Introduction to the Thermodynamics of Materials

Chapter 1

Introduction and definition of terms

1.1 INTRODUCTION

- **Thermodynamics** is concerned with the behavior of **matter.**
- **Matter** is anything that occupies space
- **The Matter,** which is the subject of a thermodynamic analysis, is called a **system.**
- Aim of applied thermo.: the determination of the effect of environment (P, T, compositions) on the state of a system

1.1 INTRODUCTION

- System : volume of interest (reaction vessel, test tube, biological cell, atmosphere, etc.)
- Surroundings : volume outside system

1.2 THE CONCEPT OF STATE

- State :

  - microscopic state: mass, vel., position etc. of all the constituent particles in a system.

  - macroscopic state: fixed when all the prop. Is fixed. Two independent variables is needed.

- Simple system: given quantity of substance of fixed composition.

THE CONCEPT OF STATE

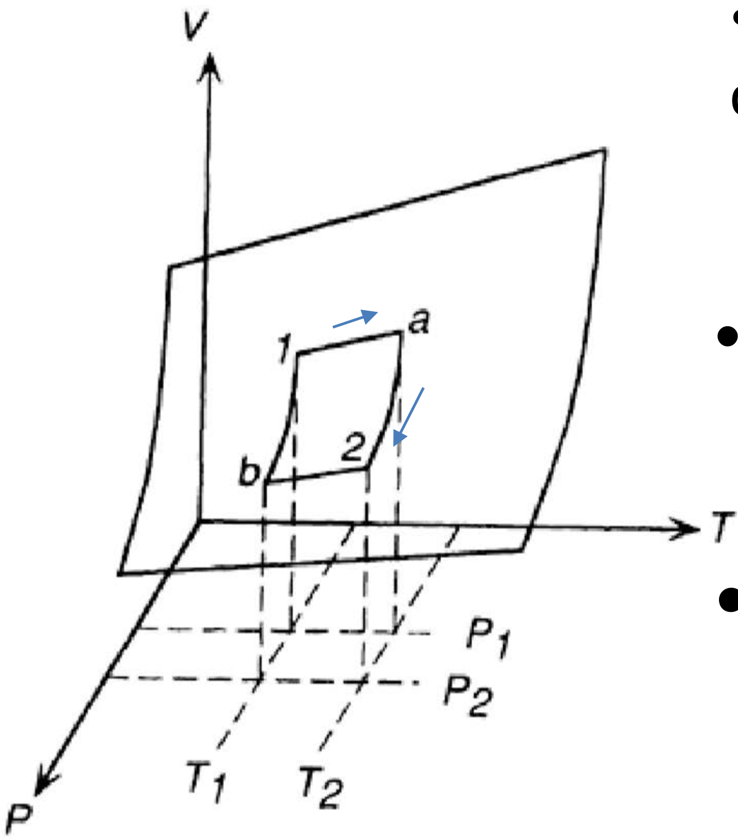

Figure 1.1 The equilibrium states of existence of a fixed quantity of gas in *P-V-T* space.

- Consider the vol. of a fixed quant. of a pure gas as property,

- $V = V(P, T)$ (eq 1.1)

  Eq. of State = math. relationship V to P & T

- $\Delta V = V_2 - V_1$

  $= (V_a - V_1) + (V_2 - V_a)$

THE CONCEPT OF STATE

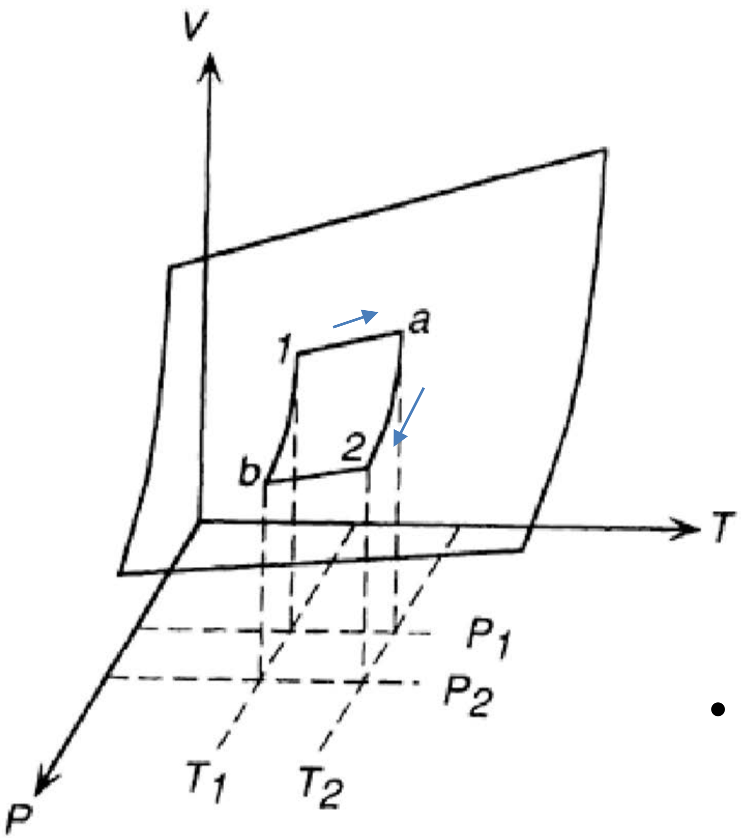

Figure 1.1 The equilibrium states of existence of a fixed quantity of gas in P-V-T space.

- $\Delta V = V_2 - V_1$
  $= (V_a - V_1) + (V_2 - V_a)$
- $(V_a - V_1) = \int_{T_1}^{T_2} \left(\frac{\partial V}{\partial T}\right)_{P_1} dT$
- $(V_2 - V_a) = \int_{P_1}^{P_2} \left(\frac{\partial V}{\partial P}\right)_{T_2} dP$
- $\Delta V = \int_{T_1}^{T_2} \left(\frac{\partial V}{\partial T}\right)_{P_1} dT + \int_{P_1}^{P_2} \left(\frac{\partial V}{\partial P}\right)_{T_2} dP$

(eq 1.2)

THE CONCEPT OF STATE

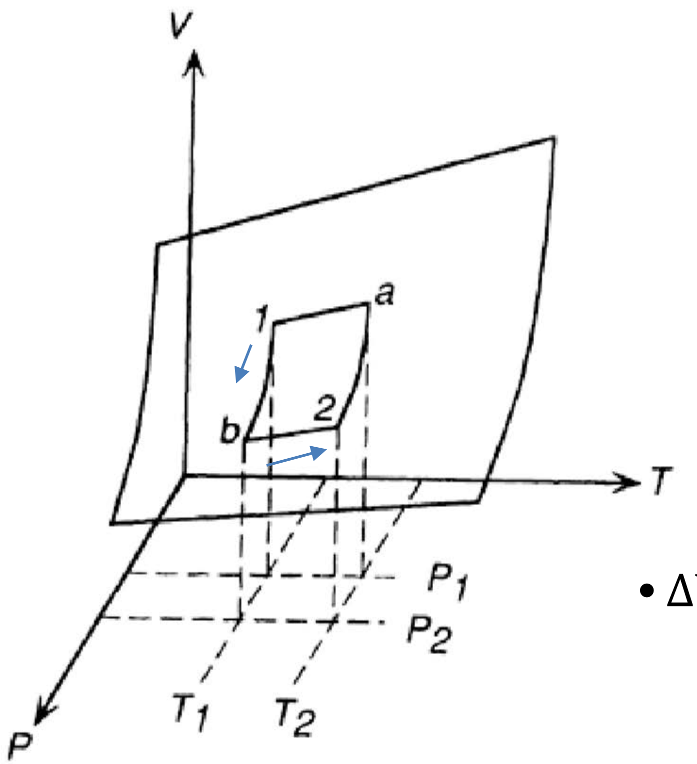

Figure 1.1 The equilibrium states of existence of a fixed quantity of gas in P-V-T space.

- $\Delta V = V_2 - V_1$
  $= (V_b - V_1) + (V_2 - V_b)$
- $(V_b - V_1) = \int_{P_1}^{P_2} \left(\frac{\partial V}{\partial T}\right)_{T_1} dP$
- $(V_2 - V_b) = \int_{T_1}^{T_2} \left(\frac{\partial V}{\partial T}\right)_{P_2} dP$
- $\Delta V = \int_{P_1}^{P_2} \left(\frac{\partial V}{\partial P}\right)_{T_1} dP + \int_{T_1}^{T_2} \left(\frac{\partial V}{\partial T}\right)_{P_2} dT$

(eq 1.3)

THE CONCEPT OF STATE

- $$\Delta \mathbf{V} = \int_{T_1}^{T_2} \left(\frac{\partial \mathbf{V}}{\partial \mathbf{T}}\right)_{P_1} \mathbf{dT} + \int_{P_1}^{P_2} \left(\frac{\partial \mathbf{V}}{\partial \mathbf{P}}\right)_{T_2} \mathbf{dP} \qquad \text{(eq 1.2)}$$

- $$\Delta \mathbf{V} = \int_{P_1}^{P_2} \left(\frac{\partial \mathbf{V}}{\partial \mathbf{P}}\right)_{T_1} \mathbf{dP} + \int_{T_1}^{T_2} \left(\frac{\partial \mathbf{V}}{\partial \mathbf{T}}\right)_{P_2} \mathbf{dT} \qquad \text{(eq 1.3)}$$

(eq 1.4)

- ΔV ($= V_2 - V_1$) depends only on $V_2 - V_1$, independent on the path taken by the gas between the states 1 & 2.

1.3 SIMPLE EQUILIBRIUM

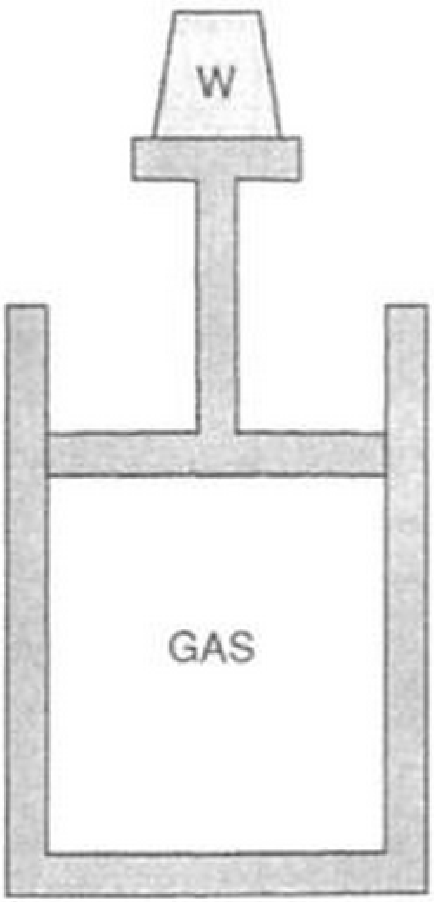

Figure 1.2 A quantity of gas contained in a cylinder by a piston.

-This is a fixed quantity of gas contained in a cylinder by a movable piston.
(at any given P & T, only one V =equil'm)

The system is at equilibrium when

(1) The pressure exerted by the gas on the piston equals the pressure exerted by the piston on the gas.
(2) The temperature of the gas is the same as the temperature of the surroundings.

1.4 THE EQ. OF STATE OF AN IDEAL GAS

Boyle's law (1660)

- **pressure-volume** relationship of a gas at **constant temperature**

$$\boxed{P \propto \frac{1}{V}} \Rightarrow \boxed{P_1 V_1 (T_1) = P_2 V_2 (T_1)}$$

P_0=standard pressure (1 atm)

T_0=standard temperature (273.15 degrees absolute)

$V(T,P)$=volume at temperature T and pressure P

Charles' law (1787)

- **Volume-temperature** relationship of a gas at **constant pressure**

$$\boxed{V \propto T} \Rightarrow \boxed{\frac{V(P_0, T_0)}{T_0} = \frac{V(P, T)}{T}}$$

P_0=standard pressure (1 atm)

T_0=standard temperature (273.15 degrees absolute)

$V(T,P)$=volume at temperature T and pressure P

Ideal gas

- In 1802 Joseph-Luis Gay-Lussac observed that the thermal coefficient of "permanent gas" was a constant.

- Later, people define Ideal gas as a gas which obeys Boyle's and Charles's laws exactly at all temperatures and pressures, and it has a value of $\alpha\ of\ \frac{1}{273.15}$, good at low pressure for gases with lower boiling points.

- The fractional decrease of volume at 0˚C leads to "the absolute 0 of temperature" at which the volume of the gas is 0.

Ideal gas

- Combination of Boyle's and Charles' law

$$\frac{(P_0 V_0)}{T_0} = \frac{PV}{T} = constant \qquad \text{(eq 1.5)}$$

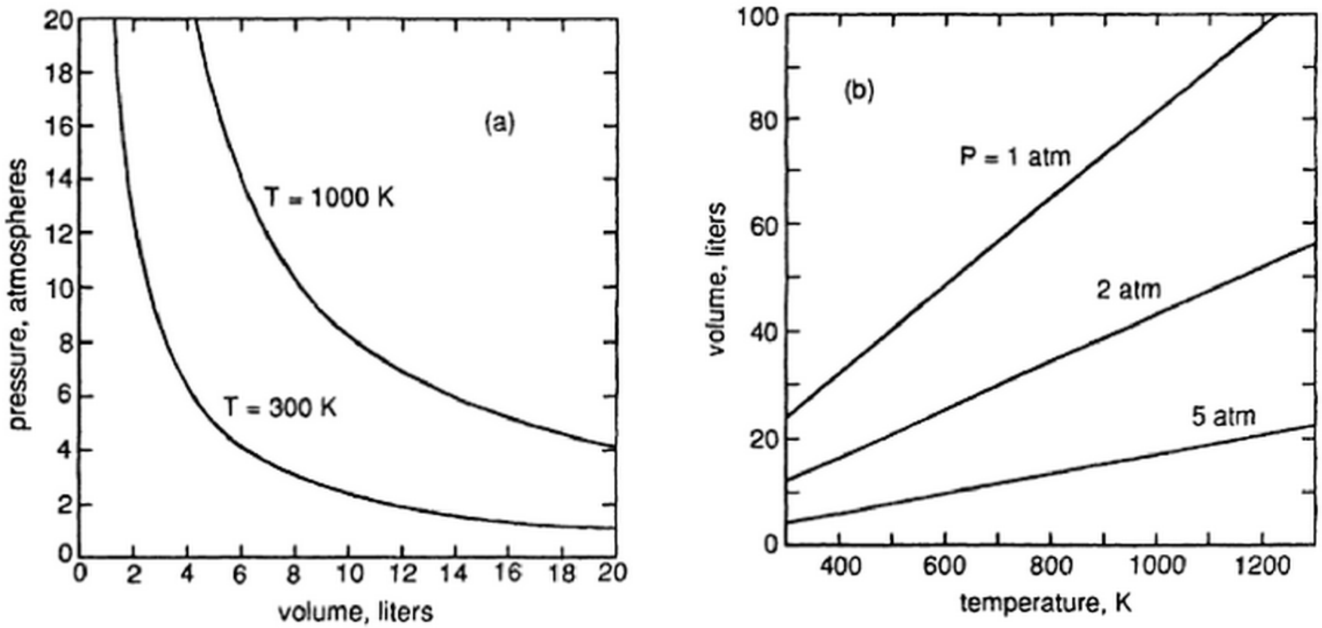

Figure 1.3 *(a)* The variations, with pressure, of the volume of 1 mole of ideal gas at 300 and 1000 K. *(b)* The variations, with temperature, of the volume of 1 mole of ideal gas at 1, 2, and 5 atm.

Gas constant

- Gas constant (R) was calculated at STP (0˚C, 1 atm) based on the Avogadro's hypothesis (the vol/g-mole of all ideal gases), and it is called a universal constant.

- This equation can thus be written as

$$PV = RT \qquad \text{(eq 1.6)}$$

and this equation is called the ideal gas law.

1.5 The units of energy and work

From Avogadro's hypothesis…

…The volume of 1 mole of ideal gas at 1 atm and 0 °C is 22.414L.

$$\frac{P_0 V_0}{T_0} = \text{constant} \quad = \mathbf{R}$$

$$= \frac{(1\ \text{atm})\ (22.4\ \text{L})}{(273.15\ \text{K})}$$

$$\mathbf{R} = 0.082057\ \text{L-atm/mol-K}$$

$$\mathbf{R} = 8.3144\ \text{J/mol-K}$$

1.6 Extensive and intensive properties

- Extensive properties have values which depend on the size of the system.

  Ex) Volume

- Intensive properties are independent of the size of the system

  Ex) Temperature, Pressure, volume/mass

- The values of extensive properties, expressed in per unit vol. or per unit mass, can be the characteristics of intensive properties.

  Ex) volume/mass

1.7 Phase diagrams and thermodynamic components

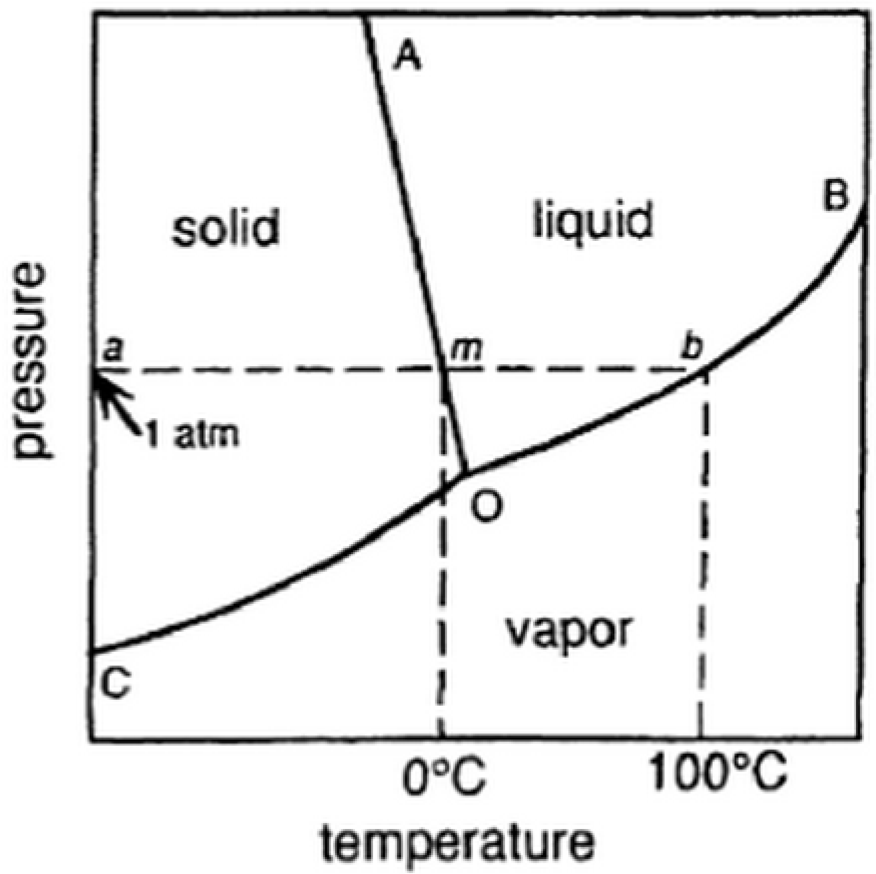

Figure 1.4 Schematic representation of part of the phase diagram for H_2O.

Phase diagrams and thermodynamic components

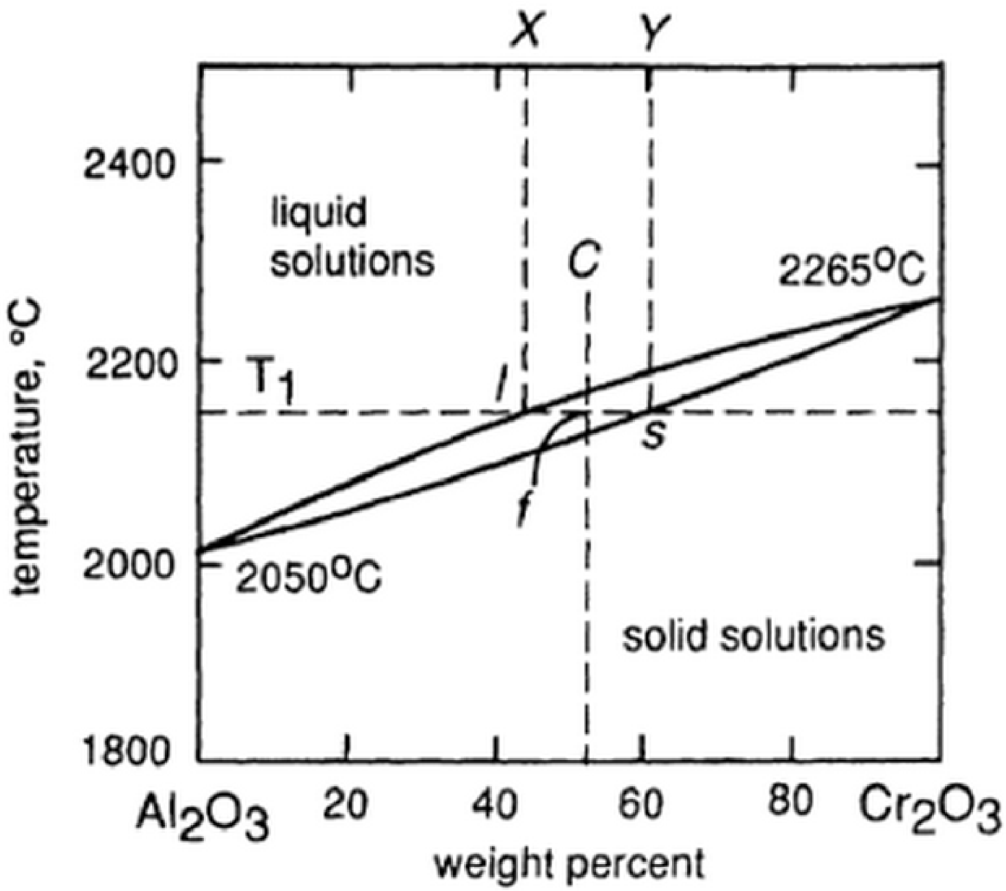

Figure 1.5 The phase diagram for the system Al_2O_3–Cr_2O_3.

Phase diagrams and thermodynamic components

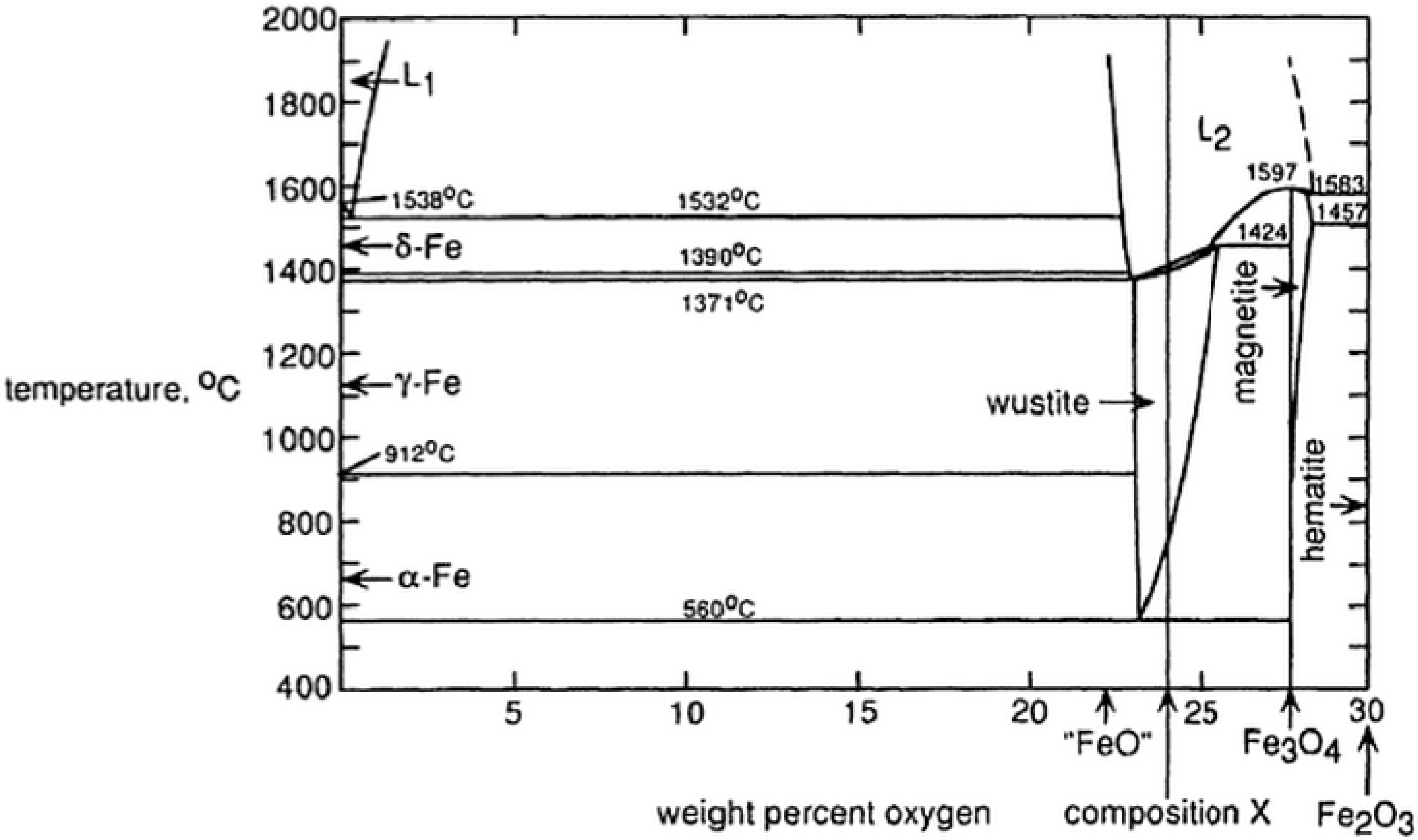

Figure 1.6 The phase diagram for the binary system Fe–O.