text{ kcal/mole (-190.4 kJ/mol).}
\end{align*}
\]

Comment on your result.

2.9 Determine the temperature above or below which reduction of MnO by carbon becomes thermodynamically feasible at 1 atm pressure (101,325 N/m²).

Given: \(2\text{C} + \text{O}_2 = 2\text{CO};\)
2.10 The standard heat of formation of solid HgO at 25°C (298 K) is -21.56 kcal/mole (-90.20 kcal/mol). The standard entropies of solid HgO, liquid Hg, and O\textsubscript{2} at 25°C are 17.5, 18.5, and 49.0 cal/deg/mole (73.22, 77.40 and 205.01 J/K/mol), respectively. Assuming that ΔH\textsuperscript{0} and ΔS\textsuperscript{0} are independent of temperature, calculate the temperature at which solid HgO will dissociate into liquid Hg and O\textsubscript{2}.

2.11 There are two allotropic forms of tin – grey and white. The enthalpy change at 25°C (298 K) for the reaction

Sn (grey) \rightarrow Sn (white)

is 0.5 kcal (2.09 kcal). The entropy change is 1.745 cal/deg (7.30 J/K). Using the free energy criterion for equilibrium, and assuming ΔH\textsuperscript{0} and ΔS\textsuperscript{0} to be independent of temperature, calculate the transition temperature, i.e. the temperature at which grey and white tin co-exist in equilibrium.

2.12 Determine the temperature above or below which the reduction of MgO by Al becomes thermodynamically feasible at 1 atm pressure (101,325 N/m\textsuperscript{2}).

Given: 2Al\textsubscript{(s)} + \frac{3}{2}O\textsubscript{2} = 2Al\textsubscript{2}O\textsubscript{3};

ΔG\textsuperscript{0} = -401,500 + 76.91 T cal (-1,679,376 + 321.79 T J).

(Mg) + \frac{1}{2}(O\textsubscript{2}) = <MgO> ;
2.13 Chromium and carbon present in stainless steel form chromium carbide at 600°C (873 K). Show by thermodynamic calculation which of the metals among Si, Ti, and V should be alloyed to stainless steel, so as to prevent the formation of chromium carbide.

Given:

\[ 3 \text{Cr} + 2\text{C} = \text{Cr}_3\text{C}_2; \]
\[ \Delta G^0 = -20,800 - 4.0 \text{ T cal} \left( -87,027 - 16.74 \text{ T J} \right). \]

\[ \text{Si} + \text{C} = \text{SiC}; \]
\[ \Delta G^0 = -12,770 + 1.66 \text{ T cal} \left( -53,430 + 6.95 \text{ T J} \right). \]

\[ \text{V} + \text{C} = \text{VC}; \]
\[ \Delta G^0 = -20,000 + 1.6 \text{ T cal} \left( -83,680 + 6.69 \text{ T J} \right). \]

\[ \text{Ti} + \text{C} = \text{TiC}; \]
\[ \Delta G^0 = -45,000 + 2.8 \text{ T cal} \left( -188,280 + 11.71 \text{ T J} \right). \]

2.14 Suggest whether the decomposition of NbC by Nb_2O_5 at 1 atm pressure is possible at 1500°C (1773 K).

Given:

\[ \Delta G^0_{1773, \text{Nb}_2\text{O}_5} = -269.0 \text{ kcal/mole} \left( -1,125.5 \text{ kJ/mol} \right). \]

\[ \Delta G^0_{1773, \text{NbC}} = -30.8 \text{ kcal/mole} \left( -128.87 \text{ kJ/mol} \right). \]

\[ \Delta G^0_{1773, \text{CO}} = -64.0 \text{ kcal/mole} \left( -267.77 \text{ kJ/mol} \right). \]
2.15 Determine which of the following metals can be produced by the reduction of metal sulphide with metal oxide at 1000°C (1273 K) and 1 atm pressure (101,325 N/m²).

Given: 

\[ \text{Cu}_2S + 2\text{Cu}_2O \rightarrow 6\text{Cu} + \text{SO}_2; \]

\[ \Delta G^0 = 28,530 + 14.06 T \log T - 70.43 T \text{cal} \]

\[ (119,370 + 58.83 T \log T - 534.66 T \text{J}). \]

\[ \text{PbS} + 2\text{Pb}_2O \rightarrow 3\text{Pb} + \text{SO}_2; \]

\[ \Delta G^0 = 98,440 + 16.1 T \log T - 121.14 T \text{cal} \]

\[ (411,873 + 67.36 T \log T - 506.85 T \text{J}). \]

\[ \text{Ni}_3\text{S}_2 + 4\text{Ni}_2O \rightarrow 7\text{Ni} + 2\text{SO}_2; \]

\[ \Delta G^0 = 139,800 - 98.59 T \text{cal} \]

\[ (584,923 - 412.5 T \text{J}). \]

2.16 Is the reaction \(<\text{Fe}_2\text{O}_3> + 3(\text{H}_2) = 2<\text{Fe}> + 3(\text{H}_2\text{O})\) spontaneous at 25°C (298 K) and 1 atm pressure (101,325 N/m²) ?

Given: 

\[ \Delta H_{298}^{\circ}(\text{H}_2\text{O}) = -57,789 \text{cal/mole} (-241,789 \text{J/mol}). \]

\[ \Delta H_{298}^{\circ}<\text{Fe}_2\text{O}_3> = -196,500 \text{cal/mole} (-822,156 \text{J/mol}). \]

\[ S_{298}^{\circ}(\text{H}_2\text{O}) = 45.10 \text{cal/deg/mole} (188.7 \text{J/K/mol}). \]

\[ S_{298}^{\circ}<\text{Fe}> = 6.49 \text{cal/deg/mole} (27.15 \text{J/K/mol}). \]

\[ S_{298}^{\circ}(\text{H}_2) = 31.21 \text{cal/deg/mole} (130.88 \text{J/K/mol}). \]

\[ S_{298}^{\circ}<\text{Fe}_2\text{O}_3> = 21.50 \text{cal/deg/mole} (89.95 \text{J/K/mol}). \]
CHAPTER 3
THE THIRD LAW OF THERMODYNAMICS

3.1 Statement of the Law

The third law of thermodynamics is stated as

The entropy of a pure, perfect and crystalline solid at absolute zero is zero.

A more general statement of the third law is

The entropy of a system at absolute zero in a state of thermodynamic equilibrium is zero.

3.2 Application

One of the important applications of this law is to determine the absolute value of entropy, $S$, at any temperature, provided that the heat capacities are known within the range of temperature under consideration and that the substance is crystalline at absolute zero.

Since

$$dS = \frac{C_p}{T} dT.$$ 

Integrating the above equation from absolute zero to a temperature $T$,

$$\int_0^T dS = \int_0^T \frac{C_p}{T} dT,$$

or

$$S_T - S_0 = \int_0^T \frac{C_p}{T} dT, \quad (3.1)$$
The Third Law of Thermodynamics

where $S_T$ and $S_0$ are the entropies of the system at $T$ and 0 K respectively. Since according to the third law $S_0$ is zero, we have

$$S_T = \int_0^T \frac{C_P}{T} \, dT.$$  (3.2)

Following Einstein's idea, Debye showed that at lower temperatures, about -258°C, (~15 K), the heat capacity of a solid may be expressed as

$$C_P = aT^3,$$  (3.3)

where $a$ is a constant. Eq.(3.3) is known as Debye's equation. Splitting the integral in Eq.(3.2) in two parts, from 0 to $T'$ and from $T'$ to $T$, where $T'$ is an intermediate temperature between 0 and $T$ K, we have

$$S_T = \int_0^{T'} \frac{C_P}{T} \, dT + \int_{T'}^{T} \frac{C_P}{T} \, dT.$$  (3.4)

If $T'$ is equal to, or below 15 K, then according to Eq.(3.3),

$$S_T = \int_0^{T'} \frac{aT^3}{T} \, dT + \int_{T'}^{T} \frac{C_P}{T} \, dT$$

$$= \int_0^{T'} aT^2 \, dT + \int_{T'}^{T} \frac{C_P}{T} \, dT$$

$$= \frac{1}{3} \left[ aT^3 \right]_{T'}^{T} + \int_{T'}^{T} \frac{C_P}{T} \, dT$$

$$= \frac{1}{3} aT'^3 + \int_{T'}^{T} \frac{C_P}{T} \, dT$$

$$= \frac{1}{3} C_{P_s}(T') + \int_{T'}^{T} \frac{C_P}{T} \, dT,$$  (3.5)

where $C_{P_s}(T')$ is the heat capacity at constant pressure at $T'$ K.
The value of the integral in Eq. (3.5) is given by the area under the curve of \( \frac{C_p}{T} \) versus \( T \) between the values of \( T = T' \) and \( T = T \). Alternatively, the value of the integral is also given by the area under the curve of \( C_p \) versus \( \ln T \) between the values of \( \ln T \) corresponding to \( T = T' \) and \( T = T \).

However, in deriving Eq. (3.5), it has been assumed that there is no phase change between the temperature 0 and \( T \) K. If there is any transformation say, at temperature \( T_t \) intermediate between \( T' \) and \( T \), we have

\[
S_T = \frac{1}{3} C_p'(T') + \int_{T'}^{T_t} \frac{C_p'}{T} \, dT + \frac{L_t}{T_t} + \int_{T_t}^{T} \frac{C_p''}{T} \, dT, \tag{3.6}
\]

where

- \( C_p' \) = heat capacity at constant pressure from \( T' \) to \( T_t \).
- \( L_t \) = latent heat of transformation, and
- \( C_p'' \) = heat capacity at constant pressure from \( T_t \) to \( T \).

The application of the third law of thermodynamics in calculating the absolute value of entropy of a metal is illustrated in the following example.

**Example 3.A**

The molar heat capacities at constant pressure of silver in the temperature range -258°C to 27°C (15 - 300 K) are given below.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_p, \text{cal/deg/mole} )</td>
<td>0.16</td>
<td>0.40</td>
<td>1.14</td>
<td>2.78</td>
<td>3.90</td>
<td>4.56</td>
<td>5.48</td>
<td>5.90</td>
<td>6.10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(Temp., K)</th>
<th>15</th>
<th>20</th>
<th>30</th>
<th>50</th>
<th>70</th>
<th>90</th>
<th>150</th>
<th>250</th>
<th>300</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_p, J/K/mol )</td>
<td>0.67</td>
<td>1.67</td>
<td>4.77</td>
<td>11.63</td>
<td>16.32</td>
<td>19.08</td>
<td>22.93</td>
<td>24.89</td>
<td>25.52</td>
</tr>
</tbody>
</table>
Calculate the standard entropy of silver at 25°C (298 K) from the third law of thermodynamics, assuming that the molar heat capacity at temperatures below -258°C (15 K) follows Debye's equation.

Solution: Since the molar heat capacity below -258°C (15 K) is followed by Debye's equation, the entropy of silver at 25°C (298 K) according to Eq.(3.5) is given by

\[ S_{298}^0 = \frac{1}{3} C_p,(15 K) + \int_{15}^{298} \frac{C_p}{T} \,dT \]

\[ = \frac{1}{3}(0.16) + \int_{15}^{298} \frac{C_p}{T} \,dT \]

\[ = 0.053 + \int_{15}^{298} \frac{C_p}{T} \,dT. \quad (3.6) \]

The integral in Eq.(3.6) can be evaluated by measuring the area under the curve of \( C_p \) versus \( \ln T \) between the values of \( \ln T \) corresponding to \( T = 15 \) K and \( T = 298 \) K. A graph is plotted between \( C_p \) and \( \ln T \) as shown in Fig. 3.1, from the following data:

<table>
<thead>
<tr>
<th>( T, K )</th>
<th>15</th>
<th>20</th>
<th>30</th>
<th>50</th>
<th>70</th>
<th>90</th>
<th>150</th>
<th>250</th>
<th>300</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \ln T )</td>
<td>2.708</td>
<td>2.995</td>
<td>3.401</td>
<td>3.912</td>
<td>4.248</td>
<td>4.499</td>
<td>5.010</td>
<td>5.520</td>
<td>5.705</td>
</tr>
<tr>
<td>( C_p )</td>
<td>0.160</td>
<td>0.400</td>
<td>1.140</td>
<td>2.780</td>
<td>3.900</td>
<td>4.560</td>
<td>5.480</td>
<td>5.900</td>
<td>6.100</td>
</tr>
</tbody>
</table>

Using the trapezoidal rule, the shaded area under the curve between the limits \( T = 15 \) K (i.e. \( \ln T = 2.708 \)) and \( T = 298 \) K (i.e. \( \ln T = 5.697 \)) in Fig. 3.1 comes out to be 10.195 cal/deg/mole.

Substituting the value in Eq.(3.6),

\[ S_{298}^0 = 0.053 + 10.195 \]

\[ = 10.248 \text{ cal/deg/mole}. \]

Thus, the standard entropy of silver at 250°C is 10.25 cal/deg/mole.
Fig. 3.1. Variation of $C_p$ with $\ln T$ (Example 3.A).

Exercises

3.1 The molar heat capacities of aluminium at different temperatures are given below.

<table>
<thead>
<tr>
<th>Temp., $^\circ$C</th>
<th>-258</th>
<th>-240.6</th>
<th>-237.9</th>
<th>-190</th>
<th>-184.7</th>
<th>-136</th>
<th>-38</th>
<th>+58</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_p$, cal/deg/mole</td>
<td>0.03</td>
<td>0.25</td>
<td>0.32</td>
<td>2.36</td>
<td>2.57</td>
<td>4.10</td>
<td>5.34</td>
<td>5.78</td>
</tr>
<tr>
<td>(Temp., K)</td>
<td>15</td>
<td>32.4</td>
<td>35.1</td>
<td>83</td>
<td>88.3</td>
<td>137</td>
<td>235</td>
<td>331</td>
</tr>
<tr>
<td>$C_p$, J/K/mol</td>
<td>0.13</td>
<td>1.05</td>
<td>1.34</td>
<td>9.87</td>
<td>10.75</td>
<td>17.15</td>
<td>22.34</td>
<td>24.18</td>
</tr>
</tbody>
</table>
The Third Law of Thermodynamics

Calculate the standard entropy of aluminium at 25°C (298 K) from the third law of thermodynamics and Debye's equation.

3.2 From the following molar heat capacities data for nickel and Debye's equation, calculate graphically the standard entropy of nickel at 25°C (298 K).

<table>
<thead>
<tr>
<th>Temp., °C</th>
<th>-258</th>
<th>-248</th>
<th>-226</th>
<th>-206</th>
<th>-191</th>
<th>-139.5</th>
<th>-69</th>
<th>-16.5</th>
<th>+10</th>
<th>+27</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_p$, cal/deg/mole</td>
<td>0.046</td>
<td>0.14</td>
<td>0.85</td>
<td>1.82</td>
<td>2.41</td>
<td>4.27</td>
<td>5.43</td>
<td>5.93</td>
<td>6.23</td>
<td>6.30</td>
</tr>
</tbody>
</table>

(Temp., K : 15 25 47 67 82 133.5 204 256.5 298 300

$C_p$, J/K/mol : 0.19 0.59 3.56 7.61 10.08 17.87 22.72 24.81 26.07 26.36).

3.3 The molar heat capacities of lead at constant pressure over a range of temperatures, are given below.

<table>
<thead>
<tr>
<th>Temp., °C</th>
<th>-258</th>
<th>-243</th>
<th>-233</th>
<th>-203</th>
<th>-123</th>
<th>27</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_p$, cal/deg/mole</td>
<td>2.01</td>
<td>3.92</td>
<td>4.72</td>
<td>5.56</td>
<td>5.98</td>
<td>6.30</td>
</tr>
</tbody>
</table>

(Temp., K : 15 30 40 70 150 300


Calculate the standard entropy of lead at 25°C (298 K) from the third law of thermodynamics. Assume that the entropy contribution below -258°C ($15K$) follows Debye's equation.

3.4 Rhombic sulphur transforms to monoclinic sulphur at 95.5°C (368.5 K) with an enthalpy change of 96 cal/mole (401.7 J/mol). Test the validity of the third law of thermodynamics for this transition from the following data:

(i) $C_p$ of rhombic sulphur at -258°C ($15K$) = 0.3 cal/deg/mole (1.26 J/K/mol).

(ii) Area under the curve drawn between $C_p/T$ and $T$ for rhombic sulphur between $T = -258°C$ ($15K$) and $T = 95.5°C$ (368.5 K) is 8.71 cal/deg/mole (38.44 J/K/mol).
(iii) For monoclinic sulphur: $S_{368.5} - S_0 = 9.07 \text{ cal/deg/mole (37.85 J/K/mol)}$, where $S_{368.5}$ and $S_0$ are the entropies at 95.5°C (368.5 K) and -273°C (0 K) respectively.

Assume that the entropy contribution of rhombic sulphur below -258°C (15 K) follows Debye's equation.
THE CLAUSIUS-CLAPEYRON EQUATION

4.1 Introduction

The Clausius-Clapeyron equation is of great importance for calculating the effect of change of pressure (P) on the equilibrium transformation temperature (T) of a pure substance, and may be represented as

\[ \frac{dP}{dT} = \frac{\Delta H}{T \Delta V} \]

where \( \Delta H \) is the heat of transformation and \( \Delta V \) is the volume change associated with the transformation. However, care should be taken in selecting the units of the quantities in Eq.(4.1). If \( \Delta H \) and \( \Delta V \) are expressed in cal and cubic centimeter respectively, then the value of \( \frac{dP}{dT} \) obtained will be in cal/c.c./deg. In order to convert the value of \( \frac{dP}{dT} \) from this unit to the more convenient unit of atm/deg, the following factor is used:

1 cal = 41.293 c.c. atm.

4.2 Application of Clausius-Clapeyron Equation to Phase Changes

The Clausius-Clapeyron equation is applicable to any phase change-fusion, vaporization, sublimation, allotropic transformation, etc.

4.2.1 Liquid-Vapour (Vaporization) Equilibria

Applying Eq.(4.1) to a liquid-vapour equilibrium, we have

\[ \frac{dP}{dT} = \frac{\Delta H_v}{T(V_{vap} - V_{liq})} \]
where $\Delta H_v$ is the molar heat of vaporization or latent heat of evaporation, $V_{\text{vap}}$ is the molar volume of vapour, and $V_{\text{liq}}$ is the molar volume of liquid. Since the molar volume of vapour is very much larger than the molar volume of liquid, $V_{\text{liq}}$ is negligible as compared to $V_{\text{vap}}$, and hence

$$\frac{dP}{dT} = \frac{\Delta H_v}{RTV_{\text{vap}}}.$$  \hspace{1cm} (4.3)

Assuming that the vapour behaves as an ideal gas, the volume $V_{\text{vap}}$ may be related to

$$V_{\text{vap}} = \frac{RT}{P}.$$ \hspace{1cm} (4.4)

Substituting the value of $V_{\text{vap}}$ in Eq.(4.3),

$$\frac{dP}{dT} = \frac{P\Delta H_v}{RT^2}.$$ \hspace{1cm} (4.5)

The equation can be rearranged in the most generally used differential form

$$\frac{d(\ln P)}{dT} = \frac{\Delta H_v}{RT^2}.$$ \hspace{1cm} (4.6)

If we assume as an approximation, however, that over the interval in question $\Delta H_v$ remains constant, then integration of Eq.(4.6) yields

$$\ln P = -\frac{\Delta H_v}{RT} + C',$$ \hspace{1cm} (4.7a)

or

$$\log P = -\frac{\Delta H_v}{2.303RT} + C,$$ \hspace{1cm} (4.7b)

where $C'$ and $C$ are integration constants.
It is evident from Eq.(4.7b) that if \( \log P \) for any liquid metal is plotted against \( 1/T \), the plot should be a straight line. The slope \( (m) \) of the straight line will be given by

\[
m = \frac{-\Delta H_v}{2.303 R},
\]

and the intercept of the line with Y-axis will give the value of constant \( C \). From the slope of line, the heat of vaporization of liquid may be calculated. However, the heat of vaporization of a liquid metal calculated in this way will be the mean value over the temperature interval concerned.

Eq.(4.6) may also be integrated between the limits \( P_1 \) and \( P_2 \) corresponding to temperatures \( T_1 \) and \( T_2 \) respectively. Assuming that the temperature range is small enough so that \( \Delta H_v \) is independent of temperature, integration of Eq.(4.6) yields

\[
\int_{P_1}^{P_2} \frac{d(ln P)}{R} = \frac{\Delta H_v}{R} \int_{T_1}^{T_2} \frac{dT}{T^2},
\]

or

\[
\log \frac{P_2}{P_1} = \frac{-\Delta H_v}{2.303 R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

Eq.(4.8) may be used to calculate the vapour pressure at any temperature if the vapour pressure at another temperature and the mean heat of vaporization over that temperature range are known.

The following example illustrates the application of the Clausius-Clapeyron
Example 4.4

The vapour pressure of liquid titanium at $2227^\circ C$ ($2500 \, K$) is $1.503 \, \text{mm Hg}$ ($200 \, \text{N/m}^2$). The heat of vaporization at the normal boiling point of titanium is $104 \, \text{kcal/mole}$ ($435.14 \, \text{kJ/mol}$). Calculate its normal boiling point.

Solution: Let us assume that the normal boiling point of titanium is $T_b$. At this temperature, the vapour pressure is equal to $1 \, \text{atm}$, or $760 \, \text{mm Hg}$. Putting the appropriate values in Eq.(4.8),

$$\log \frac{760}{1.503} = \frac{-104000}{4.575} \left( \frac{1}{T_b} - \frac{1}{2500} \right),$$

On simplification,

$$T_b = 3558 \, K = 3285^\circ C.$$

Thus the normal boiling point of titanium is $3285^\circ C$.

However, a more accurate integration of Eq.(4.6) can be carried out if the variation of heat of vaporization with temperature is taken into account. Using Kirchhoff's equation at constant pressure,

$$\left( \frac{d\Delta H_v}{dT} \right)_p = \Delta C_p,$$

or

$$\Delta H_v = \int \Delta C_p \, dT + I_1,$$  \hspace{1cm} (4.9)
The Clausius-Clapeyron Equation

where $I_1$ is an integration constant. Putting the value of $\Delta H_v$ in Eq. (4.6)

$$\frac{d(\ln P)}{dT} = \int \frac{\Delta C_p}{RT^2} dT + \frac{I_1}{RT^2}. \quad (4.10)$$

On integration,

$$\ln P = \int \frac{dT}{RT^2} \left[ \Delta C_p dT - \frac{I_1}{RT} \right] + I_2. \quad (4.11)$$

where $I_2$ is another integration constant. If $C_p$ is independent of temperature, Eq. (4.11) reduces to

$$\ln P = \frac{\Delta C_p}{R} \ln T - \frac{I_1}{RT} + I_2. \quad (4.12)$$

4.2.2 Solid-Vapour (Sublimation) Equilibria

On the basis of assumptions similar to those made in liquid-vapour equilibria, an expression similar to Eq. (4.6) may also be obtained for solid-vapour equilibria.

$$\frac{d(\ln P)}{dT} = \frac{\Delta H_s}{RT^2}, \quad (4.13)$$

where $\Delta H_s$ is the heat of sublimation.

4.2.3 Solid-Liquid (Fusion) Equilibria

Applying the Clausius-Clapeyron equation to solid-liquid equilibria,
\[
\frac{dP}{dT} = \frac{\Delta H_f}{T(V_{\text{liq}} - V_{\text{solid}})},
\]
(4.14)

or

\[
\frac{dT}{dP} = \frac{T(V_{\text{liq}} - V_{\text{solid}})}{\Delta H_f}
\]
(4.15)

where \( \Delta H_f \) is the molar heat of fusion, \( V_{\text{liq}} \) and \( V_{\text{solid}} \) are the molar volumes of liquid and solid respectively.

Eq. (4.15) may be applied to calculate the change in melting point of a metal with change of pressure, as illustrated in the following example.

**Example 4.B**

The melting point of gallium is 30°C (303 K) at 1 atm (101,325 N/m²). The densities of solid and liquid gallium are 5.885 and 6.08 g/c.c. \((5.885 \times 10^3 \text{ kg/m}^3 \text{ and } 6.08 \times 10^3 \text{ kg/m}^3)\) respectively. The heat of fusion of gallium is 18.5 cal/g \((77.40 \times 10^3 \text{ J/kg})\). Calculate the change in melting point of gallium for an increase of pressure of 1 atm \((101,325 \text{ N/m}^2)\).

**Solution:** Molar volume of liquid gallium, \( V_{\text{liq}} \)

\[
= \frac{\text{Atomic wt of gallium}}{\text{Density of Liquid gallium}}
\]

\[
= \frac{x}{6.08} \text{ c.c.},
\]

where \( x \) denotes the atomic weight of gallium.

Similarly, molar volume of solid gallium, \( V_{\text{solid}} \)

\[
= \frac{x}{5.885} \text{ c.c.}
\]
The value of heat of fusion of gallium is given in cal/g. In order to find the value in terms of cal/mole, we must multiply by its atomic weight. Thus,

\[ \text{Molar heat of fusion} = 18.5 \times \text{cal/mole}. \]

Putting the appropriate values in Eq.(4.14),

\[ \frac{dP}{dT} = \frac{18.5 \times 303}{5.885 - 6.08} \text{cal/c.c./deg.} \]

In order to change the value in atm/deg, we should use the conversion

1 cal = 41.293 c.c. atm.

Thus,

\[ \frac{dP}{dT} = \frac{18.5 \times 41.293}{5.885 - 6.08} \text{atm/deg} \]

\[ = -462.7 \text{ atm/deg}, \]

or

\[ \frac{dT}{dP} = -2.16 \times 10^{-3} \text{ deg/atm}. \]

For \( dP = 1 \text{ atm} \),

\[ dT = -2.16 \times 10^{-3} \text{ deg}. \]

Thus, the melting point of gallium will be decreased by \( 2.16 \times 10^{-3} \text{ deg} \).

4.2.4 Solid-Solid Equilibria

The rate of change of transition temperature at which two crystalline forms of a solid are in equilibrium with pressure is given by an equation similar to
that discussed earlier. If $\alpha$ is the stable form above the transition temperature, and $\beta$ is the stable form below the transition temperature $T$, then according to Eq. (4.1),

$$\frac{dP}{dT} = \frac{\Delta H_{tr}}{T(V_{\alpha} - V_{\beta})},$$

or

$$\frac{dT}{dP} = \frac{T(V_{\alpha} - V_{\beta})}{\Delta H_{tr}},$$

where $\Delta H_{tr}$ is the molar heat of transition, $V_{\alpha}$ and $V_{\beta}$ are the molar volumes of the indicated forms, all measured at temperature $T$.

4.3 Trouton's Rule

Trouton's rule states that the ratio of latent heat of evaporation to the temperature of normal boiling $T_{b}$ is constant for all liquids, and is approximately 21 cal/deg/mole, i.e.

$$\frac{\Delta H_{v}}{T_{b}} = 21 \text{ cal/deg/mole.}$$

The rule is only an approximate one, and is not followed by all liquid metals. However, this rule may be used to derive an approximate value for latent heat of evaporation.
Example 4.4

The normal boiling point of zinc is 907°C (1180 K). Calculate its vapour pressure at 800°C (1073 K), assuming that zinc follows Trouton's rule.

Solution: According to Eq.(4.7b), the vapour pressure of liquid zinc may be expressed as

\[ \log P = \frac{-\Delta H_v}{2.303 RT} + C. \]  \hspace{1cm} (4.4.1)

Since zinc follows Trouton's rule, the molar heat of vaporization is given by

\[ \Delta H_v = 21 T_b \]

\[ = 21 \times 1180 \]

\[ = 24,780 \text{ cal/mole}. \]

Substituting the value of \( \Delta H_v \) in Eq.(4.4.1),

\[ \log P = \frac{-24,780}{4.575T} + C. \]  \hspace{1cm} (4.4.2)

The value of \( C \) can be obtained by putting boundary conditions. The vapour pressure at the normal boiling point 907°C (1180 K) is 1 atm, and hence we have

\[ \log 1 = \frac{-24,780}{4.575 \times 1180} + C, \]

or

\[ C = 4.59. \]

Substituting the value of \( C \) in Eq.(4.4.2),
\[ \log P = \frac{-24,780}{4.575 T} + 4.59 \quad (4.C.3) \]

where \( P \) is in atm.

From Eq.(4.C.3), the vapour pressure of liquid at \( 800^\circ C \) (1073 K) is given as

\[ \log P = \frac{-24,780}{4.575 \times 1073} + 4.59 \]

\[ = -0.4580, \]

or

\[ P = 0.3483 \text{ atm} \]

\[ = 264.7 \text{ mm Hg}. \]

Thus, the vapour pressure of zinc at \( 800^\circ C \) is \( 264.7 \text{ mm Hg} \).

**Exercises**

4.1 Calculate the mean heat of vaporization of palladium from the following vapour pressure data:

<table>
<thead>
<tr>
<th>Temp., °C</th>
<th>1314</th>
<th>1351</th>
<th>1568</th>
</tr>
</thead>
<tbody>
<tr>
<td>V.P., mm Hg.</td>
<td>( 7.516 \times 10^{-7} )</td>
<td>( 1.614 \times 10^{-6} )</td>
<td>( 5.625 \times 10^{-5} )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temp., K</th>
<th>1587</th>
<th>1624</th>
<th>1841</th>
</tr>
</thead>
<tbody>
<tr>
<td>V.P., N/m²</td>
<td>( 1,002 \times 10^{-7} )</td>
<td>( 215 \times 10^{-6} )</td>
<td>( 760 \times 10^{-6} )</td>
</tr>
</tbody>
</table>
4.2 The vapour pressures of liquid thorium tetraiodide at 800°C (1073 K) and 825°C (1098 K) are 468 mm Hg (62,395 N/m²) and 660 mm Hg (87,993 N/m²) respectively. Calculate its mean heat of vaporization.

4.3 The heat of evaporation of copper at its normal boiling point is 74.5 kcal/mole (311.71 kJ/mol). The vapour pressure of copper at 1500°C (1773 K) is 0.256 mm Hg (34 N/m²). Calculate the boiling point of copper.

4.4 The vapour pressure of liquid zinc as a function of temperature is given as

\[ \log P (\text{mm Hg}) = -\frac{6.620}{T} - 1.255 \log T + 12.34. \]

Calculate the heat of vaporization of zinc at its boiling point 907°C (1180 K).

4.5 The densities of liquid and solid bismuth are 10.0 g/c.c. (10 x 10³ kg/m³) and 9.673 g/c.c. (9.673 x 10³ kg/m³) respectively at the normal melting point 270°C (543 K). The heat of fusion is 2.633 kcal/mole (11.08 kJ/mol). Calculate the melting point of bismuth under a pressure of 100 atm (101,325 x 10² N/m²). Atomic weight of bismuth is 209.

4.6 The melting point of cadmium at 1 atm (101,325 N/m²) is 321°C (594 K) and its heat of fusion is 13.66 cal/g (57.15 x 10³ J/kg). The volume change on the melting of cadmium is +0.0064 c.c./g (+0.0064 x 10⁻³ m³/kg). Calculate the melting point of cadmium, (a) at 2 atm (202,650 N/m²) pressure, and (b) in vacuo.
4.7 Mercury melts at -38.87°C (234.13 K) at 1 atm (101,325 N/m²) pressure. The densities of liquid and solid mercury are 13.69 g/c.c. (13.69 x 10³ kg/m³) and 14.19 g/c.c. (14.19 x 10³ kg/m³) respectively at the normal melting point. The heat of fusion of mercury is 2.33 cal/g (9.75 x 10² J/kg). Calculate the change in melting point of mercury per atmosphere change in pressure.

4.8 The vapour pressure, P, (measured in mm Hg) of liquid arsenic, is given by

\[ \log P = -\frac{2460}{T} + 6.69, \]

and that of solid arsenic by

\[ \log P = -\frac{6947}{T} + 10.8. \]

Calculate the temperature at which the two forms of arsenic will have the same vapour pressure.

4.9 The densities of ice and liquid water at 1 atm (101,325 N/m²) and 0°C (273 K) are 0.917 g/c.c. (0.917 x 10³ kg/m³) and 0.9998 g/c.c. (0.9998 x 10³ kg/m³) respectively. The heat of fusion of water is 80 cal/g (334.72 x 10³ J/kg). Calculate the melting point of ice at 0.5 atm (50,662.5 N/m²) and 101 atm (102,338 x 10² N/m²).

4.10 The heat of the reaction

\[ \text{Sn (grey) = Sn (white)} \]

is 500 cal/mole (2,092 J/mol) at the transition temperature of 13°C (286 K). The atomic weight of tin is 118.7 and the densities of grey and white tin are 5.75 g/c.c. (5.75 x 10³ kg/m³) and 7.28 g/c.c. (7.28 x 10³ kg/m³) respectively.
Calculate the change in the transition temperature if the pressure on the grey tin phase is increased by 100 atm \((101,325 \times 10^2 \text{ N/m}^2)\).

4.11 Liquid mercury boils at 357°C \((630 \text{ K})\) at 1 atm \((101,325 \text{ N/m}^2)\). Calculate its approximate vapour pressure at 100°C \((373 \text{ K})\), assuming that it follows Trouton's rule.
CHAPTER 5
FUGACITY, ACTIVITY AND EQUILIBRIUM CONSTANT

5.1 Fugacity

The combined statement of the first and second laws of thermodynamics for a system doing work against pressure is

\[ \mathrm{d}G = V \mathrm{d}P - S \mathrm{d}T. \] (5.1)

At constant temperature, Eq.(5.1) reduces to

\[ \mathrm{d}G = V \mathrm{d}P. \] (5.2)

For one mole of an ideal gas, Eq.(5.2) reduces to

\[ \mathrm{d}G = RT \ln P. \] (5.3)

If the gas is not ideal, Eq.(5.3) takes the form

\[ \mathrm{d}G = RT \ln f, \] (5.4)

where the function \( f \) is called 'fugacity' of the gas. For an ideal gas, the fugacity is numerically equal to the pressure at all pressures. Non-ideal (or real) gases approach ideal behaviour as the pressure is decreased, i.e. as \( P \to 0, \ f \to P \). Thus, for a non-ideal gas, fugacity and pressure will be numerically equal at low pressures. Fugacity can be regarded as an idealised measure of the pressure of a gas.

5.2 Activity

The activity of a substance may be defined as the ratio of fugacity of the substance to its fugacity in its standard state. Mathematically,
where \( a \) is the activity, \( f \) is the fugacity in any arbitrary state, and \( f^0 \) is the fugacity in the standard state. Putting the value of fugacity from Eq. (5.5) in Eq. (5.4),

\[
dG = RT \, d \ln (f^0 \cdot a).
\]

Since \( f^0 \) is constant at constant temperature,

\[
dG = RT \, d \ln a. \quad (5.6)
\]

Integrating the above equation from the standard state to any arbitrary state,

\[
G - G^0 = RT \ln a - RT \ln a^0,
\]

where \( a^0 \) is the activity at the standard state. Since \( a^0 \) is unity,

\[
G - G^0 = RT \ln a. \quad (5.7)
\]

A more detailed treatment of activity will be given in the chapters dealing with solutions.

### 5.3 Equilibrium Constant

Consider a chemical reaction

\[
aA + bB + \ldots = rR + sS + \ldots \quad (5.8)
\]

at constant pressure and temperature, where \( A, B, \ldots \) are reactants, \( R, S, \ldots \) are products, and prefixes are the number of g-atoms or g-molecules of the corresponding species.
The free energy change of reaction (5.8) may be written as

$$\Delta G = \sum G_{\text{product}} - \sum G_{\text{reactant}}$$

$$= (rG_R + sG_S + ....) - (aG_A + bG_B + ....). \quad (5.9)$$

If the reactants and products are present in their standard states, then the free energy change, $\Delta G^0$, may be written as

$$\Delta G = (rG_R^0 + sG_S^0 + ....) - (aG_A^0 + bG_B^0 + ....). \quad (5.10)$$

Subtracting the above two equations,

$$\Delta G - \Delta G^0 = \left[ r(G_R - G_R^0) + s(G_S - G_S^0) + .... \right] -$$

$$\left[ a(G_A - G_A^0) + b(G_B - G_B^0) + .... \right].$$

Substituting the values of $(G - G^0)$ from Eq.(5.7),

$$\Delta G - \Delta G^0 = \left[ r(RT \ln a_R) + s(RT \ln a_S) + .... \right] -$$

$$\left[ a(RT \ln a_A) + b(RT \ln a_B) + .... \right],$$

or

$$\Delta G - \Delta G^0 = RT \ln \frac{a^r R \cdot a^s S}{a_A \cdot a_B} \ldots \ldots. \quad (5.11)$$

or

$$\Delta G = \Delta G^0 + RT \ln \frac{a^r R \cdot a^s S}{a_A \cdot a_B} \ldots \ldots. \quad (5.11)$$

If the reactants and products are in equilibrium with each other, the free energy change $\Delta G$ is zero, and hence
The term \( \frac{a^r \cdot a^s \cdot \ldots}{a_A \cdot a_B \cdot \ldots} \) is called the 'thermodynamic equilibrium constant' or 'equilibrium constant', and is denoted by \( K \). Hence, at equilibrium,

\[
\Delta G^\circ = -RT \ln K.
\]

(5.12)

In the case of traditional units, \( \Delta G^\circ \) is expressed in cal, and the value of \( R \) is 1.987 cal/deg/mole. Putting the value of \( R \) and changing to common logarithm, Eq.(5.12) becomes

\[
\Delta G^\circ = -4.575 T \log K.
\]

(5.13)

In the case of SI units, \( \Delta G^\circ \) is expressed in Joules, and the value of \( R \) is 8.314 J/K/mol. The equivalent of Eq.(5.13) in the SI units is

\[
\Delta G^\circ = -19.147 T \log K.
\]

It is evident from Eq.(5.12) that the equilibrium constant of a reaction can be calculated from knowledge of the standard free energy change of the reaction.

The application of equilibrium constant in predicting the stability of a specified oxide refractory under a designated atmosphere has been illustrated in Example 5.A. Example 5.B illustrates how the value of the equilibrium constant helps in deciding the suitability of a gas mixture for the bright annealing of a metal sheet in heat-treatment practice, while calculation of the equilibrium composition of a gas mixture has been illustrated in Example 5.C.
Example 5.A

Calculate the equilibrium constant and equilibrium partial pressure of oxygen for the reaction

\[ \text{ZrO}_2 = \text{Zr} + \text{O}_2; \]

\[ \Delta G^0 = 259,940 + 4.33 \, T \log T - 59.12 \, T \, \text{cal} \]

\[ (1,087,589 + 18.12 \, T \log T - 247.36 \, T \, \text{J}), \]

at 1727°C (2000 K). Also, predict the possibility of decomposing a pure zirconia crucible under a vacuum of \(10^{-5}\) mm Hg \((133 \times 10^{-5} \text{ N/m}^2)\) at that temperature.

Solution: The standard free energy change for the reaction

\[ \text{ZrO}_2 = \text{Zr} + \text{O}_2 \quad (5.1) \]

at 1727°C (2000 K) is given by

\[ \Delta G^0_{2000} = 259,940 + 4.33 \times 2000 \times \log 2000 - 59.12 \times 2000 \]

\[ = 170,330 \, \text{cal}. \]

The equilibrium constant of reaction (5.1) can be calculated with the help of Eq.(5.13), and thus the value of \( K \) at 1727°C is given by

\[ \log K = -\frac{170,330}{4.575 \times 2000} \]

\[ = -18.61. \]

Taking antilogs,

\[ K = 2.455 \times 10^{-19}. \]

The equilibrium constant of reaction (5.1) is

\[ K = \frac{a_{\text{Zr}} \cdot a_{\text{O}_2}}{a_{\text{ZrO}_2}}. \]
where \( a_{Zr}, a_{O_2} \) and \( a_{ZrO_2} \) are the activities of \( Zr, O_2 \) and \( ZrO_2 \) respectively. Assuming that the gases behave ideally, the activity of oxygen may be replaced by its partial pressure, i.e.

\[
K = \frac{a_{Zr} \cdot p_{O_2}}{a_{ZrO_2}}
\]

where \( p_{O_2} \) is the partial pressure of oxygen in equilibrium with \( Zr \) and \( ZrO_2 \). Pressure in the expression for \( K \) is in fact a ratio of the partial pressure of the gas (expressed in atm) to the standard pressure, i.e. 1 atm, and hence has no units. The magnitude of the pressure term in the expression for \( K \) is, therefore, equal to the partial pressure of the gas expressed in atm.

Since both \( Zr \) and \( ZrO_2 \) are pure, and hence their activities may be taken as unity, it follows that

\[
K = p_{O_2}
\]  \hspace{1cm} (5.A.2)

Putting the value of \( K \) in Eq.(5.A.2),

\[
p_{O_2} = 2.455 \times 10^{-19} \text{ atm}
\]

\[
= 760 \times 2.455 \times 10^{-19} \text{ mm Hg}
\]

\[
= 1.865 \times 10^{-16} \text{ mm Hg}
\]

Thus, the partial pressure of oxygen in equilibrium with \( Zr \) and \( ZrO_2 \) at 1727\(^\circ\)C is 1.865 \( \times 10^{-16} \) mm Hg. In other words, if the partial pressure of oxygen in the system is below this value at 1727\(^\circ\)C, then zirconia will decompose. In the present problem, the vacuum is of the order of 10\(^{-5} \) mm Hg, which is equivalent to a partial pressure of oxygen of 0.21 \( \times 10^{-5} \) mm Hg (assuming that air contains 21\% oxygen on volume basis), and this value is greater than the equilibrium partial pressure of oxygen in contact with \( Zr \) and \( ZrO_2 \) at 1727\(^\circ\)C. Hence, there is no possibility of the decomposition of
Example 5.B

Calculate the equilibrium constant for the reaction

\[ <\text{NiO}> + (\text{H}_2) = <\text{Ni}> + (\text{H}_2\text{O}) \]

at 750°C (1,023 K) from the following data:

- \( <\text{Ni}> + \frac{1}{2}(\text{O}_2) = <\text{NiO}> \); \( \Delta G^o = -58,450 + 23.55 T \text{cal} \) \((=-244,555 + 98.53 T \text{J})\).
- \( (\text{H}_2) + \frac{1}{2}(\text{O}_2) - (\text{H}_2\text{O}) \); \( \Delta G^o = -58,900 + 13.1 T \text{cal} \) \((=-246,438 + 54.81 T \text{J})\).

Could pure nickel sheet be annealed at 750°C (1,023 K) in an atmosphere containing 95% H₂O and 5% H₂ by volume without oxidation?

Solution: \( (\text{H}_2) + \frac{1}{2}(\text{O}_2) = (\text{H}_2\text{O}) \); \( \Delta G^o = -58,900 + 13.1 T \text{cal} \).

- \( <\text{Ni}> + \frac{1}{2}(\text{O}_2) = <\text{NiO}> \); \( \Delta G^o = -58,450 + 23.55 T \text{cal} \).

On subtraction,

\[ <\text{NiO}> + (\text{H}_2) = <\text{Ni}> + (\text{H}_2\text{O}) \]; \( \Delta G^o = -450 - 10.45 T \text{cal} \).

At 750°C (1023 K),

\[ \Delta G^o_{1023, (5.8.1)} = -450 - 10.45 \times 1023 \]

\[ = -11,140 \text{cal}. \]

From Eq.(5.13) it follows that

\[ \log K = - \frac{\Delta G^o}{4.575T}. \]

Putting the appropriate values in the above equation,
Fugacity, Activity, and Equilibrium Constant

\[
\log K = \frac{11,140}{4.575 \times 10^{23}} = 2.38.
\]

Taking antilogs, \( K = 240 \).

Since

\[
K = \frac{p_{H_2O} \cdot a_{Ni}}{p_{H_2} \cdot a_{NiO}}
\]

and \( a_{Ni} \) and \( a_{NiO} \) are unity,

\[
K = \frac{p_{H_2O}}{p_{H_2}}.
\]  \( (5.6.2) \)

Putting the value of \( K \) in Eq.\((5.6.2)\),

\[
\frac{p_{H_2O}}{p_{H_2}} = 240.
\]

Thus, the equilibrium \( \frac{p_{H_2O}}{p_{H_2}} \) ratio for reaction \((5.6.1)\) at 750\(^\circ\)C is 240.

Now consider an enclosed system in which nickel and nickel oxide are kept at 750\(^\circ\)C in a \( H_2-H_2O \) atmosphere. If the \( p_{H_2O}/p_{H_2} \) ratio of the atmosphere is less than the equilibrium value calculated above, then the forward reaction will occur, i.e. nickel oxide will be reduced to Ni and \( H_2O \) until the \( p_{H_2O}/p_{H_2} \) ratio equals the equilibrium value. Conversely, if the \( p_{H_2O}/p_{H_2} \) ratio is greater than the equilibrium value, the backward reaction will occur, i.e. nickel will oxidise until the equilibrium \( p_{H_2O}/p_{H_2} \) value is reached.

Alternatively, suppose a constant \( p_{H_2O}/p_{H_2} \) value is maintained (as in the present example) by passing a rapid stream of \( H_2-H_2O \) gas mixture of constant composition over the nickel and nickel oxide at 750\(^\circ\)C. If the \( p_{H_2O}/p_{H_2} \) ratio of the gas mixture is less than the equilibrium value, the reaction will proceed to the right, i.e. nickel oxide will be reduced to nickel. But in doing so, the \( p_{H_2O}/p_{H_2} \) ratio of the gas stream is not significantly changed and the stable state will be pure nickel. In a similar way, if the \( p_{H_2O}/p_{H_2} \) ratio is greater than the equilibrium value, the reaction will proceed to the left, i.e. nickel will be oxidised, and thus the stable state is nickel oxide.
In the present example, the gas atmosphere contains 95% H₂O and 5% H₂, i.e. the $p_{H₂O}/p_{H₂}$ ratio is 19, which is less than the equilibrium value of 240 at 750°C, and thus reduction of NiO will take place. Hence, if a nickel sheet is heated in the given atmosphere at 750°C, it can be annealed without oxidation. Additionally, any oxide layer present on the sheet surface will be reduced.

Example 5.C

A gas mixture of the following composition by volume:

CO: 30%, CO₂: 10%, H₂: 10%, and N₂: 50%

is fed into a heat-treating furnace at 927°C (1200 K). Calculate the equilibrium composition of the gas mixture, assuming the total pressure in the furnace to be 1 atm (101,325 N/m²), from the following data:

\[
\begin{align*}
\text{\text{C}} + \frac{1}{2}\text{O}_2 &= \text{CO}; \Delta G^o = -26,700 - 21.0 T \text{ cal} (-111,713 - 87.86 T \text{ J}). \\
\text{\text{C}} + \text{O}_2 &= \text{CO}_2; \Delta G^o = -94,200 - 0.2 T \text{ cal} (-394,133 - 0.84 T \text{ J}). \\
\text{H}_2 + \frac{1}{2}\text{O}_2 &= \text{H}_2\text{O}; \Delta G^o = -58,900 + 13.0 T \text{ cal} (-246,438 + 54.39 T \text{ J}).
\end{align*}
\]

Assume that all the gases behave ideally.

Solution: When the gas mixture containing CO, CO₂, and H₂ (N₂ being inert) is fed to the furnace, the gases will tend to react with each other until equilibrium is established for the reaction

\[
\text{(CO)} + \text{(H}_2\text{O)} = \text{(CO}_2) + \text{(H}_2).
\]

Hence, the composition of the gas mixture at equilibrium will be somewhat different from the original. As is evident from reaction (5.C.1), H₂O will also be present at the equilibrium. Thus, the problem reduces to one of finding the standard free energy change of reaction (5.C.1) and calculating
the value of the equilibrium constant. Since the equilibrium constant is related to the partial pressures of the gases, the equilibrium composition of the gas mixture can be calculated.

\[
\begin{align*}
\text{<C>} + (O_2) & = (CO_2). \quad (5.C.2) \\
\text{<C>} + \frac{1}{2}(O_2) & = (CO). \quad (5.C.3) \\
(H_2) + \frac{1}{2}(O_2) & = (H_2O). \quad (5.C.4)
\end{align*}
\]

(5.C.2)-(5.C.3)-(5.C.4) gives the required reaction

\[
(CO) + (H_2O) = (CO_2) + (H_2), \quad (5.C.5)
\]

and the free energy change is given by

\[
\Delta G^\circ = (-94,200 - 0.2 T) - (-26,700 - 21.0 T) - (-58,900 + 13.0 T)
\]

\[
= -8,600 + 7.8T \text{ cal.} \quad (5.C.6)
\]

The free energy change of reaction (5.C.5) at 927°C (1200 K) is

\[
\Delta G^\circ_{1200,(5.C.5)} = -8,600 + 7.8 \times 1200
\]

\[
= 760 \text{ cal.}
\]

The value of the equilibrium constant at 927°C is

\[
K = \text{antilog} \left[ \frac{-760}{4.575 \times 1200} \right]
\]

\[
= \text{antilog} \left[ -0.1385 \right]
\]

\[
= 0.7269.
\]

Since all the gases are behaving ideally, we have

\[
K = \frac{P_{CO_2} \cdot P_{H_2}}{P_{CO} \cdot P_{H_2O}}.
\]
Putting the value of $K$ in the above,

$$\frac{p_{CO_2} \cdot p_{H_2}}{p_{CO} \cdot p_{H_2O}} = 0.7269. \quad (5.C.7)$$

This is a relation in four unknowns; hence, in order to find out the values of all the unknowns, at least three more relations between them are needed. These can be derived as follows:

(i) The total pressure in the heat-treating furnace is 1 atm, and the gas mixture contains 50% $N_2$; hence,

$$p_{H_2} + p_{CO} + p_{CO_2} + p_{H_2O} = 0.5 \text{ atm}. \quad (5.C.8)$$

(ii) The gaseous system is composed of carbon, hydrogen, and oxygen, and the molecular species at equilibrium are $CO$, $CO_2$, $H_2$, and $H_2O$. The total amount of either carbon, hydrogen, or oxygen remains constant throughout, and is independent of the molecular constitution. Hence, three expressions for the conservation of masses of carbon, hydrogen, and oxygen can be derived, which in turn can be expressed in terms of partial pressures.

If the number of g-atoms or molecules of each is represented by $n_i$, we have

$$n_C = n'_CO + n'_CO_2 = n_{CO} + n_{CO_2}, \quad (5.C.9)$$

$$n_H = 2n'_H_2 + 2n'_H_2O = 2n_{H_2} + 2n_{H_2O}, \quad (5.C.10)$$

$$n_O = n'_CO + 2n'_CO_2 = n_{CO} + 2n_{CO_2} + n_{H_2O}, \quad (5.C.11)$$

where the primed quantities refer to the gas mixture as analysed and the unprimed quantities to the equilibrium composition of the mixture at 927°C.

Since the analyses are given in volume percent, which is proportional to the number of moles, it is convenient to consider a total mass corresponding to 1 mole of the sample as analysed. The number of moles to each constituent
is equal to the volume percent divided by 100. The number of g-atoms of carbon, hydrogen, and oxygen is conserved throughout, and hence,

\[ n_C = n_{\text{CO}} + n_{\text{CO}_2} \]
\[ = \frac{30}{100} + \frac{10}{100} \]
\[ = 0.4. \]

\[ n_H = 2n_{\text{H}_2} + 2n_{\text{H}_2\text{O}} \]
\[ = \frac{20}{100} + 0 \]
\[ = 0.2. \]

\[ n_0 = n_{\text{CO}} + 2n_{\text{CO}_2} + n_{\text{H}_2\text{O}} \]
\[ = \frac{30}{100} + \frac{20}{100} + 0 \]
\[ = 0.5. \]

Putting the values of \( n_C, n_H, \) and \( n_0 \) in Eqs. (5.C.9), (5.C.10) and (5.C.11)

\[ n_{\text{CO}} + n_{\text{CO}_2} = n_C \]
\[ = 0.4. \]

\[ 2n_{\text{H}_2} + 2n_{\text{H}_2\text{O}} = n_H \]
\[ = 0.2. \]

\[ n_{\text{CO}} + 2n_{\text{CO}_2} + n_{\text{H}_2\text{O}} = n_0 \]
\[ = 0.5. \]

Changing the above equations in terms of partial pressure with the help of
equation

\[ p_i = \frac{n_i}{n_{\text{total}}} \cdot P \]

where \( P \) is total pressure, we have

\[ p_{\text{CO}} + p_{\text{CO}_2} = 0.4, \]

\[ 2p_{\text{H}_2} + 2p_{\text{H}_2\text{O}} = 0.2, \text{ and} \]

\[ p_{\text{CO}} + 2p_{\text{CO}_2} + p_{\text{H}_2\text{O}} = 0.5. \]

Thus we have five simultaneous equations relating \( p_{\text{CO}}, p_{\text{CO}_2}, p_{\text{H}_2}, \) and \( p_{\text{H}_2\text{O}} \) as follows:

\[ p_{\text{CO}} + p_{\text{CO}_2} + p_{\text{H}_2} + p_{\text{H}_2\text{O}} = 0.5, \]

\[ p_{\text{CO}_2} \cdot p_{\text{H}_2} = 0.7269 \cdot p_{\text{CO}} \cdot p_{\text{H}_2\text{O}}, \]

\[ p_{\text{CO}} + p_{\text{CO}_2} = 0.4, \]

\[ 2p_{\text{H}_2} + 2p_{\text{H}_2\text{O}} = 0.2, \text{ and} \]

\[ p_{\text{CO}} + 2p_{\text{CO}_2} + p_{\text{H}_2\text{O}} = 0.5. \]

From the above five equations, the values of \( p_{\text{CO}}, p_{\text{CO}_2}, p_{\text{H}_2}, \) and \( p_{\text{H}_2\text{O}} \) can be calculated, and the values are

\[ p_{\text{H}_2\text{O}} = 0.024 \quad p_{\text{H}_2} = 0.076 \quad p_{\text{CO}} = 0.324 \]

and \( p_{\text{CO}_2} = 0.076. \)

In terms of volume percent, the equilibrium composition of the gas mixture is

\[ \text{H}_2\text{O} = 2.4\%, \text{ H}_2 = 7.6\%, \text{ CO} = 32.4\%, \]

\[ \text{CO}_2 = 7.6\% \text{ and N}_2 = 50\%. \]
5.4 Van't Hoff Equation

The Gibbs-Helmholtz equation at constant pressure is represented as

\[ \frac{d(\Delta G^0/T)}{d(1/T)} = \Delta H^0. \]

Substituting the value of \( \Delta G^0 \) from Eq. (5.12),

\[ \frac{d(\ln K)}{d(1/T)} = -\frac{\Delta H^0}{R} . \] (5.14)

or

\[ \frac{d(\ln K)}{dT} = \frac{\Delta H^0}{RT^2}. \] (5.15)

The above equation is commonly called the Van't Hoff equation.

5.4.1. Integration of Van't Hoff Equation

From Eq. (5.14) it follows that

\[ -R \frac{d(\ln K)}{d(1/T)} = \Delta H^0 \frac{1}{T} . \] (5.16)

\( \Delta H^0 \) is not independent of temperature; hence, in order to integrate the above equation, it must be converted to a form in which there is no term dependent on temperature.

Since \( \left( \frac{\partial \Delta H}{\partial T} \right)_p = \Delta C_p \). Assuming that \( C_p \) is expressed in the form

\[ C_p = a + bT - cT^{-2}, \]

we have,
\[
\left( \frac{\partial \Delta H}{\partial T} \right)_P = \Delta a + \Delta b T - \Delta c T^{-2},
\]
or
\[
d\Delta H = (\Delta a + \Delta b T - \Delta c T^{-2})dT.
\]
For the standard state also, we have
\[
d\Delta H^0 = (\Delta a + \Delta b T - \Delta c T^{-2})dT.
\]
Integrating the above equation,
\[
\Delta H^0 = \Delta a T + \frac{\Delta b T^2}{2} + \frac{\Delta c}{T} + \Delta H_0,
\]
where \(\Delta H_0\) is an integration constant.

Putting the value of \(\Delta H^0\) in Eq.(5.16),
\[
-R \left( \ln K \right) = \Delta a T \left( \frac{1}{T} \right) + \frac{\Delta b T^2}{2} \left( \frac{1}{T} \right) - \frac{\Delta c}{T T^2} + \Delta H_0 \left( \frac{1}{T} \right).
\]
Since \(d\left( \frac{1}{T} \right) = -\frac{dT}{T^2}\), we have
\[
-R \left( \ln K \right) = -\frac{\Delta a T}{T^2} \frac{dT}{T} - \frac{\Delta b T^2}{2 T^2} \frac{dT}{T} - \frac{\Delta c}{T T^2} \frac{dT}{T} + \Delta H_0 \left( \frac{1}{T} \right)
\]
\[
= -\Delta a \frac{dT}{T} - \frac{\Delta b}{2} \frac{dT}{T} - \frac{\Delta c}{T} \frac{dT}{T^3} + \Delta H_0 \left( \frac{1}{T} \right).
\]
Integrating the above equation,
\[
-R \ln K = -\Delta a \ln T - \frac{\Delta b}{2} T - \frac{\Delta c}{2 T^2} - \frac{\Delta H_0}{T} + I,
\]
where \(I\) is an integration constant.

On rearranging,
\[
-R \ln K + \Delta a \ln T + \frac{\Delta b}{2} T - \frac{\Delta c}{2 T^2} = \frac{\Delta H_0}{T} + I.
\]  
(5.18)
The left-hand side of the above equation is commonly designated as \(\Sigma\) and is
Fugacity, Activity, and Equilibrium Constant

called 'sigma function'.

Thus,

$$
\Sigma = -R \ln K + \Delta a \ln T + \frac{\Delta b}{2} T - \frac{\Delta c}{2T^2}.
$$

(5.19)

It is evident from Eq.(5.18) that the equilibrium constant of a reaction at any temperature can be calculated from the heat capacity values of the reactants and products, provided the equilibrium constant values at two different temperatures are known, as illustrated in the following example.

**Example 5.D**

The equilibrium constants for the decomposition of nickel oxide

$$
\text{NiO} = \text{Ni} + \frac{3}{2}\text{O}_2
$$

are \(1.514 \times 10^{-11}\) and \(2.355 \times 10^{-8}\) at 527°C and 727°C (800 and 1000 K) respectively. Calculate the value of the equilibrium constant at 627°C (900 K) from the following data:

- \(\text{C}_p,\text{NiO} = 11.18 + 2.02 \times 10^{-3} T\) cal/deg/mole \((46.78 + 8.45 \times 10^{-3} T\) J/K/mol) in the range 292° - 1527°C.

- \(\text{C}_p,\text{Ni} = 7.10 + 1.0 \times 10^{-3} T - 2.23 \times 10^5 T^{-2}\) cal/deg/mole \((29.71 + 4.184 \times 10^{-3} T - 9.33 \times 10^5 T^{-2}\) J/K/mol) in the range 357°C - M.P.

- \(\text{C}_p,\text{O}_2 = 7.16 + 1.0 \times 10^{-3} T - 0.4 \times 10^5 T^{-2}\) cal/deg/mole \((29.96 + 4.184 \times 10^{-3} T - 1.67 \times 10^5 T^{-2}\) J/K/mol) in the range 20° - 272°C.

**Solution:** The heat capacity change for the reaction

$$
\text{NiO} = \text{Ni} + \frac{3}{2}\text{O}_2
$$

is written as
\[ \Delta C_p = \Sigma C_{p,\text{product}} - \Sigma C_{p,\text{reactant}} \]

Putting the appropriate values in the above,

\[ \Delta C_p = (7.10 + 1.0 \times 10^{-3} T - 2.23 \times 10^5 T^{-2}) + \frac{1}{2}(7.16 + 1.0 \times 10^{-3} T - 0.4 \times 10^5 T^{-2}) - (11.18 + 2.02 \times 10^{-3} T) \]

\[ = -0.5 - 0.52 \times 10^{-3} T - 2.43 \times 10^5 T^{-2} . \]

Thus, \( \Delta a = -0.5, \Delta b = -0.52 \times 10^{-3}, \) and \( \Delta c = 2.43 \times 10^5. \)

Substituting the values of \( \Delta a, \Delta b, \) and \( \Delta c \) in Eq.(5.18), and changing to common logarithm,

\[ -4.575 \log K = -2.303 \log T - 0.52 \times 10^{-3} T - 2.43 \times 10^5 T^{-2} \]

or \[ -4.575 \log K = -1.151 \log T - 0.26 \times 10^{-3} T - \frac{1.215 \times 10^5}{T^2} = \frac{\Delta H_0}{T} + I . \]

Putting the value of \( K \) at \( 527^\circ C \) (800 \( K \)) in Eq.(5.18),

\[ -4.575 \log(1.514 \times 10^{-11}) = 1.151 \log 800 - 0.26 \times 10^{-3} \times 800 - \frac{1.215 \times 10^5}{800^2} \]

\[ = \frac{\Delta H_0}{800} + I . \]

On simplification,

\[ \frac{\Delta H_0}{800} + I = 45.7611 . \]

Similarly, putting the value of \( K \) at \( 727^\circ C \) (1000 \( K \)) in Eq.(5.18),
\[ \frac{\Delta H_0}{1000} + I = 31.0655 \]  
\[ (5.D.3) \]

From Eqs. (5.D.2) and (5.D.3),
\[ \frac{\Delta H_0}{800} - \frac{\Delta H_0}{1000} = 14.6956, \]
or
\[ \Delta H_0 = \frac{800 \times 1000 \times 14.6956}{200} = 58,800. \]

Substituting the value of \( \Delta H_0 \) in Eq. (5.D.3),
\[ 58.80 + I = 31.0655, \]
or
\[ I = -58.80 + 31.0655 = -27.734. \]

Substituting the values of \( \Delta H_0 \) and \( I \) in Eq. (5.D.1),
\[ -4.575 \log K - 1.151 \log T - 0.26 \times 10^{-3} T - \frac{1.215 \times 10^5}{T^2} \]
\[ = \frac{58800}{T} - 27.734, \]
or
\[ 4.575 \log K = -1.151 \log T - 0.26 \times 10^{-3} T - \frac{1.215 \times 10^5}{T^2} - \frac{58800}{T} + 27.734. \]

At \( T = 627^\circ C \) (900 K), and on simplification, we have
\[ \log K = -9.046. \]

Taking antilogs,
\[ K = 8.995 \times 10^{-10}. \]

The value of equilibrium constant at 627\(^\circ\)C is \( 8.995 \times 10^{-10} \).
5.1 The equilibrium constant for the reaction

\[(H_2) + [O]_{Fe, wt\%} \rightarrow (H_2O)\]

in the range of 1563°C (1836 K) to 1750°C (2023 K) is given by

\[\log K = \frac{7250}{T} - 3.17.\]

State the expression for \(\Delta G^0\) as a function of temperature. Also, find \(\Delta G^0\) for the reaction

\[\frac{1}{2}O_2 = [O]_{Fe, wt\%}\]

at 1600°C (1873 K) from the following data:

\[(H_2) + \frac{1}{2}O_2 \rightarrow (H_2O);\]

\[\Delta G^0 = -60,180 + 13.93T \text{ cal} (-251,793 + 58.28T \text{ J}).\]

5.2 The equilibrium constants of the reactions

\[<FeO> + (CO) = <Fe> + (CO_2); K_1\]

\[<FeO> + (H_2) = <Fe> + (H_2O); K_2\]

at various temperatures, are given below:

<table>
<thead>
<tr>
<th>Temp., °C</th>
<th>600</th>
<th>700</th>
<th>800</th>
<th>900</th>
<th>1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Temp., K)</td>
<td>873</td>
<td>973</td>
<td>1073</td>
<td>1173</td>
<td>1273</td>
</tr>
</tbody>
</table>
Calculate the equilibrium constant of the reaction

\[(\text{CO}) + (\text{H}_2\text{O}) = (\text{CO}_2) + (\text{H}_2)\]

at the above temperatures. Also calculate the heat of reaction for the production of hydrogen from carbon monoxide and water vapour, assuming it to be independent of temperature.

5.3 The complete reduction of $\alpha$W$_{0.3}$ takes place in four successive stages, according to the following reactions:

\[
10 \alpha\text{W}_0.3 + \text{H}_2 = 10 \text{W}_02.9 + \text{H}_2\text{O} \quad ; \quad K_1. \\
\log K_1 = \frac{-3.792}{T} + 4.8268.
\]

\[
\frac{50}{9} \text{W}_02.9 + \text{H}_2 = \frac{50}{9} \text{W}_02.72 + \text{H}_2\text{O} \quad ; \quad K_2. \\
\log K_2 = \frac{-1.442.5}{T} + 1.684.
\]

\[
\frac{50}{36} \text{W}_02.72 + \text{H}_2 = \frac{50}{36} \text{W}_02 + \text{H}_2\text{O} \quad ; \quad K_3. \\
\log K_3 = \frac{-801.7}{T} + 0.8615.
\]

\[
\frac{1}{2} \text{W}_02 + \text{H}_2 = \frac{1}{2} \text{W} + \text{H}_2\text{O} \quad ; \quad K_4. \\
\log K_4 = \frac{-2.219}{T} + 1.5809.
\]

Find an expression for the standard free energy change for the complete reduction of $\alpha$W$_{0.3}$, i.e.

\[\alpha\text{W}_03 + 3 \text{H}_2 = \text{W} + 3 \text{H}_2\text{O}\]
as a function of temperature and, hence, calculate its value at 800°C (1073 K).

5.4 Calculate the vacuum needed for obtaining molybdenum metal according to the reaction

\[ \text{MoS}_2 = \text{Mo} + S_2 \]

at 800°C (1073 K) and 1000°C (1273 K).

Given: \[ \text{MoS}_2 + 2 \text{H}_2 = \text{Mo} + 2 \text{H}_2\text{S} ; K_1. \]

\[ 2 \text{H}_2\text{S} = 2 \text{H}_2 + S_2 ; K_2. \]

Temp., °C : 800 1000  
(Temp., K : 1073 1273)  
\[ K_1 : 7.311 \times 10^{-6} \quad 1.439 \times 10^{-3} \]

\[ K_2 : 2.2 \times 10^{-4} \quad 5.6 \times 10^{-3} \]

5.5 Calculate the \( \text{CO}/\text{CO}_2 \) ratio in equilibrium with carbon at 727°C (1000 K) assuming that the total pressure to be 2 atm (202650 N/m²).

Given: \[ 2 \text{C} + \text{O}_2 = 2 \text{CO} ; \Delta G_{1000}^0 = -95.3 \text{ kcal} (-398.7 \text{ kJ}). \]

\[ \text{C} + \text{O}_2 = \text{CO}_2 ; \Delta G_{1000}^0 = -94.0 \text{ kcal} (-393.3 \text{ kJ}) \]

5.6 Calculate the equilibrium partial pressure of Zn vapour and CO at 1200°C (1473 K) according to the following reaction:

\[ <\text{ZnO}> + <\text{C}> = (\text{Zn}) + (\text{CO}); \]
\[ \Delta G^0 = 88,720 + 10.35 T \log T - 103.33 T \text{cal} \\
(371,204 + 43.30 T \log T - 432.33 T \text{J}). \]

Assume that the reaction is carried out in a closed retort containing no air.

5.7 Evaluate the partial pressure of Mg vapour at 1200°C (1473 K) for the following reaction:

\[ 2\text{MgO} + 2\text{CaO} + \text{Si} = 2\text{Mg} + 2\text{CaO}_2\cdot\text{Si}. \]

Given: \[ 2\text{MgO} + \text{Si} = 2\text{Mg} + 2\text{CaO}_2\cdot\text{Si}; \]
\[ \Delta G^0 = 152,600 + 11.37 T \log T - 99.18 T \text{cal} \\
(638,478 + 47.57 T \log T - 414.97 T \text{J}). \]

\[ 2\text{CaO} + \text{Si}_2 = 2\text{CaO}_2\cdot\text{Si}; \]
\[ \Delta G^0 = -30,200 - 1.2 T \text{cal} (-126,357 - 5.02 T \text{J}). \]

5.8 In a copper converter, the following reaction is believed to occur in the latter stages:

\[ \{\text{Cu}_2\text{S}\} + 2\{\text{Cu}_2\text{O}\} = 6\{\text{Cu}\} + (\text{SO}_2); \]
\[ \Delta G^0 = -87.15 T \text{cal} (-364 - 21.46 T \text{J}). \]

Calculate the equilibrium partial pressure of \( \text{SO}_2 \) at 1250°C (1523 K). Assume that both \( \text{Cu}_2\text{S} \) and \( \text{Cu}_2\text{O} \) exist as pure melts.

5.9 Will a magnesia crucible decompose at 1000°C (1273 K) in a vacuum of 0.01 atm (1013 N/m²)?
Given: \[ \langle \text{MgO} \rangle = \{ \text{Mg} \} + \frac{1}{2} (\text{O}_2); \]
\[ \Delta G^0 = 145,350 + 0.24 T \log T - 26.95 T \text{cal} \]
\[ (808,144 + 1.0 T \log T - 112.35 T \text{J}). \]

5.10 Will a blast furnace gas analyzing 28% CO, 13% CO\textsubscript{2} and 59% N\textsubscript{2} reduce wustite (FeO) at 727°C (1000 K)?

Given: \[ \langle \text{Fe} \rangle + \frac{1}{2} (\text{O}_2) = \langle \text{FeO} \rangle; \]
\[ \Delta G^0 = -62,050 + 14.95 T \text{cal} \]
\[ (-256,817 + 62.55 T \text{J}). \]
\[ (\text{CO}) + \frac{1}{2} (\text{O}_2) = (\text{CO}_2); \]
\[ \Delta G^0 = -67,500 + 20.75 T \text{cal} \]
\[ (-282,420 + 86.82 T \text{J}). \]

5.11 Calculate the equilibrium constant at 727°C (1000 K) for the reaction

\[ \langle \text{FeO} \rangle + (\text{CO}) = \langle \text{Fe} \rangle + (\text{CO}_2) \]

from the following data:

\[ \langle \text{FeO} \rangle + (\text{H}_2) = \langle \text{Fe} \rangle + (\text{H}_2\text{O}); \]
\[ \Delta G^0 = 3,150 - 1.85 T \text{cal} \]
\[ (13,180 - 7.74 T \text{J}). \]
\[ (\text{CO}_2) + (\text{H}_2) = (\text{CO}) + (\text{H}_2\text{O}); \]
\[ \Delta G^0 = 8,600 - 7.8 T \text{cal} \]
\[ (35,982 - 32.63 T \text{J}). \]

Will FeO form if an iron sheet is annealed at 727°C (1000 K) in an atmosphere containing 10% CO, 2% CO\textsubscript{2} and 88% N\textsubscript{2}?
5.12 One stage of an industrial process involves the drying of moist silver carbonate in an air stream at 110°C (383 K), without decomposing it according to the following reaction:

$$\text{Ag}_2\text{CO}_3 = \text{Ag}_2\text{O} + \text{CO}_2;$$

$$\Delta G^o_{383} = 3.512 \text{ kcal (14.69 kJ).}$$

Calculate the minimum partial pressure of CO$_2$ which must be introduced into the stream of air used.

5.13 Chromium plates are bright annealed at 727°C (1000 K) in a wet hydrogen atmosphere. The pressure of wet hydrogen is 1 atm (101,325 N/m$^2$).

(i) Calculate the permissible water content in the hydrogen if there is to be no oxidation at 727°C (1000 K).

(ii) Will annealed chromium plates be oxidized when cooled to 227°C (500 K) in the furnace atmosphere, as calculated in (i)?

Neglect the possibility of dissolution of hydrogen in chromium.

Given:  

$$2\text{Cr} + 3(\text{H}_2\text{O}) = \text{Cr}_2\text{O}_3 + \text{(H}_2);$$

$$\Delta G^o = -91,050 + 22.80 \text{T cal} (-380,953 + 95.4 \text{T J}).$$
CHAPTER 6

SOLUTIONS: I

6.1 Introduction

A solution (whether solid, liquid, or gaseous) may be defined as a homogeneous phase composed of different chemical substances, whose concentration may be varied without the precipitation of a new phase. The composition of the solution may be expressed in a number of ways. In metallurgy, it is usually expressed either as 'weight percent' or 'atom percent'.

For example, consider a solution consisting of \( n \) components. Let \( w_1, w_2, \ldots, w_i, \ldots, w_n \) represent the weights of each respective component, and \( n_1, n_2, \ldots, n_i, \ldots, n_n \) represent the number of g-atoms of each respective component in the solution. Then the weight percent of component \( i \), \( \text{wt}\% \ i \), may be expressed as

\[
\text{wt}\% \ i = \frac{w_i}{w_1 + w_2 + \ldots + w_i + \ldots + w_n} \times 100.
\]

Similarly, the atom percent of component \( i \), \( \text{atom}\% \ i \), may be expressed as

\[
\text{atom}\% \ i = \frac{n_i}{n_1 + n_2 + \ldots + n_i + \ldots + n_n} \times 100.
\]

However, these two ways of expressing the proportion of any component are related to each other. In the case of a binary solution, \( A-B \), the relations are

\[
\text{wt}\% \ A = \left[ \frac{\text{atom}\% \ A \times \text{at wt } A}{\text{atom}\% \ A \times \text{at wt } A + \text{atom}\% \ B \times \text{at wt } B} \right] \times 100. \quad (6.1)
\]

\[
\text{atom}\% \ A = \left[ \frac{\text{wt}\% \ A}{\text{at wt } A + \text{wt}\% \ B \text{ at wt } B} \right] \times 100. \quad (6.2)
\]
Another way of expressing the composition is 'mole (or atom) fraction'. Mole (or atom) fraction is defined as the number of \( g \)-moles (or \( q \)-atoms) of substance divided by the total number of \( g \)-moles (or \( q \)-atoms) of all the substances comprising the solution. Thus, in a multi-component solution consisting of \( n_1, n_2, \ldots, n_i, \ldots, n_n \) \( g \)-moles of component 1, 2, \ldots, \( i \), \ldots, \( n \), respectively, the mole fraction of component \( i \), \( x_i \), may be expressed as

\[
x_i = \frac{n_i}{n_1 + n_2 + \ldots + n_i + \ldots + n_n}.
\]  

(6.3)

However, it is evident that the sum of the mole fractions of all the components must always equal one, i.e.

\[
x_1 + x_2 + \ldots + x_i + \ldots + x_n = 1.
\]  

(6.4)

Sometimes the composition of slag is expressed in terms of 'ionic fraction'. The ionic fraction of ion \( i \) may be defined as the ratio of the number of \( g \)-ions of ion \( i \) to the total number of \( q \)-ions of both signs.

**Example 6.A**

A brass contains 70 wt% of copper and the rest zinc. Calculate the composition of the brass in atom %. Also, calculate the atom fractions of copper and zinc in the above brass. Atomic weights of copper and zinc are 63.54 and 65.38 respectively.

**Solution:** Applying Eq.(6.2),

\[
\text{atom } \% \text{ Cu } = \frac{70/63.54}{70/63.54 + 30/65.38} \times 100
\]

\[
= 70.62.
\]

\[
\therefore \text{ atom } \% \text{ Zn } = (100 - 70.62)
\]

\[
= 29.38.
\]
Applying Eq. (6.3),

\[
\text{atom fraction of Cu} = \frac{70.62}{100} = 0.7062.
\]

Thus,

\[
\text{atom fraction of Zn} = (1 - 0.7062) = 0.2938.
\]

6.2 Partial Molar Quantities

The total value of any extensive function of state, \( Z' \) (e.g. \( V, H, S, G \), etc.) of a solution consisting of \( n_1, n_2, \ldots, n_i, \ldots \) moles of components 1, 2, \ldots, \( i, \ldots \) respectively may be considered as a function of temperature, pressure, and the amount of different components, i.e.

\[
Z' = f(T, P, n_1, n_2, \ldots, n_i, \ldots).
\]

The total differential may be expressed as

\[
dZ' = \left[ \left( \frac{\partial Z'}{\partial T} \right)_{P,n_1,n_2,\ldots}dT + \left( \frac{\partial Z'}{\partial P} \right)_{T,n_1,n_2,\ldots}dP + \left( \frac{\partial Z'}{\partial n_1} \right)_{T,P,n_2,\ldots}dn_1 \\
+ \left( \frac{\partial Z'}{\partial n_2} \right)_{T,P,n_1,n_3,\ldots}dn_2 + \ldots + \left( \frac{\partial Z'}{\partial n_i} \right)_{T,P,n_1,n_2,\ldots,n_{i-1},n_{i+1}}dn_i \\
+ \ldots + \ldots \right]
\]

\[
= \left[ \left( \frac{\partial Z'}{\partial T} \right)_{P,n_1,n_2,\ldots}dT + \left( \frac{\partial Z'}{\partial P} \right)_{T,n_1,n_2,\ldots}dP + \tilde{Z}_1 dn_1 + \tilde{Z}_2 dn_2 \\
+ \ldots + \tilde{Z}_i dn_i + \ldots \right], \quad (6.5)
\]
where, in general

\[ Z_i = \left( \frac{\partial Z'}{\partial n_i} \right)_{T,P,n_1,n_2,...,n_{i-1},n_{i+1},...} \]

\( Z_i \) is described as the partial molar property of component \( i \) in the solution and may be defined as the rate of change of the extensive property \( Z' \) when an infinitesimal amount of component \( i \) is added to the system, keeping the temperature, pressure and amount of all other components constant.

Partial molar properties are intensive properties. For a system at constant temperature and pressure, the total value of extensive property \( Z' \) is given by

\[ Z' = \Sigma n_i Z_i, \quad (6.6) \]

and the value of the extensive property per mole of the system \( Z \) is given by

\[ Z = \Sigma x_i Z_i, \quad (6.7) \]

where \( x_i \) is the mole fraction of component \( i \).

Since \( Z \) may be any extensive property, we may have the following relations:

\[ V = x_1 \tilde{V}_1 + x_2 \tilde{V}_2 + \ldots + x_i \tilde{V}_i + \ldots, \]
\[ H = x_1 \tilde{H}_1 + x_2 \tilde{H}_2 + \ldots + x_i \tilde{H}_i + \ldots, \]
\[ S = x_1 \tilde{S}_1 + x_2 \tilde{S}_2 + \ldots + x_i \tilde{S}_i + \ldots, \]
\[ G = x_1 \tilde{G}_1 + x_2 \tilde{G}_2 + \ldots + x_i \tilde{G}_i + \ldots, \]

where \( V, H, S, \) and \( G \) represent the molar volume, enthalpy, entropy, and free energy respectively. The partial molar free energy is also known as chemical potential, and is also designated by \( \mu \).

The various partial molar quantities are related to each other by the relations previously mentioned for a system of fixed composition. Some of the relations are as follows:
\[ \tilde{G}_i = \tilde{H}_i - \tilde{T}\tilde{S}_i \quad (6.8) \]

\[ \left( \frac{\partial \tilde{G}_i}{\partial T} \right)_P = -\tilde{S}_i. \quad (6.9) \]

\[ \left[ \frac{\partial (\tilde{G}_i/T)}{\partial (1/T)} \right]_P = \tilde{H}_i \quad (6.10) \]

\[ \left( \frac{\partial \tilde{G}_i}{\partial P} \right)_T = \tilde{V}_i. \quad (6.11) \]

In the last chapter, it has been determined that

\[ d\tilde{G} = RT \, d \ln a, \]

and hence, for a component \( i \) in the solution,

\[ d\tilde{G}_i = RT \, d \ln a_i. \quad (6.12) \]

### 6.3 Gibbs-Duhem Equation

The Gibbs-Duhem equation for any extensive function of state \( Z \) at constant temperature and pressure can be expressed as

\[ \Sigma x_i \, d\tilde{Z}_i = 0. \quad (6.13) \]

For a binary system \( A-B \), at constant temperature and pressure,

\[ x_A \cdot d\tilde{Z}_A + x_B \cdot d\tilde{Z}_B = 0. \quad (6.14) \]

Since \( Z \) can be any extensive function of state, some of the forms of Gibbs-
Duhem equation are as follows:

\[ x_A \cdot d\bar{\gamma}_A + x_B \cdot d\bar{\gamma}_B = 0. \]  \hspace{1cm} (6.15)

\[ x_A \cdot d\bar{\rho}_A + x_B \cdot d\bar{\rho}_B = 0. \]  \hspace{1cm} (6.16)

\[ x_A \cdot d\bar{\xi}_A + x_B \cdot d\bar{\xi}_B = 0. \]  \hspace{1cm} (6.17)

\[ x_A \cdot d\bar{\xi}_A + x_B \cdot d\bar{\xi}_B = 0. \]  \hspace{1cm} (6.18)

The application of the Gibbs-Duhem equation will be dealt with later.

6.4. Determination of Partial Molar Quantities from Molar Quantities

In a binary solution A-B, the partial molar quantities \( \bar{Z}_A \) and \( \bar{Z}_B \) may be related to the molar quantity \( Z \) as below

\[ \bar{Z}_A = Z + \left( 1 - x_A \right) \frac{dZ}{dx_A} x_B, \]  \hspace{1cm} (6.19)

and  \[ \bar{Z}_B = Z + \left( 1 - x_B \right) \frac{dZ}{dx_B} x_A. \]  \hspace{1cm} (6.20)

With the help of Eqs. (6.19) and (6.20), \( \bar{Z}_A \) and \( \bar{Z}_B \) can be found from a knowledge of \( Z \), either analytically or graphically. Analytically, it can be seen that if \( Z \) may be expressed by an empirical expression, then a corresponding expression for \( \bar{Z}_A \) and \( \bar{Z}_B \) results from these equations. The values of \( \bar{Z}_A \) and \( \bar{Z}_B \) may also be found graphically if the molar quantity \( Z \) is known over a range of composition. The method consists of plotting the value of molar quantity \( Z \) against concentration expressed in mole fraction.
of any one of the components (Fig. 6.1) and then drawing a tangent to the curve at the concentration at which the value of partial molar quantity is to be obtained (say at M).

The values of $\bar{Z}_A$ and $\bar{Z}_B$ are given by the intersection of the tangent with axis at $x_A = 1$ and $x_B = 1$ respectively. The evaluation of the partial molar quantities is illustrated in the following example.

![Graphical Method of Calculating Partial Molar Quantities from Molar Quantities.](image-url)
Example 6.B

The enthalpies of mixing of Cd-Sn alloys at 500°C (773 K) are given below:

<table>
<thead>
<tr>
<th>x_{Cd}</th>
<th>0</th>
<th>0.1</th>
<th>0.3</th>
<th>0.5</th>
<th>0.7</th>
<th>0.9</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔH^M, cal/mole</td>
<td>0</td>
<td>298.2</td>
<td>652.4</td>
<td>800.0</td>
<td>6,205.0</td>
<td>251.5</td>
<td>0</td>
</tr>
</tbody>
</table>

(ΔH^M, J/mol : 0 1,247.7 2,729.6 3,347.2 25,962.0 1,052.3 0).

Calculate the values of the partial molar enthalpies of mixing of cadmium and tin in a Cd-Sn alloy containing 60 atom % cadmium.

Solution: In order to find out the values of the partial molar enthalpies of mixing of cadmium, ΔH^M_{Cd}, and that of tin, ΔH^M_{Sn}, a graph is plotted between ΔH^M and x_{Cd} and a tangent is drawn at x_{Cd} = 0.6, as shown in Fig. 6.2.

Fig. 6.2. Graphical Determination of Partial Molar Enthalpies of Mixing of Cadmium and Tin.
The values of $H^M_{Cd}$ and $H^M_{Sn}$ are given by the intersection of the tangent with axis at $x_{Cd} = 1.0$ and $x_{Sn} = 1.0$ (i.e. $x_{Cd} = 0$) respectively. It follows from the graph that

$$H^M_{Cd} = 320 \text{ cal/mole}, \text{ and } H^M_{Sn} = 1,360 \text{ cal/mole}.$$
Assuming that the vapour behaves ideally, on combination with Eq.(5.5), we have

\[ a_i = x_i \]  \hspace{1cm} (6.22)

It is evident from Eq.(6.21) that the vapour pressure of any component of a solution is directly proportional to the mole fraction of that component in the solution, provided the solution obeys Raoult's law. Also, if the solution obeys Raoult's law, the activity of any component is equal to the mole fraction of that component in the solution. The solution which obeys Raoult's law is called an 'Ideal Solution'. It has been found that in actual solutions the activity of a component is directly proportional to the mole fraction of that component. It can be either greater or less than the value expected from the solution, if it followed Raoult's law, as shown in Fig.6.3.

Fig. 6.3. Relationship between Activity and Concentration of a Component in Solution, showing both Positive and Negative Deviation from Raoult's Law.
Also, it has been found that Raoult's law holds good for a number of systems at higher concentrations of solvent, as shown in the above figure.

*Example 6.C*

In the basic open-hearth process, the reaction of manganese in the bath with iron oxide (FeO) in the slag attains a condition very closely approximating to true equilibrium. The steel contains 0.065 atom % manganese and the slag analysis (by weight) is

\[
\text{FeO} - 76.94\% , \text{Fe}_2\text{O}_3 - 4.15\% , \text{MnO} - 13.86\% , \\
\text{MgO} - 3.74\% , \text{SiO}_2 - 1.06\% , \text{and CaO} - 0.25\% .
\]

Calculate the value of the equilibrium constant and standard free energy change for the above reaction at 1655°C (1928 K), assuming that the slag and Fe-Mn system behave ideally at that temperature. Neglect the effect of other metalloids present in the steel.

Given: Molecular weights of FeO: 71.85, Fe$_2$O$_3$: 159.85,
MnO: 70.94, MgO: 40.32, SiO$_2$: 60.09 and CaO: 56.08.

Solution: The reaction which occurs may be expressed as:

\[
(\text{FeO})_{\text{slag}} + [\text{Mn}]_{\text{metal}} = (\text{MnO})_{\text{slag}} + [\text{Fe}]_{\text{metal}}.
\]

The equilibrium constant of the above reaction may be written as

\[
K = \frac{[a_{\text{MnO}}] \cdot [a_{\text{Fe}}]}{(a_{\text{FeO}})_{\text{total}} \cdot [a_{\text{Mn}}]}
\]

Since slag and Fe-Mn system behave ideally at 1655°C, the activities can be changed to their respective mole fractions. The effect of other metalloids present in the steel is negligible and the atom percent of Mn is very small;
hence the mole fraction of Fe may be assumed to be one. Thus

\[ K = \frac{x_{\text{MnO}}}{(x_{\text{FeO}})_{\text{total}}} \cdot \frac{x_{\text{Mn}}}{x_{\text{Fe}}} \]

The analysis of the slag is given in weight percent. The mole fractions of FeO, Fe\(_2\)O\(_3\) and MnO can be calculated as follows:

<table>
<thead>
<tr>
<th>Slag component</th>
<th>wt % (a)</th>
<th>mol wt (b)</th>
<th>g-mole (c = (\frac{a}{b}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeO</td>
<td>76.94</td>
<td>71.85</td>
<td>1.0710</td>
</tr>
<tr>
<td>Fe(_2)O(_3)</td>
<td>4.15</td>
<td>159.85</td>
<td>0.0259</td>
</tr>
<tr>
<td>MnO</td>
<td>13.86</td>
<td>70.94</td>
<td>0.1954</td>
</tr>
<tr>
<td>MgO</td>
<td>3.74</td>
<td>40.32</td>
<td>0.0927</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>1.06</td>
<td>60.09</td>
<td>0.0176</td>
</tr>
<tr>
<td>CaO</td>
<td>0.25</td>
<td>56.08</td>
<td>0.0044</td>
</tr>
</tbody>
</table>

In the slag, iron and oxygen are also present in the form of Fe\(_2\)O\(_3\). Hence mole fraction of Fe\(_2\)O\(_3\) should be converted in terms of FeO in order to obtain total value of \(x_{\text{FeO}}\). Since reaction can take place to produce FeO according to the equation

\[ \text{Fe}_2\text{O}_3 + 2\text{FeO} + \frac{3}{2}\text{O}_2, \]

it follows that one mole of Fe\(_2\)O\(_3\) gives two moles of FeO.

\[ \therefore \text{Total g-mole of FeO} = \text{g-mole of FeO} + 2 \times \text{g-mole of Fe}_2\text{O}_3 \]

\[ = 1.0710 + 2 \times 0.0259 \]

\[ = 1.1228. \]

Total g-mole of constituents in the slag = 1.1228 + 0.1954 + 0.0927

\[ + 0.0176 + 0.0044 \]

\[ = 1.4329. \]
Mole fraction of total FeO in slag, \( x_{Fepn}^{total} \) = \( \frac{1.1228}{1.4329} \) = 0.7835.

Mole fraction of MnO in slag, \( x_{MnO} \) = \( \frac{0.1954}{1.4329} \) = 0.1363.

Mole fraction of Mn in metal, \( \left[ x_{Mn} \right] \) = \( \frac{0.065}{100} \) = 0.065 \times 10^{-2}.

Putting the appropriate values in the relation for \( K \),

\[
K = \frac{0.1363}{0.7835 \times (0.065 \times 10^{-2})}
\]

\[ = 267.6. \]

\[
\Delta \theta^o = -4.575 T \log K
\]

\[ = -4.575 \times 1928 \times \log 267.6 \]

\[ = -21,410 \text{ cal.} \]

Example 6.D

The residual zinc in lead containing no other impurity can be removed by passing chlorine gas at 390°C (663 K) according to the following reaction:

\[
[\text{Zn}]_{\text{Pb-Zn}} + (\text{PbCl}_2)_{\text{slag}} = [\text{Pb}]_{\text{Pb-Zn}} + (\text{ZnCl}_2)_{\text{slag}}.
\]

The standard free energy change of the above reaction at 390°C is -15,090 cal (-63,137 J) and the final chloride slag has a mole fraction of \( \text{ZnCl}_2 \) equal to 0.983. The activity of zinc in lead at the above temperature for very dilute solution of Zn in Pb is given as
$a_{\text{Zn}} = 29x_{\text{Zn}}$.

Calculate the level to which the removal of zinc (in wt%) can be carried out, assuming that the system $\text{PbCl}_2 - \text{ZnCl}_2$ behaves ideally. Atomic weights of lead and zinc are 207.2 and 65.38 respectively.

Solution: For the reaction

\[ [\text{Zn}]_{\text{Pb-Zn}} + (\text{PbCl}_2)_{\text{slag}} = [\text{Pb}]_{\text{Pb-Zn}} + (\text{ZnCl}_2)_{\text{slag}} \]

it can be written that

\[ \Delta G^0 = -RT \ln K = -4.575T \log \frac{[a_{\text{Pb}}] \cdot (a_{\text{ZnCl}_2})}{[a_{\text{Zn}}] \cdot (a_{\text{PbCl}_2})} \]

Since the $\text{PbCl}_2 - \text{ZnCl}_2$ system behaves ideally,

\[ \Delta G^0 = -4.575T \log \frac{[a_{\text{Pb}}] \cdot (x_{\text{ZnCl}_2})}{[a_{\text{Zn}}] \cdot (x_{\text{PbCl}_2})} \quad (6.0.1) \]

\[ x_{\text{PbCl}_2} = 1 - x_{\text{ZnCl}_2} = 1 - 0.983 = 0.017. \]

The activity of lead may then be taken as one, assuming that zinc is present in a very small quantity. Putting the appropriate values at 390°C, Eq.(6.0.1) becomes

\[ -15,090 = -4.575 \times 663 \times \log \frac{1 \times 0.983}{29 \times x_{\text{Zn}}} \times 0.017. \]

On simplification,

\[ [x_{\text{Zn}}] = 2.117 \times 10^{-5}, \]

i.e. atom % of zinc $= 2.117 \times 10^{-3}$. 

Changing the concentration of zinc to wt% with the help of Eq.(6.1),

\[ \text{wt} \% \text{Zn} = \frac{(2.117 \times 10^{-3}) \times 65.38 \times 100}{[(2.117 \times 10^{-3}) \times 65.38] + [(100 - 2.117 \times 10^{-3}) \times 207.2]} . \]

Since $2.117 \times 10^{-3}$ is extremely small,

\[ \text{wt} \% \text{Zn} = \frac{0.1385}{(0.1385 + 20720)} \times 100 \]
\[ = 6.68 \times 10^{-4} . \]

Hence, the zinc content of lead can be lowered to $6.68 \times 10^{-4}$ wt%.

6.6. Non-Ideal Solutions: Concept of Activity Coefficient

A non-ideal (or actual) solution is one for which Eq.(6.22) does not hold good for at least one component. A correction factor $\gamma_i$, known as the Raoultian activity coefficient of component $i$, is introduced to Eq.(6.22) so that it may also be applied to non-ideal solutions. Thus

\[ a_i = \gamma_i \cdot x_i, \quad (6.23) \]

Activity coefficient is dependent on the temperature, pressure and composition of the solution. Obviously, for an ideal solution

\[ \gamma_i = 1. \quad (6.24) \]
Example 6.6

The activities of aluminium at different concentrations in Al-Cu solutions at 1100°C (1373 K) are given below:

\[
\begin{align*}
\chi_{Al} & : 0.90 \ 0.75 \ 0.63 \ 0.53 \ 0.45 \ 0.38 \ 0.30 \ 0.20 \ 0.10 \\
\alpha_{Al} & : 0.89 \ 0.69 \ 0.50 \ 0.31 \ 0.20 \ 0.10 \ 0.03 \ 0.005 \ 0.008
\end{align*}
\]

Calculate the activity coefficient of aluminium in a solution containing 49 atom% aluminium.

Solution: In order to find the value of \( \alpha_{Al} \), and hence \( \gamma_{Al} \), at \( \chi_{Al} = 0.49 \), a graph is plotted between \( \chi_{Al} \) and \( \alpha_{Al} \), as shown in Fig. 6.4.

Fig. 6.4. Graph relating the Activity and Mole Fraction of Aluminium in Al-Cu Alloys.
From this graph, the value of $a_{Al}$ at $x_{Al} = 0.49$ is 0.25. Hence

$$\gamma_{Al} = \frac{0.25}{0.49} = 0.5102.$$ 

Thus the activity coefficient of aluminium at $x_{Al} = 0.49$ is $0.5102$.

6.7 Henry's Law: Dilute Solutions

Henry's law states that the partial vapour pressure of a solute in a dilute solution is proportional to its mole fraction (Fig. 6.5).

Fig. 6.5. The Activity of Solute A against its Mole Fraction. (For a negative deviation from Raoult's Law, the curve approximates to a straight line at low concentrations, thus obeying Henry's Law).
If in a solution A-B the solute is designated by A, then according to Henry's law

\[ p_A = K_A \cdot x_A, \tag{6.25} \]

where \( K_A \) is a constant at a given temperature. Dividing throughout by \( p_A^0 \),

\[ a_A = \text{constant} \cdot x_A. \tag{6.26} \]

The constant in the above relation is equal to the slope of the activity-composition curve at infinite dilution, or the slope of the curve at zero concentration of A, and is designated by \( \gamma_A^0 \). \( \gamma_A^0 \) is the activity coefficient at infinite dilution.

Like Raoult's law, Henry's law applies within a concentration range whose extent varies from one system to another, but it is valid only at low concentration.

### 6.8 Alternative Standard States

For non-ideal solutions it is sometimes more convenient to use thermodynamic quantities like standard free energy change, activity, activity coefficient, etc., relative to a standard state other than the pure substance. Henry's law offers two such alternative states: 'infinitely dilute, atom fraction' and 'infinitely dilute, weight percent' standard states.

#### 6.8.1. Infinitely Dilute, Atom Fraction Standard State

This standard state is so defined that the Henrian activity approaches the atom fraction at infinite dilution, i.e.

\[ h_A = x_A \quad \text{as} \quad x_A \rightarrow 0, \]
where $h_A$ denotes Henrian activity of $A$. In other words, in the concentration range where Henry's law is obeyed, the atom fraction is equal to the activity. Beyond this concentration range, the activity can be related to the atom fraction by the equation

$$h_A = f_A x_A,$$  \hspace{1cm} (6.27)

where $f_A$ is the Henrian activity coefficient of $A$ relative to the infinitely dilute, atom fraction standard state. The relation between the activity of $A$ relative to the pure substance standard state and the activity of $A$ relative to the infinitely dilute, atom fraction standard state, is given by

$$\frac{\text{activity of } A \text{ relative to pure subs.s.s.}}{\text{activity of } A \text{ relative to dil., atom frac.s.s.}} = \gamma_A^{\text{cons.}}$$  \hspace{1cm} (6.28)

where $\gamma_A^{\text{cons.}}$ is the Raoultian activity coefficient of $A$ at infinite dilution.

The free energy change accompanying the transfer of one mole of $A$ from pure $A$ as standard state to the infinitely dilute, atom fraction standard state, i.e.

$$A(\text{pure subs.s.s.}) \rightarrow A(\text{dil., atom frac.s.s.})$$

is given by

$$\Delta G^0 = G_A^{\text{pure subs.s.s.}} - G_A^{\text{dil., atom frac.s.s.}} = RT \ln \left[ \frac{\text{activity of } A \text{ relative to pure subs.s.s.}}{\text{activity of } A \text{ relative to dil., atom frac.s.s.}} \right] = RT \ln \gamma_A^{\text{cons.}}.$$  \hspace{1cm} (6.29)

6.8.2. Infinitely Dilute, Weight Percent Standard State

This standard state, which is most widely used in metallurgy, particularly in steel making, may be so defined that the Henrian activity approaches the
weight percent at infinite dilution, i.e.

\[ h_A = \text{wt} \% A \text{ as wt} \% A \rightarrow 0. \]

Assuming that the solution obeys Henry's law up to 1 wt\% of A, then \( h_A \) is unity at this concentration, and thus the standard state is the 1 wt\% solution. Deviations from this equality of activity and weight percent are measured in terms of Henrian activity coefficient relative to the infinitely dilute, weight percent standard state, i.e.

\[ h_A = f_A \cdot (\text{wt} \% A). \quad (6.30) \]

Though in both the equations (6.27) and (6.30) \( h_A \) and \( f_A \) have been used for denoting the Henrian activity and activity coefficient of A respectively, in Eq.(6.27) they signify relative to the infinitely dilute, atom fraction standard state, while in Eq.(6.30) they are relative to the infinitely dilute, weight percent standard state.

The relationship between the activity of A relative to the pure substance standard state and the activity of A relative to the infinitely dilute, weight percent standard state is given by

\[
\frac{\text{activity of } A \text{ relative to pure subs.s.s.}}{\text{activity of } A \text{ relative to dil., wt}\%\text{s.s.}} = \frac{\gamma_A^o \cdot x_A}{x_A = \text{cons.}}.
\quad (6.31)
\]

The free energy change accompanying the transfer of one mole of A from the pure substance standard state to the infinitely dilute, weight percent standard state, i.e.

\[ A(\text{pure subs.s.s.}) \rightarrow A(\text{dil., wt}\%\text{s.s.}) \]

is given by

\[
\Delta G^o = G_A^o(\text{dil., wt}\%\text{s.s.}) - G_A^o(\text{pure subs.s.s.})
\]

\[
= RT \ln \left[ \frac{\text{activity of } A \text{ relative to pure subs.s.s.}}{\text{activity of } A \text{ relative to dil., wt}\%\text{s.s.}} \right]
\]

\[
= RT \ln \left( \frac{\gamma_A^o \cdot x_A}{\text{wt} \% A} \right).
\quad (6.32)
\]
For a small concentration of solute A in the solution A-B, it can be shown that

\[
\frac{X_A}{\text{wt} \% A} = \frac{M_B}{100 M_A},
\]

where \( M_A \) and \( M_B \) are the molecular weights of A and B respectively. Hence, Eq.(6.32) can be rewritten as

\[
\Delta G^\circ = RT \ln \left( \gamma_A^O \cdot \frac{M_B}{100 M_A} \right)
= RT \ln \gamma_A^O + RT \ln \left( \frac{M_B}{100 M_A} \right).
\]

(6.33)

Whatever standard states are used, the equation

\[
\Delta G^\circ = -RT \ln K
= -RT \ln \left[ \frac{\text{Product of the activities of products}}{\text{Product of the activities of reactants}} \right]
\]

is valid, but the actual numerical values of \( \Delta G^\circ \) and \( K \) will depend upon the standard state used.

The application of the alternative standard state has been illustrated in the following examples.

**Example 6.F**

A heat of steel contains 0.002 wt % oxygen. Vanadium is to be added in the ladle at 1557\(^\circ\)C (1830 \( K \)) to make a product containing 1 wt % vanadium. To what extent must the oxygen content of the heat be lowered to prevent the loss of vanadium?

**Given:**

\[
2[V]_{\text{Fe,wt} \%} + 3[0]_{\text{Fe,wt} \%} = <V_2O_3>;
\]

\[
\Delta G^\circ = -186,520 + 64.0 \text{ T cal} (-780,400 + 267.8T J).
\]

**Solution:** The standard free energy change for the given reaction at 1557\(^\circ\)C
(1830 K) is given as

$$\Delta G^0_{1830} = -186,520 + 64.0 \times 1830$$

$$= -69,400 \text{ cal.}$$

The equilibrium constant of the reaction at 1557°C is given by

$$\log K = \frac{-\Delta G^0_{1830}}{4.575 \times 1830} = \frac{69,400}{4.575 \times 1830}$$

$$= 8.289.$$ 

Taking antilogs, 

$$K = 1.945 \times 10^8.$$ 

Since the standard states for vanadium and oxygen, as represented in the reaction, are 'dilute, weight percent', their weight percents can be directly substituted for activities. Thus

$$K = \frac{\left(a_{V_2O_3}\right)}{[\text{wt} \% V]^2 [\text{wt} \% O]^3}.$$ 

The activity of $V_2O_3$ is unity, because it is present in pure state, and hence

$$K = \frac{1}{[\text{wt} \% V]^2 [\text{wt} \% O]^3}.$$ 

Putting the value of $K$ in the above relation,

$$[\text{wt} \% V]^2.[\text{wt} \% O]^3 = \frac{1}{1.945 \times 10^8}$$

$$= 5.140 \times 10^{-9}.$$ 

The above expression shows that there is a fixed quantity of oxygen in equilibrium with vanadium in the steel. The amount of oxygen in equilibrium with 1 wt% V is given by

$$1 \times [\text{wt} \% O]^3 = 5.140 \times 10^{-9},$$ 

or

$$[\text{wt} \% O] = 1.726 \times 10^{-3}.$$
Thus, 0.001726 wt % oxygen is in equilibrium with 1 wt % vanadium. If there is more oxygen than this in the steel, as in the present case (0.002 wt %), vanadium will start forming $V_2O_3$. Hence, to prevent the loss of vanadium, the oxygen content of steel should be lowered from 0.002 wt % to 0.001726 wt %.

Example 6.6

The activity coefficient of chromium in iron at infinite dilution relative to pure solid chromium as the standard state is unity. Calculate the change in free energy when solid chromium is dissolved in iron so as to form an infinitely dilute, weight percent solution of chromium in liquid iron at 1800°C (2073 K) from the following data:

Heat of fusion of chromium = 5,000 cal/mole (20,920 J/mol).
Melting point of chromium = 1830°C (2103 K).
Atomic weights of Fe and Cr are 55.85 and 52.0 respectively.

Solution: Dissolution of pure liquid chromium in iron, so as to form an infinitely dilute, weight percent solution of chromium in liquid iron can be represented as

$\{\text{Cr}\}_{\text{pure subs.s.s.}} = [\text{Cr}]_{\text{Fe, wt %}}$

and the free energy change, according to Eq.(6.33), is given by

$$\Delta G^0 = RT \ln \gamma^0_{\text{Cr}} + RT \ln \left( \frac{M_{\text{Fe}}}{100 M_{\text{Cr}}} \right),$$

where $M_{\text{Fe}}$ and $M_{\text{Cr}}$ are the atomic weights of iron and chromium respectively, and $\gamma^0_{\text{Cr}}$ is the Raoultian activity coefficient of chromium at infinite dilution. Putting the appropriate values in the above equation at 1800°C,
\[ \Delta G^0_{2073} = 4.575 \times 2073 \times \log 1 + 4.575 \times 2073 \times \log \left( \frac{55.85}{100 \times 52} \right) \]

\[ = -18,670 \text{ cal.} \]

The above calculated free energy change applies to liquid chromium at 1800°C. However, we are required to find the free energy change for solid chromium at 1800°C, and hence the free energy change accompanying the fusion of chromium, i.e.

\[ <\text{Cr}> \text{ pure subs.s.s.} = \{\text{Cr}\} \text{ pure subs.s.s.} \quad (6.G.1) \]

must be taken into account.

Entropy of fusion of chromium, \( S_f \), at its M.P. is given by

\[ S_f = \text{Heat of fusion} \times \frac{\text{M.P.}}{\text{Heat of fusion}} \]

\[ = \frac{5000}{(1830 + 273)} \]

\[ = 2.378 \text{ cal/deg/mole.} \]

Assuming that the entropy of fusion, \( S_f \), and heat of fusion, \( H_f \), are independent of temperature, the free energy change of the reaction (6.G.1) at 1800°C is given by

\[ \Delta G_f = H_f - TS_f \]

\[ = 5000 - 2073 \times 2.378 \]

\[ = 71 \text{ cal.} \]

Therefore,

\[ \{\text{Cr}\} \text{ pure subs.s.s.} = [\text{Cr}]_{\text{Fe, wt\%}} ; \Delta G^0 = -18,670 \text{ cal.} \]

\[ <\text{Cr}> \text{ pure subs.s.s.} = \{\text{Cr}\} \text{ pure subs.s.s.} ; \Delta G^0 = 71 \text{ cal.} \]

Adding: \( <\text{Cr}> \text{ pure subs.s.s.} = [\text{Cr}]_{\text{Fe, wt\%}} ; \Delta G^0 = -18,599 \text{ cal.} \)
Thus, the free energy change accompanying the dissolution of pure solid chromium to an infinitely dilute, weight percent solution of chromium in iron is \(-18,599\) cal/mole.

**Exercises**

6.1 An aluminium-magnesium alloy contains 91.5 atom\% aluminium. Calculate the composition of the alloy in wt\%. The atomic weights of aluminium and magnesium are 26.98 and 24.32 respectively.

6.2 According to the ionic theory, a basic slag of the following composition:

\[
\begin{align*}
\text{CaO} & = 48.9\%, \quad \text{MgO} = 6.7\%, \quad \text{MnO} = 1.6\%, \quad \text{FeO} = 9.0\%, \\
\text{Fe}_2\text{O}_3 & = 3.3\%, \quad \text{SiO}_2 = 14.4\%, \quad \text{P}_2\text{O}_5 = 13.3\% \text{ and } \text{Al}_2\text{O}_3 = 4.1\%
\end{align*}
\]

consists of \(\text{Ca}^{2+}, \text{Mg}^{2+}, \text{Mn}^{2+}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{SiO}_4^{4-}, \text{PO}_4^{3-}, \text{AlO}_4^{3-}\) and free \(\text{O}^{2-}\) ions. Calculate the ion fraction of each ion present in the slag. Molecular weight values are \(\text{CaO} = 56.1\), \(\text{MgO} = 40.3\), \(\text{MnO} = 70.9\), \(\text{FeO} = 71.8\), \(\text{Fe}_2\text{O}_3 = 159.7\), \(\text{SiO}_2 = 60\), \(\text{P}_2\text{O}_5 = 142.0\) and \(\text{Al}_2\text{O}_3 = 101.9\).

6.3 The following table gives values for the density of Zn-Al alloys:

<table>
<thead>
<tr>
<th>wt % Al</th>
<th>Atom fraction of Zn</th>
<th>No.of g-atom in 100 g alloy</th>
<th>Density at 25°C, g/c.c.</th>
<th>Volume of 100 g alloy, c.c.</th>
<th>Volume per g-atom of alloy, c.c.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.0000</td>
<td>1.530</td>
<td>7.143</td>
<td>14.00</td>
<td>9.15</td>
</tr>
<tr>
<td>9.57</td>
<td>0.7957</td>
<td>1.738</td>
<td>6.131</td>
<td>16.31</td>
<td>9.38</td>
</tr>
<tr>
<td>19.40</td>
<td>-</td>
<td>-</td>
<td>5.345</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>25.37</td>
<td>-</td>
<td>-</td>
<td>4.953</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Complete the table, calculating the atom fraction of zinc, the number of g-atoms in 100 g of alloy, the volume of 100 g of the alloy, and the volume occupied by one g-atom of the alloy. Also, find the partial molar (atomic) volumes of zinc and aluminium at 25°C in an alloy containing 0.75 atom fraction of zinc. Atomic weights of Zn and Al are 65.38 and 26.96 respectively.

6.4 The molar heat of formation of liquid brass according to the reaction

\[(1-x)\{Cu\} + x\{Zn\} = \{Cu-Zn\}\]

is given by

\[\Delta H^M = -7100.x.(1 - x) \text{ cal} \quad (-29,706.x.(1 - x) J)\]

where \(x\) is the atom fraction of zinc. Determine the expressions relating the partial molar heats of formation of copper and zinc in liquid brass to the alloy composition.

6.5 Calculate the partial molar heats of mixing of zinc and of cadmium in a Zn-Cd alloy, containing 0.6 atom fraction zinc, from the following data at 700°C (973 K):

<table>
<thead>
<tr>
<th>(x_{\text{Zn}})</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
<th>0.6</th>
<th>0.7</th>
<th>0.8</th>
<th>0.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Integral heat of mixing, cal/mole</td>
<td>180</td>
<td>317</td>
<td>413</td>
<td>468</td>
<td>491</td>
<td>478</td>
<td>424</td>
<td>329</td>
<td>188</td>
</tr>
<tr>
<td>Integral heat of mixing, J/mol</td>
<td>753</td>
<td>1,326</td>
<td>1,728</td>
<td>1,958</td>
<td>2,054</td>
<td>2,000</td>
<td>1,774</td>
<td>1,377</td>
<td>787</td>
</tr>
</tbody>
</table>

6.6 The integral free energies of mixing \(\Delta G^M\), of Cr-Ti alloys at 1380°C (1653 K) are as follows:
6.7 Calculate the equilibrium composition of a Cu-Ni alloy (in wt%) capable of existing in equilibrium with Cu$_2$O and NiO at 727°C (1000 K) from the following data:

At 727°C (1000 K) $\Delta G^0_{\text{Cu}_2\text{O}} = -18,230$ cal/mole ($-76,274$ J/mol),
and $\Delta G^0_{\text{NiO}} = -30,150$ cal/mole ($-126,148$ J/mol).

Atomic weights of Cu and Ni are 63.54 and 58.7 respectively.

6.8 The liquid solutions of MnO in FeO and of Mn in Fe are virtually ideal at 1600°C (1873 K). Calculate the concentration of manganese in iron in wt% which is in equilibrium with a slag containing 40% MnO and 60% FeO at this temperature.

Given: $(\text{FeO})_{\text{slag}} + [\text{Mn}]_{\text{Fe-Mn}} = (\text{MnO})_{\text{slag}} + [\text{Fe}]_{\text{Fe-Mn}}$;
$\Delta G^0 = -29,080 + 3.67T$ cal ($-121,671 + 15.35T$ J).

Atomic weights of Fe and Mn are 55.85 and 54.94 respectively.

6.9 The peritectic decomposition of the compound ZrZn$_{14}$ at 545°C (818 K) may be represented as
ZrZn$_{14}$ = ZrZn$_6$ + 8[Zn]$_{Zn-Zr}$ alloy

The alloy at the peritectic temperature contains 99.2 atom% zinc. Calculate the activity coefficient of zinc in the alloy.

Given: At 545°C (818 K), ($\Delta G^o_{ZrZn_{14}} - \Delta G^o_{ZrZn_6}$) = -678 cal (-2837 J).

6.10 Liquid iron contains 0.2% aluminium and 0.05% nitrogen by weight at 1620°C (1893 K). Determine the possibility of precipitating aluminium nitride, AlN, by thermodynamic calculation.

Given: AlN = [Al]$_{Fe,wt\%}$ + [N]$_{Fe,wt\%}$; $K_{1893} = 6 \times 10^{-3}$.

6.11 Show thermodynamically that with a given amount of ferro-silicon, the deoxidation of steel improves as the temperature is lowered, keeping all the other variables constant. Base your calculation on the following data:


6.12 The aluminium left in steel after deoxidation can be removed by vacuum treatment at 1600°C (1873 K) in either a silica, magnesia, or alumina crucible, according to the following reactions:

$<SiO_2> + 2[Al]_{Fe,wt\%} = (SiO) + (Al_2O)$

$<MgO> + 2[Al]_{Fe,wt\%} = (Al_2O) + (Mg)$

$<Al_2O_3> + 4[Al]_{Fe,wt\%} = 3(Al_2O)$
If the minimum pressure attained by the vacuum pump is $10^{-4}$ atm (10.1 N/m$^2$), which of the crucible/crucibles can be used to obtain aluminium-free steel?

Given: (a) At 1600°C (1873 K)

\[
\Delta G_{\text{SiO}_2}^0 = -130.44 \text{ kcal/mole } (-545.76 \text{ kJ/mol}),
\]

\[
\Delta G_{\text{SiO}}^0 = -57.70 \text{ kcal/mole } (-241.42 \text{ kJ/mol}),
\]

\[
\Delta G_{\text{Al}_2\text{O}}^0 = -71.60 \text{ kcal/mole } (-299.57 \text{ kJ/mol}),
\]

\[
\Delta G_{\text{MgO}}^0 = -82.70 \text{ kcal/mole } (-346.02 \text{ kJ/mol}),
\]

\[
\Delta G_{\text{Al}_2\text{O}_3}^0 = -256.04 \text{ kcal/mole } (-1071.3 \text{ kJ/mol}).
\]

(b) $\Delta G$ for the transfer of one atom of aluminium from the pure liquid state to an infinitely dilute, wt% solution of aluminium in liquid iron at 1600°C (1873 K) is -13 kcal/mole (-54.39 kJ/mol).

(c) Aluminium left after deoxidation = 0.2 wt%.

6.13 The melting point of cobalt is 1480°C (1753 K). Calculate the free energy change for the transfer of one g-atom of cobalt from pure liquid to a 1 wt% solution in liquid iron at 1500°C (1773 K). Assume that cobalt behaves ideally in iron at that temperature. Atomic weights of Co and Fe are 58.9 and 55.85 respectively.

6.14 Vanadium melts at 1720°C (1993 K). The Raoultian activity coefficient of vanadium at infinite dilution in liquid iron at 1620°C (1893 K) is 0.068. Calculate the free energy change accompanying the transfer of the standard state from pure solid vanadium to the infinitely dilute, weight percent solution of vanadium in pure iron at 1620°C.

Given: (a) Heat of fusion of vanadium = 4,500 cal/mole (18,828 J/mol).

(b) Atomic weights of vanadium and iron are 50.95 and 55.85 respectively.
6.15 The activity coefficient of copper in iron at infinite dilution, relative to pure copper as the standard state, is 8.5 at 1600°C (1873 K). Calculate the free energy change for the reaction

\[
\{\text{Cu}\} = [\text{Cu}]_{\text{Fe}, \text{wt%}}
\]

at 1600°C (1873 K). Assume the atomic weights of copper and iron to be 63.5 and 55.85 respectively.

6.16 Calculate the free energy change when the standard state of manganese is transferred from the pure liquid state to the infinitely dilute, weight percent solution of manganese in iron at 1627°C (1900 K).

Given: (a) Melting point of manganese = 1245°C (1518 K).

(b) Atomic weights of manganese and iron are 54.94 and 55.85 respectively.

(c) Fe-Mn system can be regarded as an ideal solution.
CHAPTER 7

SOLUTIONS: II

7.1 Sievert's Law

Diatomic gases, e.g. H₂, O₂, N₂, etc., generally dissociate when they are dissolved in metals. In this event, Henry's law takes the form

\[ P_A = \text{constant} \cdot x_A^n, \]  

(7.1)

where \( n \) is the number of atoms per molecule. The relation has been found to hold good for the solubility, \( S \), of diatomic gases in many metals, and is known as Sievert's law. Since \( x_A \) is proportional to \( S_A \), Sievert's law may be written as

\[ S_A = K' \sqrt{P_A}, \]  

(7.2)

where \( K' \) designates the constant.

In the case where the gas is not entirely diatomic, Eq.(7.2) is still valid provided \( P_A \) is expressed as the partial pressure of the diatomic gaseous species.

Example 7.1

The solubility of oxygen in liquid silver at 1075°C (1348 K) is given below for a range of partial pressures of oxygen:

<table>
<thead>
<tr>
<th>Partial pressure of oxygen</th>
<th>Solubility of oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>mm Hg</td>
<td>(N/m²)</td>
</tr>
<tr>
<td>128</td>
<td>(17066)</td>
</tr>
<tr>
<td>488</td>
<td>(65061)</td>
</tr>
<tr>
<td>760</td>
<td>(101325)</td>
</tr>
<tr>
<td>1203</td>
<td>(160386)</td>
</tr>
</tbody>
</table>

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Show that the solubility of oxygen in silver follows Sievert's law, and calculate the amount of oxygen dissolved in 100 g of liquid silver at 1075°C, from atmospheric air, assuming that the air contains 21% oxygen by volume.

Solution: Applying Eq. (7.2) to the solubility of oxygen in silver at 1075°C,

$$SO_2 = K' \sqrt{P_{O_2}}$$

(7.1)

where $S_{O_2}$ is the solubility of oxygen in silver expressed in c.c./100 g Ag, $P_{O_2}$ is the partial pressure of oxygen expressed in mm Hg, and $K'$ is the constant. The value of $K'$ at different $P_{O_2}$ values, as calculated from Eq. (7.1) is given below.

<table>
<thead>
<tr>
<th>$P_{O_2}$ (mm Hg)</th>
<th>$\sqrt{P_{O_2}}$</th>
<th>$S_{O_2}$ (c.c./100 g Ag)</th>
<th>$K'$ ( = $S_{O_2}/\sqrt{P_{O_2}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>128</td>
<td>11.313</td>
<td>81.5</td>
<td>7.206</td>
</tr>
<tr>
<td>488</td>
<td>22.090</td>
<td>156.9</td>
<td>7.104</td>
</tr>
<tr>
<td>760</td>
<td>27.568</td>
<td>193.6</td>
<td>7.026</td>
</tr>
<tr>
<td>1203</td>
<td>34.680</td>
<td>254.8</td>
<td>7.347</td>
</tr>
</tbody>
</table>

From the above it is clear that the value of $K'$ is substantially constant, and therefore the solubility of oxygen in silver at 1075°C obeys Sievert's law.

Air contains 21% oxygen by volume, i.e. the partial pressure of oxygen is

$$P_{O_2} = 0.21 \text{ atm}$$

$$= 0.21 \times 760 \text{ mm Hg}$$

$$= 159.6 \text{ mm Hg}.$$  

The value of $K'$ at 128 mm Hg is 7.206. It can be assumed that the value of $K'$ at 159.6 mm Hg is also 7.206, because the difference in the $P_{O_2}$ values is small. Thus, the solubility of oxygen at 159.6 mm Hg, according to Eq. (7.1), is given by
Alternatively, this problem can be solved by plotting a graph between $S_{O_2}$ and $\sqrt{P_{O_2}}$. If a straight line results, then the system follows Sievert's law. The slope of the line gives the mean value of $K'$ and from this the solubility of oxygen at an oxygen partial pressure of 159.6 mm Hg can be calculated. The value of $S_{O_2}$ obtained from this method may be slightly different from the value calculated above.

### 7.2 Mixing Functions

When the components $A$ and $B$ are mixed together to form a solution $A-B$

$$A + B = A-B$$

there are changes in thermodynamic properties like free energy, entropy, enthalpy, etc. Taking the example of free energy, the change is the 'free energy of solution formation', 'free energy of mixing', or 'integral free energy of mixing', and its value per mole of solution is denoted by $\Delta G^M$. This may be defined as the difference between the free energy of solution and the sum of the free energies of the pure components at the same temperature and pressure. Thus, for the solution $A-B$,

$$\Delta G^M = G_{\text{real soln.}} - (\text{sum of the free energies of } A \text{ and } B)$$

$$= (x_A \tilde{G}_A + x_B \tilde{G}_B) - (x_A G_A^0 + x_B G_B^0)$$

$$= x_A (\tilde{G}_A - G_A^0) + x_B (\tilde{G}_B - G_B^0), \quad (7.3)$$

where, in general, $\tilde{G}_i$ and $G_i^0$ are the molar free energies of component $i$ in the solution and in the chosen standard state respectively. The quantity
\((G_1 - G_1^0)\) is called the 'partial molar free energy of mixing', or 'relative partial molar free energy' of component \(i\), and is denoted by \(G_i^M\). Thus, Eq.(7.3) takes the shape

\[ \Delta G^M = x_A G_A^M + x_B G_B^M. \]  

(7.4)

Similarly, other mixing functions like integral molar entropy and enthalpy of mixing may be defined. Thus, for the solution under consideration,

\[ \Delta S^M = x_A S_A^M + x_B S_B^M, \]  

(7.5)

and

\[ \Delta H^M = x_A H_A^M + x_B H_B^M. \]  

(7.6)

The various mixing functions are related to each other through all the expressions discussed in earlier chapters. Thus

\[ \Delta G^M = \Delta H^M - T \Delta S^M, \]

\[ G_i^M = H_i^M - T S_i^M, \]

\[ \frac{\partial}{\partial T} \left( \frac{\Delta G^M}{T} \right)_P = -\frac{\Delta H^M}{T^2}, \text{ etc.} \]

From Eq.(5.7) it follows that

\[ G_i^M = RT \ln a_i, \]  

(7.7)

and hence, for the solution under consideration

\[ \Delta G^M = RT(x_A \ln a_A + x_B \ln a_B). \]  

(7.8)

Integrating Eq.(7.8) w.r.t. temperature at constant pressure and composition,

\[
\left( \frac{\partial \Delta G^M}{\partial T} \right)_P, x_A = R(x_A \ln a_A + x_B \ln a_B) 
+ RT \left[ x_A \left( \frac{\partial \ln a_A}{\partial T} \right)_P, x_A \right] + x_B \left( \frac{\partial \ln a_B}{\partial T} \right)_P, x_B, \right],
\]
or \[ \Delta S^M = - R(x_A \ln a_A + x_B \ln a_B) - RT \left[ x_A \left( \frac{\partial \ln a_A}{\partial T} \right)_P x_A \right. \]
\[ \left. + x_B \left( \frac{\partial \ln a_B}{\partial T} \right)_P x_B \right]. \] (7.9)

Since \( \Delta G^M = \Delta H^M - T \Delta S^M \), it follows from Eqs.(7.8) and (7.9) that
\[ \Delta H^M = - RT \left[ x_A \left( \frac{\partial \ln a_A}{\partial T} \right)_P x_A \right. \]
\[ \left. + x_B \left( \frac{\partial \ln a_B}{\partial T} \right)_P x_B \right]. \] (7.10)

For an ideal solution, activity is equal to mole fraction, and hence it is independent of temperature. The following mixing functions can be obtained for an ideal solution A-B:

\[ \Delta G^M_{\text{ideal}} = RT(x_A \ln x_A + x_B \ln x_B). \] (7.11)
\[ \Delta S^M_{\text{ideal}} = - R(x_A \ln x_A + x_B \ln x_B). \] (7.12)
\[ \Delta H^M_{\text{ideal}} = 0. \] (7.13)

Apart from the above, the volume of mixing for an ideal solution is also zero.

### 7.3 Excess Functions

The excess thermodynamic function may be defined as the difference between the thermodynamic function for the real solution and the thermodynamic function for the solution assumed to be ideal. Thus

\[ Z^{xs} = Z_{\text{real soln.}} - Z_{\text{ideal soln.}}, \]

where \( Z \) represents thermodynamic functions like \( H, S, G, \) etc., and \( Z^{xs} \) is the corresponding excess function.
Considering a binary solution A-B, the excess integral molar free energy of solution, $G^{\text{xs}}$, is given by

$$G^{\text{xs}} = \Delta G_{\text{real soln.}}^M - \Delta G_{\text{ideal soln.}}^M.$$ 

Putting the values of $\Delta G_{\text{real soln.}}^M$ and $\Delta G_{\text{ideal soln.}}^M$ from Eqs. (7.8) and (7.11) respectively,

$$G^{\text{xs}} = RT(x_A \ln \gamma_A + x_B \ln \gamma_B).$$  \hspace{1cm} (7.14)

Similarly, excess integral molar entropy and enthalpy of solution may be written as

$$S^{\text{xs}} = -RT(x_A \ln \gamma_A + x_B \ln \gamma_B) - RT \left[ x_A \left( \frac{\partial \ln \gamma_A}{\partial T} \right)_{P,x_B} + x_B \left( \frac{\partial \ln \gamma_B}{\partial T} \right)_{P,x_A} \right].$$ \hspace{1cm} (7.15)

$$H^{\text{xs}} = -RT(x_A \ln \gamma_A + x_B \ln \gamma_B) - RT \left[ x_A \left( \frac{\partial \ln \gamma_A}{\partial T} \right)_{P,x_B} + x_B \left( \frac{\partial \ln \gamma_B}{\partial T} \right)_{P,x_A} \right].$$ \hspace{1cm} (7.16)

This approach of excess functions can also be extended to partial molar quantities. Thus, the excess partial molar free energy of component $i$, $\bar{G}_i^{\text{xs}}$, can be written as

$$\bar{G}_i^{\text{xs}} = RT \ln \gamma_i.$$ \hspace{1cm} (7.17)

Hence, for a binary solution A-B,

$$G^{\text{xs}} = x_A \bar{G}_A^{\text{xs}} + x_B \bar{G}_B^{\text{xs}}.$$ \hspace{1cm} (7.18)

The excess partial and integral quantities are related through the thermodynamic relations previously discussed. Thus

$$\frac{\partial}{\partial T} \left( \frac{G^{\text{xs}}}{T} \right)_{P} = - \frac{H^{\text{xs}}}{T^2},$$ \hspace{1cm} etc.
7.4 Regular Solutions

A regular solution may be defined as that solution of which the enthalpy of mixing is different from zero, but the entropy of mixing is the same as for an ideal solution. The various mixing functions of a binary regular solution A-B may be written as

\[ \Delta G^M = RT(x_A \ln a_A + x_B \ln a_B) \]  
(7.19)

\[ \Delta S^M = -R(x_A \ln x_A + x_B \ln x_B) \]  
(7.20)

\[ \Delta H^M = RT(x_A \ln \gamma_A + x_B \ln \gamma_B) \]  
(7.21)

Also, for a regular solution,

\[ \Delta H^M_i = RT \ln \gamma_i, \]  
(7.22)

\[ G^{xs}_i = RT \ln \gamma_i, \]  
(7.23)

and \[ \Delta H^M = G^{xs}. \]  
(7.24)

A simple test for 'regularity' of a binary solution A-B is that

\[ RT \ln \gamma_A = \alpha x_B^2, \]  
(7.25)

and \[ RT \ln \gamma_B = \alpha x_A^2. \]  
(7.26)

where \( \alpha \) is a constant and is independent of composition and has the same value for all the components of the system.

Example 7.B

From the e.m.f. measurements at 527°C (800 K), the following values of the activity coefficient of cadmium in zinc-cadmium solutions have been obtained:

\[
\begin{array}{ccccc}
  x_{Cd} & 0.2 & 0.3 & 0.4 & 0.5 \\
  \gamma_{Cd} & 2.153 & 1.817 & 1.544 & 1.352 \\
\end{array}
\]
(i) Determine whether the Zn-Cd solution exhibits regular behaviour.

(ii) Calculate the values of the partial molar heat of mixing of Zn and Cd, integral molar heat of mixing, integral molar entropy of mixing, partial molar free energy of mixing of cadmium and integral molar free energy of mixing for an equiatomic solution of Zn-Cd, assuming regular behaviour at 527ºC (800 K).

Solution: (i) If the Zn-Cd solution is regular, then according to Eq.(7.25) it should follow the relation:

\[ \frac{\ln \gamma_{Cd}}{x_{Zn}^2} = \alpha, \]  

(7.B.1)

where \( \alpha \) is a constant, irrespective of composition. Eq.(7.B.1) may also be written as

\[ \frac{\log \gamma_{Cd}}{(1-x_{Cd})^2} = \text{constant}. \]

The following table shows the value of \( \frac{\log \gamma_{Cd}}{(1-x_{Cd})^2} \) as a function of \( x_{Cd} \):

<table>
<thead>
<tr>
<th>( x_{Cd} )</th>
<th>( (1-x_{Cd})^2 )</th>
<th>( \gamma_{Cd} )</th>
<th>( \log \gamma_{Cd} )</th>
<th>( \log \gamma_{Cd}/(1-x_{Cd})^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.64</td>
<td>2.153</td>
<td>0.3330</td>
<td>0.5202</td>
</tr>
<tr>
<td>0.3</td>
<td>0.49</td>
<td>1.817</td>
<td>0.2593</td>
<td>0.5291</td>
</tr>
<tr>
<td>0.4</td>
<td>0.36</td>
<td>1.544</td>
<td>0.1886</td>
<td>0.5240</td>
</tr>
<tr>
<td>0.5</td>
<td>0.25</td>
<td>1.352</td>
<td>0.1309</td>
<td>0.5236</td>
</tr>
</tbody>
</table>

From the above calculation, it is clear that \( \frac{\log \gamma_{Cd}}{(1-x_{Cd})^2} \) is virtually constant, irrespective of the solution composition, and hence the solution exhibits regular behaviour.
(ii) Since the solution is regular,

\[ \frac{\log \gamma_{Cd}}{(1-x_{Cd})^2} = \frac{\log \gamma_{Zn}}{(1-x_{Zn})^2} . \]

At \( x_{Zn} = x_{Cd} = 0.5 \),

\[ \frac{\log 1.352}{(0.5)^2} = \frac{\log \gamma_{Zn}}{(0.5)^2} , \]

or

\[ \gamma_{Zn} = 1.352. \]

According to Eq.(7.22), the partial molar heat of mixing of zinc is given as

\[ \mu_{Zn}^N = RT \ln \gamma_{Zn} = 4.575 \times 800 \times \log 1.352 = 479 \text{ cal/mole}. \]

Similarly, the partial molar heat of mixing of cadmium is given as

\[ \mu_{Cd}^N = 4.575 \times 800 \times \log 1.352 = 479 \text{ cal/mole}. \]

Thus the integral molar heat of mixing is given as

\[ \Delta H^M = x_{Zn} \mu_{Zn}^N + x_{Cd} \mu_{Cd}^N = 0.5 \times 479 + 0.5 \times 479 = 479 \text{ cal/mole}. \]

According to Eq.(7.20), the integral molar entropy of mixing is given as

\[ \Delta S^M = -4.575(0.5 \log 0.5 + 0.5 \log 0.5) = 1.377 \text{ cal/deg/mole}. \]
The partial molar free energies of mixing of zinc and cadmium can be calculated with the help of Eq. (7.19), and thus

\[ \frac{M}{M} G^M_{\text{Zn}} = RT \ln a_{\text{Zn}} = 4.575 \times 800 \times \log(1.352 \times 0.5) = -622.4 \text{ cal/mole}. \]

Similarly,

\[ \frac{M}{M} G^M_{\text{Cd}} = -622.4 \text{ cal/mole}. \]

Thus the integral molar free energy of mixing is given as

\[ \Delta G^M = x_{\text{Zn}} \frac{M}{M} G^M_{\text{Zn}} + x_{\text{Cd}} \frac{M}{M} G^M_{\text{Cd}} = -0.5 \times 622.4 - 0.5 \times 622.4 = -622.4 \text{ cal/mole}. \]

Example 7.C

Using data given in the previous example, calculate the values of the excess partial molar free energy of zinc and cadmium, excess integral molar free energy of solution, and excess integral molar entropy of solution at 527°C (800 K) for the equiatomic Zn-Cd solution.

Solution: It has been shown in the previous example that Zn-Cd solutions behave regularly, and it has also been calculated that at \( x_{\text{Zn}} = 0.5 \) the value of \( \gamma_{\text{Zn}} \) is 1.352. According to Eq. (7.23), the excess partial molar free energy of zinc is given as

\[ \frac{X}{X} G^X_{\text{Zn}} = RT \ln \gamma_{\text{Zn}} = 4.575 \times 800 \times \log 1.352 = 479 \text{ cal/mole}. \]
Similarly, the value of excess partial molar free energy of cadmium can be obtained as

\[ \overline{G}_{\text{Cd}}^{\text{xs}} = 479 \text{ cal/mole.} \]

Thus the excess integral molar free energy of solution is given as

\[ \overline{G}^{\text{xs}} = x_{\text{Zn}} \overline{G}_{\text{Zn}}^{\text{xs}} + x_{\text{Cd}} \overline{G}_{\text{Cd}}^{\text{xs}} \]

\[ = 0.5 \times 479 + 0.5 \times 479 \]

\[ = 479 \text{ cal/mole.} \]

Since Zn-Cd solution exhibits regular behaviour, the excess integral molar entropy of solution is zero.

7.5 Application of the Gibbs-Duhem Equation

7.5.1 Determination of the Partial Molar Quantity of One Component in a Binary Solution when the Variation of the Partial Molar Quantity of the Other with Concentration is known

The Gibbs-Duhem equation can be used in calculating the partial molar quantity of one component in a binary solution, when the variation of the partial molar quantity for the other with concentration is known. Let us consider that in a binary solution A-B, the partial molar quantity \( \overline{Z}_B \) as a function of mole fraction of B, \( x_B \), is known, and it is required to calculate the partial molar quantity \( \overline{Z}_A \) at the desired composition (say at \( x_A = x_A \)). From Eq.(6.14),

\[ d\overline{Z}_A = - \frac{x_B}{x_A} d\overline{Z}_B. \]

Expressing the above equation in terms of an indefinite integral,
The limits of integration may be chosen as desired. The upper limit will obviously be that corresponding to $x_A^* = x_A^*$. The lower limit should be that at which the value of $Z_A$ is known. However, the most convenient lower limit will correspond to $x_A^* = 1$, i.e.

$$\int_{x_A^*=1}^{x_A^*} dZ_A = - \int_{x_A^*=1}^{x_A^*} \frac{x_B}{x_A} dZ_B.$$  

or

$$\left[ \frac{Z_A}{x_A^*} \right]_{x_A^*=1}^{x_A^*} = - \int_{x_A^*=1}^{x_A^*} \frac{x_B}{x_A} dZ_B. \quad (7.27)$$

The integral in the above equation may be solved graphically, and hence the value of $Z_A$ may be calculated, as illustrated in the following example.

**Example 7.D**

Calculate the partial molar heat of mixing of zinc in a solid Cd-Zn alloy containing 20 atom % zinc at 530°C (803 K) from the following data:

<table>
<thead>
<tr>
<th>$x_{Cd}$</th>
<th>1.0 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_{Cd}^M$, cal/mole</td>
<td>0 30 90 190 300 440 630 870 1170 1710</td>
</tr>
<tr>
<td>$H_{Cd}^M$, J/mol</td>
<td>0 126 377 795 1265 1841 2636 3640 4825 7155</td>
</tr>
</tbody>
</table>

**Solution:** From Eq.(6.16), the appropriate Gibbs-Duham equation for the Cd-Zn alloy can be written as
The value of $H_{Zn}^M$ can be calculated by expressing the above equation in the form of a definite integral. The upper limit will obviously be that corresponding to $x_{Zn} = 0.2$. The lower limit, for convenience, can be taken as that corresponding to $x_{Zn} = 1.0$. Thus,

$$
\int_{x_{Zn} = 1.0}^{x_{Zn} = 0.2} x_{Zn}^M \frac{dH_{Zn}^M}{x_{Zn}} = - \int_{x_{Zn} = 1.0}^{x_{Zn} = 0.2} \frac{x_{Cd}^M}{x_{Zn}} dH_{Cd}^M.
$$

or

$$
\left[ \frac{H_{Zn}^M}{x_{Zn}} \right]_{x_{Zn} = 0.2} - \left[ \frac{H_{Zn}^M}{x_{Zn}} \right]_{x_{Zn} = 1.0} = - \int_{x_{Zn} = 1.0}^{x_{Zn} = 0.2} \frac{x_{Cd}^M}{x_{Zn}} dH_{Cd}^M.
$$

Since at $x_{Zn} = 1.0$, $H_{Zn}^M = 0$, we have

$$
\left[ \frac{H_{Zn}^M}{x_{Zn}} \right]_{x_{Zn} = 0.2} + \int_{x_{Zn} = 0.2}^{x_{Zn} = 1.0} \frac{x_{Cd}^M}{x_{Zn}} dH_{Cd}^M.
$$

(7.0.1)

In order to solve the above integral, a graph is plotted relating $\frac{x_{Cd}}{x_{Zn}}$ to $H_{Cd}^M$ as shown in Fig. 7.1 from the following calculated data:

<table>
<thead>
<tr>
<th>$x_{Cd}$</th>
<th>0.9</th>
<th>0.8</th>
<th>0.7</th>
<th>0.6</th>
<th>0.5</th>
<th>0.4</th>
<th>0.3</th>
<th>0.2</th>
<th>0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x_{Zn}$</td>
<td>0.1</td>
<td>0.2</td>
<td>0.3</td>
<td>0.4</td>
<td>0.5</td>
<td>0.6</td>
<td>0.7</td>
<td>0.8</td>
<td>0.9</td>
</tr>
<tr>
<td>$x_{Cd}$</td>
<td>9.00</td>
<td>4.00</td>
<td>2.33</td>
<td>1.50</td>
<td>1.00</td>
<td>0.66</td>
<td>0.42</td>
<td>0.25</td>
<td>0.11</td>
</tr>
<tr>
<td>$H_{Cd}^M$, cal/mole</td>
<td>30</td>
<td>90</td>
<td>190</td>
<td>300</td>
<td>440</td>
<td>630</td>
<td>870</td>
<td>1170</td>
<td>1710</td>
</tr>
</tbody>
</table>
The area bounded by the curve and the axis for $\overline{H}^M_{Cd}$ between the values of $\overline{H}^M_{Cd}$ corresponding to $x_{Zn} = 0.2$ (i.e. $\frac{x_{Cd}}{x_{Zn}} = 4.0$), and $x_{Zn} = 1.0$ (i.e. $\frac{x_{Cd}}{x_{Zn}} = 0$) gives the value of $\overline{H}^M_{Zn}$ at $x_{Zn} = 0.2$. The area can be calculated by the trapezoidal rule, taking a chord width of $\overline{H}^M_{Cd} = 100$ cal/mole. From the graph, the shaded area is equivalent to 1,113 cal/mole, and hence the partial molar heat of mixing of zinc in a Cd-20 atom% Zn alloy is 1,113 cal/mole.
However, the above graphical integration of the Gibbs-Duhem equation is rather unsatisfactory because of the asymptotic nature of the curve.

### 7.5.2 Determination of the Activity of One Component in a Binary Solution, when the Activity of the Other is known

It is often troublesome to measure the activity of both components in a binary solution. Let us consider a binary solution A-B. The activity of B, $a_B$, as a function of mole fraction $x_B$ is known. The activity of A, $a_A$, can be calculated at the desired composition (say at $x_A = x_A$) with the help of Gibbs-Duhem equation. From Eq.(6.18) the following expression can be obtained:

$$x_A \, d \bar{G}_A + x_B \, d \bar{G}_B = 0 .$$

On substituting the values of $d \bar{G}_A$ and $d \bar{G}_B$,

$$x_A \cdot RT \, d \ln a_A + x_B \cdot RT \, d \ln a_B = 0 ,$$

or

$$x_A \cdot d \ln a_A + x_B \cdot d \ln a_B = 0 , \quad (7.28)$$

or

$$x_A \cdot d \log a_A + x_B \cdot d \log a_B = 0 ,$$

or

$$d \log a_A = - \frac{x_B}{x_A} \, d \log a_B . \quad (7.29)$$

In principle, the above equation permits the calculation of one activity from the other. Thus, expressed as an indefinite integral,

$$\int d \log a_A = - \int \frac{x_B}{x_A} \, d \log a_B . \quad (7.30)$$

The limits of integration may be chosen as desired. The upper limit will
obviously be that corresponding to \( x_A = x_A' \). The lower limit must be that at which the value of \( a_A \) is known. Since \( a_A = 1 \) at \( x_A = 1 \), the most convenient lower limit will correspond to pure \( A \), i.e. \( x_A = 1 \). Thus,

\[
\int_{x_A=1}^{x_A=x_A'} d\log a_A = - \int_{x_A=1}^{x_A=x_A'} \frac{x_B}{x_A} d\log a_B ,
\]

or

\[
\left[ \log a_A \right]_{x_A=x_A'}^{x_A=1} - \left[ \log a_A \right]_{x_A=1}^{x_A=x_A'} = - \int_{x_A=1}^{x_A=x_A'} \frac{x_B}{x_A} d\log a_B ,
\]

or

\[
\left[ \log a_A \right]_{x_A=x_A'}^{x_A=1} = - \int_{x_A=1}^{x_A=x_A'} \frac{x_B}{x_A} d\log a_B . \tag{7.31}
\]

The above integral can be solved graphically. To evaluate this integral, a graph should be plotted relating \( \frac{x_B}{x_A} \) to \(-\log a_B\). The area bounded by the curve and the axis for \(-\log a_B\) between the values of \(-\log a_B\) corresponding to \( x_A = x_A' \) (i.e. \( x_B = \frac{1-x_A}{x_A} \)), and \( x_A = 1 \) (i.e. \( x_B = 0 \)), will give the value of \(-\log a_B\) at \( x_A = x_A' \), and hence the value of \( a_A \) can be calculated. However, integration is difficult because the area under the curve approaches infinity as \( x_A \) becomes small (i.e. \( \frac{x_B}{x_A} \to \infty \)) and \( \log a_B \) approaches minus infinity when \( x_A \) tends to one. Thus, the activity value obtained from the above method is not very accurate.

A more precise value of the activity can be determined with the help of a relation similar to Eq.(7.28), expressed in terms of activity coefficients. Since,

\( x_A + x_B = 1 \),

Differentiating,

\( dx_A + dx_B = 0 \).
Multiplying the first term by \( \frac{x_A}{x_A} \) and the second by \( \frac{x_B}{x_B} \) in the above expression,

\[
x_A \frac{dx_A}{x_A} + x_B \frac{dx_B}{x_B} = 0 ,
\]
or

\[
x_A \cdot d \ln x_A + x_B \cdot d \ln x_B = 0 . \tag{7.32}
\]

Subtracting the above equation from Eq.(7.28),

\[
x_A \cdot d \ln y_A + x_B \cdot d \ln y_B = 0 ,
\]
or

\[
x_A \cdot d \log y_A + x_B \cdot d \log y_B = 0 , \tag{7.33}
\]
or

\[
d \log y_A = -\frac{x_B}{x_A} d \log y_B . \tag{7.34}
\]

Integrating Eq.(7.34) between the limits \( x_A = x_A \) and \( x_A = 1 \),

\[
\left[ \log y_A \right]_{x_A=x_A}^{x_A=1} - \left[ \log y_A \right]_{x_A=1}^{x_A=1} = - \int_{x_A=1}^{x_A=x_A} \frac{x_B}{x_A} d \log y_B .
\]

Since at \( x_A=1 \), \( y_A=1 \),

\[
\left[ \log y_A \right]_{x_A=x_A}^{x_A=1} = - \int_{x_A=1}^{x_A=x_A} \frac{x_B}{x_A} d \log y_B . \tag{7.35}
\]

The above integral can be solved graphically in a similar way to that described previously, and thus the value of \( y_A \) and hence \( a_A \), can be calculated.

Hence, in order to find out a more precise value of activity of \( A \) at a desired composition, the activities of \( B \) should be changed to the corresponding activity coefficient values, and then the value of the activity coefficient
of $A$, $\gamma_A$, at the desired composition is calculated with the help of Eq.(7.35). From this value of the activity coefficient, the activity can be determined, as illustrated in Example 7.E.

Since $\gamma_B$ is always finite, the graphical evaluation of the integral in Eq. (7.35) presents no difficulty in the vicinity of $x_A = 1$, as did the graphical integration of Eq.(7.31). But there is still difficulty where $x_A$ is small, because $x_B/x_A$ again approaches infinity.

However, the above difficulty of calculating the activity (or activity coefficient) of component $A$ in a solution where $x_A$ is small as compared to $x_B$, can be overcome if the integration is done in a somewhat different way, as described below.

Dividing Eq.(7.33) by $dx_B$,

$$\frac{d \log \gamma_A}{dx_B} + \frac{x_A}{x_B} \frac{d \log \gamma_B}{dx_B} = 0,$$

or

$$d \log \gamma_A = - \frac{x_B}{x_A} \frac{d \log \gamma_B}{dx_B} \cdot dx_B.$$

Integrating within the limits $x_A = x_A$ and $x_A = 1$,

$$\int_{x_A=1}^{x_A=x_A} d \log \gamma_A = - \int_{x_A=1}^{x_A=x_A} \frac{x_B}{x_A} \frac{d \log \gamma_B}{dx_B} \cdot dx_B.$$

Integrating by parts,

$$[\log \gamma_A]_{x_A=x_A}^{x_A=x_A} = - \left[ \frac{x_B}{x_A} \log \gamma_B \right]_{x_A=1}^{x_A=x_A} + \int_{x_A=1}^{x_A=x_A} \frac{x_B}{x_A} \frac{d \log \gamma_B}{dx_B} \cdot dx_B. \quad (7.36)$$
The integral in Eq.(7.36) can be solved graphically by plotting a curve between \( \log \gamma_B \) and \( x_B \). The value of the integral will be given by the area under the curve between the limits \( x_A = x_A^0 \) and \( x_A = 1 \). The curve will not be asymptotic to either of the axes. Thus, the value of activity coefficient, and hence activity, can be calculated as illustrated in Example 7.F.

**Example 7.E**

The following data have been obtained for Cr-Ti solutions at 1250°C (1523 K):

<table>
<thead>
<tr>
<th>( x_{Cr} )</th>
<th>0.09</th>
<th>0.19</th>
<th>0.27</th>
<th>0.37</th>
<th>0.47</th>
<th>0.67</th>
<th>0.78</th>
<th>0.89</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a_{Cr} )</td>
<td>0.302</td>
<td>0.532</td>
<td>0.660</td>
<td>0.778</td>
<td>0.820</td>
<td>0.863</td>
<td>0.863</td>
<td>0.906</td>
</tr>
</tbody>
</table>

Calculate the activity of titanium in a Cr-Ti solution containing 60 atom % Ti.

**Solution:** Expressing the Eq.(7.30) for Cr-Ti solutions,

\[
\int d \log a_{Ti} = - \int \frac{x_{Cr}}{x_{Ti}} d \log a_{Cr}.
\]

Integrating the above between the limits \( x_{Ti} = 0.6 \) and \( x_{Ti} = 1.0 \),

\[
\left. \frac{x_{Cr}}{x_{Ti}} \right|_{x_{Ti}=0.6}^{x_{Ti}=1.0} \int d \log a_{Ti} = \left. \frac{x_{Cr}}{x_{Ti}} \right|_{x_{Ti}=0.6}^{x_{Ti}=1.0} \int d \log a_{Cr},
\]

or

\[
\log a_{Ti} \bigg|_{x_{Ti}=0.6} = + \left. \frac{x_{Cr}}{x_{Ti}} \right|_{x_{Ti}=0.6} \int d \log a_{Cr}.
\]  \hspace{1cm} (7.E.1)

In order to find the value of the above integral, a graph is plotted relating
$x_{Cr}/x_{Ti}$ to $(-\log a_{Cr})$, as shown in Fig. 7.2, from the following calculated data:

<table>
<thead>
<tr>
<th>$x_{Cr}$</th>
<th>$x_{Cr}/x_{Ti}$</th>
<th>$a_{Cr}$</th>
<th>$(-\log a_{Cr})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.09</td>
<td>0.0989</td>
<td>0.302</td>
<td>0.520</td>
</tr>
<tr>
<td>0.19</td>
<td>0.2346</td>
<td>0.532</td>
<td>0.274</td>
</tr>
<tr>
<td>0.27</td>
<td>0.3699</td>
<td>0.660</td>
<td>0.180</td>
</tr>
<tr>
<td>0.37</td>
<td>0.5873</td>
<td>0.778</td>
<td>0.109</td>
</tr>
<tr>
<td>0.47</td>
<td>0.8867</td>
<td>0.820</td>
<td>0.086</td>
</tr>
<tr>
<td>0.67</td>
<td>2.0310</td>
<td>0.863</td>
<td>0.064</td>
</tr>
<tr>
<td>0.78</td>
<td>3.5460</td>
<td>0.863</td>
<td>0.064</td>
</tr>
<tr>
<td>0.89</td>
<td>8.0910</td>
<td>0.906</td>
<td>0.043</td>
</tr>
</tbody>
</table>

Fig. 7.2. Graphical Solution of the Integral in Eq.(7.E.1).
The area bounded by the curve and the axis for \((-\log a_{Cr}\)) between the values of \(-\log a_{Cr}\) corresponding to \(x_{Ti} = 0.6\) (i.e. \(x_{Cr} = 0.666\)), and \(x_{Ti} = 1.0\) (i.e. \(x_{Cr} = 0\)) is calculated by the trapezoidal rule, taking a chord width of 0.05. This area gives the value of \((-\log a_{Ti}\)). However, from Fig. 7.2, it is clear that the area to be measured is under a curve tending to infinity, and hence a precise value of the area cannot be determined. From the graph, it follows that

\[
\text{Shaded area} = 0.09465,
\]

and hence,

\[
-\log a_{Ti} \bigg|_{x_{Ti} = 0.6} = 0.09465,
\]

or

\[
[a_{Ti}] \bigg|_{x_{Ti} = 0.6} = 0.8041.
\]

Thus, the activity of titanium in a Cr-Ti solution containing 60 atom% Ti is 0.8041.

A more accurate value of the activity can be obtained from Eq.(7.35), and thus

\[
[\log \gamma_{Ti}] \bigg|_{x_{Ti} = 0.6} = + \int_{x_{Ti} = 0.6}^{x_{Ti} = 1.0} \frac{x_{Cr}}{x_{Ti}} \, d \log \gamma_{Cr}.
\]

In order to calculate the value of this integral, a graph is plotted relating \(x_{Cr}/x_{Ti}\) to \(\log \gamma_{Cr}\) from the following calculated data, as shown in Fig. 7.3.
<table>
<thead>
<tr>
<th>$x_{Cr}$</th>
<th>$\frac{x_{Cr}}{x_{Ti}}$</th>
<th>$\alpha_{Cr}$</th>
<th>$\gamma_{Cr}$</th>
<th>$\log \gamma_{Cr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.09</td>
<td>0.0989</td>
<td>0.302</td>
<td>3.356</td>
<td>0.5258</td>
</tr>
<tr>
<td>0.19</td>
<td>0.2346</td>
<td>0.532</td>
<td>2.800</td>
<td>0.4472</td>
</tr>
<tr>
<td>0.27</td>
<td>0.3699</td>
<td>0.660</td>
<td>2.444</td>
<td>0.3881</td>
</tr>
<tr>
<td>0.37</td>
<td>0.5873</td>
<td>0.778</td>
<td>2.103</td>
<td>0.3228</td>
</tr>
<tr>
<td>0.47</td>
<td>0.8867</td>
<td>0.820</td>
<td>1.745</td>
<td>0.2417</td>
</tr>
<tr>
<td>0.67</td>
<td>2.0310</td>
<td>0.863</td>
<td>1.288</td>
<td>0.1100</td>
</tr>
<tr>
<td>0.78</td>
<td>3.5460</td>
<td>0.863</td>
<td>1.106</td>
<td>0.0437</td>
</tr>
<tr>
<td>0.89</td>
<td>8.0910</td>
<td>0.906</td>
<td>1.018</td>
<td>0.0076</td>
</tr>
</tbody>
</table>

Shaded area = 0.08765

Fig. 7.3. Graphical Solution of the Integral in Eq.(7.E.2).

The area bounded by the curve and the axis for ($\log \gamma_{Cr}$) between the values of $\log \gamma_{Cr}$ corresponding to $x_{Ti} = 0.6$ (i.e. $x_{Cr}/x_{Ti} = 0.666$) and $x_{Ti} = 1.0$ (i.e. $x_{Cr}/x_{Ti} = 0$) is calculated by the trapezoidal rule, taking a chord width
of 0.05, which gives the value of \( \log \gamma_{T_i} \) at \( x_{T_i} = 0.6 \). From the graph, it follows that
\[
\text{Shaded area} = 0.08765
\]
Hence,
\[
[\log \gamma_{T_i}]_{x_{T_i}=0.6} = 0.08765,
\]
or
\[
[\gamma_{T_i}]_{x_{T_i}=0.6} = 1.224.
\]
Since
\[
a_{T_i} = \gamma_{T_i} x_{T_i},
\]
\[
[a_{T_i}]_{x_{T_i}=0.6} = 1.224 \times 0.6 = 0.7344.
\]
The value of the activity of titanium in a Cr-Ti solution containing 60 atom\% Ti is 0.7344. The value of activity obtained by this method is more accurate as compared to the value obtained by the first method.

**Example 7.**

The activities of copper in Al-Cu alloys at 1100°C (1873 K) are given below.

<table>
<thead>
<tr>
<th>( x_{\text{Al}} )</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
<th>0.6</th>
<th>0.7</th>
<th>0.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a_{\text{Cu}} )</td>
<td>0.86</td>
<td>0.61</td>
<td>0.34</td>
<td>0.18</td>
<td>0.08</td>
<td>0.045</td>
<td>0.02</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Calculate the activity of aluminium in an Al-Cu alloy containing 5 atom\% aluminium at 1100°C (1873 K).

**Solution:** As illustrated in the previous example, the use of the Gibbs-Duhem equation expressed in terms of activity coefficients is quite satisfactory when the value of activity of the unknown component is required for a solution containing an appreciable amount of that component. But if the value of the activity of the unknown component is required in a solution containing very
little of that component (as in the present example), difficulties are encoun-
tered due to the asymptotic nature of the curve with respect to the ordinate.
In such a case, the activity is best determined by the use of Eq.(7.36). Apply-
ing this to the present example,

$$\log \gamma_{Al} \bigg|_{x_{Al}=0.05} = - \int_{x_{Al}=0.05}^{x_{Al}=1.0} \log \gamma_{Cu} \frac{dx_{Cu}}{x_{Al}^2}$$

(7.6.1)

The value of the integral in Eq.(7.6.1) is given by the area under a curve of
$$\frac{\log \gamma_{Cu}}{x_{Al}^2}$$
versus $$x_{Cu}$$ between the values of $$x_{Al} = 0.05$$ (i.e. $$x_{Cu} = 0.95$$), and
$$x_{Al} = 1.0$$ (i.e. $$x_{Cu} = 0$$). The curve is drawn from the following calculated
data, as shown in Fig. 7.4.

<table>
<thead>
<tr>
<th>$$x_{Al}$$</th>
<th>$$x_{Cu}$$</th>
<th>$$a_{Cu}$$</th>
<th>$$\gamma_{Cu}$$</th>
<th>$$\frac{\log \gamma_{Cu}}{x_{Al}^2}$$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.9</td>
<td>0.860</td>
<td>0.9557</td>
<td>- 1.970</td>
</tr>
<tr>
<td>0.2</td>
<td>0.8</td>
<td>0.610</td>
<td>0.7625</td>
<td>- 2.945</td>
</tr>
<tr>
<td>0.3</td>
<td>0.7</td>
<td>0.340</td>
<td>0.4857</td>
<td>- 3.484</td>
</tr>
<tr>
<td>0.4</td>
<td>0.6</td>
<td>0.180</td>
<td>0.3000</td>
<td>- 3.268</td>
</tr>
<tr>
<td>0.5</td>
<td>0.5</td>
<td>0.080</td>
<td>0.1600</td>
<td>- 3.184</td>
</tr>
<tr>
<td>0.6</td>
<td>0.4</td>
<td>0.045</td>
<td>0.1125</td>
<td>- 2.636</td>
</tr>
<tr>
<td>0.7</td>
<td>0.3</td>
<td>0.020</td>
<td>0.0666</td>
<td>- 2.400</td>
</tr>
<tr>
<td>0.8</td>
<td>0.2</td>
<td>0.010</td>
<td>0.0500</td>
<td>- 2.032</td>
</tr>
</tbody>
</table>

From the graph, the area of the shaded portion is -2.4075 (measured using the
trapezoidal rule, chord width = 0.05).
The other term in Eq. (7.1) requires the value of $\log \gamma_{\text{Cu}}$ at $x_{\text{Al}} = 0.05$, which can be obtained by extrapolating the curve in Fig. 7.4. Thus

$$\log \gamma_{\text{Cu}} = \frac{\log \gamma_{\text{Cu}}}{x_{\text{Al}}} = -1.58,$$

and hence $\log \gamma_{\text{Cu}} = -0.00395$. 

Fig. 7.4. Graphical Solution of the Integral in Eq. (7.1).
Putting the appropriate values in Eq.(7.F.1),

\[
\left[ \log \gamma_{\text{Al}} \right]_{x_{\text{Al}}=0.05} = -\left[ \frac{0.95}{0.05} \times (-0.00395) \right] + (-2.4075)
\]

\[
= 0.0750 - 2.4075
\]

\[
= -2.3325.
\]

Taking antilogs,

\[
\gamma_{\text{Al}} = 0.00465.
\]

Hence,

\[
\left[ a_{\text{Al}} \right]_{x_{\text{Al}}=0.05} = 0.00465 \times 0.05
\]

\[
= 0.0002325.
\]

The activity of aluminium in an Al-Cu solution containing 5 atom% Al is 0.0002325.

Sometimes the thermodynamic data are expressed in the form of an empirical equation. For example, the activity coefficient of a component in a solution is often expressed as a function of composition in terms of an empirical equation. In such cases, the Gibbs-Duhem equation can be solved analytically instead of graphically. The following example illustrates the analytical integration of the Gibbs-Duhem equation.

**Example 7.G**

Al-Zn alloys exhibit the following relation at 477°C (750 K):

\[ RT \ln \gamma_{\text{Zn}} = 1750 (1-x_{\text{Zn}})^2, \]

where \( R \) and \( T \) are expressed in cal/deg/mole and \( K \), respectively.
Calculate the activity of aluminium at 477°C (750 K) in an Al-Zn alloy containing 40 atom% zinc.

**Solution:** The activity coefficient of zinc at 477°C (750 K) is given by

$$4.575 \times 750 \times \log \gamma_{Zn} = 1750 \left(1 - x_{Zn}\right)^2,$$

or

$$\log \gamma_{Zn} = 0.5099 \left(1 - x_{Zn}\right)^2.$$

Differentiating,

$$d \log \gamma_{Zn} = -2 \times 0.5099 \left(1 - x_{Zn}\right) dx_{Zn}$$

$$= -1.0198 \left(1 - x_{Zn}\right) dx_{Zn}. \quad (7.6.1)$$

From Eq.(7.34),

$$d \log \gamma_{Al} = - \frac{x_{Zn}}{x_{Al}} d \log \gamma_{Zn}.$$

Putting the value of $d \log \gamma_{Zn}$ from Eq.(7.6.1) in the above equation,

$$d \log \gamma_{Al} = \frac{x_{Zn}}{x_{Al}} \times 1.0198 \left(1 - x_{Zn}\right) dx_{Zn}$$

$$= \frac{x_{Zn}}{1 - x_{Zn}} \times 1.0198 \left(1 - x_{Zn}\right) dx_{Zn}$$

$$= 1.0198 x_{Zn} dx_{Zn}. \quad (7.6.2)$$

The value of $\gamma_{Al}$ at $x_{Zn} = 0.4$ can be obtained by expressing Eq.(7.6.2) in terms of a definite integral. The upper limit of integration will obviously be that corresponding to $x_{Zn} = 0.4$ (i.e. $x_{Al} = 0.6$). The lower limit, for convenience, may be taken as that corresponding to $x_{Zn} = 0$ (i.e. $x_{Al} = 1.0$). Thus,

$$\int_{x_{Al} = 1.0}^{x_{Al} = 0.6} d \log \gamma_{Al} = \int_{x_{Zn} = 0}^{x_{Zn} = 0.4} 1.0198 x_{Zn} dx_{Zn},$$

$$x_{Al} = 0.6 \quad x_{Zn} = 0.4$$

$$x_{Al} = 1.0 \quad x_{Zn} = 0$$
or 
\[ \log \gamma_{Al}^{x_{Al}=0.6} - \log \gamma_{Al}^{x_{Al}=1.0} = \left[ \frac{1.0198}{2} \right]^{x_{Zn}=0.4} \times \] 

Since at \( x_{Al} = 1.0, \gamma_{Al} = 1.0, \)
\[ \log \gamma_{Al}^{x_{Al}=0.6} = 0.5099 [0.16 - 0] \]
\[ = 0.0815. \]

Taking antilogs,
\[ \gamma_{Al}^{x_{Al}=0.6} = 1.206, \]

or
\[ a_{Al}^{x_{Al}=0.6} = 1.206 \times 0.6 \]
\[ = 0.7236. \]

Hence, the activity of aluminium in an Al-Zn solution containing 40 atom\% Zn at 477°C is 0.7236.

7.6 Multicomponent Solutions

The activity coefficient of a solute in a binary solution can be obtained from the relation

\[ \text{activity coefficient} = \frac{\text{activity}}{\text{mole fraction}}, \]

if the activity and concentration are known. However, the numerical value of the activity coefficient will be different for different chosen standard states.
The above relation does not hold good for a multi-component solution. The solutes, even present in small amounts, exert their influence on the solvent as well as on each other. When a solvent metal, A, contains a number of solute metals, B, C, D, ..., the Henrian activity coefficient of one of these (say $f_B$) may be expressed as a product of factors which represent the effect of each of the other components. Thus, in a solution of mole fraction, $x_B$, $x_C$, $x_D$, ..., 

$$f_B = f_B^B \cdot f_B^C \cdot f_B^D \ldots \, , \quad (7.37)$$

where $f_B^B$ is the activity coefficient of B in a binary solution A-B, having the mole fraction of B as $x_B$ and $f_B^C$, the 'interaction coefficient', is a measure of the effect of C on the activity coefficient of B. Similarly, other interaction coefficients may be defined. However, Eq.(7.37) does not take into consideration any interaction between the solutes C, D, ..., and hence it is only approximate where more than three components are concerned.

Wagner(1) has derived the following expression for the activity coefficient of a solute in a multi-component system:

$$\ln f_B(x_B, x_C, x_D, \ldots) = \ln f_B^0 + \left[ x_B \left( \frac{\partial \ln f_B}{\partial x_B} \right) + x_C \left( \frac{\partial \ln f_B}{\partial x_C} \right) + x_D \left( \frac{\partial \ln f_B}{\partial x_D} \right) + \ldots \right] + \frac{1}{2} x_B x_C \frac{\partial^2 \ln f_B}{\partial x_B \partial x_C} + \ldots \ldots \ldots \, , \quad (7.38)$$

where the derivatives are to be taken for the limiting case of zero concentration of all solutes. If all except the first-order terms are neglected, the expression for the logarithm of the activity coefficient becomes linear with respect to the mole fraction of the solute present in the dilute alloy solution. Hence,

$$\ln f_B(x_B, x_C, x_D, \ldots) = \ln f_B^0 + x_B \left( \frac{\partial \ln f_B}{\partial x_B} \right) + x_C \left( \frac{\partial \ln f_B}{\partial x_C} \right) + x_D \left( \frac{\partial \ln f_B}{\partial x_D} \right) + \ldots \, . \quad (7.39)$$
The derivatives in the above equation are represented by the symbol $\varepsilon_B^B, \varepsilon_B^C, \varepsilon_B^D, \ldots$, defined as

$$\varepsilon_B^B = \left( \frac{\partial \ln f_B}{\partial x_B} \right),$$

$$\varepsilon_B^C = \left( \frac{\partial \ln f_B}{\partial x_C} \right),$$

and are called 'interaction parameters'. Hence Eq.(7.39) becomes

$$\ln f_B(x_B, x_C, x_D, \ldots) = \ln f_B^0 + x_B\varepsilon_B^B + x_C\varepsilon_B^C + x_D\varepsilon_B^D + \ldots \quad (7.40)$$

At infinite dilution, the term $\ln f_B^0$ can be made zero by putting $f_B \approx 1$. Hence,

$$\ln f_B(x_B, x_C, x_D, \ldots) = x_B\varepsilon_B^B + x_C\varepsilon_B^C + x_D\varepsilon_B^D + \ldots \quad (7.41)$$

Though the derivatives represented for $\varepsilon_B^B, \varepsilon_B^C, \ldots$ are taken for the limiting case of the infinitely dilute solution, it has been found in many systems that the value of the derivatives, say $\varepsilon_B^B$, derived for the infinitely dilute solution is constant over a finite, sometimes large, range of concentration.

It can be easily demonstrated from the Gibbs-Duhem equation that

$$\varepsilon_B^C = \varepsilon_C^B \quad (7.42)$$

It should be remembered that the activity coefficient expressed in Eq.(7.41) is relative to the infinitely dilute, atom fraction standard state. For convenience, common logarithms are used and concentrations are expressed in wt%.

Thus Eq.(7.41) becomes

$$\log f_B(\%B, \%C, \%D, \ldots) = \%B\varepsilon_B^B + \%C\varepsilon_B^C + \%D\varepsilon_B^D + \ldots \quad (7.43)$$

where

$$\varepsilon_B^B = \left( \frac{\partial \log f_B}{\partial \%B} \right), \quad \varepsilon_B^C = \left( \frac{\partial \log f_B}{\partial \%C} \right) \text{ etc.}$$
and the derivatives are taken for the limiting case of zero concentration of all solutes. The activity coefficient expressed in the above equation is relative to the infinitely dilute, weight percent standard state. The reciprocal relationship for this parameter is

\[ e^C_B = \frac{M_B}{M_C} e^C_C. \]  

(7.44)

where \( M_B \) and \( M_C \) are the molecular weights of \( B \) and \( C \) respectively.

The above formulae are strictly applicable only at infinite dilution, but they are suitable for approximate calculations in the region over which Henry's law is valid.

Example 7.7

The activity coefficient of zinc relative to the infinitely dilute atom fraction standard state in a binary Bi-Zn solution containing 0.015 mole fraction of zinc at 450°C \((723 \text{ K})\) is 3.974. The interaction parameters in bismuth, \( \varepsilon^\text{Pb}_Zn \) and \( \varepsilon^\text{Ag}_Zn \) are 1.3 and -2.5 respectively. Calculate the activity coefficient of zinc in a Bi-Zn-Pb-Ag solution containing mole fractions of Zn, Pb, and Ag equal to 0.015 at 450°C.

Solution: From Eq.(7.37), it follows that

\[ \ln f_{Zn} = \ln f^\text{Zn}_{Zn} + \ln f^\text{Pb}_{Zn} + \ln f^\text{Ag}_{Zn} \]

\[ = \ln f^\text{Zn}_{Zn} + x^\text{Pb}_{Zn} \varepsilon^\text{Zn}_{Zn} + x^\text{Ag}_{Zn} \varepsilon^\text{Zn}_{Zn}. \]

Putting the appropriate values in the above equation,

\[ \ln f_{Zn} = (2.303 \log 3.974) + (0.015 \times 1.3) + (0.015 \times -2.5) \]

\[ = 1.362. \]
Solutions: II

or \[ \log f_{\text{Zn}} = 0.5913. \]

Taking antilogs, \( f_{\text{Zn}} = 3.902. \)

Thus, the activity coefficient of zinc in the given solution relative to infinitely dilute atom fraction standard state is 3.902.

**Example 7.1**

A liquid Fe-P alloy containing 0.65 wt% phosphorus is equilibrated with a H$_2$O-H$_2$ mixture in which P$_{H_2O}$ is equal to 0.0494 at 1600°C (1873 K). The equilibrated alloy is found to contain 0.0116 wt% oxygen. The activity coefficient \( f^0_0 \) of oxygen relative to the infinitely dilute, weight percent standard state in Fe-0 binary alloys at 1600°C is represented by

\[ \log f^0_0 = -0.2[\text{wt}\% \text{O}] \].

Calculate the interaction parameter \( e^p_0 \) at 1600°C if the equilibrium constant of the reaction

\[(H_2)^{[\text{O}]_{\text{Fe,wt\%}}}(H_2O)\]

at 1600°C is 3.855.

**Solution:** Assuming that the gases behave ideally, the equilibrium constant for the reaction

\[(H_2)^{[\text{O}]_{\text{Fe,wt\%}}}(H_2O)\]

can be written as

\[ K = \frac{\frac{P_{H_2O}}{P_{H_2} \times (\text{wt}\% \times f_0)}}{f_0} \],

where \( f_0 \) is the activity coefficient of oxygen in the ternary Fe-P-O alloy. Putting the values of \( \frac{P_{H_2O}}{P_{H_2}} \), \( \text{wt}\% \), and \( K \),
According to Eq. (7.37),

\[ f_0 = f_0^0 \cdot f_0^p, \]  \hspace{1cm} (7.1.2)

where \( f_0^0 \) is the activity coefficient of oxygen in the binary Fe-0 alloy containing the same concentration of oxygen as the Fe-P-0 alloy, and \( f_0^p \) is the effect of phosphorus on this activity coefficient. Taking logarithms on both sides,

\[ \log f_0 = \log f_0^0 + \log f_0^p. \]

Putting the value of \( f_0^0 \) in the above,

\[ \log f_0 = -0.2[\text{wt}\%O] + \log f_0^p. \]

Putting the value of \( f_0 \) from Eq. (7.1.1), and also the value of wt\%O,

\[ \log 1.105 = -0.2 \times 0.0116 + \log f_0^p, \]

or

\[ \log f_0^p = 0.0456. \]

Taking antilogs,

\[ f_0^p = 1.110. \]

The interaction parameter \( e_0^p \) may be written as

\[ e_0^p = \left( \frac{\partial \log f_0^p}{\partial \text{wt}\%P} \right). \]

Making the assumption that \( \log f_0^p \) is a linear function of the phosphorus content up to at least 0.65 wt\% (i.e. composition of P in alloy), then

\[ e_0^p = \frac{\log f_0^p}{\text{wt}\%P}. \]
or

\[ p \log 1.110 = 0.65 \]

\[ = 0.0698. \]

Thus, the value of the interaction parameter \( e_0 \) is 0.0698.

Reference:

Exercises

7.1 100 g (0.1 kg) of silver at 1077°C (1350 K) and 1 atm (101325 N/m²) pressure dissolves 194 c.c. (194 \( \times 10^{-6} \) m³) of oxygen, measured at S.T.P. Calculate the solubility of oxygen in silver under a partial pressure of 130 mm Hg (17332 N/m²) at the same temperature. How much oxygen does 100 g (0.1 kg) of silver absorb at 1077°C (1350 K) from atmospheric air? Assume air contains 21% oxygen by volume.

7.2 The solubility of hydrogen in an Al-10%Si alloy at 720°C (993 K) is 0.7 c.c. per 100 g (7 \( \times 10^{-6} \) m³ per kg) of alloy under an equilibrium hydrogen pressure of 700 mm Hg (93325 N/m²). Calculate the limiting pressure to which this alloy should be subjected in order to have 0.1 c.c. hydrogen per 100 g (1 \( \times 10^{-6} \) m³ hydrogen per kg) of alloy.

7.3 The solubility of hydrogen in liquid iron under 1 atm (101325 N/m²) partial pressure of hydrogen is found to obey the following equation:
\[
\log S_{H_2} = - \frac{1670}{T} - 1.68,
\]
where the solubility \( S_{H_2} \) is expressed in wt%. Can the hydrogen content be brought down to 1 ppm (10^{-4} \text{ wt%}) by reducing the pressure in the vacuum chamber to 1 \text{ \mu m Hg} (0.133322 \text{ N/m}^2) at 1600°C (1873 K)?

7.4 At 1 atm (101325 \text{ N/m}^2) pressure and 1500°C (1773 K), 150 g (0.15 kg) of plain carbon steel containing 0.1% carbon dissolves 40 c.c. \((40 \times 10^{-6} \text{ m}^3)\) of hydrogen measured at S.T.P. Under the similar condition, 150 g (0.15 kg) of the above steel dissolves 40 c.c. \((40 \times 10^{-6} \text{ m}^3)\) of nitrogen. How much gas will 150 g (0.15 kg) of the above steel dissolve at 1500°C (1773 K) at 1 atm (101325 \text{ N/m}^2) pressure under an atmosphere which consists of: (i) 40% \( \text{N}_2 \) and 60% \( \text{H}_2 \); (ii) 40% \( \text{N}_2 \) and 60% argon; and (iii) 30% \( \text{N}_2 \), 40% \( \text{H}_2 \), and 30% argon? Assume that argon is insoluble in the steel.

7.5 At 1540°C (1813 K) liquid iron dissolves 0.039 wt% nitrogen in equilibrium with nitrogen at 1 atm (101325 \text{ N/m}^2) pressure, and 0.0025 wt% hydrogen in equilibrium with hydrogen at 1 atm (101325 \text{ N/m}^2) pressure. Ammonia gas was passed over iron at that temperature at such a rate that equilibrium was attained with fully dissociated ammonia at a net pressure of 1 atm. Calculate the hydrogen and nitrogen contents of the melt.

7.6 The iron in an Fe-Ni alloy containing 85.4 atom% Fe oxidises more readily than nickel when equilibrated with a gas mixture consisting of 57.5% \( \text{H}_2 \) and 42.5% \( \text{H}_2\text{O} \) by volume at 1 atm (101325 \text{ N/m}^2) pressure and 840°C (1113 K):

\[
[\text{Fe}]_{\text{alloy}} + (\text{H}_2\text{O}) = <\text{FeO}> + (\text{H}_2);
\]

\[
\Delta G^0 = -3150 + 1.85 \text{ T cal} (-13180 + 7.74 \text{ T J}) .
\]

Calculate the excess partial molar free energy of iron in the alloy, assuming that the \( \text{FeO} \) formed is insoluble in iron.
7.7 The vapour pressure of copper over Cu-Fe alloys at 1550°C (1823 K), as a function of composition, is given below.

\[
\begin{array}{c|cccc}
 x_{\text{Cu}} & 1.0 & 0.792 & 0.476 & 0.217 \\
 p_{\text{Cu}} (\text{mm Hg}) & 0.547 & 0.486 & 0.449 & 0.399 \\
 (p_{\text{Cu}} (N/m^2)) & 72.93 & 64.79 & 59.86 & 52.20 \\
\end{array}
\]

Calculate the activity of iron at \( x_{\text{Cu}} = 0.217 \), assuming that the alpha-function is the same for both iron and copper at this concentration at 1550°C (1823 K).

7.8 Solid Au-Cu alloys are regular in their thermodynamic behaviour. The integral enthalpy of mixing, \( \Delta H^M \), at 447°C (720 K) is given below as a function of composition.

\[
\begin{array}{c|cccc}
x_{\text{Cu}} & 0.2 & 0.3 & 0.4 & 0.5 \\
\Delta H^M, \text{ cal/mole} & -585 & -850 & -1075 & -1220 \\
(\Delta H^M, J/mol) & -2448 & -3556 & -4498 & -5104 \\
\end{array}
\]

Calculate the integral molar free energy of mixing of the above solution at \( x_{\text{Cu}} = 0.3 \) and \( x_{\text{Cu}} = 0.5 \).

7.9 The activity coefficient of copper in Cu-Zn alloys at 1027°C (1300 K) is given below.

\[
\begin{array}{c|cccc}
x_{\text{Cu}} & 0.9 & 0.8 & 0.7 & 0.6 \\
\gamma_{\text{Cu}} & 0.981 & 0.922 & 0.837 & 0.728 \\
\end{array}
\]

Calculate the integral molar free energy of mixing and excess integral molar free energy of solution for an alloy containing 80 atom% Cu, assuming Cu-Zn to
be a regular solution.

7.10 The partial molar entropy of mixing of gold in solid Au-Cu alloys, determined at 500°C (773 K) over the complete solution range, is tabulated below.

\[
\begin{array}{cccccccccc}
 x_{Au} & 0.1 & 0.2 & 0.3 & 0.4 & 0.5 & 0.6 & 0.7 & 0.8 & 0.9 \\
 S_{Au}^M, \text{cal/deg/mole} : & 4.56 & 2.87 & 2.20 & 1.84 & 1.42 & 1.04 & 0.72 & 0.44 & 0.21 \\
 (S_{Au}^M, J/K/mol: & 19.08 & 12.00 & 9.20 & 7.70 & 5.94 & 4.35 & 3.01 & 1.84 & 0.88 )
\end{array}
\]

Calculate the partial molar entropy of mixing of copper and integral molar entropy of mixing of the solution containing 40 atom% copper.

7.11 The excess partial molar free energy of iron at 1600°C (1873 K) in Fe-Ni solutions at different compositions is given below.

\[
\begin{array}{cccccccccc}
 x_{Ni} & 0.1 & 0.2 & 0.3 & 0.4 & 0.5 & 0.6 & 0.7 & 0.8 & 0.9 \\
\end{array}
\]

Calculate the excess partial molar free energy of nickel in an equiatomic solution.

7.12 Calculate the activity of bismuth in a Bi-Zn alloy containing 70 atom% Zn at 600°C (873 K) from the following data obtained from vapour pressure measurements:
7.13 Calculate the activity of tin in an Al-Sn alloy containing 40 atom% Sn at 727°C (1000 K) from the following data:

\[
\begin{align*}
X_{Zn} & : 0.1 \quad 0.2 \quad 0.3 \quad 0.4 \quad 0.5 \quad 0.6 \quad 0.7 \quad 0.8 \quad 0.9 \\
Y_{Zn} & : 2.591 \quad 2.303 \quad 2.098 \quad 1.898 \quad 1.721 \quad 1.551 \quad 1.384 \quad 1.219 \quad 1.089
\end{align*}
\]

7.14 The excess partial molar free energy of zinc in liquid Cu-Zn alloys at 1027°C (1300 K) can be represented as

\[
\bar{U}_{Zn}^{ex} \text{ (cal/mole)} = -5150 (1 - x_{Zn})^2.
\]

Calculate the activity of copper at 1027°C (1300 K) in an equiatomic solution.

7.15 Liquid brasses conform to the following relationship:

\[
RT \ln \gamma_{Zn} = -5000 x_{Cu}^2,
\]

where \( R \) and \( T \) are in cal/deg/mole and K respectively. The vapour pressures of pure copper and pure zinc (in mm Hg) are given as

\[
\log p_{Cu} = -\frac{17520}{T} - 1.21 \log T + 13.21,
\]

and

\[
\log p_{Zn} = -\frac{6850}{T} - 0.755 \log T + 11.24.
\]

Calculate (i) the vapour pressure of copper over a brass containing 40 atom%
zinc at 1227°C (1500 K), and (ii) the vapour pressure of zinc over the above brass at the same temperature.

7.16 The activity coefficient of zinc in Mg-Zn alloys may be represented by

$$\log \gamma_{Zn} = ( - \frac{1750}{T} + 0.831 ) \left( x_{Zn}^{2.5} - 1.667 x_{Zn}^{1.5} + 0.667 \right).$$

Calculate the activity coefficient and the activity of magnesium in a Mg-Zn alloy containing 0.32 atom fraction of magnesium at 727°C (1000 K).

7.17 Liquid iron containing 0.0105 wt% aluminium is equilibrated with an alumina crucible at 1727°C (2000 K). The equilibrium is represented by

$$\text{Al}_2\text{O}_3 = 2[\text{Al}]_{\text{Fe},\text{wt}} + 3[\text{O}]_{\text{Fe},\text{wt}};$$

$$K_{2000} = 3.162 \times 10^{-12}.$$  

Calculate the residual oxygen in the melt.

Given:  
(a) Activity coefficient of oxygen in binary Fe-O alloy is unity.  
(b) Activity coefficient of aluminium in binary Fe-Al alloy is unity.  
(c) $e_{\text{Al}}^{\text{A1}} = -3.15$.  
(d) Atomic weights of Al and O are 27 and 16 respectively.

7.18 An iron-chromium alloy is brought to equilibrium with a $\text{H}_2-\text{H}_2\text{O}$ mixture in which $P_{\text{H}_2\text{O}}/P_{\text{H}_2} = 0.00353$, in a pure alumina crucible at 1700°C (1973 K). The equilibrium is represented by
The alloy at equilibrium contains Cr: 1.90%, Al: 0.031%, and O: 0.0032% by weight. The values of various interaction parameters are

\[ e^0 = 0, \quad e^{Cr} = -0.058, \quad \text{and} \quad e^{Al} = -3.15. \]

Calculate the free energy change of the above reaction at 1700°C (1973 K).

7.19 During carbon dioxide arc welding, carbon and oxygen from the CO\(_2\) enter into solution in iron at 1600°C (1873 K) according to

\[ (CO_2) = [C]_{Fe, wt\%} + 2[O]_{Fe, wt\%}; \]

\[ \Delta G^0 = 43,855 - 11.4T \text{ cal (183,489 - 47.70 T J).} \]

The final oxygen content of the weld is represented by

\[ \log[\% O] = \frac{-6320}{T} + 2.734. \]

Calculate the equilibrium carbon content of the weld if the partial pressure of CO\(_2\) is 1 atm (101325 N/m\(^2\)). Assume the following interaction parameter values:

\[ e^0 = -0.13, \quad e^C = -0.1, \quad e^O = -0.2, \quad \text{and} \quad e^C = 0.22. \]

7.20 Calculate the nitrogen content of liquid iron at the end of a converter blow for high carbon steel containing 1 wt% C and 0.5 wt% P. The temperature at the end of the heat is 1600°C (1873 K), and the pressure of nitrogen is...
Given: \( \frac{1}{2}(N_2) = [N]_{Fe, wt\%} \); \( \Delta G^0 = 860 + 5.71T \text{ cal} \ (3598 + 23.89T \text{ J}) \).

\[ e_N^N = 0, \quad e_N^C = 1.3 \times 10^{-2}, \quad \text{and} \quad e_N^P = 5.1 \times 10^{-2}. \]
CHAPTER 8

THE THERMODYNAMICS OF ELECTROCHEMICAL CELLS

8.1 Introduction

An electrochemical cell converts energy liberated in a chemical or physical change into electrical energy. An electrochemical cell is reversible only if it satisfies the following conditions:

(i) there is a stable equilibrium, when no current passes through the cell, and

(ii) all the processes occurring in the cell are reversed, when the direction of infinitesimal current passing through it is reversed.

Electrochemical cells are of two types: galvanic cells, and concentration cells. In galvanic cells, the electrodes are made of different metals, while in concentration cells, they are of the same metal. A typical example of a galvanic cell is a Daniell cell, which consists of a copper electrode (positive) dipping into an aqueous copper sulphate solution, and a zinc electrode (negative) dipping into a zinc sulphate solution. The solutions are in electrical contact. When the copper and zinc electrodes are connected externally by a metallic conductor, a current flows due to the energy released by the following reaction:

\[
Zn + CuSO_4 = Cu + ZnSO_4
\]

A typical example of a concentration cell is one containing two solutions of copper sulphate of different concentrations (i.e. of different \(Cu^{2+}\) activities), separated by a porous pot. Copper electrodes dip into each copper sulphate solution. The tendency of copper to ionise and pass into solution is greater the lower its activity in the solution. Thus, when the cell reaction is allowed to proceed in the spontaneous direction, it consists of dissolution of copper from the electrode in the weaker solution and the deposition of copper on the electrode in the stronger solution. In other words, the overall reaction is equivalent to the transfer of copper sulphate from the stronger to the weaker solution.
8.1.1 Convention

Usually, the Daniell cell is represented as follows:

\[ \text{Zn} | \text{ZnSO}_4(aq) | \text{CuSO}_4(aq) | \text{Cu} \]

in which the vertical lines represent the phase boundary. The convention used in representing the cell in the above manner is that the negative electrode is written on the left side, while the positive electrode is written on the right side; and the e.m.f. is assigned a positive value. Thus, the spontaneous reaction associated with positive e.m.f. involves the passage of positive ions through the cell from left to right.

According to this convention, the concentration cell discussed earlier may be represented as

\[ \text{Cu} | \text{CuSO}_4(aq, \text{conc.} C_1) | \text{CuSO}_4(aq, \text{conc.} C_2) | \text{Cu} \]

if the concentration \( C_1 \) is less than \( C_2 \), so that the copper electrode on the left is negative.

8.2 Determination of Thermodynamic Quantities using Reversible Electrochemical Cells

For an electrochemical cell operating under reversible conditions, the free energy change of the cell reaction is given by

\[ \Delta G = -zFE \quad (8.1) \]

where \( z \) is the number of electrons transferred, \( F \) is one Faraday (96487 coulombs/g-equivalent) and \( E \) is the reversible e.m.f. of the cell. If the value of \( \Delta G \) is expressed in calories, and \( E \) is measured in volts, the Faraday must be converted from coulombs/g-equivalent to cal/V/g-equivalent. In SI units, \( \Delta G \) is expressed in joules, and therefore Faraday must be
converted from coulombs/g-equivalent to J/V/g-equivalent. The value of $F$ is
23,061 cal/V/g-equivalent (96,487 J/V/g-equivalent).

Changes in other thermodynamic properties of the cell reaction can be deter­
mined with the help of the reversible e.m.f. of an electrochemical cell. Since

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

it follows that

$$\Delta S = zF \left( \frac{\partial E}{\partial T} \right)_p, \quad (8.2)$$

where the term $\left( \frac{\partial E}{\partial T} \right)_p$ is called the temperature coefficient of the e.m.f.

From the Gibbs-Helmholtz equation, it follows that

$$\Delta H = -zF \left[ E - T \left( \frac{\partial E}{\partial T} \right)_p \right]. \quad (8.3)$$

Thus, the entropy and enthalpy change of the cell reaction may be calculated
from knowledge of the reversible e.m.f. and its temperature coefficient. The
value of $\left( \frac{\partial E}{\partial T} \right)_p$ at the desired temperature may be found by plotting the
values of $E$ against $T$. The tangent to the curve at the desired temperature
gives the value of $\left( \frac{\partial E}{\partial T} \right)_p$.

The heat capacity change of the cell reaction at constant pressure, $\Delta C_P$, can
be obtained by differentiating Eq.(8.3) w.r.t. temperature. Since

$$\left( \frac{\partial \Delta H}{\partial T} \right)_P = \Delta C_P,$$

it follows that

$$\Delta C_P = zFT \left( \frac{\partial^2 E}{\partial T^2} \right)_p, \quad (8.4)$$

The activity of a component $A$ in an alloy can be determined by measuring the
 reversible e.m.f. of the following cell:
Pure metal A | electrolyte containing ions of metal A in an
metal A (valency $z_A$) | alloy.

Since one g-atom of metal A is transferred from left to right, the cell reaction may be represented as

$$A\text{(pure metal)} = A\text{(in alloy)}.$$ 

The free energy change of the above reaction is given by

$$\Delta G = \Delta G^0 + RT \ln \frac{a_A}{1} = \Delta G^0 + RT \ln a_A,$$

where $a_A$ denotes the activity of A in the alloy. In the specific case when both electrodes are of pure A (standard state), there will be no e.m.f. developed (i.e. $E^0 = 0$), and hence the standard free energy change, $\Delta G^0$, will be zero. Hence, it follows that

$$\Delta G = RT \ln a_A.$$  (8.7)

Combining Eq.(8.7) with Eq.(8.1),

$$RT \ln a_A = -z_AFE,$$

or

$$\log a_A = - \frac{z_AFE}{4.575T}.$$  (8.8)

It must be remembered that F in the above equation is expressed in cal/V/g-equivalent. The partial molar quantities can also be calculated from knowledge of the e.m.f. Thus,

$$\bar{G}_A^M = RT \ln a_A = -z_AFE,$$  (8.9)

$$\bar{S}_A^M = z_AF \left(\frac{\partial E}{\partial T}\right)_P,$$  (8.10)

and

$$\bar{H}_A^M = -z_AF \left[E - T \left(\frac{\partial E}{\partial T}\right)_P\right].$$  (8.11)
Similarly, the excess thermodynamic quantities may also be related to the reversible e.m.f. Thus

\[ \overline{G}^{\text{xs}}_A = RT \ln \gamma_A = - [z_A F E + RT \ln x_A], \quad (8.12) \]

and

\[ \overline{S}^{\text{xs}}_A = [z_A F \left( \frac{\partial E}{\partial T} \right)_P] + R \ln x_A. \quad (8.13) \]

The following examples illustrate how the value of the reversible e.m.f. can be used in calculating the various thermodynamic quantities.

**Example 8.A**

The e.m.fs. of the reversible cells

\[ \text{Pb}(s)|\text{PbCl}_2(s),\text{KCl},\text{AgCl}(s)|\text{Ag}(s) \]

and

\[ \text{Pb}(s)|\text{PbI}_2(s),\text{KI},\text{AgI}(s)|\text{Ag}(s) \]

at 25°C (298 K) are 0.4902 and 0.2111 V respectively. The temperature coefficients of e.m.f. of the above cells are -186 x 10^{-6} and -127 x 10^{-6} V/deg (V/K) respectively. Calculate the values of \( \Delta G^0 \) and \( \Delta H^0 \) for the reaction

\[ <\text{PbI}_2> + 2<\text{AgCl}> = <\text{PbCl}_2> + 2<\text{AgI}> \]

at 25°C (298 K).

If the standard enthalpies of \( \text{PbI}_2 \), \( \text{AgCl} \) and \( \text{PbCl}_2 \) at 25°C (298 K) are -41.9 kcal/mole (-175.3 kJ/mol), -30.3 kcal/mole (-126.8 kJ/mol) and -85.8 kcal/mole (-359.0 kJ/mol) respectively, calculate the standard enthalpy of \( \text{AgI} \) at 25°C (298 K).

**Solution:** The reactants and products of both the cells are present in their
respective standard states, and hence the free energy change, is the standard free energy change, $\Delta G^0$, and the observed e.m.f. is the e.m.f. of the cell under standard condition, i.e.

$$\Delta G^0 = -zF E^0.$$  \hspace{1cm} (8.A.1)

Now, for the cell

$$\text{Pb(s)} \mid \text{PbCl}_2(s), \text{KCl}, \text{AgCl(s)} \mid \text{Ag}$$

lead is the negative electrode, and silver is the positive electrode. The spontaneous reaction involves dissolution of the lead electrode and simultaneous conversion of silver ions to metallic silver. Thus, the net spontaneous reaction of the cell may be represented as

$$<\text{Pb}> + 2<\text{AgCl}> = <\text{PbCl}_2> + 2<\text{Ag}>.$$  \hspace{1cm} (8.A.2)

In other words, the passage of 2 Faradays of electricity through the cell causes the dissolution of one g-atom of lead, and the deposition of 2 g-atoms of silver.

Similarly, for the cell

$$\text{Pb(s)} \mid \text{PbI}_2(s), \text{KI}, \text{AgI(s)} \mid \text{Ag(s)}$$

the cell reaction may be represented as

$$<\text{Pb}> + 2<\text{AgI}> = <\text{PbI}_2> + 2<\text{Ag}>.$$  \hspace{1cm} (8.A.3)

Applying Eq.(8.A.1),

$$\Delta G^0_{298,(8.A.2)} = -2 \times 23061 \times 0.4902$$

$$= -22,610 \text{ cal.}$$

Similarly,

$$\Delta G^0_{298,(8.A.3)} = -2 \times 23061 \times 0.2111$$

$$= -9,736 \text{ cal.}$$
Subtracting reaction (8.A.3) from reaction (8.A.2),

\[ \text{PbI}_2 + 2\text{AgCl} = \text{PbCl}_2 + 2\text{AgI}, \quad (8.A.4) \]

and the free energy change is given by

\[ \Delta G°_{298,(8.A.4)} = -22,610 - (-9,736) \]
\[ = -12,874 \text{ cal} \]
\[ = -12.87 \text{ kcal}. \]

Thus, the standard free energy change of the required reaction at 25°C is -12.87 kcal.

From Eq.(8.3),

\[ \Delta H° = -zF [E° - T(\frac{\partial E°}{\partial T})]. \]

Thus,

\[ \Delta H°_{298,(8.A.2)} = -2 \times 23061(0.4902 + 298 \times 186 \times 10^{-6}) \]
\[ = -25,160 \text{ cal}. \]

Similarly,

\[ \Delta H°_{298,(8.A.3)} = -2 \times 23061(0.2111 + 298 \times 127 \times 10^{-6}) \]
\[ = -11,480 \text{ cal}. \]

The enthalpy change of reaction (8.A.4) is given by

\[ \Delta H°_{298,(8.A.4)} = \Delta H°_{298,(8.A.2)} - \Delta H°_{298,(8.A.3)} \]
\[ = -25,160 - (-11,480) \]
\[ = -13,680 \text{ cal} \]
\[ = -13.68 \text{ kcal}. \]

Thus, the standard enthalpy change of the required reaction at 25°C is -13.68 kcal.
The enthalpy change of reaction (8.A.4) at 25°C can also be represented as

$$\Delta H^{\circ}_{298,(8.A.4)} = \Delta H^{\circ}_{298,PbCl_2} + 2\Delta H^{\circ}_{298,AgI} - \Delta H^{\circ}_{298,PbI_2} - 2\Delta H^{\circ}_{298,AgCl}.$$ 

Putting in the appropriate values,

$$-13.68 = -85.8 + (2 \times \Delta H^{\circ}_{AgI}) + 41.9 + (2 \times 30.3),$$

or

$$2\Delta H^{\circ}_{298,AgI} = 85.8 - 41.9 - 60.6 - 13.68,$$

or

$$\Delta H^{\circ}_{298,AgI} = -15.19 \text{ kcal/mole}.$$ 

Thus, the standard enthalpy of AgI at 25°C is -15.19 kcal/mole.

Example 8.B

The e.m.f. of the reversible cell

$$\text{Zn}(1, \text{pure})|\text{KCl-NaCl-LiCl-ZnCl}_2|\text{Zn(in Cd-10.3 atom% Zn alloy)}$$

has been found to be 85.80 x 10^{-3} V at 800°C (1073 K). Calculate (i) the activity of zinc in the alloy; (ii) the values of the partial molar free energy, entropy and enthalpy of mixing of zinc in the alloy, assuming that the temperature coefficient of e.m.f. is 0.111 x 10^{-3} V/deg (V/K).

Solution: The cell reaction may be represented as

$$\text{Zn}(1, \text{pure}) = \text{Zn(in Cd-10.3 atom% Zn alloy)}.$$ 

Applying Eq.(8.8),

$$\log a_{Zn} = \frac{-2 \times 23061 \times 85.80 \times 10^{-3}}{4.575 \times 1073} = -0.8061.$$
Taking antilogs,
\[ a_{Zn} = 0.1562. \]

The partial molar free energy of mixing of zinc in the Cd-Zn alloy can be calculated from Eq. (8.9) and is given by
\[ \overline{G}_{Zn}^M = RT \ln a_{Zn} \]
\[ = 4.575 \times 10^73 \times \log 0.1562 \]
\[ = -3957 \text{ cal/mole}. \]

The partial molar entropy of mixing of zinc in the Cd-Zn alloy can be calculated from Eq. (8.10) and is given by
\[ \overline{S}_{Zn}^M = \frac{\partial F}{\partial T} \]
\[ = 2 \times 23061 \times 0.111 \times 10^{-3} \]
\[ = 5.119 \text{ cal/deg/mole}. \]

Since
\[ \overline{H}_{Zn}^M = \overline{G}_{Zn}^M + T \overline{S}_{Zn}^M \]
therefore
\[ \overline{H}_{Zn}^M = -3957 + 1073 \times 5.119 \]
\[ = 1,535 \text{ cal/mole}. \]

Example 8. C

The reversible e.m.f. between pure magnesium and magnesium-zinc alloy containing 63.5 atom% magnesium in a fused KCl-LiCl-MgCl₂ electrolyte may be represented by
E = 16.08 \times 10^{-3} + 1.02 \times 10^{-5} T,

where E and T are in V and K respectively. Calculate the activity coefficient and excess partial molar free energy of mixing of magnesium in the above alloy at 727°C (1000 K).

Solution: The cell reaction may be represented as

\[ \text{Mg(pure)} \rightarrow \text{Mg(in alloy)}. \]

At 727°C (1000 K), the value of E is given by

\[
E = 16.08 \times 10^{-3} + 1.02 \times 10^{-5} \times 10^3 \\
= 26.28 \times 10^{-3} \text{ V}.
\]

The activity of magnesium in the alloy can be obtained from Eq.(8.8). Thus,

\[
\log a_{\text{Mg}} = - \frac{2 \times 23061 \times 26.28 \times 10^{-3}}{4.575 \times 1000}.
\]

Taking antilogs, \( a_{\text{Mg}} = 0.5433 \).

The activity coefficient of magnesium is given by

\[
\gamma_{\text{Mg}} = \frac{a_{\text{Mg}}}{\chi_{\text{Mg}}} \\
= \frac{0.5433}{0.6350} \\
= 0.8555.
\]
The excess partial molar free energy of mixing of magnesium can be calculated from its activity coefficient value with the help of the following equation:

\[ \Delta G_{\text{Mg}}^{\text{xs}} = RT \ln \gamma_{\text{Mg}} \]

Thus, at 727°C,

\[ \Delta G_{\text{Mg}}^{\text{xs}} = 4.575 \times 1000 \times \log 0.8555 \]
\[ = -310 \text{ cal/mole.} \]

Alternatively, the value of \( \Delta G_{\text{Mg}}^{\text{xs}} \) may also be obtained from Eq.(8.12), and thus

\[ \Delta G_{\text{Mg}}^{\text{xs}} = [Z_{\text{Mg}}FE + RT \ln x_{\text{Mg}}] \]
\[ = - [2 \times 23061 \times 26.28 \times 10^{-3} + 4.575 \times 1000 \times \log 0.635] \]
\[ = -310 \text{ cal/mole.} \]

8.3 Electrochemical Cells Based on Solid Electrolytes

It was proposed by Wagner\(^1\) in 1943 that certain oxide solid solutions such as \( \text{ZrO}_2-\text{CaO} \) contain vacant oxygen ion sites and thus can be used as solid electrolytes for the transport of oxygen ions. Kingery et al.\(^2\) calculated the oxygen ion mobilities for this electrolyte and concluded that the conductivity is wholly ionic and the transference number is near unity for the oxygen ion. Although the electrolyte exhibits virtually exclusive ionic conduction at high temperatures it has been reported\(^3\) that the electronic conduction is a significant factor below \( P_{\text{O}_2} = 10^{-18} \text{ atm} \times 10^{-18} \text{ atm}^{-1} \text{N/m}^2 \) at 1000°C (1273 K). Other solid electrolytes based on thorium with lime, yttria, or lanthana additions have been found to be ionic conductors at oxygen pressures below those applicable to zirconia base electrolytes. Such electrolytes are important in the field of metallurgy and have been used in determining the thermodynamic properties of metallic oxides, oxy-compounds, partial...
pressures of oxygen in vacuum and other atmospheres, properties of oxygen dissolved in metals and alloys, activity determination, etc.\( (4, 5) \).

The free energy of formation of an oxide can be determined from knowledge of the e.m.f. developed by a cell of the type

\[
A, A_0 | \text{solid electrolyte} | B, B_0
\]

such that the oxygen ion transfers from the right-hand side to the left-hand side (A0 and B0 are oxides of metal A and B respectively). At equilibrium, the e.m.f. developed may be related to

\[
E = \frac{\mu^\circ_{O_2} - \mu_{O_2}^\circ}{zF}, 
\]

(8.14)

where \( \mu^\circ_{O_2} \) and \( \mu_{O_2}^\circ \) are the chemical potentials (partial molar free energies) of oxygen at the right-hand and left-hand sides respectively, \( z \) is the number of electrons involved in the reaction, and \( F \) is the Faraday constant. If the free energy of formation of one of the oxides is known, that of the other may be calculated as illustrated in the following example.

**Example 8.D**

The e.m.f. of the cell

\[
\text{Mo}_2 \text{O}_3 | (\text{ZrO}_2)^{(\text{CaO})_{0.85}} | \text{Ni}_2 \text{O}_3
\]

at 900\(^\circ\)C (1173 K) has been found to be 284.7 mV. Calculate the standard free energy of formation of \( \text{Mo}_2 \text{O}_3 \) at 900\(^\circ\)C (1173 K) if the standard free energy of formation of \( \text{Ni}_2 \text{O}_3 \) is given by

\[
\Delta G^\circ_{\text{Ni}_2 \text{O}_3} = -56,000 + 20.3T \text{cal/mole} (-234,300 + 84.94T \text{J/mol}).
\]
Solution: Since oxygen ions transfer from the \((\text{Ni}, \text{NiO})\) electrode to the \((\text{Mo}, \text{MoO}_2)\) electrode, the overall reaction can be represented as

\[
2\text{NiO} + \text{Mo} = \text{MoO}_2 + 2\text{Ni}. \quad (8.D.1)
\]

The number of electrons involved in the above reaction is four. At equilibrium, the free energy change is given by

\[
\Delta G^0(8.D.1) = -2F\epsilon.
\]

Putting the appropriate values in the above equation,

\[
\Delta G^0_{1173,(8.D.1)} = -2 \times 2306 \times 284.7 \times 10^{-3} \text{ cal.}
\]

\[
= -26,260 \text{ cal.}
\]

But

\[
\Delta G^0_{1173,(8.D.1)} = \Delta G^0_{1173, \text{MoO}_2} - 2\Delta G^0_{1173, \text{NiO}}
\]

or

\[
\Delta G^0_{1173, \text{MoO}_2} = \Delta G^0_{1173,(8.D.1)} + 2\Delta G^0_{1173, \text{NiO}}.
\]

Putting in the values of \(\Delta G^0(8.D.1)\) and \(\Delta G^0_{\text{NiO}}\),

\[
\Delta G^0_{1173, \text{MoO}_2} = -26,260 + 2(-56,000 + 20.3 \times 1173)
\]

\[
= -90,640 \text{ cal/mole}
\]

\[
= -90.64 \text{ kcal/mole.}
\]

Thus, the free energy of formation of \(\text{MoO}_2\) is \(-90.64 \text{ kcal/mole}\) at 900°C.

An interesting application of a solid electrolyte is the direct determination of oxygen in molten metals. If a cell of the type

\[
\text{Oxygen in liquid metal} \mid \text{solid electrolyte} \mid A, A^0
\]

is set up, oxygen ions will flow in the direction of the fall in the pressure.
Assuming that the chemical potential of oxygen in the liquid metal is less than in pure A0, the chemical reaction for the above cell may be represented as

\[
\langle A0 \rangle = \langle A \rangle + [O]^{-}_{\text{metal, liquid}}. \tag{8.15}
\]

The free energy change of the above reaction, \( \Delta G \), may be related to the e.m.f. \( E \),

\[
\Delta G = \Delta G^0 + RT \ln a_0 = -zFE, \tag{8.16}
\]

if pure solid A and A0 are taken to be in their standard state. In Eq. (8.16), \( \Delta G^0 \) is the standard free energy change of reaction (8.15), \( a_0 \) is the activity of oxygen in the liquid metal w.r.t. a reference state of pure oxygen gas at 1 atm (101325 N/m\(^2\)) pressure, and \( z \) is the number of electrons involved in the reaction. However, \( E \) will be negative for the cell as written, if the chemical potential of oxygen in the liquid metal is higher than in pure A0, whereupon the spontaneous reaction would occur in the opposite direction to that written above. The following example illustrates the use of a solid electrolyte for determination of the activity of oxygen in a molten metal.

**Example 8.E**

The reaction for the electrochemical cell,

\[
\text{Oxygen dissolved in liquid Cu}_{0.85}[\text{ZrO}_2]_{0.15}(\text{CaO})_n - |\text{Ni}, \text{NiO}
\]

may be represented as

\[
\text{NiO} = \text{Ni} + [O]_{\text{Cu, liquid}}. 
\]

The e.m.f. is 138 mV at 1200°C (1473 K). The standard free energy of formation of NiO at 1200°C (1473 K) is -23.76 kcal/mole (-99.41 kJ/mol). Calculate the activity of oxygen in liquid copper at 1200°C (1473 K) w.r.t. a reference state of oxygen as pure gas at 1 atm (101325 N/m\(^2\)).
Solution: \( \text{NiO} \rightarrow \text{Ni} + [0]_{\text{Cu \text{, liquid}}} \) \hspace{1cm} (8.E.1)

Assuming that Ni and NiO are present in their respective standard states, the free energy change of (8.E.1) at temperature \( T \) may be represented as

\[
\Delta G_T(8.E.1) = \Delta G^0_T(8.E.1) + RT \ln a_0 ,
\]

(8.E.2)

where \( \Delta G^0_T(8.E.1) \) is the standard free energy change of reaction (8.E.1) (i.e. negative of the standard free energy of formation of NiO) at temperature \( T \), and \( a_0 \) is the activity of oxygen in liquid copper w.r.t. a reference state of oxygen as pure gas at 1 atm pressure. However, the free energy change \( \Delta G_T(8.E.1) \) is related to the e.m.f., \( E \), according to

\[
\Delta G_T(8.E.1) = -zFE ,
\]

(8.E.3)

where \( z \) is equal to 2.

From Eqs.(8.E.2) and (8.E.3), it follows that

\[
\Delta G^0_T(8.E.1) + RT \ln a_0 = -zFE ,
\]

or

\[
-\Delta G^0_T, \text{NiO} + RT \ln a_0 = -zFE .
\]

Substituting the values for \( T = 1200^\circ C \) \((1473 \text{ K})\) in the above,

\[
-(-23760) + 4.575 \times 1473 \times \log a_0 = -2 \times 23061 \times 138 \times 10^{-3} .
\]

On simplification,

\[
a_0 = 3.388 \times 10^{-5} .
\]

Thus, the activity of oxygen in liquid copper at 1200\(^\circ\)C is \( 3.388 \times 10^{-5} \) w.r.t. a reference state of oxygen as pure gas at 1 atm pressure.
REFERENCES:


Exercises

8.1 The reaction of a cadmium-calomel cell is represented as

\[ \text{Cd} + \text{Hg}_2\text{Cl}_2 = \text{Cd}^{++} + 2\text{Cl}^- + 2\text{Hg}, \]

where all the components are present in their standard states. The reversible e.m.f. (in V) of the above cell varies with temperature (in K) according to the following relation:

\[ E^0 = 0.67 - 1.02 \times 10^{-4} (T - 298) - 2.4 \times 10^{-6} (T - 298)^2. \]

Calculate the values of \( \Delta G^0 \), \( \Delta S^0 \) and \( \Delta H^0 \) for the above reaction at 40°C (313 K).

8.2 The e.m.f. of a cell having the following reaction:

\[ \text{Zn} + 2\text{AgCl} = \text{ZnCl}_2 + 2\text{Ag} \]

at atmospheric pressure is 1.005 V at 25°C (298 K) and 1.015 V at 0°C (273 K). Assuming the temperature coefficient of e.m.f. to be constant, calculate the change in enthalpy for the reaction at 25°C (298 K).
8.3 For the reaction
\[ 2Ca + ThO_2 = 2CaO + Th \]
the following e.m.f. values are obtained in a reversible electrochemical cell at 1 atm (101325 N/m²) pressure:

<table>
<thead>
<tr>
<th>Temp., °C</th>
<th>1002</th>
<th>1102</th>
<th>1202</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp., K</td>
<td>1275</td>
<td>1375</td>
<td>1475</td>
</tr>
<tr>
<td>E°, V</td>
<td>0.0738</td>
<td>0.0542</td>
<td>0.0345</td>
</tr>
</tbody>
</table>

Calculate the values of \( \Delta G^0 \), \( \Delta S^0 \) and \( \Delta H^0 \) for the cell reaction at 1102°C (1375 K). Also calculate the maximum temperature at which calcium will reduce thorium dioxide at 1 atm (101325 N/m²) pressure.

8.4 The following cell is set up for determination of the activity of zinc in a Zn-Sn-Cd-Pb alloy:

\[ \text{Zn(pure)}|\text{LiCl-KCl-ZnCl}_2|\text{Zn(in the alloy)}. \]

The reversible e.m.fs. are as follows:

<table>
<thead>
<tr>
<th>Temp., °C</th>
<th>441</th>
<th>484</th>
<th>532</th>
<th>569</th>
<th>604</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp., K</td>
<td>714</td>
<td>757</td>
<td>805</td>
<td>842</td>
<td>877</td>
</tr>
<tr>
<td>E,mV</td>
<td>12.76</td>
<td>16.30</td>
<td>20.26</td>
<td>23.32</td>
<td>26.20</td>
</tr>
</tbody>
</table>

Calculate the activity of zinc in the above alloy at these temperatures.

8.5 An electrolytic cell has pure liquid cadmium as one electrode and a liquid cadmium-lead alloy as the other, and the electrolyte consists of a fused salt mixture containing cadmium ions (Cd²⁺). When the atom fraction of cadmium in the alloy electrode is 0.4, the reversible e.m.f. of the cell is found to be 14.35 x 10⁻³ V at 500°C (773 K).
Calculate the activity, activity coefficient, and the partial molar free energy of cadmium in the alloy electrode w.r.t. pure cadmium as standard state.

8.6 The reversible e.m.f. of the following electrochemical cell:

\[ \text{Cd(pure)} \mid \text{LiCl-KCl-CdCl}_2 \mid \text{Cd(in Cd-Sb alloy)} \]

has been found to be 28.48 mV at 500°C (773 K).

Calculate the activity of cadmium relative to pure cadmium as standard state and the partial molar free energy, entropy, and enthalpy of mixing of cadmium in a Cd-Sb alloy containing 60.2 atom% Cd. Assume the temperature coefficient of e.m.f. at 500°C (773 K) to be 33.63 μV/deg (μV/K).

8.7 The reversible e.m.f. of the cell

\[ \text{U(pure,solid)} \mid \text{KCl-LiCl-UCl}_3 \text{eutectic} \mid \text{U(in Cd-U alloy)} \]

at 398°C (671 K) is 49.76 mV. The temperature coefficient of e.m.f. is -41.0 μV/deg (μV/K). Calculate the excess partial molar free energy, entropy, and enthalpy of uranium in a Cd-U alloy containing 1.6 x 10⁻³ mole fraction of U at 398°C (671 K).

8.8 The e.m.f. of the cells

\[ \text{Mo}_x\text{MoO}_2|\text{ZrO}_2|\text{(CaO)}_{0.15}|\text{Fe}_x\text{Fe}_0,_{0.85} \]

and

\[ \text{Mo}_x\text{MoO}_2|\text{ZrO}_2|\text{(CaO)}_{0.15}|\text{Ni}_x\text{NiO}_{0.85} \]

at 800°C (1073 K) is 17.8 and 284.0 mV respectively. Calculate the standard free energy change for the reaction

\[ \text{Fe}_0 + \text{Ni} = \text{Ni}_0 + \text{Fe}. \]
A chemical or metallurgical reaction is thermodynamically possible only when there is a decrease in free energy. All the equations which we use in the thermodynamic treatment of a metallurgical reaction refer to equilibrium conditions. A reaction may be thermodynamically possible, but in practice the reaction may not proceed to completion in a measurable period of time. In other words, the thermodynamic treatment does not provide information on the rate of reaction. For this reason, another theoretical approach - 'kinetics' - has been used to study the rate of reaction.

The rate or velocity of a reaction may be defined as the rate of decrease of the concentration of a reactant or as the rate of increase of a product of the reaction. If a reactant of initial concentration $C_0$ has a concentration $C$ at any time $t$, the rate is expressed as $(-dC/dt)$. If the concentration of the product is $x$ at any time $t$, the rate is expressed as $(dx/dt)$.

### 9.2 Effect of Concentration on the Reaction Rate

The rate of a chemical reaction is proportional to the concentration of the reacting substances. The sum of the powers to which the concentration of the reacting atoms or molecules must be raised to determine the rate of reaction, is known as the 'order of reaction'. The order of reaction does not bear any relation to the molecularity of the reaction. The expressions for the rates of reactions of different orders can be evaluated as follows.
9.2.1 First-Order Reaction

In a first-order reaction, for example,

\[ A = X + Y, \]

the rate of reaction is given by

\[ -\frac{dC}{dt} = kC, \quad (9.1) \]

where \( C \) is the concentration of \( A \) at any time \( t \), and \( k \) is a constant known as the velocity constant, rate constant, or specific reaction rate. On integrating Eq.(9.1) within the limits \( C = C_0 \) at \( t = 0 \), and \( C = C \) at \( t = t \),

\[ k = \frac{2.303}{t} \log \frac{C_0}{C_0 - x}, \quad (9.2) \]

where \( x \) is the amount of \( A \) reacted in time \( t \). It is evident from Eq.(9.2) that for a first-order reaction a plot of \( \log \frac{C_0}{C_0 - x} \) (along y-axis) against \( t \) (along x-axis) will result in a straight line. The slope of the line will be equal to \( \frac{k}{2.303} \).

The time required for 50 percent completion of a first-order reaction, i.e. half-life period \( t_{0.5} \), can be calculated from Eq.(9.2). Thus,

\[ t_{0.5} = \frac{2.303 \log 2}{k}. \quad (9.3) \]

9.2.2 Second-Order Reaction

If the rate of reaction

\[ A + B = X + Y \]

depends upon the concentration of \( A \) and \( B \), the reaction is second-order. If \( C_a \) and \( C_b \) are the concentrations of \( A \) and \( B \) respectively at time \( t \), the reaction rate can be expressed as
\[- \frac{dC_a}{dt} = - \frac{dC_b}{dt} = k C_a C_b. \quad (9.4)\]

Alternatively, if the amount of each (A and B) reacted after time \(t\) is \(x\), Eq.\((9.4)\) can also be written as

\[- \frac{d(C_A - x)}{dt} = - \frac{d(C_B - x)}{dt} = k(C_A - x)(C_B - x), \]

or

\[\frac{dx}{dt} = k(C_A - x)(C_B - x), \quad (9.5)\]

where \(C_A\) and \(C_B\) are the initial concentrations of A and B respectively. On integrating Eq.\((9.5)\) within the limits \(x = 0\) at \(t = 0\), and \(x = x\) at \(t = t\),

\[k = \frac{2.303 \cdot C_B(C_A - x)}{t(C_A - C_B)} \log \frac{C_B(C_A - x)}{C_A(C_B - x)}. \quad (9.6)\]

If \(C_A = C_B = C\), the integration of Eq.\((9.5)\) gives

\[k = \frac{1}{t} \cdot \frac{x}{C(C - x)}. \quad (9.7)\]

The half-life period, \(t_{0.5}\), for a second-order reaction, in which both the reactants have the same initial concentration, can be obtained from Eq.\((9.7)\). Thus,

\[t_{0.5} = \frac{1}{\kappa C}. \quad (9.8)\]

The rate constants of higher order reactions can be calculated in a similar manner.

---

Example 9.A

The radioactive decay of uranium 238 is first-order and the half-life is \(4.51 \times 10^9\) years \((1.42 \times 10^{17}\) s\). Calculate the specific reaction rate. In how
many days will 75 percent of a given amount of uranium disappear?

**Solution:** Using Eq.(9.3), and putting in the appropriate values,

\[ 4.51 \times 10^9 = \frac{2.303 \log 2}{k} \]

or \[ k = 1.532 \times 10^{-10} \text{ year}^{-1}. \]

Thus, the specific rate of radioactive decay of uranium 238 is \( 1.532 \times 10^{-10} \text{ year}^{-1} \).

The time for 75 percent completion, \( t_{0.75} \), can be calculated from Eq.(9.2), and hence

\[ t_{0.75} = \frac{2.303}{1.532 \times 10^{-10}} \log \frac{100}{100-75} \text{ years} \]

\[ = \frac{2.303 \times 365}{1.532 \times 10^{-10}} \log 4 \text{ days} \]

\[ = 330.4 \times 10^{10} \text{ days.} \]

Thus, the time required for 75 percent of a given amount of uranium 238 to disappear, is \( 330.4 \times 10^{10} \) days.

**Example 9.B**

A second-order reaction has an initial concentration of the reactants of 0.4 moles/litre \((0.4 \text{ mol/dm}^3)\). The reaction is 30 percent complete in 80 min \((4800 \text{ s})\). Calculate the rate constant and the time it would take for the reaction to be 80 percent complete.

**Solution:** Using Eq.(9.7) and inserting the appropriate values,
Thus, the rate constant of the reaction is \(2.232 \times 10^{-4}\) litre/mole/sec.

The time required for 80 percent completion, \(t_{0.8}\), of reaction can also be calculated from Eq.(9.7).

\[
2.232 \times 10^{-4} = \frac{1}{t_{0.8}} \cdot \frac{0.80 \times 0.4}{0.4(0.4 - 0.80 \times 0.4)}
\]

or

\[
t_{0.8} = \frac{0.80 \times 0.4}{0.4 \times (0.4 - 0.32) \times 2.232 \times 10^{-4}} \text{ sec}
\]

\[
= 4.48 \times 10^4 \text{ sec.}
\]

Thus, 80 percent of the reaction will be completed in \(4.48 \times 10^4\) sec.

9.3 Effect of Temperature on Reaction Rate

The dependence of the rate constant, \(k\), on temperature, \(T\), is given by the following expression, which is commonly known as the Arrhenius equation:

\[
k = A e^{-E/RT},
\]

(9.9)

where \(A\) is a constant known as the 'frequency factor', and \(E\) is the activation energy of the reaction. Taking logarithms of both sides of Eq.(9.9),

\[
\log k = \log A - \frac{0.4342 E}{R} \left(\frac{1}{T}\right).
\]

(9.10)
The Arrhenius law can be tested by plotting \( \log k \) against the reciprocal of the absolute temperature. According to Eq.(9.10), a straight line having a slope equal to \( \left( -\frac{0.4342E}{R} \right) \) should result, and hence the activation energy can be calculated. The intercept at \( 1/T = 0 \) gives the value of \( \log A \), from which the frequency factor can be calculated. The following example illustrates the use of Eq.(9.10) for calculating the activation energy of a reaction.

**Example 9.C**

The rate constants \((k)\) for the leaching of galena in an aqueous medium containing ammonium acetate under oxygen pressure at different temperatures are listed below:

<table>
<thead>
<tr>
<th>log ( k )</th>
<th>-10.9</th>
<th>-11.1</th>
<th>-11.2</th>
<th>-11.5</th>
<th>-12.1</th>
<th>-12.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{1}{T} \times 10^3 )</td>
<td>2.30</td>
<td>2.35</td>
<td>2.38</td>
<td>2.45</td>
<td>2.61</td>
<td>2.75</td>
</tr>
</tbody>
</table>

where \( k \) and \( T \) are expressed in mole²/cm⁴/min and K respectively.

Calculate the activation energy of the leaching process.

**Solution:** In order to obtain the value of the activation energy, \( \log k \) was plotted against \((1/T)\), which resulted in a straight line, as shown in Fig.9.1. The slope of the line, which is equal to \( \left( -\frac{0.4342E}{R} \right) \) is \(-3.82 \times 10^3\).

Thus,

\[
-3.82 \times 10^3 = -\frac{0.4342E}{R}
\]

\[
= -\frac{0.4342E}{1.987}
\]

or

\[
E = \frac{3.82 \times 10^3 \times 1.987}{0.4342}
\]

\[
= 17,480 \text{ cal/mole.}
\]

Thus, the activation energy of the leaching process is \( 17,480 \text{ cal/mole} \).
9.4 Determination of the Order of Reaction

Some of the important methods of determining the order of reaction are as follows:
9.4.1 Integration Method

In this method, the experimental data are put into equations for the different orders of reaction, until an equation is found which satisfies the data. For example, if a reaction

\[ nA \rightarrow \text{Products} \]

is \( n \)-th order and involves substances that initially have a concentration \( C_0 \), the rate is given by

\[ \frac{d(C_0 - x)}{dt} = \frac{dx}{dt} = k(C_0 - x)^n , \]

where \( x \) is the amount of \( A \) that has disappeared in time \( t \). The integrated rate equations for various values of order of reaction are tabulated in Table 9.1.

An easier way consists of presenting the integrated rate equation in such a form that a linear plot can be obtained. For example, in the case of a first-order reaction, a plot of \( \log \frac{C_0}{C_0 - x} \) (along y-axis) against \( t \) (along x-axis) will result in a straight line passing through the origin and having a slope equal to \( k/2.303 \). A deviation from linearity will indicate that the reaction is not first-order. Similar linear plots can be obtained for reactions of other orders.

9.4.2 Half-Life Method

If the reactant concentrations are equal, the half-life period, \( t_{0.5} \), for a reaction of overall order \( n \) is given by

\[ t_{0.5} = \frac{1}{C_0(n-1)} , \quad (9.11) \]

where \( C_0 \) denotes the initial concentration. Taking logarithms of both sides of Eq.(9.11),

\[ \log t_{0.5} = \text{constant} - (n-1)\log C_0, \quad (9.12) \]

If the half-lives of a reaction are known for different initial concentrations,
<table>
<thead>
<tr>
<th>Order</th>
<th>Rate equation</th>
<th>Unit of rate constant, if the units of concentration and time are</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Differential form</td>
<td>Integrated form</td>
</tr>
<tr>
<td>0</td>
<td>( \frac{dx}{dt} = k )</td>
<td>( k = \frac{x}{t} )</td>
</tr>
<tr>
<td>( \frac{1}{2} )</td>
<td>( \frac{dx}{dt} = k(C_0 - x)^{\frac{1}{2}} )</td>
<td>( k = \frac{2 [C_0^{\frac{1}{2}} - (C_0 - x)^{\frac{1}{2}}]}{t} )</td>
</tr>
<tr>
<td>1</td>
<td>( \frac{dx}{dt} = k(C_0 - x) )</td>
<td>( k = \frac{2.303}{t} \log \frac{C_0}{(C_0 - x)} )</td>
</tr>
<tr>
<td>( \frac{3}{2} )</td>
<td>( \frac{dx}{dt} = k(C_0 - x)^{\frac{3}{2}} )</td>
<td>( k = \frac{2 [\frac{1}{t(C_0 - x)^{\frac{1}{2}}} - \frac{1}{C_0^{\frac{1}{2}}}]}{t} )</td>
</tr>
<tr>
<td>2</td>
<td>( \frac{dx}{dt} = k(C_0 - x)^2 )</td>
<td>( k = \frac{1}{t} \left[ \frac{x}{C_0(C_0 - x)} \right] )</td>
</tr>
<tr>
<td>3</td>
<td>( \frac{dx}{dt} = k(C_0 - x)^3 )</td>
<td>( k = \frac{1}{2t} \left[ \frac{2C_0x - x^2}{C_0^2(C_0 - x)^2} \right] )</td>
</tr>
</tbody>
</table>
Eq.(9.12) can be used for calculating the order of reaction. The slope of the straight line obtained by plotting \( \log t_{0.5} \) against \( \log C_0 \) gives the value of \(- (n-1)\) and hence that of \( n \).

9.4.3 Van't Hoff's Differential Method

According to this method, the reaction rate \( v \) for an isothermal reaction can be related to the concentration of a reactant \( C \) by the following equation:

\[
v = k C^n, \tag{9.13}
\]

where \( n \) is the order of reaction. Taking logarithms of both sides of Eq. (9.13),

\[
\log v = \log k + n \log C. \tag{9.14}
\]

If the reaction rate \( v \) is known at various values of reactant concentration, a plot of \( \log v \) against \( \log C \) will result in a straight line, and the slope of the line gives the value of the order of reaction with respect to the substance whose concentration is being varied.

Two different methods may be used for calculating reaction rates at different reactant concentrations. One consists of plotting reactant concentration against time. The slopes (negative) at different reactant concentrations give the values of the rates at the respective reactant concentrations. The order of reaction obtained on the basis of the above rate values is called 'order with respect to time', \( n_t \). The other method involves plotting reactant concentration against time for different values of initial concentration of reactant. Tangents are drawn at the beginning of the reaction (i.e. at time \( t = 0 \)). The rate corresponding to a particular initial reactant concentration is given by the negative of the respective slope value. When these initial rate values at different initial reactant concentrations are used for calculating the order according to Eq.(9.14), the order obtained is known as 'order with respect to concentration' or 'true order', \( n_c \).

In case the reaction involves more than one reactant, experiments are carried out with different initial concentrations of one reactant, while keeping the
concentration of other reactants constant. The order of reaction with respect to this reactant is determined. In order to determine the total order, this order is added to the orders with respect to other reactants determined in a similar manner.

Example 9.D

For the reaction A + B = C, the following data were determined:

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Initial Concentration</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>A</td>
<td>B</td>
<td>A</td>
<td>B</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>moles/litre</td>
<td>mol/dm^3</td>
<td>moles/litre</td>
<td>mol/dm^3</td>
<td>moles/litre</td>
<td>mol/dm^3</td>
<td>moles/litre</td>
</tr>
<tr>
<td>1</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.5</td>
<td>9000</td>
<td>372</td>
</tr>
<tr>
<td>2</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>1.0</td>
<td>3600</td>
<td>107</td>
</tr>
</tbody>
</table>

Calculate the order of reaction and the specific reaction rate.

Solution: If two experiments are carried out at the initial reactant concentrations \((C_0)_1\) and \((C_0)_2\) and if their half-life periods are \((t_{0.5})_1\) and \((t_{0.5})_2\) respectively, then according to Eq. (9.12),

\[
n = 1 + \frac{\log(t_{0.5})_1 - \log(t_{0.5})_2}{\log(C_0)_2 - \log(C_0)_1} \tag{9.0.1}
\]

Putting the appropriate values in Eq. (9.0.1),

\[
n = 1 + \frac{\log 2.5 - \log 1}{\log 5 - \log 2}
\]
Thus the reaction is second-order.

The specific reaction rate for a second-order reaction when both the reactants are at the same concentration can be calculated from Eq.(9.8), and thus,

\[ k = \frac{1}{C \cdot t^{0.5}} \]

\[ = \frac{1}{2 \times 2.5} \]

\[ = 0.2 \, \text{litre/mole/hour}. \]

Thus the specific reaction rate of the reaction is 0.2 litre/mole/hour.

Example 9.5

The following data are obtained for the kinetics of reduction of FeO in slag by carbon in molten pig iron at a certain temperature:

<table>
<thead>
<tr>
<th>Time, min</th>
<th>0</th>
<th>1.0</th>
<th>1.5</th>
<th>2.0</th>
<th>3.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of FeO in slag, wt%</td>
<td>20.00</td>
<td>11.50</td>
<td>9.35</td>
<td>7.10</td>
<td>4.40</td>
</tr>
</tbody>
</table>

Calculate the order of reaction w.r.t. FeO by Van't Hoff's differential method. Also calculate the rate constant.

Solution: The concentration of FeO in the slag is plotted against time, as shown in Fig.9.2. Tangents are drawn at the points corresponding to 18, 16, 10, and 6 wt% FeO. The slopes of these four tangents are measured to
Fig. 9.2. Variation of the Concentration of FeO in Slag with Time.

obtain the rates of reduction of FeO corresponding to the four values of FeO concentration, as shown below:

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Concentration of FeO in slag, wt% (C)</th>
<th>log C</th>
<th>Slope of the tangent</th>
<th>Rate of reduction of FeO, %FeO/min (v)</th>
<th>log v</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>18</td>
<td>1.2553</td>
<td>-11.88</td>
<td>11.88</td>
<td>1.0749</td>
</tr>
<tr>
<td>2</td>
<td>16</td>
<td>1.2041</td>
<td>-8.94</td>
<td>8.94</td>
<td>0.9513</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>1.0000</td>
<td>-4.63</td>
<td>4.63</td>
<td>0.6656</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>0.7782</td>
<td>-3.13</td>
<td>3.13</td>
<td>0.4955</td>
</tr>
</tbody>
</table>
Again, log $v$ is plotted against log $C$, giving the straight line shown in Fig. 9.3. The slope is 1.09, and the reaction can be regarded as first-order w.r.t. FeO. Also, the intercept of the line at log $C = 0$ is equal to $-0.34$, and hence, according to Eq. (9.14):

$$\log k = -0.34$$

or

$$k = 0.4571 \text{ min}^{-1}.$$ 

Thus, the specific reaction rate is equal to $0.4571 \text{ min}^{-1}$. 

Fig. 9.3. Log-log Plot between the Rate of Reduction of FeO ($v$) and Concentration of FeO in Slag ($C$).
There are two important theories of reaction kinetics - the collision theory, and absolute reaction rate theory. With the aid of these theories, the rate of a reaction can be calculated.

### 9.5.1 Collision Theory

Consider a homogeneous bimolecular reaction between two gas molecules A and B. According to this theory, for the reaction to occur, the molecules A and B must collide. The reaction rate is given by

\[ v = z_{AB} e^{-E/RT} \text{ molecules/c.c./sec}, \quad (9.15) \]

where \( z_{AB} \) is the number of collisions per sec between A and B in 1 c.c. of gas, \( E \) is the activation energy, \( R \) is the gas constant, and \( T \) is the temperature in K. According to kinetic theory, the value of \( z_{AB} \) is given by

\[ z_{AB} = \frac{n_A n_B d_{AB}^2}{\left( 8\pi kT \frac{m_A + m_B}{m_A m_B} \right)^{\frac{1}{2}}} \quad (9.16) \]

where \( n_A \) and \( n_B \) are the concentrations of molecules A and B respectively in molecules/c.c., \( m_A \) and \( m_B \) are the masses of A and B molecules respectively, \( d_{AB} \) is the average diameter of A and B and \( k \) is the Boltzmann's constant. Putting the value of \( z_{AB} \) in Eq.(9.15),

\[ v = n_A n_B d_{AB}^2 \left( 8\pi kT \frac{m_A + m_B}{m_A m_B} \right)^{\frac{1}{2}} e^{-E/RT} \text{ molecules/c.c./sec}. \quad (9.17) \]

In many cases, the observed rate does not agree with the value calculated on the basis of Eq.(9.17). In order to account for deviation from the collision theory, Eq.(9.15) is modified to
\[ v = P \cdot z_{AB} \cdot e^{-E/RT} \text{ molecules/c.c./sec,} \quad (9.18) \]

where \( P \) is referred to as the probability or steric factor.

### 9.5.2 Absolute Reaction Rate Theory

Consider the chemical reaction

\[ A + B + C + D. \quad (9.19) \]

This theory assumes that before a chemical reaction takes place, the molecules \( A \) and \( B \) have to collide and then form an activated complex, which then decomposes to give the products. Thus, the reaction (9.19) can be rewritten as

\[ A + B \rightarrow A \ldots B + C + D, \]

where \( A \ldots B \) represents the activated complex. The two basic principles of this theory are

(i) The activated complex may be treated as any other chemical species and is in equilibrium with the reactants. It has a very short life.

(ii) The specific reaction rate of decomposition of the activated complex into products is a universal rate, independent of the nature of the reactants and the form of the activated complex.

The rate of the overall reaction (9.19), which is equal to the rate at which the activated complex \( A \ldots B \) decomposes to form the products, is given by

\[ v = \frac{RT}{Nh} c^+ = \frac{kT}{h} c^+, \quad (9.20) \]
where $C^+$ is the concentration of activated complex, $k$ is the Boltzmann's constant, and $h$ is the Planck's constant.

The equilibrium constant $K^+$ for the reaction

$$A + B \rightarrow A...B$$

is given as

$$K^+ = \frac{a^+}{a_A a_B}$$  \hspace{1cm} (9.21)

where $a^+$, $a_A$ and $a_B$ are the activities of activated complex, $A$ and $B$ respectively. Assuming ideal behaviour,

$$K^+ = \frac{C^+}{c_A c_B}$$  \hspace{1cm} (9.22)

where $C$ represents the concentration. Putting the value of $C^+$ from Eq. (9.22) in Eq.(9.20),

$$v = C_A C_B \frac{kT}{h} K^+.$$  \hspace{1cm} (9.23)

Since

$$K^+ = e^{-\Delta G^+/RT},$$

it follows that

$$v = C_A C_B \frac{kT}{h} e^{-\Delta G^+/RT}$$

$$= C_A C_B \frac{kT}{h} e^{-\Delta H^+/RT} e^{\Delta S^+/R},$$  \hspace{1cm} (9.24)

where $\Delta G^+$, $\Delta H^+$, and $\Delta S^+$ are the free energy, enthalpy, and entropy changes respectively when the activated complex is formed.

For most reactions, it has been found that all activated complexes formed from the reactants dissociate into the products. However, in some reactions it is
possible that not all activated complexes dissociate into the products, and
therefore a term 'transmission coefficient' is introduced in the rate equation
to account for this. Thus, Eq.(9.24) reduces to
\[ v = C_A \cdot C_B \cdot \kappa \cdot \frac{kT}{h} \cdot \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \cdot \exp\left(-\frac{\Delta S^\ddagger}{R}\right), \] (9.25)

where \( \kappa \) is the transmission coefficient.

However, it should be noted that \( \Delta G^\ddagger, \Delta H^\ddagger \) and \( \Delta S^\ddagger \) refer to the free
energy, enthalpy, and entropy of activation, when both the reactants and acti­
vated complex are in their standard state. The choice of standard state is
automatically determined by the units chosen to express the concentration of
reactants. For example, if the concentrations are expressed in moles/c.c.,
the standard state is 1 mole/c.c. On the other hand, if the concentration
is expressed in the form of atm pressure, the standard state is a gas at 1 atm
pressure.

Eq.(9.25) may also be expressed in a form which takes into account the experi­
mental activation energy, \( E_{\text{exp}} \), instead of enthalpy of activation, \( \Delta H^\ddagger \)
For example, for a bimolecular reaction, the rate may be expressed as
\[ v = C_A \cdot C_B \cdot \exp\left(-\frac{E_{\text{exp}}}{RT}\right) \cdot \exp\left(-\frac{\Delta S^\ddagger}{R}\right). \] (9.26)

The reaction rate, \( v \), of the reaction (9.19) can also be expressed in the form
of partition functions,
\[ v = C_A \cdot C_B \cdot \frac{kT}{h} \cdot \frac{F^\ddagger}{F_A \cdot F_B} \cdot \exp\left(-\frac{E_0}{RT}\right) \] (9.27)

where \( F_A \) and \( F_B \) are the partition functions of A and B respectively,
\( F^\ddagger \) is the partition function of activated complex which lacks the contribution
for one very loose vibrational degree of freedom, and \( E_0 \) is the difference
between zero-point energy per mole of the activated complex and reactants.
9.6 Rate of Heterogeneous Reactions

Most metallurgical reactions, e.g. slag-metal reactions, reduction of metal oxides by gaseous reductants, oxidation of metals, etc., are heterogeneous in character. In all these reactions, the reacting components are in different phases. In general, heterogeneous reactions involve the following principal steps:

(i) Transport of the reactants from the bulk phases (across the boundary layers) to the place of reaction, i.e. interface.

(ii) The phase boundary reaction at the interface, which may be composed of several individual steps.

(iii) Transport of the reaction products from the interface into the bulk phases.

It is evident that the slowest of the above three possible steps determines the overall reaction rate. Steps (i) and (iii) are similar to the diffusion process, and their rates are governed by the diffusion theory. Step (ii) obeys the basic laws of chemical kinetics as discussed previously, and will be temperature-dependent according to the Arrhenius equation. In many metallurgical processes the temperature is high, and the rate of phase boundary reaction at the interface is also high. Therefore, step (ii) is unlikely to be the rate controlling in those cases. Hence, it is apparent that the rate of transport of substances is of considerable importance in many metallurgical processes. A few important metallurgical reactions are considered below, for the purpose of calculating their rates.

The decarburization rate of steel in the basic open-hearth process is controlled by the diffusion of oxygen through a thin metal film from an oxidizing slag for reaction with carbon (1). Applying the diffusion theory, the decarburization rate \( \frac{d[C]}{dt} \) is given by
where \( [O]_{\text{sat}} \) = oxygen concentration at the interface, wt%,
\([O]\) = oxygen concentration of the main bath, wt%,
\(\lambda\) = bath depth, cm,
\(\Delta l\) = thickness of oxygen-rich metal layer in contact with slag, cm,
and \(D\) = diffusivity of oxygen, cm\(^2\)/sec.

The rate of metal oxidation is generally controlled by the diffusion of either metal or oxygen ion across the oxide film. The oxidation rates of most metals over an intermediate range of temperature follow the parabolic rate law\(^{(2)}\), i.e.

\[
\frac{dy}{dt} = \frac{k'}{y},
\]

where \(y\) = thickness of oxide layer,
\(k'\) = constant,
and \(t\) = time.

Integrating Eq.(9.29),

\[
y^2 = 2 k' t + A',
\]

where \(A'\) is an integration constant.

Assuming that the increase in weight due to oxidation, \(\Delta m\), is proportional to the thickness, \(y\), it follows that

\[
\Delta m^2 = 2 k t + A',
\]

where \(k\) is the parabolic rate constant and \(A\) is a constant.
Example 9.F

Calculate the rate of decarburization in % per hr for a steel bath, 40 cm (0.4 m) deep in an open-hearth furnace from the following data:

(i) Difference between the oxygen content at the slag-metal interface and the main bath = 0.04%.

(ii) Thickness of the metal film rich in oxygen = 0.004 cm (0.04 mm).

(iii) Diffusivity of oxygen = $2 \times 10^{-4}$ cm$^2$/sec ($2 \times 10^{-8}$ m$^2$/s).

Solution: Using Eq.(9.28) and putting in the appropriate values,

$$\frac{-d[C]}{dt} = \frac{2 \times 10^{-4} \times 0.04 \times 12}{40 \times 0.004 \times 16} = 0.375 \times 10^{-4} \text{ % per sec}$$

$$= 0.375 \times 10^{-4} \times 60 \times 60 \text{ % per hr}$$

$$= 1350 \times 10^{-4} \text{ % per hr}$$

$$= 0.135 \text{ % per hr}.$$ 

Thus, the rate of decarburization is 0.135 % per hr.

Example 9.G

The following data were obtained for the oxidation of niobium in pure oxygen atmosphere at 200°C (473 K):

<table>
<thead>
<tr>
<th>Time, min</th>
<th>20</th>
<th>60</th>
<th>100</th>
<th>120</th>
<th>180</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Time, s</td>
<td>1200</td>
<td>3600</td>
<td>6000</td>
<td>7200</td>
<td>10800)</td>
</tr>
</tbody>
</table>
Weight gain, \(\text{mg/cm}^2\):

<table>
<thead>
<tr>
<th>Weight gain, (\text{mg/cm}^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.45</td>
</tr>
<tr>
<td>45.82</td>
</tr>
<tr>
<td>59.16</td>
</tr>
<tr>
<td>65.00</td>
</tr>
<tr>
<td>80.00</td>
</tr>
</tbody>
</table>

Calculate the parabolic rate constant.

Solution: It is apparent from Eq.(9.31) that a plot of \((\text{weight gain})^2, \Delta m^2\), against time, \(t\), will result in a straight line having a slope equal to \(2k\). For the present example, a similar graph, plotted from the given data, is shown in Fig.9.4. The slope of the line is 35.71, and hence the parabolic rate constant is \(17.85 \text{ mg}^2/\text{cm}^4/\text{min}\).
REFERENCES


Exercises

9.1 The rate constant of a first-order reaction is $4.8 \times 10^{-5} \text{ sec}^{-1}$. The initial concentration of reactant is 0.2 moles/litre ($0.2 \text{ mol/dm}^3$). Calculate the initial rate in moles/c.c./min.

9.2 The half-life period for the decomposition of radium is 1600 years ($5.04 \times 10^{10} \text{ a}$). Calculate the rate constant in min$^{-1}$ and sec$^{-1}$, assuming that the reaction is first-order. In how many years will 90 percent of a given amount of radium disappear?

9.3 The reaction between FeO in slag with carbon in pig iron may be regarded as first-order, and at a certain temperature, the reaction is 50 percent complete at the end of 90 min ($5400 \text{ s}$). In how many min will the reaction be 90 percent complete at that temperature? Calculate the rate constant.

9.4 Calculate the ratio of the time required for the reaction to be 75 percent complete to that required for 50 percent complete, if it is a first-order reaction.

9.5 Two similar carbon-saturated molten pig irons, one containing 0.8% S and...
the other 0.8% S and 1.46% Si are in contact with a sulphur-free slag at 1500°C (1773 K) for desulphurization. The concentrations of sulphur in the metals at different intervals of time are as follows:

<table>
<thead>
<tr>
<th>Time, min</th>
<th>Sulphur in metal, wt%</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0% Si in iron</td>
<td>1.46% Si in iron</td>
<td></td>
</tr>
<tr>
<td>10 (600 s)</td>
<td>0.67</td>
<td>0.64</td>
<td></td>
</tr>
<tr>
<td>20 (1200 s)</td>
<td>0.56</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>30 (1800 s)</td>
<td>0.47</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td>40 (2400 s)</td>
<td>0.40</td>
<td>0.32</td>
<td></td>
</tr>
</tbody>
</table>

Show graphically that silicon does not affect the first-order kinetics of desulphurization and calculate the rate constant in both cases.

9.6 The concentration of sulphur in pig iron after desulphurization with a basic slag at 1470°C (1743 K) at various intervals of time is as follows:

<table>
<thead>
<tr>
<th>Time, min</th>
<th>Conc. of sulphur, g/cm² of interface</th>
<th>Conc. of sulphur, kg/m² of interface</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.71</td>
<td>87.1</td>
</tr>
<tr>
<td>9</td>
<td>5.74</td>
<td>57.4</td>
</tr>
<tr>
<td>20</td>
<td>3.02</td>
<td>30.2</td>
</tr>
<tr>
<td>40</td>
<td>1.00</td>
<td>10.0</td>
</tr>
<tr>
<td>64</td>
<td>0.275</td>
<td>2.75</td>
</tr>
</tbody>
</table>

Show that the desulphurization is a first-order reaction.

9.7 Show that the time required for the reaction of any given fraction of the material initially present is independent of the initial concentration for
a first-order reaction, but varies with the initial concentration for a second-order reaction.

9.8 Two second-order reactions have similar frequency factors and activation energies differing by 8 kcal/mole (33.47 kJ/mol). Calculate the ratio of their rate constants at 227°C (500 K).

9.9 The rate constants of fluorination of uranium oxide at various temperatures are listed below.

<table>
<thead>
<tr>
<th>Temp., °C</th>
<th>600</th>
<th>630</th>
<th>660</th>
<th>690</th>
<th>720</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Temp., K</td>
<td>873</td>
<td>903</td>
<td>933</td>
<td>963</td>
<td>993</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Rate constant (x 10^3), g/cm²/min</th>
<th>0.69</th>
<th>1.21</th>
<th>2.10</th>
<th>3.46</th>
<th>5.37</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Rate constant (x 10^5), kg/m²/s</td>
<td>0.12</td>
<td>0.20</td>
<td>0.35</td>
<td>0.58</td>
<td>0.90</td>
</tr>
</tbody>
</table>

Determine the activation energy for fluorination.

9.10 Calculate the activation energy of cementation of copper by iron from a copper sulphate solution containing 1.32 g Cu/litre (1.32 kg Cu/m³) from the following data:

<table>
<thead>
<tr>
<th>(1/T\ \times 10^3)</th>
<th>2.80</th>
<th>2.90</th>
<th>2.95</th>
<th>3.05</th>
<th>3.15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate constant (x 10^5), cm/sec</td>
<td>3.9</td>
<td>3.0</td>
<td>2.5</td>
<td>2.0</td>
<td>1.5</td>
</tr>
<tr>
<td>(Rate constant (x 10^6), m/s</td>
<td>(3.9 \times 10^{-2})</td>
<td>(3.0 \times 10^{-2})</td>
<td>(2.5 \times 10^{-2})</td>
<td>(2.0 \times 10^{-2})</td>
<td>(1.5 \times 10^{-2})</td>
</tr>
</tbody>
</table>

where \(T\) represents absolute temperature.
9.11 The diffusion coefficients for zinc in copper are given below.

Temp., °C : 1049 980 903 734 605
(Temp., K : 1322 1253 1176 1007 878)

Diffusion coefficient, cm²/sec : 1.0x10⁻⁸ 4.0x10⁻⁹ 1.1x10⁻⁹ 4.0x10⁻¹¹ 1.6x10⁻¹²

(Diffusion coefficient, m²/s : 1.0x10⁻¹² 4.0x10⁻¹³ 1.1x10⁻¹³ 4.0x10⁻¹⁵ 1.6x10⁻¹⁶)

Calculate the activation energy for the diffusion process.

9.12 The specific rate constant of a reaction at 400°C (673 K) is double that at 300°C (573 K). Calculate the activation energy of the reaction.

9.13 During a creep test carried out at constant stress, the creep rate was exactly doubled by a sudden increase in the test temperature from 230°C (503 K) to 240°C (513 K). Calculate the activation energy for creep.

9.14 The kinetics of the rapid reduction of FeO in slag by carbon in pig iron have been studied at various temperatures. The values of percent FeO reduced as a function of time and temperature are given below:

<table>
<thead>
<tr>
<th>Time, min</th>
<th>Percent FeO reduced</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1430°C (1703 K)</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1.0 (60s)</td>
<td>33.93</td>
</tr>
<tr>
<td>1.5 (90s)</td>
<td>47.52</td>
</tr>
<tr>
<td>2.0 (120s)</td>
<td>56.35</td>
</tr>
<tr>
<td>3.0 (180s)</td>
<td>69.80</td>
</tr>
<tr>
<td>4.0 (240s)</td>
<td>80.00</td>
</tr>
</tbody>
</table>
Determine graphically the order of reaction and also calculate the activation energy of the process.

9.15 74.40 g (0.0744 kg) of carbon saturated liquid iron of composition 4% C, 0.3% S, and 0.002% O₂ was agitated at 1450°C (1723 K) with 25.60 g (0.0256 kg) of synthetic slag of composition 40% CaO, 40% SiO₂ and 20% Al₂O₃, in order to produce a homogeneous solution. The average density of the solution is 5.42 g/c.c. (5.42 x 10³ kg/m³). The desulphurization reaction which is taking place can be represented as follows:

\[ [S]_{\text{metal}} + [(O)]_{\text{slag}} = [O]_{\text{metal}} + (S)_{\text{slag}}. \]

The mean ionic diameter for sulphur and oxygen is 3.24 x 10⁻⁸ cm (3.24 x 10⁻¹⁰ m). The activation energies for the forward and backward reactions are 75,000 cal/mole (313 3800 J/mol) and 50,710 cal/mole (212,170 J/mol) respectively. The steric factor for both forward and backward reactions is 10⁻⁷.

Calculate the percent sulphur left in the iron after 20 min (1200 s) from the start of reaction, according to the collision theory. Assume that the solution consists of independent atoms of Fe, C, \([O]_{\text{metal}}\), \((O)_{\text{slag}}\), \([S]_{\text{metal}}\), \((S)_{\text{slag}}\), Ca, Si, and Al, and the total number of atoms within the solution remains constant.

9.16 The rate determining step in the leaching of cuprite with H₂SO₄ at 31°C (304 K) has been found to be the thermal decomposition of surface sites containing adsorbed H₂SO₄ molecules:

\[ \text{Cu}_2\text{O.H}_2\text{SO}_4 \rightarrow \text{Cu}^{++} + \text{Cu}^{0} + \text{H}_2\text{O} + \text{SO}_4^{--}. \]

The enthalpy of activation for the decomposition is 10,300 cal/mole (43,085 J/mol) and the entropy of activation is negligible. Total number of bare surface sites is 10¹⁵ per cm² (10¹⁸ per m²), and 92% of these are covered with the adsorbed H₂SO₄. Calculate the rate of leaching according to the absolute reaction rate theory if the transmission coefficient is unity.
9.17 According to the absolute reaction rate theory, the rate of bimolecular reaction between the surface sites of a metal oxide and CO and Cl₂ gas molecules is given by

\[
v = \frac{h^9}{2} \frac{S}{C_s} C_g^1 C_g^2 \frac{1}{(2\pi m_1)^{3/2}(2\pi m_2)^{3/2}(8\pi^2 I_1)(8\pi^2 I_2)(kT)^4} e^{-E_0/RT}
\]

molecules/cm²/sec

where

- \( C_s \) = concentration of bare surface sites per cm²,
- \( C_g \) = concentration of gas, molecules/c.c.
- \( m \) = mass of gas per molecule, g,
- \( I \) = moment of inertia of gas molecule, g.cm²,
- \( h \) = Planck's constant,
- \( k \) = Boltzmann's constant,
- \( E_0 \) = activation energy at absolute zero, cal/mole,
- \( S \) = number of possible sites adjacent to any one site,
- \( R \) = gas constant, cal/deg/mole,

and the subscripts 1 and 2 refer to CO and Cl₂ gas molecules respectively.

The activation energy of the reaction at 600°C is 7,600 cal/mole and the concentration of bare surface sites is \( 10^{15} \) sites/cm². Total number of possible sites adjacent to any one site is 4, and the interatomic distance between Cl-Cl and C-O atoms is \( 10^{-8} \) cm in each case.

Calculate the rate of reaction if the partial pressure of each of the gases is 0.33 atm. Assume that the activation energy at 600°C is not very far from that at absolute zero.
APPENDIX 1

SI UNITS

The International System of Units are of three kinds: base, derived, and supplementary. The names and symbols of the SI base Units are given in Table A1.1.

Table A1.1
SI Base Units

<table>
<thead>
<tr>
<th>Physical quantity</th>
<th>Name of SI Unit</th>
<th>Symbol for SI Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>metre</td>
<td>m</td>
</tr>
<tr>
<td>Mass</td>
<td>kilogramme</td>
<td>kg</td>
</tr>
<tr>
<td>Time</td>
<td>second</td>
<td>s</td>
</tr>
<tr>
<td>Electric current</td>
<td>ampere</td>
<td>A</td>
</tr>
<tr>
<td>Temperature</td>
<td>kelvin</td>
<td>K</td>
</tr>
<tr>
<td>Amount of substance</td>
<td>mole</td>
<td>mol</td>
</tr>
<tr>
<td>Luminous intensity</td>
<td>candela</td>
<td>cd</td>
</tr>
</tbody>
</table>

Some of the SI derived Units pertinent to the subject matter of this book are given in Table A1.2.
### Table A1.2

**Some SI derived Units**

<table>
<thead>
<tr>
<th>Physical quantity</th>
<th>Name of SI Unit</th>
<th>Symbol for SI Unit</th>
<th>Definition of SI Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy</td>
<td>joule</td>
<td>J</td>
<td>( \text{kg m}^2/\text{s}^2 )</td>
</tr>
<tr>
<td>Force</td>
<td>newton</td>
<td>N</td>
<td>( \text{kg m/s}^2 = \text{J/m} )</td>
</tr>
<tr>
<td>Pressure</td>
<td>newton per square metre</td>
<td>( N/\text{m}^2 )</td>
<td>( \text{kg/m/s}^2 )</td>
</tr>
<tr>
<td>Electric charge</td>
<td>coulomb</td>
<td>C</td>
<td>As</td>
</tr>
<tr>
<td>Electrical potential</td>
<td>volt</td>
<td>V</td>
<td>( \text{kg m}^2/\text{s}^3/\text{A} = \text{J/A/s} )</td>
</tr>
<tr>
<td>Area</td>
<td>square metre</td>
<td>( \text{m}^2 )</td>
<td></td>
</tr>
<tr>
<td>Volume</td>
<td>cubic metre</td>
<td>( \text{m}^3 )</td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>kilogramme per cubic metre</td>
<td>( \text{kg/m}^3 )</td>
<td></td>
</tr>
<tr>
<td>Heat capacity, entropy</td>
<td>joules per kelvin</td>
<td>J/K</td>
<td>( \text{kg m}^2/\text{s}^2/\text{K} )</td>
</tr>
</tbody>
</table>

Two supplementary units are at present defined, the radian, and the steradian, which are the units for plane and solid angles respectively.

The internationally agreed prefixes for fractions and multiples of the SI
Units are given in Table A1.3.

### Table A1.3

Prefixes used in the SI Units

<table>
<thead>
<tr>
<th>Multiplication factor</th>
<th>SI prefix</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-1}$</td>
<td>deci</td>
<td>$d$</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>centi</td>
<td>$c$</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>milí</td>
<td>$m$</td>
</tr>
<tr>
<td>$10^{-6}$</td>
<td>micro</td>
<td>$\mu$</td>
</tr>
<tr>
<td>$10^{-9}$</td>
<td>nano</td>
<td>$n$</td>
</tr>
<tr>
<td>$10^{-12}$</td>
<td>pico</td>
<td>$p$</td>
</tr>
<tr>
<td>$10^{-15}$</td>
<td>femto</td>
<td>$f$</td>
</tr>
<tr>
<td>$10^{-18}$</td>
<td>atto</td>
<td>$a$</td>
</tr>
<tr>
<td>$10^{1}$</td>
<td>deca</td>
<td>$da$</td>
</tr>
<tr>
<td>$10^{2}$</td>
<td>hecto</td>
<td>$h$</td>
</tr>
<tr>
<td>$10^{3}$</td>
<td>kilo</td>
<td>$k$</td>
</tr>
<tr>
<td>$10^{6}$</td>
<td>mega</td>
<td>$M$</td>
</tr>
<tr>
<td>$10^{9}$</td>
<td>giga</td>
<td>$G$</td>
</tr>
<tr>
<td>$10^{12}$</td>
<td>tera</td>
<td>$T$</td>
</tr>
</tbody>
</table>
APPENDIX 2.

CONSTANTS AND CONVERSION FACTORS

A 2.1. Values of Selected Constants

The values of some useful constants are listed in Table A2.1.

Table A2.1
Some Useful Constants

<table>
<thead>
<tr>
<th>Name</th>
<th>Value in Traditional Units</th>
<th>Value in SI Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avagadro's number</td>
<td>$6.02 \times 10^{23}$ molecules/mole</td>
<td>$6.02 \times 10^{23}$ molecules/mole</td>
</tr>
<tr>
<td>Boltzmann's constant</td>
<td>$3.30 \times 10^{-24}$ cal/deg</td>
<td>$1.38 \times 10^{-23}$ J/K</td>
</tr>
<tr>
<td></td>
<td>$1.38 \times 10^{-16}$ erg/deg</td>
<td></td>
</tr>
<tr>
<td>Faraday's constant</td>
<td>96487 C/g-equivalent</td>
<td>96487 C/g-equivalent</td>
</tr>
<tr>
<td></td>
<td>23061 cal/V/g-equivalent</td>
<td>96487 J/V/g-equivalent</td>
</tr>
<tr>
<td>Gas constant</td>
<td>$1.987$ cal/deg/mole</td>
<td>$8.314$ J/K/mol</td>
</tr>
<tr>
<td></td>
<td>$8.314 \times 10^{7}$ erg/deg/mole</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$82.07$ c.c.atm/deg/mole</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$0.08207$ litre atm/deg/mole</td>
<td></td>
</tr>
<tr>
<td>Planck's constant</td>
<td>$1.584 \times 10^{-34}$ cal sec</td>
<td>$6.626 \times 10^{-24}$ J/s</td>
</tr>
<tr>
<td></td>
<td>$6.626 \times 10^{-27}$ erg sec</td>
<td></td>
</tr>
<tr>
<td>Volume of 1 mole of an</td>
<td>$22400$ c.c. at $0^\circ$C and</td>
<td>$2.24 \times 10^{-2}$ m$^3$ at 273 K</td>
</tr>
<tr>
<td>ideal gas</td>
<td>$1$ atm</td>
<td>and $101325$ N/m$^2$</td>
</tr>
</tbody>
</table>
A 2.2 Conversion Factors

Absolute temperature (K) = (Centigrade temperature (°C) + 273)

1 atm = 760 mm Hg
= 1033.2 g/cm²
= 101325 N/m²
= 101325 Pa

1 mm Hg = 133.32 N/m²
1 torr = 1 mm Hg
1 cal = 4.184 x 10⁷ erg
= 41.293 c.c. atm
= 4.184 J

1 erg = 2.39 x 10⁻⁸ cal
= 10⁻⁷ J
1 C = 1 As
1 litre = 1 dm³

ln x (i.e. logₑ x) = 2.303 log₁₀ x
= 2.303 log x

R ln x = 4.575 log x (if R is expressed in cal/deg/mole)
= 19.147 log x (if R is expressed in J/K/mol)
APPENDIX 3.
MATHEMATICAL OPERATIONS

A 3.1 Solution of Simultaneous Equations with the help of Determinant

The system of $n$ equations in $n$ unknowns

\[
\begin{align*}
    a_{11} x_1 + & \cdots + a_{1n} x_n = b_1 \\
    a_{21} x_1 + & \cdots + a_{2n} x_n = b_2 \\
    \vdots \hspace{2cm} & \vdots \\
    a_{n1} x_1 + & \cdots + a_{nn} x_n = b_n
\end{align*}
\]

(A3.1)

with a non-zero determinant of the system

\[
D = \begin{vmatrix}
    a_{11} & \cdots & a_{1n} \\
    a_{21} & \cdots & a_{2n} \\
    \vdots & \ddots & \vdots \\
    a_{n1} & \cdots & a_{nn}
\end{vmatrix} \neq 0
\]

has a unique solution $(x_1, \ldots, x_n)$, where $x_i = \frac{D_i}{D}$. $D_i$ is the determinant obtained by replacing the $i$th column of $D$ by the column of the elements forming the right-hand side of Eq.(A3.1)
A 3.2 Solution of Quadratic and Cubic Equations

(i) Quadratic Equations

In terms of the coefficients, the roots of the equation

$$ax^2 + bx + c = 0$$

is given by

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

If $b^2 - 4ac > 0$ the roots are real and distinct; if $b^2 - 4ac = 0$, the roots are identical; while if $b^2 - 4ac < 0$, the roots are complex.

(ii) Cubic Equations

Consider the following cubic equation in its standard form

$$y^3 + 3py + 2q = 0. \quad (A3.2)$$

Let coefficients $p$ and $q$ of Eq.(A3.2) be real and different from zero. Let the roots of the above equation be $y_1$, $y_2$, and $y_3$. Put $r = \varepsilon^{\sqrt{|p|}}$, where $\varepsilon = 1$ if $q > 0$, and $\varepsilon = -1$ if $q < 0$. The roots can be determined by means of the trigonometric or hyperbolic functions according to Table A3.1(1).

Table A3.1

Roots of Equation (A3.2)

<table>
<thead>
<tr>
<th></th>
<th>$p &lt; 0$</th>
<th>$p &gt; 0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p^3 + q^2 &lt; 0$</td>
<td>$p^3 + q^2 &gt; 0$</td>
<td></td>
</tr>
<tr>
<td>$\cos \alpha = \frac{q}{r^3}$</td>
<td>$\cosh \alpha = \frac{q}{r^3}$</td>
<td>$\sinh \alpha = \frac{q}{r^3}$</td>
</tr>
<tr>
<td>$y_1 = -2r \cos \frac{\alpha}{3}$</td>
<td>$y_1 = -2r \cosh \frac{\alpha}{3}$</td>
<td>$y_1 = -2r \sinh \frac{\alpha}{3}$</td>
</tr>
<tr>
<td>$y_2 = 2r \cos (60^\circ - \frac{\alpha}{3})$</td>
<td>$y_2 = r \cosh \frac{\alpha}{3}$</td>
<td>$y_2 = r \sinh \frac{\alpha}{3}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$y_2 = r \sinh \frac{\alpha}{3}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(imaginary)</td>
</tr>
<tr>
<td>$y_3 = 2r \cos (60^\circ + \frac{\alpha}{3})$</td>
<td>$y_3 = r \cosh \frac{\alpha}{3}$</td>
<td>$y_3 = r \sinh \frac{\alpha}{3}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$y_3 = r \sinh \frac{\alpha}{3}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(imaginary)</td>
</tr>
</tbody>
</table>

* $\alpha$ is the interval $(0^\circ, 90^\circ)$, and $r = \frac{\varepsilon}{\sqrt{|p|}}$
A3.3 Graphical Solution of Equations in One Unknown

Algebraic or trigonometrical methods are not always convenient in solving equations. An approximate solution can be determined by graphical method, as described below.

Let the given equation be \( ax^2 + bx + c = 0 \). To solve such an equation graphically, \( x \) is regarded as an independent variable, and the left-hand side of the equation as the function of this variable. A graph is plotted between \( ax^2 + bx + c \) and \( x \). The intersections of the curve with the \( x \)-axis give the solutions of the equation. Similarly, other types of equations can be solved.

The graphical method for solving an equation yields only an approximate solution. A more accurate value may be obtained by enlarging the scale in the region of the solution. Enlarging the scale is not very effective because an increase in accuracy requires a proportionate enlargement of the scale. However, there exists an algebraic method for finding a more accurate value which is as follows:

If \( x_1 \) is an approximate value of a root of a given equation unknown in \( x \), \( x = (x_1 + h) \) is substituted in the equation, where \( h \) is a new unknown which is small. Discarding the terms containing \( h \) to more than first power, the equation is solved for \( h \). The value \( (x_1 + h) \) is a better approximation to the original value, i.e. \( x_1 \). The process may be repeated, depending upon the accuracy required.

A3.4 Graphical or Numerical Integration

Let \( f(x) \) be continuous for \( a \leq x \leq b \). The graphical integration of the integral

\[
\int_{a}^{b} f(x) \, dx
\]

(A3.3)
consists of plotting \( f(x) \) as a function of \( x \). The value of the integral is given by the area under the curve between the values of \( x = a \) and \( x = b \) and \( x \)-axis. The most simple way of calculating the area is to count all the squares. However, the area can also be approximated in several other ways, as described below:

1. **Weighing** - If the graph paper is reasonably uniform in thickness, a very satisfactory method consists of cutting the figure out with a sharp knife, and weighing it. The area can be computed from the weight of the graph paper of known area.

2. **Trapezoidal Rule** - In order to determine the area by this rule, the interval \((a, b)\) is divided into \( n \) equal intervals of length \( h = \frac{b-a}{n} \). Let the values of \( f(x) \) corresponding to the values of \( x = a, x_1, x_2, ..., x_{n-1} \) and \( b \) be \( f(x) = f(a), f(x_1), f(x_2), ..., f(x_{n-1}), f(b) \) respectively, as shown in Fig. A3.1.

According to the trapezoidal rule, the area \( S \) is given by

\[
S = \frac{h}{2} \left[ f(a) + 2f(x_1) + 2f(x_2) + ... + 2f(x_{n-1}) + f(b) \right]
\]

\[
= h \left[ \frac{f(a) + f(b)}{2} + f(x_1) + f(x_2) + ... + f(x_{n-1}) \right]
\]

3. **Simpson's Rule**: This rule is very much similar to the trapezoidal rule except that the area is divided into an even number, \( n \), of vertical strips. The area \( S \) according to the Simpson's rule is given by

\[
S = \frac{h}{3} \left[ f(a) + f(b) + 4\{f(x_2) + f(x_4) + ... + f(x_{n-2})\} + 2\{f(x_3) + f(x_5) + ... + f(x_{n-1})\} \right]
\]
Fig. A 3.1. Graphical Solution of Integral (A 3.3).
BIBLIOGRAPHY

Thermodynamics


Kinetics


Chapter 1

1.1) -302.49 kcal/mole of $\text{B}_2\text{O}_3$, -4.343 kcal/g of $\text{B}_2\text{O}_3$.
1.2) (i) 8940 kg, (ii) 15285 kg, (iii) 12745 kg.
1.3) -8878 kcal/100 kg of ore.
1.4) -6.5 kcal.
1.5) 318.6 kcal.
1.6) (a) -35.79 kcal/mole, (b) 21.71 kcal/mole.
1.7) -69.25 kcal, -66.0 kcal.
1.8) -57.98 kcal/mole.
1.9) -211.9 kcal, -212.85 kcal.
1.10) $\Delta H^0 = (0.58 \times 10^{-3} T^2 - 3.66 T - 4.17 \times 10^5 T^{-1} + 59240)$ cal.
1.11) $H^0 - H^0_{298} = 5.335(T - 298) + \frac{3.74 \times 10^{-3}}{2} (T^2 - 298^2)$ cal/g-atom,

$$C_p = (5.335 + 3.74 \times 10^{-3} T) \text{ cal/deg/g-atom.}$$
1.12) 62.76 kcal/mole, 2.549 kcal/mole.
1.13) 1511 kcal/kg of zinc.
1.14) -27.85 kcal.
1.15) 328 kcal/kg of scrap.
1.16) -223.08 kcal/mole of $\text{TiO}_2$.
1.17) -93.17 kcal/mole of MnO.
1.18) (a) 2031°C, (b) 2956 cal/cu.ft. of exhaust gas.
Chapter 2

(2.1) Zero.

(2.2) (a) $\Delta H = 125,000$ cal, $\Delta S = 129.23$ cal/deg.
     (b) $\Delta H = 329,000$ cal, $\Delta S = 138.33$ cal/deg.

(2.3) 7.07 cal/deg/mole.

(2.4) 0.121 cal/deg/mole, process spontaneous.

(2.5) -79.94 cal/deg.

(2.6) 0.35 cal/deg.

(2.7) 0.218 cal/deg.

(2.8) -16.5 kcal/mole of Mo, 34.5 kcal/mole of Cr, not possible to reduce $\text{Cr}_2\text{O}_3$ by $\text{H}_2$.

(2.9) 1420°C.

(2.10) 572.5°C.

(2.11) 13.5°C.

(2.12) At or above 1472°C.

(2.13) Titanium.

(2.14) Not possible.

(2.15) Copper.

(2.16) Not spontaneous.

Chapter 3

(3.1) 6.72 cal/deg/mole.

(3.2) 7.10 cal/deg/mole.

(3.3) 15.43 cal/deg/mole.

(3.4) Valid.

Chapter 4

(4.1) 99 kcal/mole

(4.2) 32.2 kcal/mole.

(4.3) 2577°C.

(4.4) 27.35 kcal/mole.
Chapter 5

(5.1) \( \Delta S^0 = -32,250 + 14.51 T \) cal, -29,016 cal.

(5.2) \( 2.711, 1.595, 1.073, 0.7626, 0.5928, \Delta H^0 = -8320 \) cal.

(5.3) \( \Delta G^0 = 25,840 - 20.89 T \) cal, 3420 cal.

(5.4) \( 1.608 \times 10^{-9} \) atm, \( 8.058 \times 10^{-6} \) atm.

(5.5) 1.57.

(5.6) 13.40 atm each.

(5.7) \( 8.71 \times 10^{-3} \) atm.

(5.8) 13.58 atm.

(5.9) Will not decompose.

(5.10) Will reduce.

(5.11) 0.78, no.

(5.12) 7.53 mm Hg.

(5.13) <1.072 \times 10^{-3} \) volume\% \( \text{H}_2\text{O} \), oxidise.

Chapter 6

(6.1) 92.30 wt\% Al, 7.70 wt\% Mg.

(6.2) \( \text{Ca}^{2+} = 0.415, \text{Mg}^{2+} = 0.079, \text{Mn}^{2+} = 0.011, \text{Fe}^{2+} = 0.06, \text{Fe}^{3+} = 0.02, \text{SiO}_4^{4-} = 0.114, \text{PO}_4^{3-} = 0.089, \text{AlO}_3^{3-} = 0.038, \) and free \( \text{O}_2^- = 0.174. \)

(6.3) | wt\% Al | \( x_{\text{Zn}} \) | No. of g-atoms in 100 g alloy | Density at 25°C, g/c.c. | Volume of 100 g of alloy, c.c. | Volume per g-atom of alloy, c.c. |
<table>
<thead>
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</tr>
</thead>
<tbody>
<tr>
<td>19.40</td>
<td>0.6314</td>
<td>1.952</td>
<td>5.345</td>
<td>18.71</td>
<td>9.585</td>
</tr>
<tr>
<td>25.37</td>
<td>0.5479</td>
<td>2.083</td>
<td>4.953</td>
<td>20.18</td>
<td>9.692</td>
</tr>
</tbody>
</table>
Partial molar volume of zinc = 9.15 c.c./mole, partial molar volume of aluminium = 10.35 c.c./mole.

(6.4) $\Delta H^M_{\text{Cu}} = -7100 x^2$ cal/mole and $\Delta H^M_{\text{Zn}} = -7100 (1 - x)^2$ cal/mole.

(6.5) $\Delta H^M_{\text{Cd}} = 665$ cal/mole and $\Delta H^M_{\text{Al}} = 350$ cal/mole.

(6.6) $\Delta G^M_{\text{Cr}} = -1830$ cal/mole and $\Delta G^M_{\text{Ti}} = -1490$ cal/mole.

(6.7) 99.77 wt% Cu and 0.23 wt% Ni.

(6.8) 0.167 wt% Mn.

(6.9) 0.9570.

(6.10) Will precipitate.

(6.12) Silica and magnesia.

(6.13) -16,410 cal/mole.

(6.14) -26,840 cal/mole.

(6.15) -9,650 cal/mole.

(6.16) -17,330 cal/mole.

---

Chapter 7

(7.1) 80.26 and 88.9 c.c.

(7.2) 14.29 mm Hg.

(7.3) Yes.

(7.4) (i) 25.30 c.c. $H_2$ and 30.98 c.c. $N_2$.  (ii) 25.30 c.c. $N_2$,

(iii) 21.91 c.c. $N_2$ and 25.30 c.c. $H_2$.

(7.5) 0.0195 wt% $N_2$ and 0.002165 wt% $H_2$.

(7.6) -73.84 cal/mole.

(7.7) $a_{\text{Fe}} = 0.8594$.

(7.8) -1724 and -2212 cal/mole.

(7.9) -2132 and -840 cal/mole.

(7.10) 1.73 cal/deg/mole and 1.32 cal/deg/mole.

(7.11) -1040 cal/mole.
(7.12) 0.5112
(7.13) 0.5448
(7.14) 0.304
(7.15) (i) $2.236 \times 10^{-3}$ mm Hg, (ii) 4128 mm Hg.
(7.16) 0.4458.
(7.17) 0.0034 wt%.
(7.18) -2262 cal.
(7.19) 0.059 wt%.
(7.20) 0.03134 wt%.

Chapter 8

(8.1) -30,800 cal, -8.017 cal/deg and -33,310 cal.
(8.2) -51,830 cal.
(8.3) -5 kcal, -18.12 cal/deg, -29.92 kcal and 1650 K.
(8.4) 0.6606, 0.6066, 0.5576, 0.5258 and 0.4999.
(8.5) 0.65, 1.625 and -662 cal/mole.
(8.6) 0.4253, -1313 cal/mole, 1.551 cal/deg/mole and -114 cal/mole.
(8.7) 5138 cal/mole, -15,616 cal/deg/mole and -5332 cal/mole.
(8.8) 12,274 cal.

Chapter 9

(9.1) $5.759 \times 10^{-7}$ moles/c.c./min.
(9.2) $8.243 \times 10^{-10}$ min$^{-1}$, $1.374 \times 10^{-11}$ sec$^{-1}$, 5315 years.
(9.3) 299 min, $1.283 \times 10^{-4}$ sec$^{-1}$.
(9.4) 2.
(9.5) $K_{0.0\% Si} = 0.018$ min$^{-1}$, $K_{1.4\% Si} = 0.024$ min$^{-1}$.
(9.6) 3.183 $\times 10^{-4}$.
(9.7) 29.5 kcal/mole.
(9.8) 5420 cal/mole.
(9.9) 46.5 kcal/mole.
(9.12) 5.3 kcal/mole.
(9.13) 35.53 kcal/mole.
(9.14) First order, 54.9 kcal/mole.
(9.15) 0.188% S.
(9.16) $2.278 \times 10^{20}$ molecules/cm$^2$/sec.
(9.17) $1.188 \times 10^4$ molecules/cm$^2$/sec.
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