

2. EQUILIBRIUM RELATIONSHIPS

2.1 Introduction

On firing ceramic bodies solid state reactions take place. Typical of such reactions are the formation of mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) through the reaction between silica and alumina or the formation of anorthite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) in firing of ceramic wall tiles. Besides, the start and end of melting can be assessed by considering the equilibrium between the different phases. The study of such equilibria is of major importance for the following reasons:

- It represents a first approximation regarding the different phases present at any temperature.
- It can be used to obtain the relative amount of such phases. In case of liquid phase formation, an equilibrium study can predict the percent liquid formed and hence decide upon the maximum temperature to be maintained so as not to cause warping.
- If an undesirable phase turns out to be present, then it is possible to alter the initial composition or the firing conditions so as to avoid its formation.
- Sometimes, an increase in the amount of a certain phase can be either beneficial or detrimental to the properties of the fired body. This can be fixed by either altering the initial composition or firing temperature.

2.2 Thermodynamic considerations

2.2.1 The chemical potential

When an equilibrium state is reached between several phases then the sum of their chemical potentials is nil. By chemical potential is meant the ability of a system to shift from an equilibrium state to another. Thermodynamically, this is related to the definition of the Gibb's free energy in the following way:

$$dG = V.dP - S.dT + \sum_{i=1}^n \mu_i . dn_i \quad (2.1)$$

Where: μ_i is the chemical potential of the i^{th} species.

It turns out from this equation that:

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,P} \quad (2.2)$$

That is, the chemical potential of any phase is the variation of free energy of that phase when one mol of it is transferred to another phase at constant temperature and pressure.

It can be proved that the chemical potential is related to temperature for a solid phase through the relation:

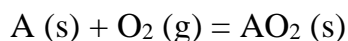
$$\mu_i = \mu_0 + R.T . \ln a_i \quad (2.3)$$

Where: a_i is the activity (or effective concentration) of the phase and μ_0 the chemical potential under standard conditions. For solids these conditions are a pure solid at the given temperature. For gases it is the equilibrium pressure at the given temperature. For ideal gases, the activity is equal to the partial pressure. For pure solid compounds, the activity = 1, while for gases, it is substituted by the partial pressure of the gas.

The equilibrium criterion from equation (2.1) hence takes the following form under constant pressure and temperature conditions:

$$\mu_1 \cdot dn_1 + \mu_2 \cdot dn_2 + \mu_3 \cdot dn_3 + \dots = 0 \quad (2.4)$$

As an example, consider the oxidation reaction:



Combining equations (2.3) and (2.4), we can write:

$$\mu_{0A} + \mu_{0O_2} + RT \ln p_{O_2} - \mu_{0AO_2} = 0$$

$$\mu_{0AO_2} - (\mu_{0A} + \mu_{0O_2}) = RT \ln p_{O_2}$$

The LHS is the standard free energy of reaction ΔG^0 so that we can write:

$$\Delta G^0 = RT \ln p_{O_2} \quad (2.5)$$

$$\text{Since } \Delta G^0 = \Delta H^0 - T \cdot \Delta S^0 \quad (2.6)$$

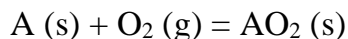
We get:

$$\Delta H^0 - T \cdot \Delta S^0 = RT \ln p_{O_2} \quad (2.7)$$

Here, ΔH^0 and ΔS^0 are the enthalpy and entropy changes of the reaction, respectively. We notice from Equation (2.6) that the standard free energy decreases with an increase in temperature. The slope of this relation is the standard entropy of reaction. Since both enthalpy and entropy are sensibly constant the plot is generally linear.

2.2.2 Free energy curves

Consider an oxidation reaction in the form:



Plots related to oxidation reactions are shown in Figure (2.1). These are known as Ellingham plots.

The outer right axis is the oxygen partial pressure axis. By joining a point corresponding to any partial pressure on that axis to the point labeled OK on the outer left axis, the intercept of that line with an Ellingham line gives the temperature at which the metal is in equilibrium with its oxide at that pressure. This is equivalent to solving an equation like (2.7). From equation (2.6), a decrease in entropy will produce a positive slope of the $\Delta G^0 - T$ line. As seen in the figure, all slopes are positive since the reaction of a solid with a gas to produce a solid is accompanied with a decrease in disorder, and hence in entropy.

For example, consider the oxidation of titanium. At an oxygen partial pressure of one atmosphere the two lines intersect at about 1300°C. This means that titanium will oxidize in pure oxygen at that temperature. If the oxygen partial pressure is decreased to 10^{-2} atm, then the oxidation temperature will increase to about 1600°C.

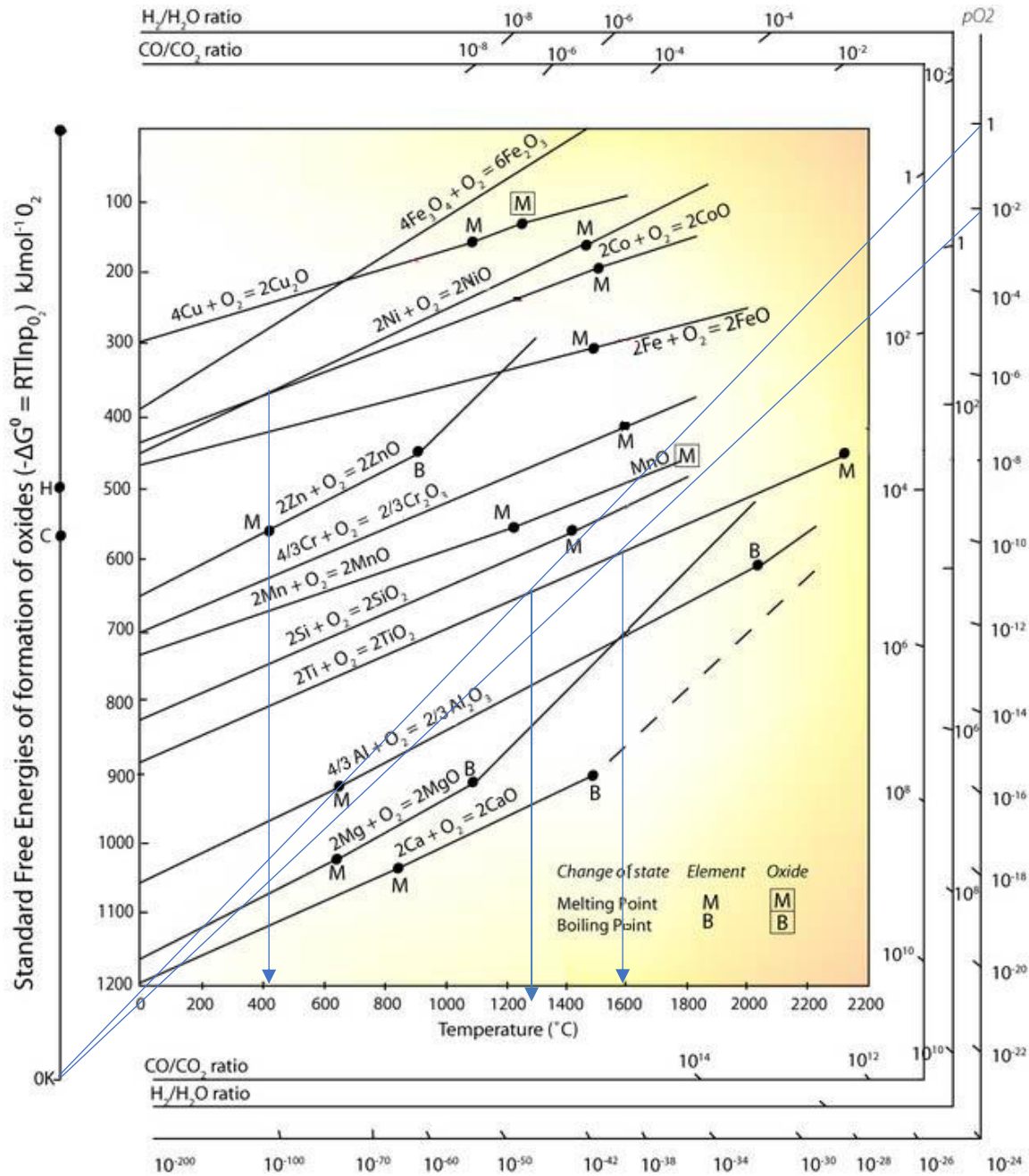


Fig (2.1) Ellingham plots

There are also corresponding scales for the equilibrium temperatures at different CO/CO_2 or $\text{H}_2\text{O}/\text{H}_2$ ratios.

The lower the position of a metal's line in the Ellingham diagram, the greater is the stability of its oxide. For example, the line for Al (oxidation of aluminum) is found to

be below that for Fe (formation of Fe_2O_3). This means that if the curves for two metals at a given temperature are compared, the metal with the lower free energy of oxidation on the diagram will reduce the oxide with the higher free energy of formation. For example, metallic aluminum can reduce iron oxide to metallic iron, the aluminum itself being oxidized to aluminum oxide.

Also consider the oxidation reactions of Co and Ni. Their free energy curves intersect at about 410°C . Below that temperature, the line corresponding to the oxidation of Ni is lower than that of Co. This means that NiO is more stable than CoO below that temperature. Hence Ni will reduce CoO below 400°C and oxidizes to NiO.

2.3 The Phase Rule

Consider a system where P phases are at equilibrium. Let the number of components in that system = C . In principle, there will be $P.C$ degrees of freedom for that system. Since temperature and pressure can also be varied then the initial number of degrees of freedom = $P.C + 2$.

Now, there are some restrictions in such systems: First, the sum of mol fractions of all components in each phase = 1. This means that we have P conditions corresponding to the P phases.

Also, considering that equilibrium prevails then the chemical potentials of any component (i) in all the P phases must be equal. That is:

$$\mu_i \text{ (in phase 1)} = \mu_i \text{ (in phase 2)} = \mu_i \text{ (in phase 3)} = \dots = \mu_i \text{ (in phase P)}$$

For each component there are $P - 1$ such restrictions. For the C components the number of restrictions is therefore: $C.(P - 1)$

The total number of restrictions is therefore $P + C.(P - 1) = C.P - C + P$

Hence the number of degrees of freedom = $P.C + 2 - (C.P - C + P)$ or:

$$F = C - P + 2 \quad (2.12)$$

This is the well-known phase rule.

If under certain conditions $F = 0$, this is known as an **invariant situation** where all conditions are fixed and any slight change in any of these conditions will shift the equilibrium to a new state.

2.3 One component systems

2.3.1 Application of the phase rule

If the system consists of one component, then the phase rule yields: $F = 1 - P + 2 \rightarrow F = 3 - P$.

Since the minimum number of phases is one, there will be at most 2 degrees of freedom, namely, temperature and pressure.

2.3.1 Types of transitions

When a material transforms from one phase to another, $F = 1$, meaning that at each pressure, there will correspond one single temperature. This results in classifying one – component transitions into two categories:

- Transition not accompanied by any appreciable change in volume: Like in melting or allotropic transformations.
- Transitions accompanied with a large change in volume: Like in vaporization and sublimation.

The general expression relating temperature to pressure is known as the **Clapeyron equation**:

$$\frac{dp}{dT} = \frac{\Delta H_t}{\Delta V \cdot T_t} \quad (2.8)$$

Where: ΔH_t is the enthalpy change accompanying the transition ($\text{J} \cdot \text{mol}^{-1}$)
 ΔV is the change in molar volume of the material ($\text{m}^3 \cdot \text{mol}^{-1}$)
 T_t is the transition temperature (K)

If there is no appreciable change in volume (as in melting), then $\Delta V \approx 0$, and the RHS of the above equation $\rightarrow \infty$, resulting in an almost vertical $p - T$ line. This means that any variation in pressure will hardly affect the transition temperature. Most solids slightly expand in volume on melting so that the line possesses a faint positive slope. Only in some rare cases, does the solid contract on melting as in water and bismuth, in which case the vertical line will be slightly deviated to the left, having a negative slope (Figure 2.2).

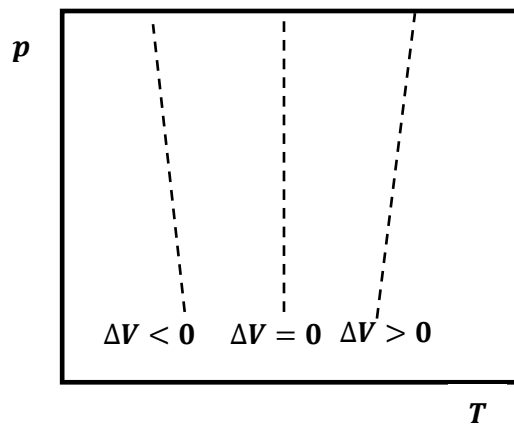


Fig 2.2: Different cases of volume change on melting

Consider now the case of vaporization of a liquid or a solid (sublimation). If the vapor formed is assumed to behave ideally, then we may write, for 1 g mole of vapor:

$$pV = RT$$

Also, in this case, the volume of solid can be neglected compared to that of the vapor, so that: $\Delta V \approx V_g$ and equation (2.8) can be rewritten as:

$$\frac{dp}{dT} = \frac{\Delta H_t}{V_g.T} = \frac{p.\Delta H_t}{RT^2}$$

This equation, known as the **Clausius – Clapeyron equation**, is best written as:

$$\frac{d \ln p}{dT} = \frac{\Delta H_t}{RT^2} \quad (2.9)$$

If the temperature range investigated is relatively narrow, then ΔH_t may be assumed constant, in which case this equation is integrated to yield:

$$\ln p = -\frac{\Delta H_t}{RT} + C \quad (2.10)$$

Equation (2.10) may be integrated between two temperature and pressure limits to yield:

$$\ln \frac{p_2}{p_1} = \frac{\Delta H_t}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (2.11)$$

Example 2.1

Tin melts at 505K and possesses a heat of melting = 7029 J.mol⁻¹. The density of solid tin = 7.28 g.cm⁻³ while that of liquid tin is 6.98 g.cm⁻³ and its atomic mass = 118.7. Estimate the change in its melting temperature when the pressure is raised from 1 to 100 atm.

Solution:

First, equation (2.8) can be rewritten to read:

$$\frac{\Delta p}{\Delta T} = \frac{\Delta H_t}{\Delta V.T_t}$$

$$\Delta p = (100 - 1) \times 1.0132 \times 10^5 = 1.003 \times 10^7 \text{ Pa}$$

$$\Delta H_t = 7029 \text{ J.mol}^{-1}$$

$$T_t = 505 \text{ K}$$

$$\text{Atomic volume of solid} = V_1 = \frac{118.7}{7.28} = 16.264 \text{ cm}^3.\text{mol}^{-1} \equiv 1.6264 \times 10^{-5} \text{ m}^3.\text{mol}^{-1}$$

$$\text{Atomic volume of liquid} = V_2 = \frac{118.7}{6.98} = 17 \text{ cm}^3.\text{mol}^{-1} \equiv 1.7 \times 10^{-5} \text{ m}^3.\text{mol}^{-1}$$

$$\Delta V = 0.736 \times 10^{-6} \text{ m}^3.\text{mol}^{-1} \quad \text{Substituting in equation (2.2):}$$

$$\frac{1.003 \times 10^7}{\Delta T} = \frac{7029}{0.736 \times 10^{-6} \times 505}$$

$$\text{Hence: } \Delta T = \mathbf{0.53 \text{ K}}$$

Example 2.2

The vapor pressure of PbO (s) is 10⁻⁵Pa at 475 °C. When the temperature is raised to 610 °C, the vapor pressure increases to 10⁻²Pa. evaluate the enthalpy of sublimation of PbO over that temperature range.

Solution:

Equation (2.11) is applied:

$$\ln \frac{10^{-2}}{10^{-5}} = \frac{\Delta H_t}{8.314} \left(\frac{1}{475+273} - \frac{1}{610+273} \right) \quad \text{We get: } \Delta H = 280980 \text{ J. mol}^{-1}$$

2.3.2 An example: The silica diagram

Figure (2.2) illustrates the $p - T$ diagram of silica. This oxide exhibits several allotropic forms: At low pressures, the stable room temperature form is trigonal α - quartz. This transforms to hexagonal β - quartz at temperatures varying from 570 to 1370°C, depending on the applied pressure. At pressures below 60MPa, this latter transforms to another hexagonal form: tridymite at temperatures ranging from 870°C at atmospheric pressure to 1400°C, as the applied pressure reaches 60MPa. This allotrope converts to a tetragonal form: cristobalite at temperatures ranging from 1390 to 1470°C, depending on the applied pressure. At low temperatures and at pressures ranging from 2.3GPa to 8.1GPa, the stable form is a monoclinic allotrope (coesite), while a tetragonal form, named stishovite, is the stable allotrope at high pressures. The melting point increases from 1720°C at atmospheric pressure to more than 2600°C under extremely high pressures. Table (2.1) summarizes the different allotropic forms.

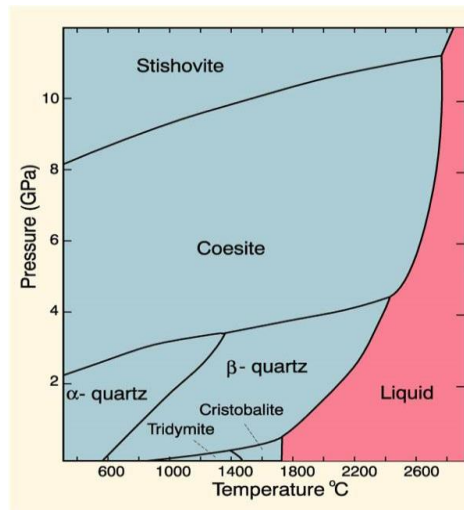


Fig 2.2: The phase diagram of SiO₂

Table 2.1: Crystal structure of silica allotropes

Allotrope	α - quartz	β - quartz	Tridymite	Cristobalite	Coesite	Stishovite
	Trigonal	Hexagonal	Hexagonal	Tetragonal	Monoclinic	Tetragonal
Structure						

We note that all allotropic transitions lines, except for the tridymite – cristobalite transition, are of positive slope, implying that the volume of the high temperature form is higher than that of the low temperature form. Also, the liquid volume is always higher than that of the solid, as evidenced by the positive slopes of the melting curves.

Also, there are five points where three phases are present in equilibrium. These are summarized in Table (2.2). under such conditions, $F = 1 - 3 + 2 = 0$. This means that such points can only occur at a definite combination of temperature and pressure. They are called **invariant points**.

Table 2.2: Invariant situations in the silica system

T°C	1390	1720	1370	2400	2660
p GPa	0.35	0.70	3.42	4.15	11.0
Phases	β-quartz – Tridymite – Cristobalite	β-quartz – Cristobalite – Liquid	α-quartz – β-quartz – Coesite	β-quartz – Coesite – Liquid	Stishovite – Coesite – Liquid

2.4 Two component systems

Binary phase diagrams reveal the equilibrium phases that will appear upon heating a mixture of two solids to melt. In most cases, pressure being maintained constant, will result in decreasing the number of degrees of freedom by 1, resulting in a modified rule: $F = C - P + 1$

The following cases represent some common types encountered in the ceramic field.

2.4.1 A and B form a complete series of solid solutions (Isomorphous systems)

In some rare cases, the two components are similar in chemical nature, in atomic size and in valence. In that case it is possible that the atoms (or ions) of one of the two compounds substitute the other by diffusion at all possible percentages. This situation while being common in metals is very rare in ceramics. One example is the system CoO – MgO shown in Fig (2.4). The melting points of the two oxides are 1930 and 2850°C respectively.

At low temperatures the two solids are totally soluble in each other and form one phase consisting of a solid solution (S.S.). Consider the composition 75% MgO (mol.). If this mixture is heated to about 3000°C, it will consist of one molten liquid phase. On cooling down, a solid phase will precipitate at about 2650°C consisting of a solid solution consisting mostly of MgO. On further cooling the amounts of solid increase until the liquid completely disappears at about 2300°C. The last liquid left will contain about 18% MgO.

The lower boundary between S.S. and the two-phase region is called **solidus** line which represents the locus of final freezing (or initial melting). On the other hand, the upper boundary curve between liquid and the two-phase region is called **liquidus** line. It represents the locus of initial freezing (or final melting). On following up the temperature behavior with time on cooling, the difference between the specific heats of solid solution and liquid will cause a break in the cooling curve. Nowhere on that

curve will the temperature remain constant since, according to the phase rule: $F = 2 - 2 + 1 = 1 \neq 0$. The temperature – time curve is called a **cooling curve**.

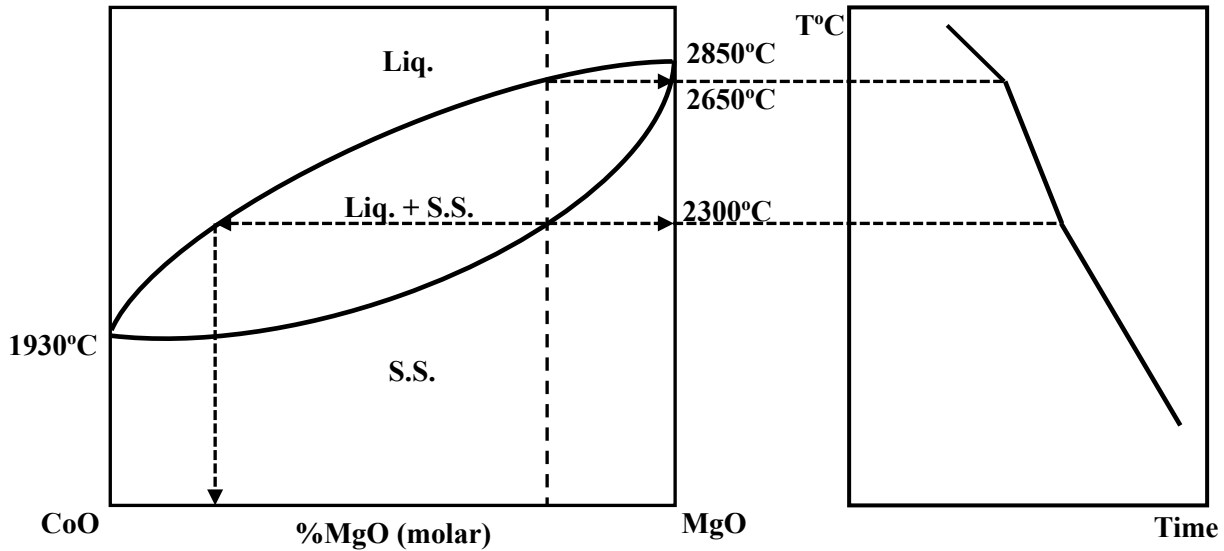


Fig (2.4) CoO – MgO system

Sometimes, it may happen that the solidus and liquidus curve touch at a point and exhibit either minimum or maximum melting temperature. For example, in Fig. (2.5), the liquidus and solidus lines of the system NaCl – LiCl exhibit a minimum melting temperature of 537°C. The relative amount of liquid and solid solution within the two-phase region may be determined using the “**lever arm principle**” which goes as follows: Consider the hypothetical system A – B in Fig (2.6), where the percentage B is expressed as **weight percent**.

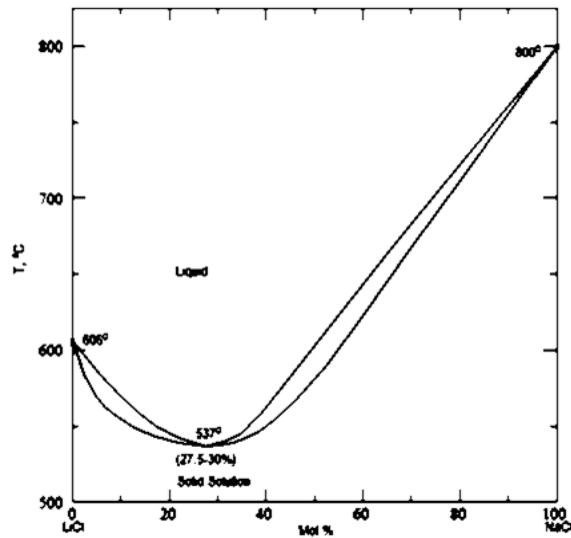


Fig (2.5) LiCl – NaCl system

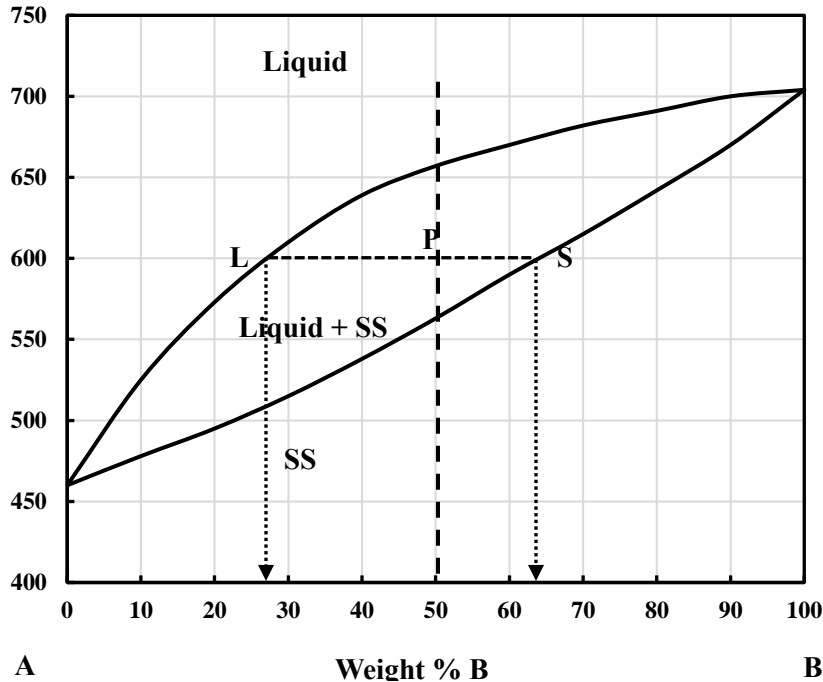


Fig (2.6) The lever arm principle

Let a melt of composition 50% B be cooled down. At 600°C, two phases coexist in equilibrium at point P: A liquid phase represented by point L, of composition 27% B and a solid solution phase represented by point S of composition 63% B. the isothermal line LS is termed **tie line**. The percentage liquid in the two-phase mixture is calculated from the rule:

$$\% \text{ Liquid} = \frac{PS}{LS} \times 100\% = \frac{63 - 50}{63 - 27} \times 100\% = 36.11\%$$

Whereas the percent solid solution will be obtained from $\frac{LP}{LS} \times 100\%$

Since this rule is deduced from a simple mass balance in the two-phase region, it cannot be applied when compositions are expressed as mole %.

2.4.2 Systems with solid immiscibility

In the latter case, it often happens that there is some immiscibility in the solid solution region. This means that the solid solution may split into two phases, each consisting of a solid solution. For example, in Fig (2.7) the solid solution formed between KI and NaI splits below 240°C into two S.S. At a temperature of 200°C, one of the two phases will consist of 40% NaI while the other contains 85%. Above 240°C, the two phases dissolve into one single phase. The maximum temperature of immiscibility is called the **consolute temperature** while the region below the solid boundary is termed **miscibility gap**.

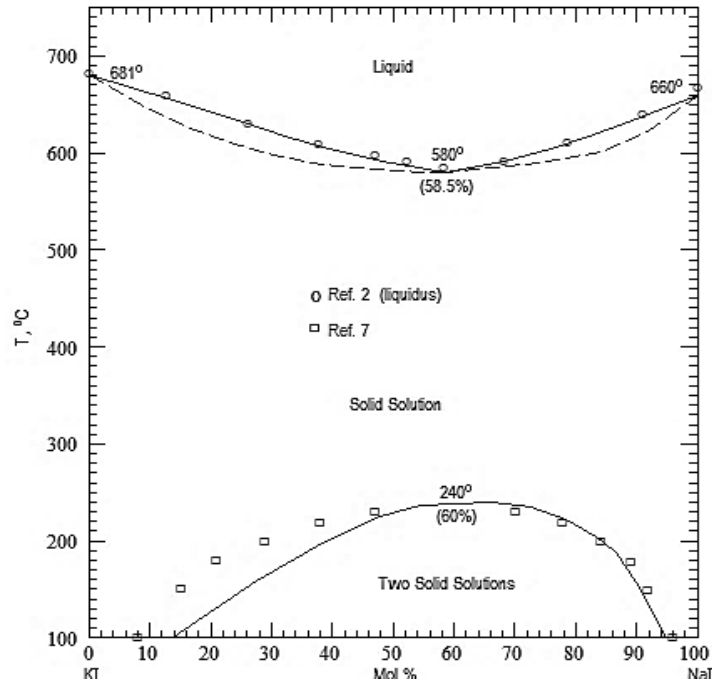


Fig (2.7) KI – NaI system

Eventually, the consolute temperature may exceed the solidus temperature at the consolute composition. This situation is pictured in Fig (2.8) and as the gap boundary crosses the solidus line, three phases will coexist at equilibrium: The two S.S. and liquid. This means that the number of degrees of freedom = 0 and the temperature must be constant in that situation. That is why, the phase diagram takes the form shown in Fig (2.9) for the CaO – MgO system where the liquidus line meets the isothermal solidus line at one point of minimum melting point known as the **eutectic point**.

A schematic diagram is shown in Fig (2.10) to detail that type of diagram. We consider the cooling curves of three compositions X, Y and Z.

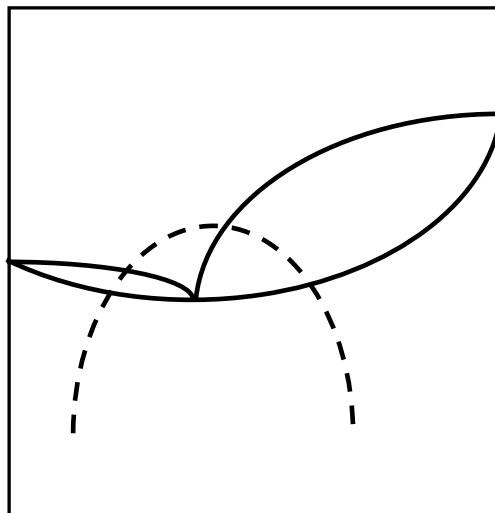


Fig (2.8) Miscibility gap interfering with solidus line

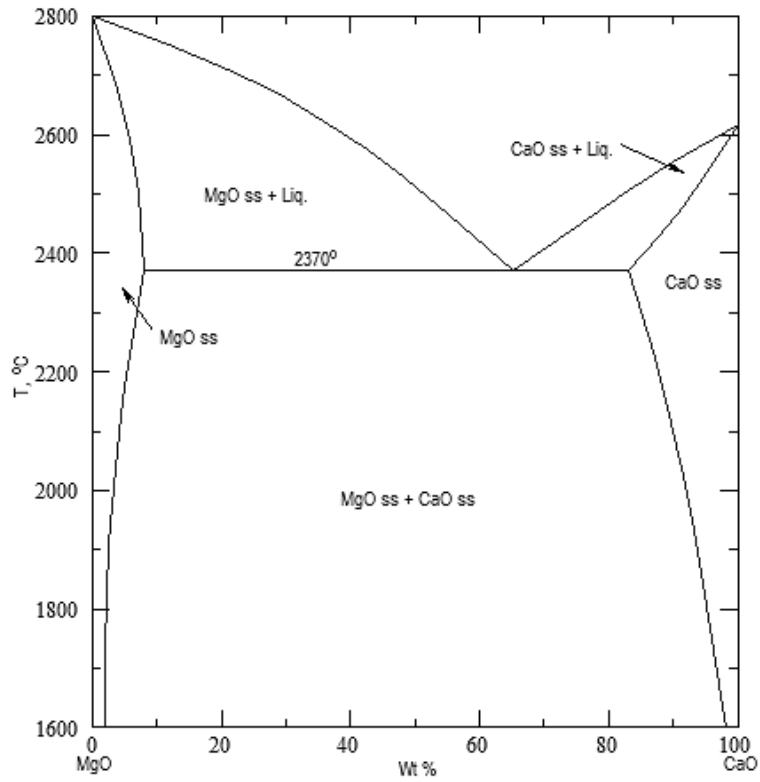


Fig (2.9) The MgO – CaO system

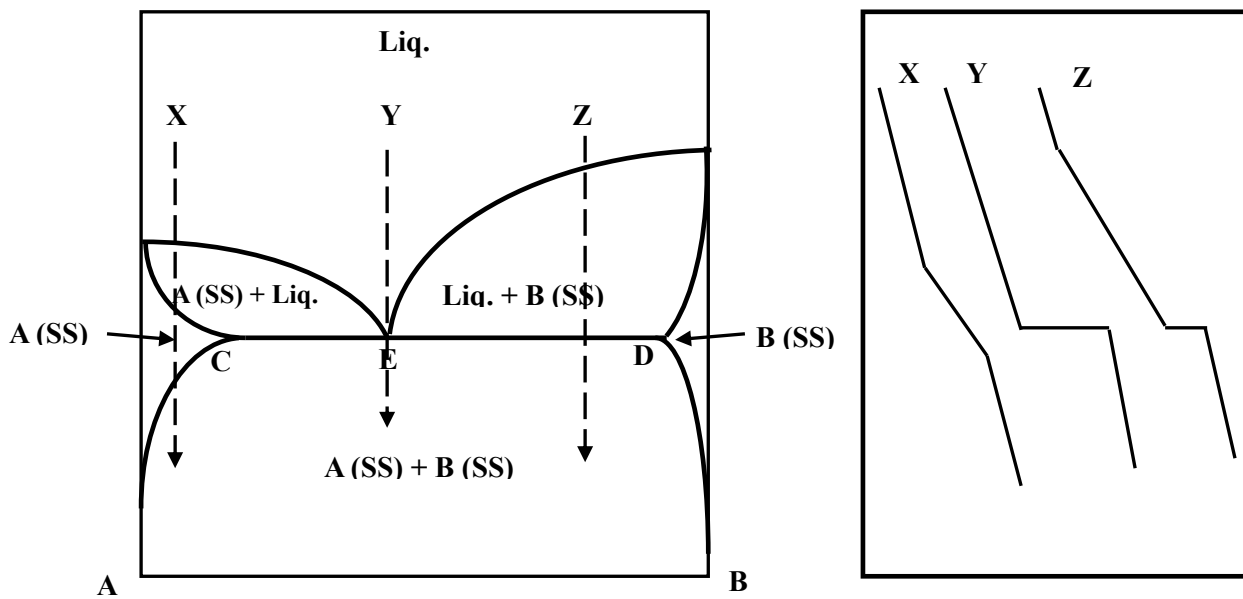
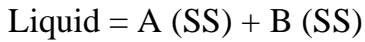


Fig (2.10) Formation of a eutectic with partial solid solubility

Consider a mixture Y of composition identical to that of the eutectic. Freezing occurs on cooling to that temperature as the following reaction takes place (Eutectic reaction):



This reaction takes place isothermally as $F = 2 - 3 + 1 = 0$ (Invariant point) and the temperature – time cooling curve displays an isothermal arrest. Below the eutectic temperature, the two solid solutions phases remain.

At the left and right corners of the diagram there exists two regions of solid solutions whereby A (SS) consists of A dissolving small amounts of B whereas B (SS) consists of B dissolving small amounts of A. the maximum solubility of B in A and A in B occur at points C and D respectively. The corresponding solid solubility curves extending from the eutectic temperature down to room temperature are called the **solvus lines**. Any melt of percent B less than that corresponding to point C or above that corresponding to point D will not undergo the eutectic reaction on cooling. Consider composition X: As its composition vertical line crosses the liquidus curve, A (SS) precipitates the amount of which increases on expense of the liquid on cooling. When the vertical line crosses the solidus curve, all liquid disappears to be left with A (SS). On further cooling and as the vertical line crosses the solvus line and B (SS) starts forming so that the two solid phases A(SS) and B (SS) are left at room temperature. On the cooling curve of composition X, all crossings are accompanied with a break in the cooling curve following changes occurring in heat capacities.

Finally, any composition, like Z, lying between points C and D will undergo the eutectic reaction and its cooling curve will display an isothermal arrest as its vertical composition line crosses the eutectic line.

In many cases, the two components A and B do not exhibit any solid solubility. In that case, the phase diagram simplifies to that shown in Fig (2.11) representing the equilibrium phases in the system NaF – PbF₂.

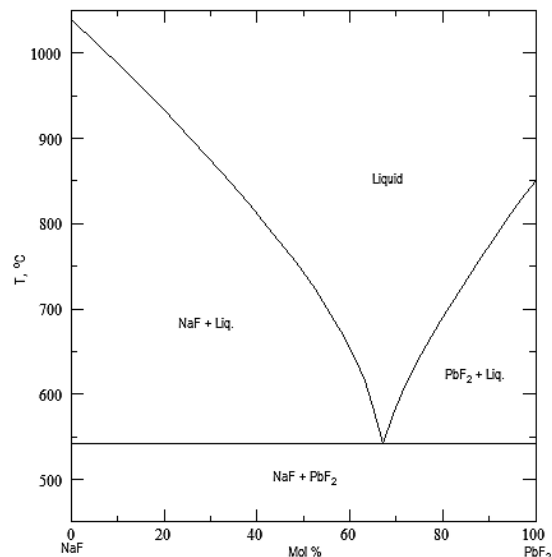
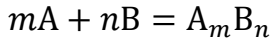


Fig (2.11) The NaF – PbF₂ system

2.4.3 Formation of an intermediate compound

More often than not, the two end members of a binary system can react to form an intermediate compound as described by the generalized reaction:



Such compounds are generally classified into two categories.

(a) Congruently melting intermediate compounds

An intermediate compound is said to be “congruently melting” if the composition of the liquid formed upon melting is like the composition of the solid compound. In that case the diagram shows as two simple eutectic diagrams “welded” together at the composition of the compound. Fig (2.12) illustrates the MnO – Al₂O₃ diagram where an intermediate compound MnO.Al₂O₃ is formed. Two different eutectic points appear: The first between MnO and MnO.Al₂O₃ at 1520°C and 23% Al₂O₃ and the second between MnO.Al₂O₃ and Al₂O₃ at 1770°C and 77% Al₂O₃. Therefore, depending on the initial composition of the melt, one of the following two eutectic reactions will take place on cooling:

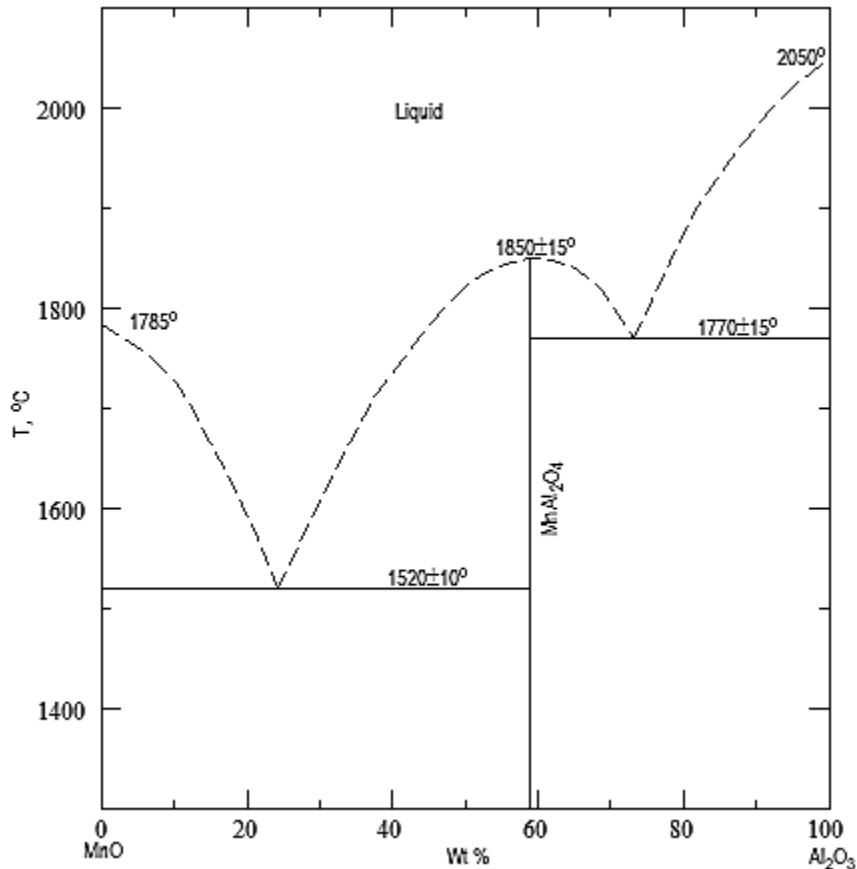
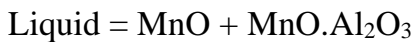


Fig (2.12) The MnO – Al₂O₃ system

It is more common, however, that the intermediate compound formed may dissolve one or both end members of the system. Consider, for instance, the system MgO – Al₂O₃ (Fig 2.13). In that system, a congruently melting compound MgO·Al₂O₃ is formed. Its composition is not fixed at a molar ratio MgO:Al₂O₃ = 1:1 (Corresponding to about 71% Al₂O₃). Instead, its composition extends over a range starting from about 69% alumina to about 92% alumina. This is an example of a **non – stoichiometric compound**. In that case, the compound (Known as spinel type) can dissolve an appreciable amount of Al₂O₃ (Expressed as corundum) in solid state, while the solubility of MgO (Periclase) in that compound is practically nil.

It is more common, however, that the intermediate non – stoichiometric compound dissolves both end members of the diagram. A typical example is shown in the system SiO₂ – Al₂O₃ which will be discussed later.

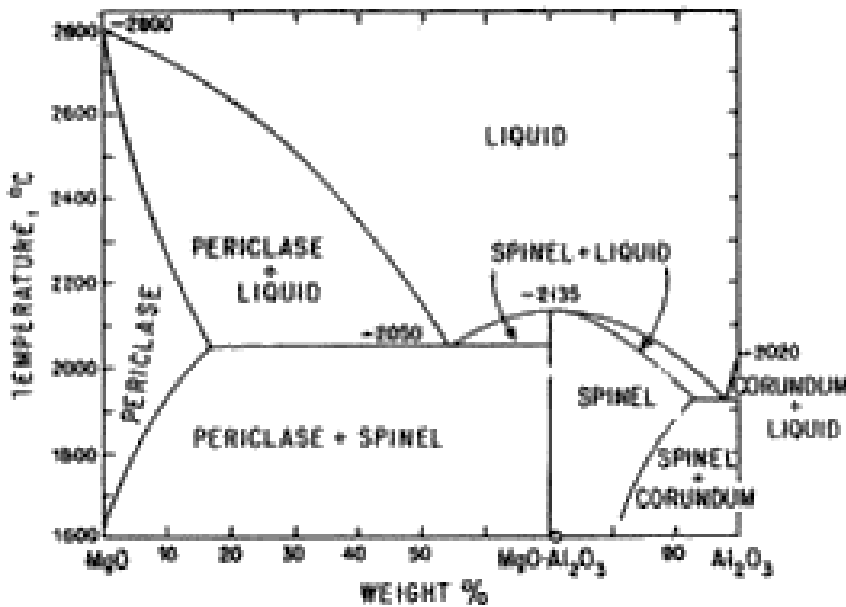
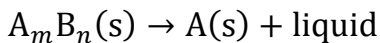


Fig (2.13) The phase diagram MgO – Al₂O₃

It is also common that more than one intermediate compound may form between the end members as will be discussed in a coming section.

(b) Incongruently melting intermediate compounds

It may happen that the intermediate compound formed dissociates while melting to another compound such that a reaction can take place such as, for example:



This situation is illustrated in Fig (2.14) where a compound $A_m B_n$ in the hypothetical system A – B is formed. This compound melts at a temperature T_p , known as the **peritectic temperature**. The liquid formed on melting contains about 40% B. This is called a **peritectic point** and involves an isothermal arrest on the cooling curve diagram (Composition X) since three phases co-exist at equilibrium.

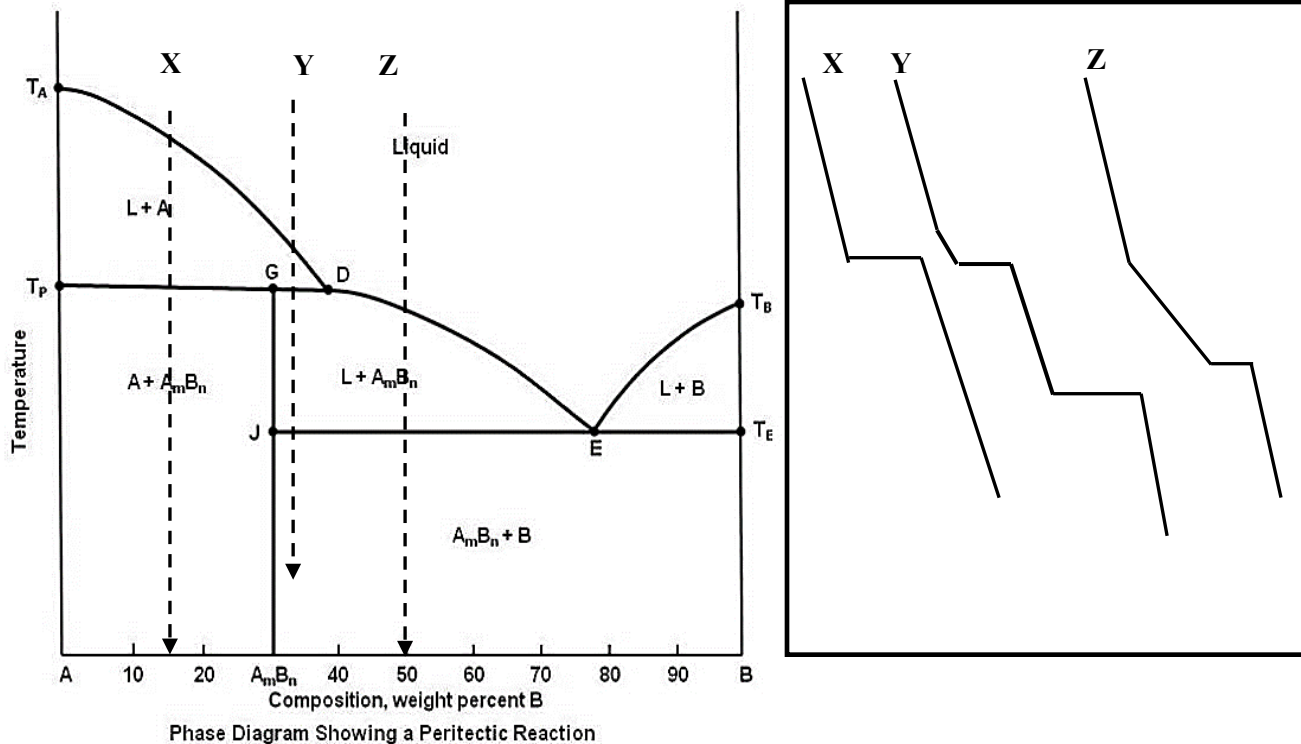
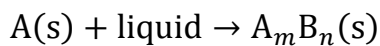
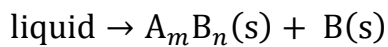


Fig (2.14) Formation of a peritectic melting compound

On the other hand, a melt of composition Y will go on cooling, through two invariant situations accompanied by isothermal arrests: The peritectic reaction at T_p accompanied with the complete disappearance of the A solid phase taking the form:



On further cooling and as the eutectic temperature T_e is reached, another isothermal invariant situation appears as the following eutectic reaction takes place accompanied with total disappearance of the liquid phase:



If the intermediate compound is non – stoichiometric, then it can dissolve either A or B or even both. A typical example is the $ZrO_2 - TiO_2$ system shown in Fig. (2.15) where the intermediate incongruently melting compound $ZrTiO_4$ ($ZrO_2 \cdot TiO_2$) dissolves both oxides. Here, the dissolution is mutual as both TiO_2 and ZrO_2 exist as solid solutions. The following peritectic reaction occurs at $1820^\circ C$ and the peritectic point composition is about 55% TiO_2 (molar).



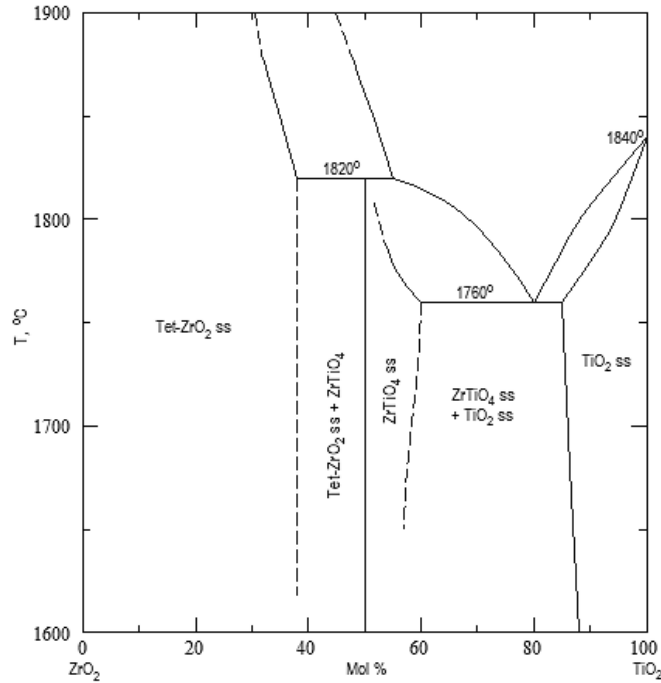


Fig (2.15) The ZrO₂ – TiO₂ system

Finally, it often happens that the intermediate incongruently melting compound can form a complete series of solid solutions with one of the end members. In that case this solid solution is considered to melt peritectically. This situation is shown in Fig (2.16) in the FeO – MnO diagram where the FeO rich solid solution melts incongruently at 1430°C splitting into MnO solid solution and liquid. This situation is however more common in metals than in ceramics.

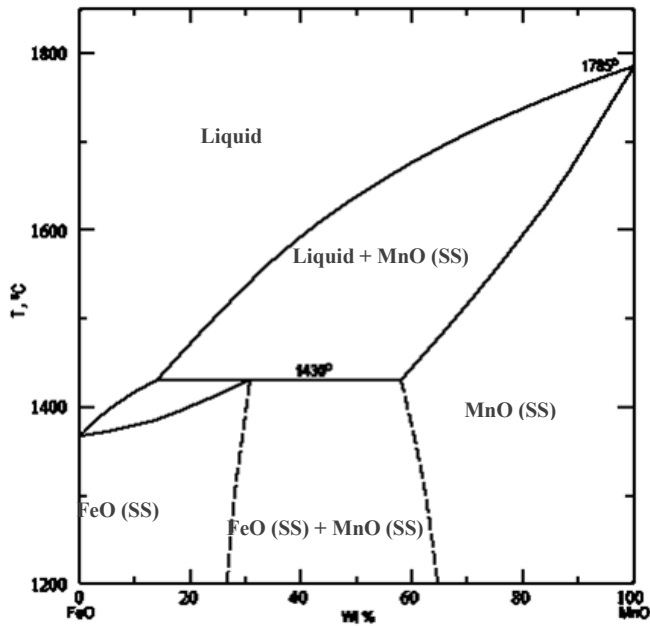


Fig (2.16) The FeO – MnO system (In air)

2.4.4 Formation of an immiscibility gap in the liquid phase

In some cases, particularly in some oxide systems of the type $\text{MO}_2 - \text{NO}$ on the high MO_2 side, as a melt is cooled it splits into two immiscible liquids. In the hypothetical figure (Fig 2.17), as a composition X is melted and cooled, the single-phase liquid splits

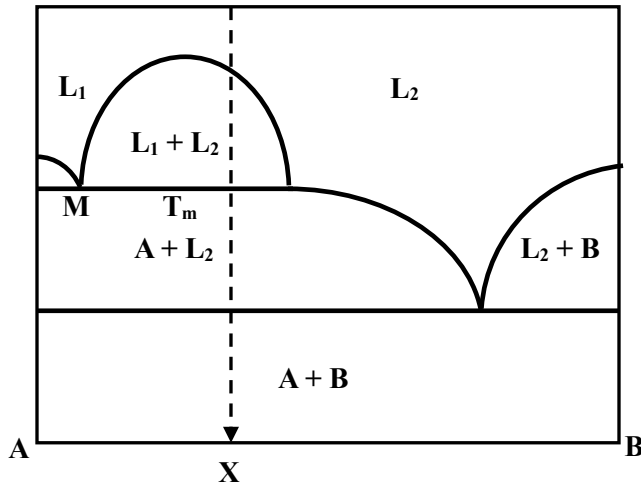
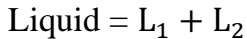


Fig (2.17) Formation of a monotectic

into two liquids: liquid rich in A (L_1) and another liquid poorer in A (L_2). A miscibility gap is formed defining an invariant situation for all compositions lying within the range of the gap. M is termed **monotectic point** and T_m , monotectic temperature. The **monotectic reaction** is:



As will be explained later, the presence of a monotectic situation plays an important role in the refractory industry.

2.4.5 Sub-solidus reactions

Some intermediate compounds may be stable over a certain temperature range such that they decompose to two solids either above or below a certain temperature. This type of decomposition is termed sub-solidus since it doesn't involve the formation of any liquid phase. In the following are explained the main types of invariant situations occurring in the solid state.

(a) The Eutectoid reaction

Consider a compound A_mB_n that is only stable above a certain temperature T_e where the following decomposition reaction takes place:

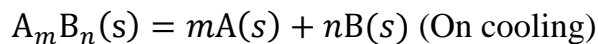


Fig (2.18) illustrates that invariant situation which is known as a **eutectoid reaction**.

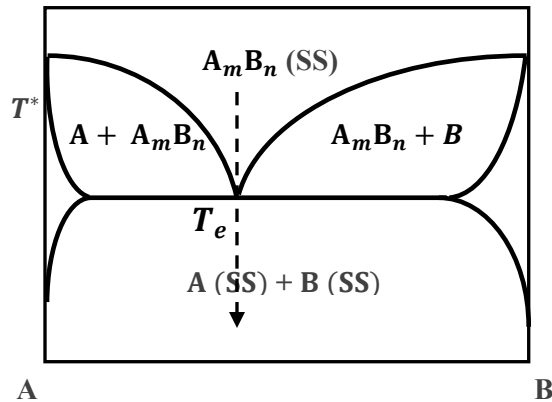


Fig (2.18) The eutectoid reaction

(a) The Peritectoid reaction

Consider now that the compound $A_m B_n$ is only stable below a certain temperature T_p where the following decomposition reaction takes place:

This situation defines a new invariant point known as the **peritectoid point**.



Fig (2.19) illustrates a peritectoid situation.

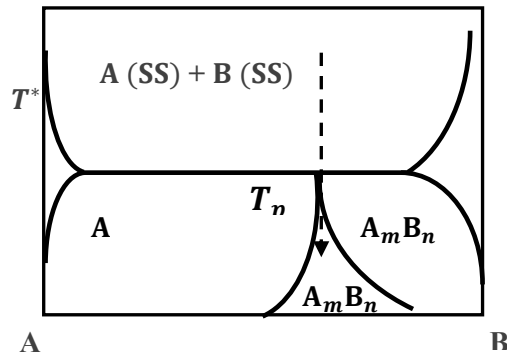


Fig (2.19) The peritectoid reaction

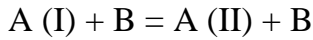
2.4.6 Allotropic transitions

In the ceramic industry, some compounds like silica (SiO_2) and zirconia (ZrO_2) can exist in more than one allotropic form with different crystal structure. The allotropic transitions occurring on either firing or cooling the products containing such compounds are usually associated with dimensional changes that can cause problems in operation.

For example, silica can exist in three main allotropic forms under atmospheric conditions. These undergo irreversible slow transformations in the following way:

Quartz → tridymite → Cristobalite → SiO₂ (liq.)

In a two components system A – B where such an allotropic transition takes place for the component A, the reaction will take the form:



At the transition temperature, there will exist three phases and $F = 0$ so that the allotropic transition will take place at the same temperature at which it occurs for pure A.

If, however, A forms a solid solution with B, the situation becomes more complicated since the transition will involve two phases only: S.S. (A I in B) and S.S. (A II in B). Therefore, the transition temperature will not remain constant and one of two situations will occur depending on whether the presence of B in solid solution with A will decrease or increase the transition temperature. This way, either a eutectoid or peritectoid point will be formed as illustrated in Fig (2.20)

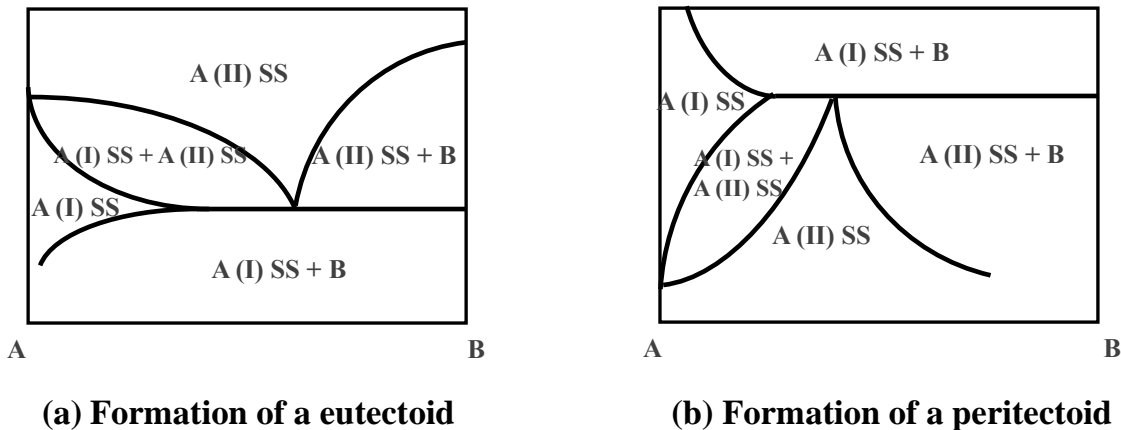


Fig (2.20) Allotropic transitions in solid solutions

2.4.7 Complex diagrams

Many phase diagrams in the ceramic field are more complex than the above-mentioned cases. This is since they are complicated by the presence of more than one intermediate compound or large regions of solid solutions or allotropic transitions or a combination of all these features. In the following are some examples:

(a) The CaO – TiO₂ system

This system is illustrated in Fig (2.21) and displays the following features:

- The melting point of TiO₂ = 1830°C while that of CaO is not shown on figure. Its value is about 2570°C.
- There are three intermediate compounds in that system:
 - CaO.TiO₂ (CaTiO₃ or CT) that melts congruently at 1960°C.
 - 5CaO.4TiO₂ (Ca₅Ti₄O₁₃ or C₅T₄) that melts incongruently at 1840°C dissociating to CaO.TiO₂ and a liquid containing 49% TiO₂.

- $3\text{CaO} \cdot 2\text{TiO}_2$ ($\text{Ca}_3\text{Ti}_2\text{O}_7$ or C_3T_2) that melts incongruently at 1750°C dissociating to $5\text{CaO} \cdot 4\text{TiO}_2$ and a liquid containing 45% TiO_2 .

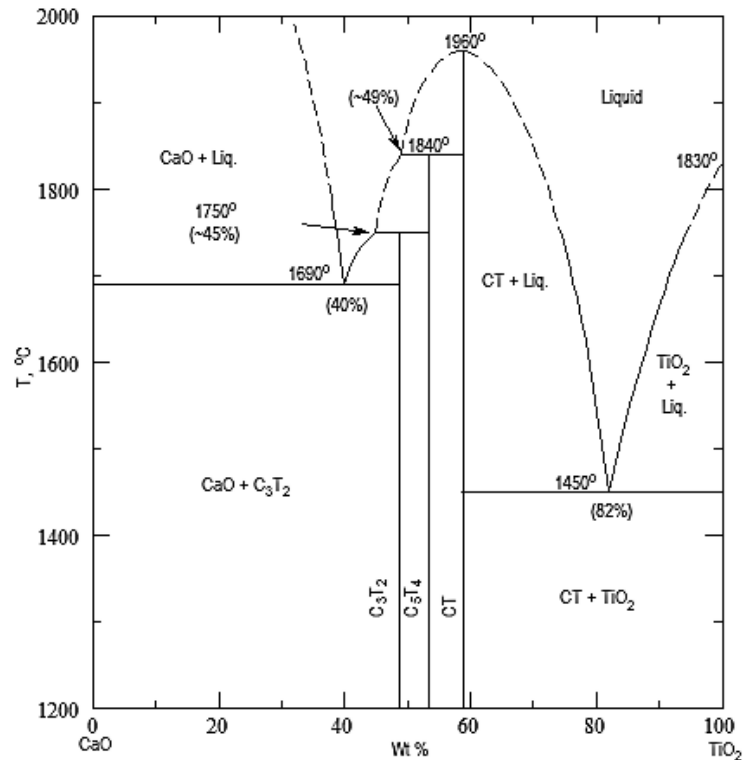


Fig (2.22) The CaO – TiO₂ system

- There are four invariant situations associated with the following reactions:
 - A eutectic is formed between TiO_2 and $\text{CaO} \cdot \text{TiO}_2$ at 1450°C and 82% TiO_2 according to the reaction: $\text{Liquid} = \text{TiO}_2 + \text{CaO} \cdot \text{TiO}_2$
 - A peritectic point exists at 1840°C and 49% TiO_2 according to the reaction: $\text{Liquid} + \text{CaO} \cdot \text{TiO}_2 = 5\text{CaO} \cdot 4\text{TiO}_2$
 - A peritectic point exists at 1750°C and 45% TiO_2 according to the reaction: $\text{Liquid} + 5\text{CaO} \cdot 4\text{TiO}_2 = 3\text{CaO} \cdot 2\text{TiO}_2$.
 - A eutectic is formed between CaO and $3\text{CaO} \cdot 2\text{TiO}_2$ at 1690°C and 40% TiO_2 according to the reaction: $\text{Liquid} = \text{CaO} + 3\text{CaO} \cdot 2\text{TiO}_2$

(b) The ZrO₂ – Y₂O₃ system

This system is displayed in Fig (2.23) and shows extensive solid solution formation. It possesses the following features:

- The melting point of ZrO_2 is 2715°C while that of Y_2O_3 ($\text{YO}_{1.5}$) is 2420°C .
- ZrO_2 exists in two main allotropic forms: Monoclinic (Mon.) and tetragonal (Tet.). The transition from the low monoclinic to the high tetragonal form occurs for the pure oxide at 1170°C . However, owing to the formation of a solid solution, a eutectoid is formed at 560°C that lowers the transition temperature according to the reaction: $\text{ZrO}_2 (\text{Tet.}) = \text{ZrO}_2 (\text{Mon.}) + \text{Cubic S.S.}$

- Due to the presence of Y_2O_3 , ZrO_2 forms an extensive solid solution with Y_2O_3 extending to 69% Y_2O_3 (molar). The tetragonal form of ZrO_2 converts to the cubic form at 2235°C for the pure compound. The transition temperature decreases to about 1900°C as the percent Y_2O_3 reaches 12.5% (molar). When the percent Y_2O_3 exceeds that value, ZrO_2 can only exist in cubic solid solution.
- Y_2O_3 forms a solid solution above 87% which melts incongruently at 2480°C according to the peritectic reaction: Y_2O_3 (S.S.) = cubic S.S. + Liquid (90% Y_2O_3)

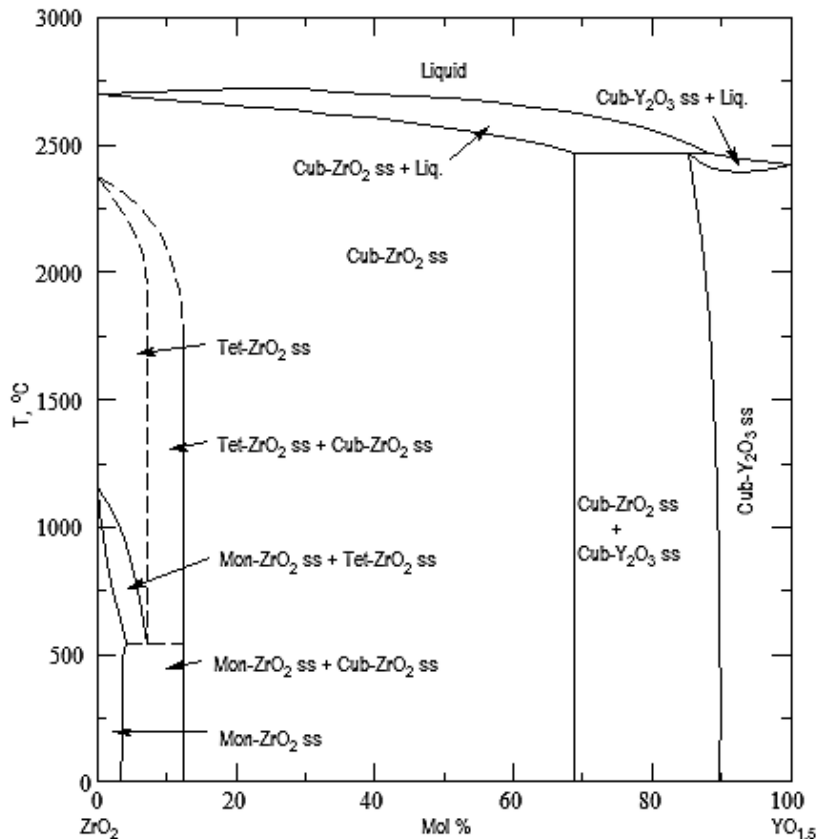


Fig (2.23) The $ZrO_2 - Y_2O_3$ system

2.4.8 Application to the ceramic industry

(a) The system $Al_2O_3 - SiO_2$

This system shown in Fig (2.24) is of major importance in understanding the reactions occurring on firing ceramic bodies based on clays and in assessing the properties of the so – called acid refractories.

The two end members of this diagram, silica and alumina melt at 1710°C and 2025°C respectively. There exists one equilibrium non – stoichiometric intermediate compound between the two end members: Mullite ($3.Al_2O_3.2SiO_2$) that melts congruently at about 1850°C. This compound forms a eutectic with silica at 1590°C and 5% alumina and with alumina at 1830°C and 78% alumina.

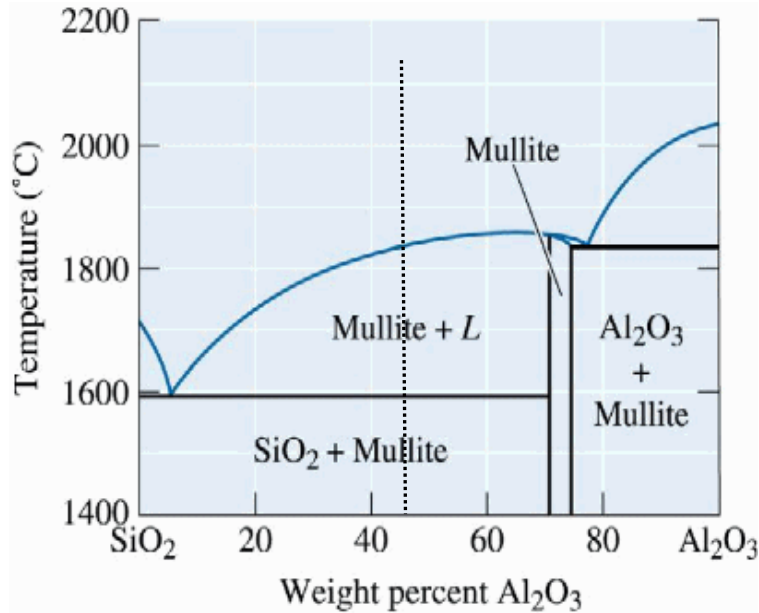


Fig (2.24) Phase diagram SiO₂– Al₂O₃

Kaolin clays widely used in ceramic industries usually contain from 35 to 42% alumina. In theory the alumina content of a kaolinite type clay should be about 45%. The dashed line in Fig (2.8) shows such composition. The prevailing phases at sufficiently high temperatures (Though below 1600°C) are mullite + silica. As the eutectic reaction occurs at 1590°C, silica totally melts while part of mullite remains. This situation persists as temperature is raised with an increase in the amount of liquid phase until total melting takes place at about 1820°C. The phases at equilibrium upon starting of melting are silica + mullite + liquid. Just above the initial melting point there exists a liquid of 5% alumina and a solid containing about 72% alumina. Considering that the initial composition of clay is 45% alumina then the percent liquid present just above melting is obtained by the lever arm principle as:

$$\frac{70 - 45}{70 - 5} \times 100\% \approx 38\%$$

Owing to the high viscosity of the liquid melt formed this percentage can still keep the fired body without warping. A rise in temperature will increase the amount of liquid formed and hence the possibility of warping.

On the other hand, it is clear from this diagram that an increase in the amount of alumina has the effect to generally increase the final melting temperature starting from a composition of 5% alumina. That is why refractory bricks and shapes manufactured from clays must have high alumina content. This is done in practice by adding bauxite (an alumina ore) to clay. High alumina refractories contain more than 80% alumina and will therefore withstand temperatures exceeding 1600°C on service.

The following table shows the different types of alumino – silicate refractories and their industrial uses.

Table 2.1 Types and uses of alumino – silicate refractory bricks

Type of brick	% Al ₂ O ₃	Uses
Fire clay	45%	Blast furnace stove, Incinerators, Roofs of electric furnaces, Enameling furnaces.
Sillimanite	60%	Glass tank ports, Oil fired boiler walls, air heaters, Rotary cement kiln, Lime kilns, Various metallurgical furnaces.
Mullite	70 %	Steel ladles, Rotary cement kiln, Lime kilns, Electric furnace roofs,
High Alumina	80%	Burning zone in cement kilns, Aluminum arc furnace, Electric furnace roofs.

(b) The system Na₂O – SiO₂

The following figure shows the high silica region of this diagram. This is the region of industrial interest in refractory, glass and ceramic industries. We will confine the following discussion to applications in refractory industries.

Silica exists in three main allotropic forms: Quartz, tridymite and cristobalite. As it passes from one form to another with a rise in temperature, its volume expands. This is the basis of the use of refractory silica bricks in the arch of glass tank furnaces. On service such bricks will tend to expand and impart more strength to the arch. In the glass industry the raw mix consists of limestone, quartz and soda ash. At the high temperature prevailing there is a high content of sodium in the vapor phase so that attack of the silica bricks roof is unavoidable.

The phase diagram in Fig (2.25) shows that a low melting compound (Na₂Si₂O₅) is formed that melts congruently at 865°C. This compound forms a eutectic with silica at 790°C. The liquidus curve sharply drops from 1710°C to 790°C as the percent soda increases.

The percent sodium oxide in contact with the silica roof does not usually exceed 3%. This composition is shown as dotted line in the figure. As the temperature exceeds the eutectic temperature (795°C) a viscous liquid is formed at a percentage ≈ 10%. This level does not cause any harm to the brick since its extremely high viscosity keeps it adhering to the brick. Warping will not occur before the percent liquid exceeds 30%. This takes place at about 1560°C which means that any overheating inside the furnace will cause refractory failure.

This situation can also present itself in another situation if the brick contains soda impurities at levels exceeding 3%. On service warping can take place at relatively low temperatures. That is why standards do not allow the presence of more than 1% sodium in their composition.

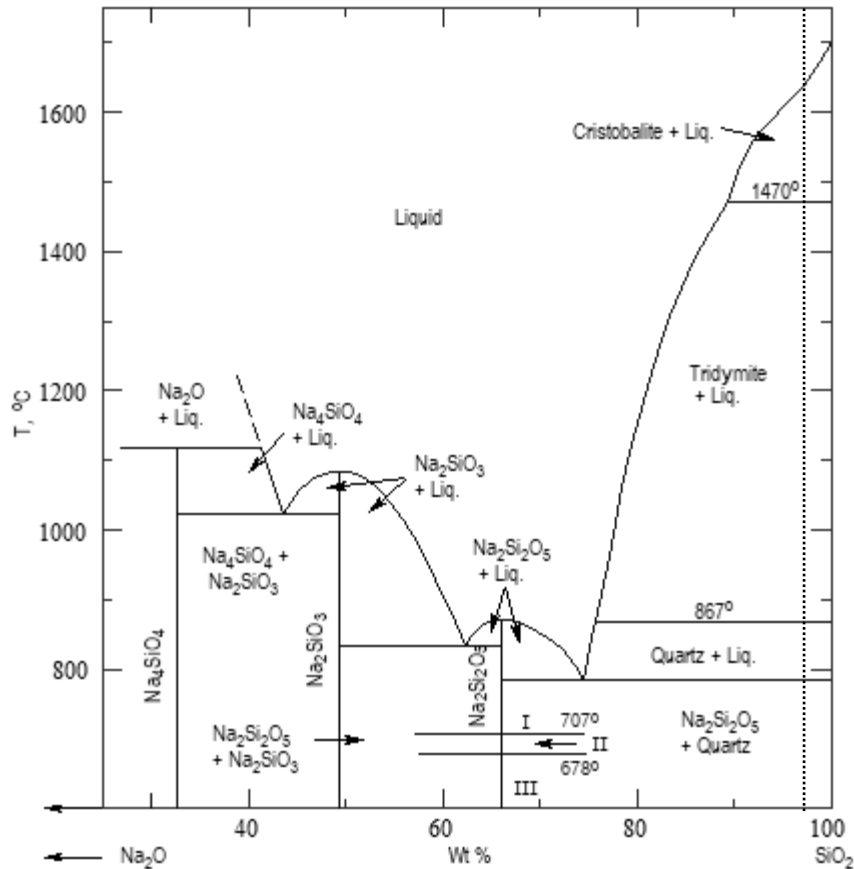


Fig (2.25) The system SiO₂ – Na₂O

(c) The system CaO – SiO₂

This system shown in Fig (2.26) is also of use in the manufacture of silica bricks. Generally, the transformation of quartz to cristobalite is accompanied by an increase in volume. This transformation should take place during the manufacture of silica bricks and not on service since in this latter case expansion of built – in bricks will cause refractory wall failure.

Unfortunately, such a transformation is extremely slow and must be accelerated to proceed at a reasonable rate. This is done by using a catalyst known as “mineralizer” that allows for most quartz to transform to cristobalite in a few days. This is added in 5 – 7% by weight. The most common mineralizer, CaO emphasizes the importance of the diagram under study.

As was shown in section 2.4.2, the presence of sodium is extremely detrimental to silica bricks. That is why sodium oxide (or any alkali metal oxide) cannot be used as mineralizer.

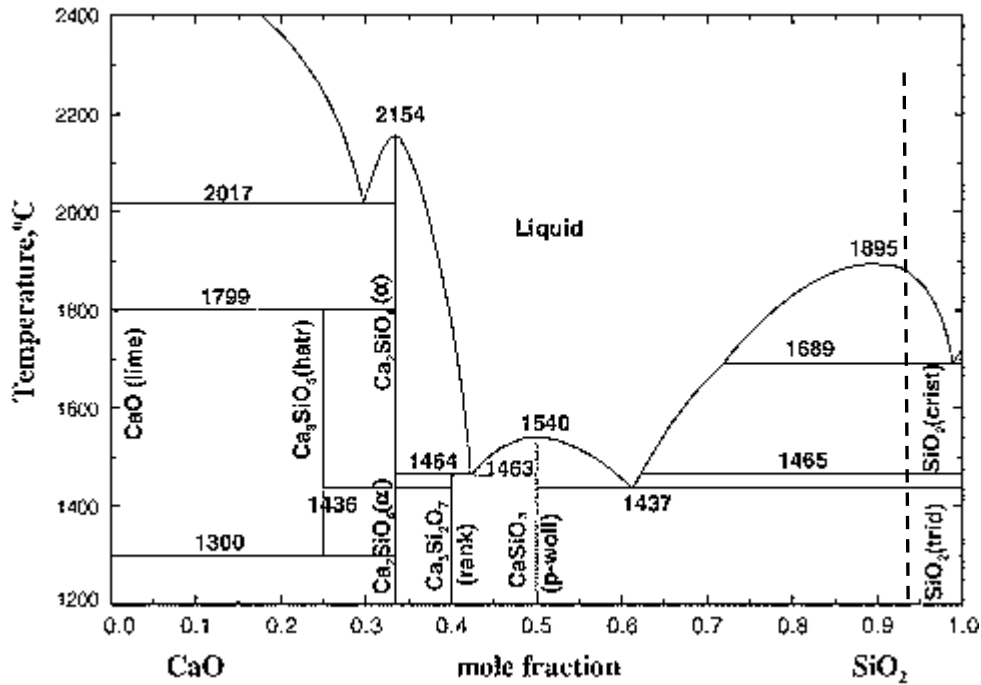


Fig (2.26) Phase diagram SiO₂ – CaO

The effect of the presence of CaO in contact with silica bricks can be understood by considering Fig (2.26). CaO forms SiO₂ several compounds the richest in silica being pseudo – wollastonite (CaO.SiO₂) which forms a eutectic with silica at 1437°C and 62 % mol silica. The diagram also shows that a monotectic situation is formed at 1689°C and 2% mol silica. It is clear that the drop in melting temperature is negligible (1710°C to 1689°C, as contrasted with 1710 °C to 790°C in case of Na₂O – SiO₂).

Consider a typical case where 6% by weight CaO is added as mineralizer (6.6% by mol). Owing to the presence of a monotectic reaction the percent liquid in the two-phase region SiO₂ + liquid increases from about 17.4% by mol at 1437°C to about 22.7% at 1689°C which is a relatively small increase. So, the presence of lime as addition to silica does not drastically affect the refractoriness of silica bricks besides that this percentage of viscous liquid is not enough to cause warping.

(iv) The system CaO – ZrO₂

Zirconia is a ceramic material of diverse uses: it is used in the manufacture of special refractory blocks, piezo – electric ceramics, ceramic knives, artificial diamond, dental prostheses etc...This oxide has a high melting temperature (2715°C) and a high compressive strength (2000MPa). It also has a high resistance to wear and abrasion and is chemically inert. It has three well-defined polymorphic forms: the monoclinic (m), tetragonal (t) and cubic (c) phases. Only the monoclinic form is stable at room temperature (although the tetragonal phase can be quenched to the ambient condition). The transition from the monoclinic form to tetragonal is accompanied by a large drop in volume at about 1170°C. This causes serious trouble when zirconia bodies are

cooled down from the high temperatures at which they are manufactured down to room temperature. The addition of appropriate dopants, however, is known to stabilize the tetragonal phase so that the change in volume is minimized. One of the first such dopants is lime (CaO) which is added at a level of 10 – 15% (by weight). Lime (CaO) stabilized zirconia (LSZ) based on the $ZrO_2 - CaO$ diagram.

The phase diagram shown in Fig (2.27) reveals the formation of a cubic phase that melts incongruently at about 2600°C when 8 to 15% (by weight) lime is added. As a lime stabilized zirconia body is cooled down there is no phase change and hence no appreciable increase in volume will occur.

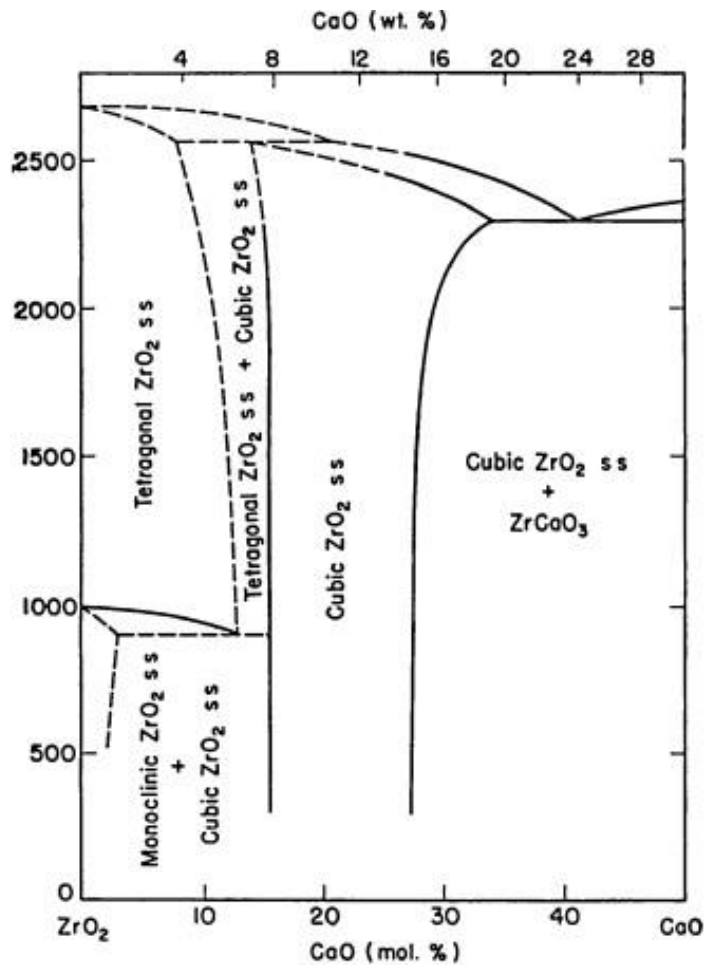


Fig (2.27) Phase diagram $ZrO_2 - CaO$

The use of CaO as ZrO_2 stabilizer has been replaced using Y_2O_3 . A comparison between Figures (2.26) and (2.27) reveals that the solid solution formed in the $ZrO_2 - Y_2O_3$ system is much wider than in the $ZrO_2 - CaO$ system, giving more room for proper control of the cooling rate.

A final comment

This chapter cannot be concluded before a final warning: The results that can be obtained from phase diagrams are subjected to two main cautions. First, these results assume that equilibrium is reached on firing, which is not always the case. Second, the presence of impurities can have an impact on the results. In the former case, the kinetics of reactions occurring on firing should be taken into consideration while in the latter more complex phase diagrams (Involving more than three components) should be considered.