CHAPTER 1

Basic Laws of Thermodynamics

1.1 The first law of thermodynamics

1.1.1 Systems and processes

A **system** is defined as a definite portion of space separated by its surroundings by a definite boundary. A classical system in thermodynamics is the piston – cylinder duet.

A **process** is a mechanism by which the state of the system (temperature, pressure, etc.) is changed. It is termed **reversible** if as the system reaches equilibrium, any infinitesimal change in the conditions of the system (such as temperature) can cause the process to reverse. The main thermodynamic processes are:

- Isothermal processes, in which the temperature of the system remains constant.
- Adiabatic processes, in which no heat is transferred to or from the system.
- Isochoric processes, in which the volume of the system remains constant.
- Isobaric processes, in which the pressure of the system remains constant.

1.1.2 State properties

A state property is a property that only depends on the initial and final states of a system. If an amount of heat Q is supplied to a system so that this system performs an amount of work W on its surroundings, then the internal energy of that system will decrease by an amount ΔU that does not depend on any particular path chosen to perform the heat supply or work performed (isothermal, adiabatic, etc.). This way, the internal energy is a state function, while heat and work are not. Later, some other state properties like enthalpy and entropy will be introduced.

1.1.3 Statement of the first law

Following the previous discussion, it can be deduced that:

$$\Delta U = Q - W \tag{1.1}$$

Conventionally, heat supplied to a system and work done by the system are considered positive, while the reverse actions confer negative values to the two variables.

If an infinitesimal amount of heat δQ is supplied to the system, and an amount of work δW is performed, then the internal energy change takes the form:

$$dU = \delta Q - \delta W \tag{1.2}$$

It is to be noted that heat (and work) cannot be written as dQ since upon integration between an initial state Q_1 and a final state Q_2, one gets $Q_2 - Q_1$. This would indicate that the change in heat supplied does not depend on the way it is supplied, which contradicts the fact that the amount of heat supplied depends on the path taken by the system (The type of the thermodynamic process). That is why δQ simply integrates to Q and, as well, δW integrates to W.

1.1.4 Calculation of work

Consider the classical example of a frictionless piston of cross-sectional area A that moves along the internal surface of a cylinder a distance dL due to the expansion of the gas inside it (Figure 1).

The infinitesimal work done by the cylinder equals:

$$\delta W = F.dL = \frac{F}{A} A.dL = p.dV \qquad (1.3)$$

For example, in case of an isothermal process, T remains constant so that, if the gas is considered to behave ideally, then for 1 mole one can write: $p = \frac{RT}{V}$. Substitution in equation (1.3), we get:

$$\delta W = \frac{RT}{V}.dV$$

Assuming the initial and final volumes to be V_1 and V_2 , we get on integration:

$$W = RT \ln\frac{V_2}{V_1} \qquad (1.4)$$

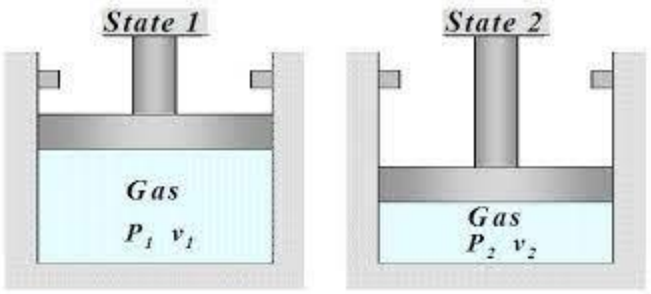


Fig 1.1: Cylinder – piston system

1.1.5 Enthalpy and heat capacity

The enthalpy of a system is defined as:

$$H = U + pV \qquad (1.5)$$

The heat capacity of a system, on the other hand, is defined as follows:

$$C = \frac{\delta Q}{dT} \qquad (1.6)$$

Substituting by equations (1.3) and (1.6) in (1.2), one gets:

$$dU = C.dT - p.dV \qquad (1.7)$$

Differentiation of equation (1.5) yields:

$$dH = dU + pdV + V.dp \qquad (1.8)$$

From the above two equations, one gets:

$$dH = C.dT + V.dp \tag{1.9}$$

Since, in dealing with solids, the pressure is usually maintained constant, then $dp = 0$ and the above equation becomes: $dH = C.dT$.

This defines the heat capacity of a system at constant pressure:

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \tag{1.10}$$

From equation (1.8), if pressure is kept constant, then, referring to equation (1.2):

$$dH = dU + pdV = \delta Q$$

So that the heat supplied to a system under isobaric conditions is equal to the change in enthalpy of the system.

Heat capacities of solids are usually expressed in the unit: J.mol^{-1}.K^{-1} and identify with their specific heats. At moderate to elevated temperatures, it is usually related to temperature through an empirical relation in the form:

$$C_p = a + bT + cT^{-2} \tag{1.11}$$

The constants a, b and c are empirical and can be obtained for any specific solid from special tables. Some values are reported in Table 1.1

Table 1.1: Heat capacity constants for some substances (J.mol^{-1}K^{-1})

Substance	a	$b \times 10^3$	$c \times 10^{-5}$	T range (K)
SiO_2 (quartz)	46.9	34.2	–11.32	298–848
BCl_3 (*l*)	70.41	11.89	–10.20	298–1000
$MnSiO_3$ (*s*)	110.0	16.21	–25.79	298–1500
TiO_2 (rutile)	67.31	18.71	–14.85	750–950
Ag (*s*)	21.20	8.55	1.50	298–1235
Ag (*l*)	30.5	-	-	1235–1600
AgCl (*s*)	32.11	4.19	–11.32	298–735
MnO (*s*)	47.9	10.2	–4.59	298–1500

1.1.6 Heats of formation

Calculations of heat effects need the definition of a standard sate for each physical state of the material. The usual **standard states** for the three common states of mater are:

- **For solids and liquids:** The stable form of the material at the specified temperature and 1 atm. pressure.
- **For gases:** The specified temperature and 1 atm. pressure.

In general, the common practice is to consider 298K as the reference temperature. Since solid reactions frequently take place at constant pressures, it is customary to use the term enthalpy rather than heat of formation. Table 1.2 illustrates the values of the enthalpies of formation (ΔH_f^0) of some common substances in kJ.mol^{-1}.

Table 1.2: Enthalpy of formation of some solids (kJ.mol^{-1})

Substance	SiO_2 (quartz)	$MnSiO_3$ (s)	TiO_2 (rutile)	Al_2O_3 (s)	CaO (s)	$CaCO_3$ (s)	MnO (s)	CO_2 (g)
$\boldsymbol{\Delta H_f^0}$	–860	–1320	–944	–1670	–636	–1206	–384	–394

1.1.7 Heats of reaction

To estimate the heat of a certain reaction, it is customary to use the heats of formation of both reactants and products and apply the simple rule:

$$\Delta H_r = \sum \alpha_{ip} \Delta H_{fi} \text{ (products)} - \sum \alpha_{ir} \Delta H_{fi} \text{ (reactants)} \qquad (1.11)$$

Where α_{ip} and α_{ir} are the stoichiometric coefficients of products and reactants respectively.

The heat calculated using standard states of reactants and products is termed the standard heat of reaction, normally reported at 298 K.

For example, if it is required to estimate the heat of calcination of $CaCO_3$ (s) to CaO (s) and CO_2 (g) at 298 K, then, using the data in Table 1.2, one gets:

$\Delta H_r = (-636 - 394) - (-1206) = 176$ kJ.mol^{-1}.

If now, it is required to estimate ΔH_r at any other temperature, like T K, then it is necessary to follow a cycle in the following form:

Reactants at T K → Reactants at 298 K → Products at 298 K → Products at T K

The determination of the enthalpy associated with the first and third steps, one uses the integrated form of equation (1.10) written as follows for the first step:

$$\Delta H = \int_T^{298} C_{pr}.dT \qquad (1.12)$$

Example 1.1

Using the data in Tables 1.1 and 1.2, estimate the enthalpy of the following reaction at 800 K.

$MnSiO_3$ (s) = MnO (s) + SiO_2 (quartz)

Solution:

First, the heat of reaction at 298 K is calculated:

$\Delta H_R^0 = (-860 - 384) - (-1320) = \mathbf{76}$ **kJ.mol^{-1}**.

Next, the enthalpy of the first step is calculated from:

$$\Delta H_1 = \int_{800}^{298} 110 + 16.21 \times 10^{-3}T - 25.79 \times 10^{5}T^{-2}.dT = -54256\text{J.mol}^{-1}$$

$$\equiv -54.26\ \text{kJ.mol}^{-1}$$

Similarly, for the third step:

$\Delta H_3 = \int_{298}^{800}(46.9 + 47.9) + (10.2 + 34.2) \times 10^{-3}T - (11.32 + 4.59) \times 10^{5}T^{-2}.dT =$ $56476\ \text{J.mol}^{-1} \equiv 56.48\ \text{kJ.mol}^{-1}$.

Hence: $\Delta H_{800} = \Delta H_1 + \Delta H_R^0 + \Delta H_3 = \mathbf{78.22\ kJ.mol^{-1}}$

Note that in most cases involving similar reactions, the heat of reaction does not depend much on temperature. The difference between the heat of reaction at 298K and 800K does not exceed 3%. The reason is the comparable values of specific heats of solid materials.

1.2 The second law of thermodynamics

1.2.1 Definition of entropy

Whereas the first law predicts the thermal characteristics of a chemical reaction, yet it cannot predict the possibility of its occurrence in the first place. For example, as we write a reaction in the form A (s) + B(s) = C (s), one cannot predict beforehand, by mere application of the first law, that this reaction will take place as written. The thermodynamic entity that is used for that prediction is termed **entropy**, the definition of which will be given later.

If we consider a system (*s*) and its surroundings (*surr*), then an infinitesimal change in the entropy of both will result in what is known as the total change of entropy of the process:

$$dS = dS_S + dS_{surr}$$

One interesting property of entropy changes is that the total variation in entropy $dS = 0$ for reversible processes and $dS > 0$ for irreversible processes. As a matter of fact, this is a way of stating the second law. The formal definition of the entropy of a system undergoing a **reversible process** is as follows:

$$dS = \frac{\delta Q}{T} \qquad (1.13)$$

Although Q is not a function of state, the entropy is. So that, if the process involves changing the temperature from T_1 to T_2, then this equation can be integrated to give:

$$\Delta S = \int_{T_1}^{T_2} \frac{dQ}{T} \qquad (1.14)$$

Hence, for a reversible process, the first law can be written in the form:

$$dU = T.dS - \delta W$$

When dealing with ideal gases, for example, from equation (1.3), one gets:

$$dU = T.dS - p.dV \qquad (1.15)$$

Example 1.2

Deduce a formula to calculate the entropy change when one mole of an ideal gas is heated reversibly from T_1 to T_2 under conditions of constant pressure p.

Solution:

From equation (1.10), one can write for a constant pressure process: $dQ = C_p . dT$

From equation (1.14):

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p . dT}{T}$$

Assuming the heat capacity to be fairly constant over the temperature range, then:

$\Delta S = C_p . \ln(T_2/T_1)$ J.mol^{-1}K^{-1}

Since p is constant, then the volume of the gas is proportional to its temperature so that:

$\Delta S = C_p . \ln(V_2/V_1)$ J.mol^{-1}K^{-1}

1.2.2 Entropy change for isothermal phase transitions.

By phase transitions is meant one of the following cases:

- Melting: Solid ↔ Liquid
- Allotropic transition: A (I) ↔ A (II)
- Boiling: Liquid ↔ Vapor
- Sublimation: Solid ↔ Vapor

According to the phase rule, these changes occur at a constant temperature = T_t. In that case, if the enthalpy change associated with the transition = ΔH_t, then, the corresponding entropy change will simply equal:

$$\Delta S_t = \frac{\Delta H_t}{T_t} \qquad (1.16)$$

1.2.3 Entropy change for irreversible processes.

The definition of entropy by equation (1.13) is restricted to reversible processes. To illustrate the method of calculation for irreversible processes, consider the following example:

Let the freezing point of a substance = T_m and let a certain temperature = $T^* < T_m$. Accordingly, while it is possible to melt or freeze the material reversibly at T_m, it is impossible to do so at T^*. This is since reversibility assumes that the process can be reversed by an infinitesimal change in temperature. To calculate the entropy of melting at T^* for the transition: A (*s*) → A (*l*), the following cycle is adopted that consists of consecutive reversible processes:

A (*s*) at T^*= A (*s*) at T_m (i)

A (*s*) at T_m = A (*l*) at T_m (ii)

A (*l*) at T_m =A (*l*) at T^* (iii)

The entropy of the process can be calculated by adding the entropies of the three steps as follows:

$$\Delta S = \int_{T^*}^{T_m} \frac{C_p(s).dT}{T} + \frac{\Delta H_m}{T_m} + \int_{T_m}^{T^*} \frac{C_p(l).dT}{T}$$

The following example illustrates these steps.

Example 1.3

Silver melts at 1235 K. The latent heat of fusion = 11.2 kJ.mol^{-1}. Calculate the entropy change of the system and surroundings in case of freezing of undercooled liquid silver at 1073.

Solution:

As explained above, the following steps are undertaken:

Ag (*l*) → Ag (*l*): 1073 K to 1235 K:

$\Delta S_1 = \int_{1073}^{1235} \frac{C_p(l).dT}{T} = 30.5 \ln \frac{1235}{1073} = 4.29$ J.mol^{-1}K^{-1} (See table 1.1).

Ag (*l*) → Ag (*s*): at 1235 K: $\Delta S_2 = \frac{-11200}{1235} = -9.07$ J.mol^{-1}K^{-1} (Exothermic heat)

Ag (*s*) → Ag (*s*): 1235 K to 1073 K:

$\Delta S_3 = \int_{1235}^{1073} \frac{C_p(s).dT}{T} = \int_{1235}^{1073} \frac{(21.2+8.55\times10^{-3}T+1.5\times10^{5}T^{-2}.dT}{T} = -4.39$ J.mol^{-1}K^{-1}

Thus, the change in entropy of the system = $4.29 - 9.07 - 4.39 = \mathbf{-9.17}$ **J.mol^{-1}K^{-1}**

To obtain the entropy change of surroundings, one first must calculate the amount of heat transferred to the surroundings which is the amount of heat produced by the cycle.

Ag (*l*) → Ag (*l*): 1073 K to 1235 K: $\Delta H_1 = \int_{1073}^{1235} C_{pl}.dT = 30.5 \times (1235 - 1073) =$ 4941 J.mol^{-1}

Ag (*l*) → Ag (*s*): at 1235 K: $\Delta H_2 = -11200$ J.mol^{-1}

Ag (*s*) → Ag (*s*): 1235 K to 1073 K:

$$\Delta H_3 = \int_{1235}^{1073} 21.2 + 8.55 \times 10^{-3}T + 1.5 \times 10^{5}T^{-2}.dT = -5051 \text{ J. mol}^{-1}$$

Thus, the heat transferred to surroundings = $4941 - 11200 - 5051 = -11310$ J. mol^{-1}

The heat gained by surroundings is therefore 11310 J. mol^{-1}

The change in entropy of surroundings = $\Delta S_{surr} = \frac{11310}{1073} = 10.54$ J. mol^{-1}K^{-1}

We note that the total change in entropy = $-9.17 + 10.54 = \mathbf{1.37\ J.\,mol^{-1}K^{-1}} > 0$, which conforms to what has been previously mentioned in Section 1.2.1.

1.2.4 An application: The difference between C_v and C_p

As previously explained, solid state processes usually take place at constant pressure so that we are usually concerned with isobaric changes occurring in the system. However, since the volume changes in solids are minor, it is also necessary to consider the case of constant volume behavior. To that aim, on defines the heat capacity at constant volume in a manner like that used in equation (1.10) for C_p.

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V \tag{1.17}$$

A relation between the two heat capacities will be derived for solid materials. The proof is too complicated to be presented. So, only the main definitions are shown:

It can be proved that:

$$C_p = C_V + \left(\frac{\partial V}{\partial T}\right)_p T \left(\frac{\partial p}{\partial T}\right)_V \tag{1.18}$$

We now define the volume expansion coefficient of a solid as follows:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \ \mathrm{K}^{-1} \tag{1.19}$$

While the compressibility coefficient is defined as:

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \ \mathrm{Pa}^{-1} \tag{1.20}$$

Now, we expand dV as a perfect differential as function of T and p:

$$dV = \left(\frac{\partial V}{\partial p}\right)_T . dp + \left(\frac{\partial V}{\partial T}\right)_p . dT \tag{1.21}$$

At constant volume, $dV = 0$. If the expression is then divided by dT, we get:

$$0 = \left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V + \left(\frac{\partial V}{\partial T}\right)_p \tag{1.22}$$

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T} \tag{1.23}$$

Combining equations (1.18), (1.19), (1.20) and (1.23), we finally get:

$$C_p = C_V + \frac{\alpha^2 VT}{\beta} \tag{1.24}$$

The importance of this result is that it is usually easy to experimentally determine C_p, while the determination of C_V is extremely difficult since it is not practical to keep a solid from expanding when heated. The following table illustrates some typical values of the parameters investigated for copper at different temperatures.

Table 1.3: Properties of copper

T K	$a \times 10^{6}$ K^{-1}	$\beta \times 10^{11}$ Pa^{-1}	C_p J.mol^{-1}K^{-1}	C_V J.mol^{-1}K^{-1}
100	31.5	0.72	16.2	16.1
200	45.6	0.748	22.6	22.2
300	48	0.762	23.6	23.1
800	60.7	0.922	28	25.7
1200	69.7	1.03	30.7	26.3

Example 1.4

Determine the work done on one mol of a copper body when the pressure is increased from 1 to 1000 atm at 300 K. (Density of copper = 8.96 g.cm^{-3})

Solution:

Since the atomic weight of copper = 63.55, then:

Molar volume = $\frac{63.55}{8.96} = 7.0926$ cm^3.mol^{-1} ≡ 7.0926×10^{-6} m^3.mol^{-1}

The pressure increased from $p_1 = 101325$ to $p_2 = 101325000$ Pa

The work is obtained from: $W = \int_{p_1}^{p_2} p.dV = -\int_{p_1}^{p_2} V\beta p.dp$ (From equation 1.20)

$W = -7.0926 \times 10^{-6} \times 0.762 \times 10^{-11} \times 0.5 \times [1.013 \times 10^{8})^2 - (101325)^2] =$ $\mathbf{-0.277\ J.mol^{-1}}$ **.**

1.2.5 Some empirical rules for entropy of transition

In this section are presented two common empirical rules that can be used to predict the entropy of fusion and that of vaporization of solids at their transition temperatures.

- **Richard's rule**

According to that rule, the entropy of melting of a solid at its melting point is approximately equal to **9.2** $\mathbf{J.mol^{-1}K^{-1}}$ **.** However, this rule serves only as a rough guide whenever experimental values are not available. Table 1.5 shows the entropy of fusion of some solid materials, revealing that this rule is far from being universal.

Table 1.5: Entropy of fusion and vaporization of some solids (J.mol^{-1}K^{-1})

Material	Cu	Fe	Ni	Co	SiO_2	CaO	MgO	Al_2O_3	TiO_2	NaCl
ΔS_f	6.73	8.49	9.96	9.16	4.79	18.9	24.8	48.1	7.3	23.83
ΔS_v	113.6	111.5	116.1	96.4	ND	98.6	85.3	ND	103.2	126.6

- **Trouton's rule**

This rule states that the entropy of vaporization of melts is about **89** $\mathbf{J.mol^{-1}K^{-1}}$.

As can be seen in Table 1.5, this rule is of approximate character, although the values of entropy of vaporization fluctuate around the Trouton value.

1.2.6 The physical meaning of entropy

The best way to understand the concept of entropy is through its statistical meaning. Without going into details, it suffices to say that entropy is a measure of the disorder in a system. Heating a gas will cause the velocity of its particles to increase, thus increasing disorder and hence entropy. A cooler gas will therefore possess lower value of entropy so that if the two gases are connected, heat will flow from the higher to the lower temperature system. It can be proved that the entropy of the final state of the system will be higher than the sum of entropies of the two initial systems:

Consider two similar bodies possessing an equal number of moles n and having the same heat capacities C. Let the first be heated to 500K, while the second is at 300K. If they are allowed to contact, heat will flow from the first to the second until an equilibrium temperature is attained. Because of their similarity, this temperature will be 400K.

The change in entropy of the first body $\Delta S_1 = n\int_{500}^{400}\frac{C}{T}.dT = -0.233nC$

The change in entropy of the second body $\Delta S_2 = n\int_{300}^{400}\frac{C}{T}.dT = 0.287nC$

The net change in entropy of the entire system = $\Delta S_1 + \Delta S_2 = 0.054nC > 0$

We see therefore that the entropy of the final state is higher than of entropy of the two initial systems.

1.2.7 The statistical interpretation of entropy

(a) Introduction

The concept of entropy is closely related to some statistical concepts to the extent that a special branch of thermodynamics, known as statistical thermodynamics, is devoted to the subject. In the following are presented some preliminary principles.

Consider 9 different objects to be distributed to three people so that the first takes 4, the second 3 and the third takes the remaining 2. It can be proved that the total number of ways of performing that task is:

$$N = \frac{9!}{4!3!2!}$$

In general, if n objects are to be distributed on i cells, so that n_1 are to be placed in the first cell, n_2 in the second, etc., then the total number of ways to perform this distribution is:

$$w = \frac{n!}{n_1!n_2!n_3!\dots} \qquad (1.25)$$

It is obvious that $n = n_1 + n_2 + n_3 \dots + n_i$

The variable W is known as the **thermodynamic probability** and refers to the number of ways n particles can be distributed into i positions. Strictly speaking, it is not a probability term, but rather the number of different probabilities related to the process.

Boltzmann has defined the absolute entropy of a system as follows:

$$S = k.\ln W \qquad (1.26)$$

Where, k is **Boltzmann constant** (1.3806×10^{-23}J.K^{-1}). This constant is related to the general gas constant R as follows:

$$R = k.N_0 \qquad (1.27)$$

Where N_0 is Avogadro's number = 6.022×10^{23} mol^{-1}.

It is worth noticing that if the n objects are identical, then the number of ways to distribute them on i cells is:

$$w = \frac{n+i-1!}{n!i-1!} \qquad (1.28)$$

(b) An application

A famous application of that principle is the determination of the entropy of mixing of two different species.

First, it should be noted that on dealing with molecules present in any species, the numbers involved are enormous, being in the 10^{20} range. In that case, the factorial $n!$ can be obtained using the Stirling approximation:

$$n! \approx \sqrt{2n\pi}.n^n.e^{-n}$$

Taking logarithms:

$$\ln n! \approx \ln\sqrt{2\pi} + \frac{1}{2}\ln n + n\ln n - n$$

For extremely large values of n, the first two terms can be neglected. One gets:

$$\ln n! \approx n\ln n - n \qquad (1.29)$$

For example, although 50 is not an extremely large number, still we have:

$50! = 3.0414 \times 10^{64} \rightarrow \ln 50! = 148.48$

While, if equation (1.28) is applied, we get:

$\ln 50! \approx 50\ln 50 - 50 = 145.60$

The error is about 1.94%.

Consider now a component A consisting of n_A molecules mixed with a component B consisting of n_B molecules such that $n = n_A + n_B$ so that the solution consists of 1 mole. In that case, the number of molecules in the solution is the Avogadro's number N_0.

If the entropies of A, B and the solution are S_A, S_B, S_{AB} respectively, then the entropy of mixing is the change in entropy associated with the mixing operation is:

$\Delta S_m = S_{AB} - S_A - S_B$

From equation (1.26), we can write:

$\Delta S_m = k(\ln W_{AB} - \ln W_A - \ln W_B)$

W_A is the number of ways to distribute n_A molecules in n_A sites so that every site will contain one molecule. Since all A molecules are indistinguishable, then $W_A = 1$. Likewise, $W_B = 1$. Hence the above equation simplifies to:

$$\Delta S_m = k \ln W_{AB} \tag{1.30}$$

W_{AB} is the number of ways of distributing n_A molecules of A and n_B molecules of B in the same n sites. Following equation (1.25), this results in:

$$W_{AB} = \frac{n!}{n_A! n_B!} \tag{1.31}$$

$$\Delta S_m = k(\ln n! - \ln n_A! - \ln n_B\,!) \tag{1.32}$$

Applying equation (1.29):

$\Delta S_m = k(n \ln n - n - n_A \ln n_A + n_A - n_B \ln n_B + n_B)$

Since $n = n_A + n_B$, this reduces to:

$$\begin{aligned}\Delta S_m &= k(n \ln n - n_A \ln n_A - n_B \ln n_B)\\ &= k[n_A(\ln(n_A + n_B) - n_A \ln n_A + n_B(\ln(n_A + n_B) - n_B \ln n_B\end{aligned}$$

$$\Delta S_m = -k(n_A + n_B)\left(\frac{n_A}{n_A + n_B} \ln \frac{n_A}{n_A + n_B} + \frac{n_B}{n_A + n_B} \ln \frac{n_B}{n_A + n_B}\right)$$

Denoting $\frac{n_A}{n_A+n_B}$ by X_A and $\frac{n_B}{n_A+n_B}$ by X_B (mol. fractions) and $= -k(n_A + n_B) = -k.N_0 = -R$ (general gas constant). We get the following expression:

$$\Delta S_m = -R(X_A \ln X_A + X_B \ln X_B) \tag{1.33}$$

This result will be proved later in Chapter 3 from a classical thermodynamic point of view.

1.3 The free energy function

1.3.1 Definition and meaning

Consider a system that loses heat reversibly to its surroundings. Then its entropy will change by:

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

Under isobaric conditions, this is written as:

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

Therefore, $dH - T.dS = 0$

If the process is irreversible, it may be proved that in that case:

$$dH - T.dS < 0 \tag{1.34}$$

This equation offers a criterion for deciding whether a process will occur spontaneously or not. In other words, it can be used to judge, for example, the possibility of the occurrence of a chemical reaction under a specified set of conditions.

This has led to defining the **free energy** function as follows:

$$G = H - T.S \tag{1.35}$$

Upon differentiation, one gets:

$$dG = dH - T.dS - S.dT$$

Under isothermal conditions, this equation yields:

$$dG = dH - T.dS \tag{1.36}$$

This shows that the change in free energy is appropriate to judge whether a process can take place spontaneously or not, using the following criterion as per equation (1.34):

For spontaneous processes under isothermal conditions: $dG < 0$.

1.3.2 Important relations for ΔG

In the following is presented the proof of two important expression in thermodynamics that relates free energy to other thermodynamic properties.

(a) First relation:

$$G = H - T.S$$

Dividing by T and differentiating with respect to T, we get:

$$\left(\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right)_P = \left(\frac{\partial\left(\frac{H}{T}\right)}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_P \tag{1.37}$$

$$\left(\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P + H\left(\frac{\partial\left(\frac{1}{T}\right)}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_P \tag{1.38}$$

Now, $\frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P = \frac{C_p}{T}$ and $\left(\frac{\partial\left(\frac{1}{T}\right)}{\partial T}\right)_P = -\frac{1}{T^2}$

Substituting in equation (1.38):

$$\left(\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right)_P = -\frac{C_p}{T} - \frac{H}{T^2} - \left(\frac{\partial S}{\partial T}\right)_P \tag{1.39}$$

On the other hand, for reversible isobaric processes:

$dS = \frac{dH}{T}$ Thus, $dH = T.dS \rightarrow C_p.dT = T.dS$, which can be written in the form:

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T} \tag{1.40}$$

Substituting in equation (1.38):

$$\left(\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right)_P = \frac{C_p}{T} - \frac{H}{T^2} - \frac{C_p}{T} = -\frac{H}{T^2} \tag{1.42}$$

This is usually written in the form:

$$\left(\frac{\partial\left(\frac{G}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right)_P = H \tag{1.43}$$

Usually, the following form is more of use:

$$\left(\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right)_P = \Delta H \tag{1.44}$$

Example 1.5

When a reaction was carried out at 300K, the change in free energy = -38.5 kJ. mol^{-1}, while it reached -23.6 kJ. mol^{-1} when carried out at 350K. Calculate the average value of the enthalpy of that reaction over the temperature range 300K – 350K.

Solution:

$T_1 = 300 \rightarrow \Delta G_1 = -38.5$ $\qquad$ $T_2 = 350 \rightarrow \Delta G_2 = -23.6$

Hence:

$\frac{\Delta G_1}{T_1} = -0.128$ $\qquad$ $\frac{\Delta G_2}{T_2} = -0.0674$

The net variation in $\frac{\Delta G}{T}$ due to change in temperature = $-0.0674 - (-0.128) = 0.061$

The variation in $\frac{1}{T} = \frac{1}{350} - \frac{1}{300} = -0.00476$

Hence: $\Delta\left(\frac{\Delta G}{T}\right) = 0.061$ $\qquad$ $\Delta\left(\frac{1}{T}\right) = -0.00476$

$$\left(\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right)_P \approx \left(\frac{\Delta\left(\frac{\Delta G}{T}\right)}{\Delta\left(\frac{1}{T}\right)}\right)_P = \Delta H = \frac{0.061}{-0.00476} = \mathbf{-12.82\ kJ.\,mol^{-1}}$$

(b) Second relation:

From equation (1.8):

$dH = dU + pdV + V.dp$

And since:

$dG = dH - T.dS - S.dT$

Therefore:

$dG = dU + pdV + V.dp - T.dS - S.dT$

From the first law, we get:

$dG = \delta Q + V.dp - T.dS - S.dT$ And from equation (1.13), $\delta Q = T.dS$.

We therefore obtain the following important relation:

$$dG = V.dp - S.dT \qquad (1.45)$$

PROBLEMS (Any missing data must be obtained by online search)

1. Calculate the amount of enthalpy change when the temperature of $MnSiO_3$ (s) is raised from 300K to 1000K.
2. Calculate the enthalpy change for the calcination of $CaCO_3$ (s) at 1000K.
3. Prove that in an isothermal reversible process at temperature T, the change in entropy of a mole of an ideal gas when its pressure is raised from p_1 to p_2 can be obtained from the expression:
   $$\Delta S = R \ln \frac{p_1}{p_2}$$
4. Sodium chloride melts at 801°C and its latent heat of fusion = 27.95 $kJ.mol^{-1}$. Calculate the entropy change of the system and surroundings in case of freezing of undercooled liquid NaCl at 700°C. (Heat capacity of NaCl (s) = 50 $J.mol^{-1}.K^{-1}$ and for NaCl (*l*) ≈ 61.5 $J.mol^{-1}.K^{-1}$).
5. Determine the entropy change when the pressure applied on a copper body of volume 5 L is raised reversibly from 1 to 10^4 atm at 300K.
6. The free energy of a reaction can be obtained from the expression:
   $\Delta G = -16.8 + 0.00368T - 0.0721 \ln T$ $kJ.mol^{-1}$ (T in K)
   Calculate ΔS and ΔH for that reaction at 400K.
7. 100 identical molecules of gas are to be distributed to 50 sites. Evaluate the number of ways this can be done.
8. Calculate the change in free energy when one mole of ideal gas is compressed isothermally from atmospheric pressure to 100 atm at 298K.

CHAPTER 2

Thermodynamics of chemical reactions

2.1 Physical transitions

2.1.2 Order of transitions

When the free energy of a transition is plotted against one of the state variables (T, p, V) then the shape of the curve determines the order of transition. The transition is said to be of first order if the plot of G against T (for example) is continuous, but that of $\left(\frac{\partial G}{\partial T}\right)_P$ is not. For example, it is clear from Figure1 that the plot of G against T is continuous at the transition temperature T_t. On the other hand, a plot of $\left(\frac{\partial G}{\partial T}\right)_P$ against T shows a discontinuity at the transition temperature.

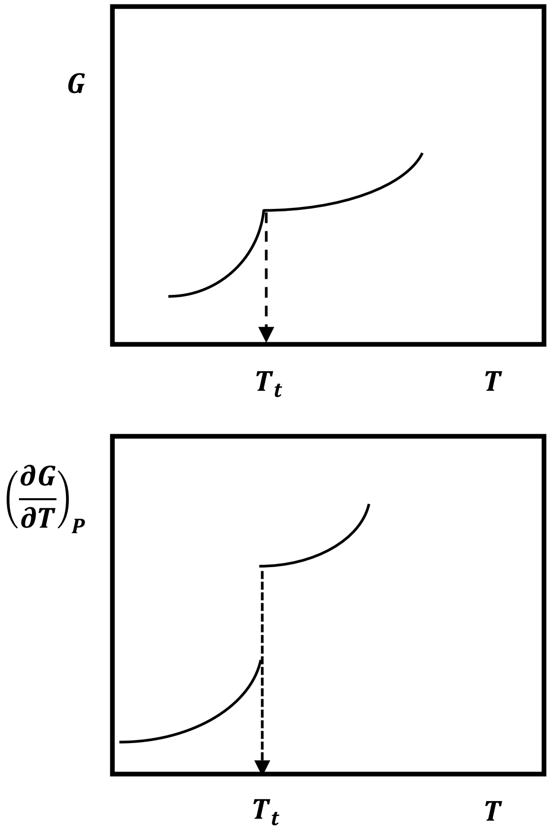


Fig 2.1: Fist order transition

In the same way, a plot of H against T will be continuous at the transition temperature from solid to liquid, whereas a plot of $C_p = \left(\frac{\partial H}{\partial T}\right)_P$ against T will show discontinuity at the melting temperature (Figure 2.1)

In second order transitions, such as order – disorder transformations in alloys, will display continuous behavior for both $G - T$ and $\left(\frac{\partial G}{\partial T}\right)_P - T$ plots. However, a plot of $\frac{\partial^2 G}{\partial T^2}$ will show discontinuity at the transition temperature.

2.1.3 Effect of pressure on phase transition temperature

Since for a reversible process, $dG = dH - T.dS = 0$, then the free energies of both phases must be equal. If a reversible transition takes place in the form:

A (I) ↔ A(II)

Then $dG_{\mathrm{I}} = dG_{\mathrm{II}}$

From equation (1.45):

$$dG = V.dp - S.dT$$

Hence, at the transition temperature T_t:

$$V_1.dp - S_1.dT = V_2.dp - S_2dT$$

Rearranging, we get:

$$\frac{dp}{dT} = \frac{S_2 - S_1}{V_2 - V_1} \qquad (2.1)$$

From equation (1.16):

$$S_2 - S_1 = \Delta S_t = \frac{\Delta H_t}{T_t}$$

So that equation (2.1) takes the following form, known as **Clapeyron equation**:

$$\frac{dp}{dT} = \frac{\Delta H_t}{\Delta V.T_t} \qquad (2.2)$$

This is particularly applied in cases of melting – freezing and allotropic transitions.

Example 2.1

Tin melts at 505K and possesses a heat of melting = 7.029 kJ.kg^{-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 (2.2) can be rewritten to read:

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

$\Delta p = (100 - 1) \times 1.013 \times 10^5 = 1.0029 \times 10^7$ Pa

$\Delta H_t = 7.029 \times 118.7 = 834.34$ J.mol^{-1}

$T_t = 505$ K

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

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

$\Delta V = 0.736 \times 10^{-6}$ m^3.mol^{-1}

Substituting in equation (2.2):

$$\frac{1.0029 \times 10^7}{\Delta T} = \frac{834.34}{0.736 \times 10^{-6} \times 505}$$

Hence: $\boldsymbol{\Delta T = 4.467}$ **K**

We can conclude from the previous result that there is an increase of about 1% in melting temperature corresponding to a one-hundred-fold increase in pressure. This means that a $p - T$ plot will result in an almost vertical line. 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).

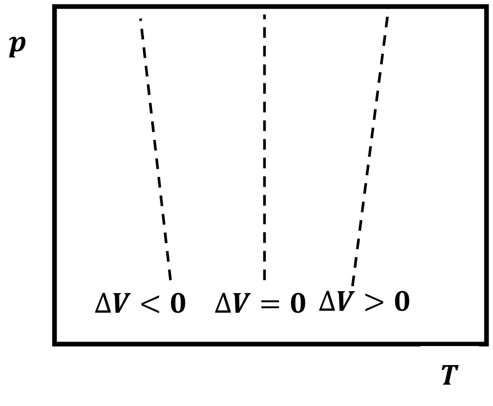


Fig 2.2: Different cases of volume change on melting

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:

$p^0 V = RT$ (p^0 is the vapor pressure at that temperature)

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 (2.2) can be rewritten as:

$$\frac{dp^0}{dT} = \frac{\Delta H_t}{V_g.T} = \frac{p.\Delta H_t}{RT^2}$$

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

$$\frac{d\ln p^0}{dT} = \frac{\Delta H_t}{RT^2} \tag{2.3}$$

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

$$\ln p = -\frac{\Delta H_t}{RT} + C \tag{2.4}$$

This means that a plot of $\ln p$ against the reciprocal of temperature will yield a straight line of slope = $-\frac{\Delta H_t}{R}$.

Example 2.2

The vapor pressure of molten silver (Pa) is related to temperature (K) by the relation:

$$\log p^0 = -14900T^{-1} - 0.85\log T + 14.32$$

From a suitable plot, deduce the latent heat of vaporization of silver at its melting temperature (1235K). Compare with the published data of 251 kJ.mol^{-1}.

Solution:

The following table summarizes the calculations.

T **K**	**log *p***	**1/*T* K^{-1}**	**ln *p*^{0}**
1235	-0.37269	0.00081	-0.85816
1300	0.21161	0.00077	0.48725
1350	0.62218	0.00074	1.43262
1400	1.00293	0.00071	2.30934
1450	1.35698	0.00069	3.12455
1500	1.68699	0.00067	3.88444
1550	1.99531	0.00065	4.59438
1600	2.284	0.00063	5.2591

A plot of $\ln p^0$ against $1/T$ is shown in Figure 2.3.

The slope of the line = -34075

This slope corresponds to a latent heat of vaporization = 275.4 kJ.mol^{-1} which is slightly different from the experimental reported value of 251, the error being 9.71%.

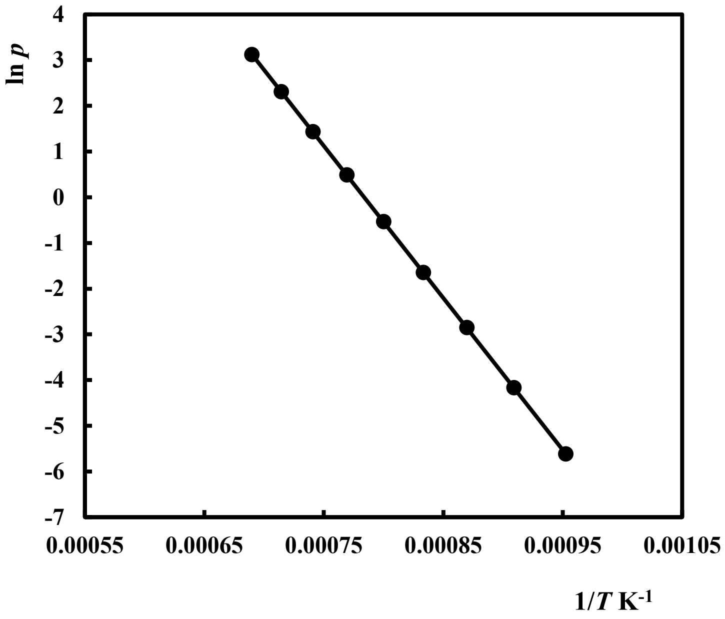


Fig 2.3: Plot of $\ln p^0$ against $1/T$ for liquid Ag

2.2 Chemical reactions

2.2.1 Standard free energy of a chemical reaction

As previously mentioned, (equation 1.34) a reaction can proceed spontaneously if the change in free energy is negative. Despite this, some reactions with negative free energy change are not observed to occur. This is mainly due to the extremely low rate of reaction, which is accelerated by a rise in temperature.

Consider a system of solid reactants A and B **at their standard states**, due to react according to the following equation to yield products at their standard states (1 atm. and the fixed reaction temperature):

$$a\mathrm{A}(s) + b\mathrm{B}(s) = c\mathrm{C}(s) + d\mathrm{D}(s) \qquad \Delta G^0 \qquad \text{(i)}$$

$(a, b, c, d$ are stoichiometric coefficients).

The free energy change for that reaction is termed the **standard free energy of reaction ΔG^0**. Its sign cannot be taken as a general criterion of irreversibility (spontaneity) for that reaction unless all species are at their standard states.

Under equilibrium conditions, each component will be in equilibrium with its vapor at the vapor pressure corresponding to the reaction temperature:

$$a\mathrm{A}(v, p_A^0) = a\mathrm{A}(s) \qquad \Delta G_1^0 = 0 \qquad \text{(ii)}$$

$$b\mathrm{B}(v, p_B^0) = b\mathrm{B}(s) \qquad \Delta G_2^0 = 0 \qquad \text{(iii)}$$

$$c\mathrm{C}(v, p_C^0) = c\mathrm{C}(s) \qquad \Delta G_3^0 = 0 \qquad \text{(vi)}$$

$$d\mathrm{D}(v, p_D^0) = d\mathrm{D}(s) \qquad \Delta G_4^0 = 0 \qquad \text{(v)}$$

If equations from (i) to (v) are added, we get:

$$a\mathrm{A}(v, p_A^0) + b\mathrm{B}(v, p_B^0) = c\mathrm{C}(v, p_C^0) + d\mathrm{D}(v, p_D^0) \qquad \Delta G^0 \qquad \text{(vi)}$$

The free energies of sublimation of the solid species are zero since vapor is in equilibrium with its solid in each case. The last equation (vi) infers that the standard free energy of the reaction can be calculated by dealing with vapor instead of solid phases.

Let us assume that the vapor pressures were changed to new values p_A, p_B, p_C, p_D still in equilibrium with their corresponding solid phases (**but not at their standard states**) to obtain the following reaction:

$$a\mathrm{A}(v, p_A) + b\mathrm{B}(v, p_B) = c\mathrm{C}(v, p_C) + d\mathrm{D}(v, p_D) \qquad \text{(vii)}$$

To evaluate the free energy change caused by the change in vapor pressures, we refer to equation (1.45):

$$dG = V.dp - S.dT$$

Since the temperature of reaction is assumed constant, then $dT = 0$ and we get:

$$dG = V.dp$$

Assuming the vapors of all components to behave ideally, then: $V = \frac{RT}{p}$

Substituting, one gets:

$$dG = \frac{RT}{p}.dp$$

Integration is now performed for all four components from the initial state to the final state involving the new values of vapor pressures. We get:

$$\Delta G_I = RT \ \ln\frac{p_i}{p^0} \qquad (2.5)$$

This equation is now written for all four components:

$$a\mathrm{A}(v, p_A^0) = a\mathrm{A}(v, p_A) \qquad \Delta G_5 = aRT \ \ln\frac{p_A}{p_A^0} \qquad \text{(viii)}$$

$$bB(v, p_B^0) = bB(v, p_B) \qquad \Delta G_6 = bRT \ \ln\frac{p_C}{p_B^0} \qquad \text{(ix)}$$

$$c\mathrm{C}(v, p_C^0) = c\mathrm{C}(v, \ p_C) \qquad \Delta G_7 = cRT \ \ln\frac{p_C}{p_C^0} \qquad \text{(x)}$$

$$d\mathrm{D}(v, p_D^0) = d\mathrm{D}(v, p_D) \qquad \Delta G_8 = dRT \ \ln\frac{p_D}{p_D^0} \qquad \text{(xi)}$$

When equilibrium is reached, the free energy for the global reaction = 0, we can add the equations from (viii) to (xi) together with (vi):

$$a\mathrm{A}(v, p_A^0) + b\mathrm{B}(v, p_B^0) = c\mathrm{C}(v, p_C^0) + d\mathrm{D}(v, p_D^0) \qquad \Delta G^0$$

$$a\mathrm{A}(v, p_A) + b\mathrm{B}(v, p_B) = c\mathrm{C}(v, p_C) + d\mathrm{D}(v, p_D) \qquad \Delta G_7 + \Delta G_8 - (\Delta G_5 + \Delta G_6)$$

$$\Delta G_7 + \Delta G_8 - (\Delta G_5 + \Delta G_6) + \Delta G^0 = 0$$

$$cRT\ \ln\frac{p_C}{p_C^0} + dRT\ \ln\frac{p_D}{p_D^0} - aRT\ \ln\frac{p_A}{p_A^0}\ - bRT\ \ln\frac{p_B}{p_B^0} + \Delta G^0 = 0$$

This can be written in the form:

$$RT.\ln\frac{\left(\frac{p_C}{p_C^0}\right)^c}{\left(\frac{p_A}{p_A^0}\right)^a} \times \frac{\left(\frac{p_D}{p_D^0}\right)^d}{\left(\frac{p_B}{p_B^0}\right)^b} + \Delta G^0 = 0$$

The expression following the logarithm is called the **equilibrium constant** of reaction K_e and the latter equation takes the form:

$$\Delta G^0 + RT\ln K_e = 0$$

$$\Delta G^0 = -RT\ln K_e \qquad (2.6)$$

The quantity $\frac{p_i}{p^0}$ is known as the **activity** of the component (a_i).

The expression for the equilibrium constant K_e can therefore be written as:

$$K_e = \frac{a_C^c}{a_A^a} \times \frac{a_D^d}{a_B^b} \qquad (2.7)$$

In the case of ideal gases, the standard state is taken as 1 atm and the activity equal to the mol fraction of the gas = $\frac{p_{gas}}{1} = p_{gas}$. However, when we deal with solutions, the concept of activity must be expanded to regard it as the effective concentration of a component in the solution. Following this principle, the activity of a component in solution will be 1 if the solution is constituted from this component only: $a_i^0 = 1$.

Equation (2.5) can now be written as follows:

$$\Delta G_i = RT\ \ln a_i \qquad (2.8)$$

Returning to the original reaction, where the components are **not at their standard states**. We can then write:

$a\mathrm{A}(a_A) + b\mathrm{B}(a_B) = c\mathrm{C}(a_C) + d\mathrm{D}(a_D)$ (xii) ΔG

If all components are at their standard sates, then:

$a\mathrm{A}(a_A = 1) + b\mathrm{B}(a_B = 1) = c\mathrm{C}(a_C = 1) + d\mathrm{D}(a_D = 1)$ ΔG^0

To move any component from its standard state to its actual state, one uses equation (2.8):

$a\mathrm{A}(a_A = 1) = a\mathrm{A}(a_A)$ $\Delta G_1 = G_1 - G_1^o = aRT\ln a_A$

$bB(a_B = 1) = b\mathrm{B}(a_B)$ $\Delta G_2 = G_2 - G_2^o = bRT\ln a_B$

$c\mathrm{C}(a_C = 1) = c\mathrm{C}(a_C)$ $\Delta G_3 = G_3 - G_3^o = cRT\ln a_C$

$d\mathrm{D}(a_D = 1) = d\mathrm{D}(a_D)$ $\Delta G_3 = G_4 - G_4^o = dRT\ln a_D$

The free energy of equation (xii) is therefore:

$$\Delta G = \sum G_i = \sum G_i^0 + RT \ln \frac{a_C^c}{a_A^a} \times \frac{a_D^d}{a_B^b}$$

$$\Delta G = \Delta G^0 + RT \ln \frac{a_C^c}{a_A^a} \times \frac{a_D^d}{a_B^b} \qquad (2.9)$$

Example 2.3

Consider the equilibrium reaction mixture of Ca, Si and CaSi, dissolved in a solvent at 1000 K. Suppose that the initial activity of Ca = 0.5 and that CaSi is pure. If the standard free energy of the reaction Ca + Si = CaSi at that temperature is -172 kJ.mol^{-1}, find the activity of Si in the equilibrium mixture. Then find the partial pressure of Ca (v) in equilibrium with the dissolved Ca (Vapor pressure of Ca at 1000 K = 14.6 Pa). Also find the change in free energy for the reaction:

Ca $(a = 0.5)$ + Si $(a = 0.4)$ = CaSi $(a = 0.8)$

Solution:

$\Delta G^0 = -172000$ J.mol^{-1} $= -RT \ln K_e = -8.314 \times 1000 \ln K_e \rightarrow K_e = 9.65 \times 10^8$

$9.65 \times 10^8 = \frac{a_{\text{CaSi}}}{a_{\text{Ca}} \times a_{\text{Si}}} = \frac{1}{0.5 \times a_{\text{Si}}} \rightarrow \boldsymbol{a_{\text{Si}} = 2.072 \times 10^{-8}}$

The activity of Ca is 0.5, meaning that $\frac{p_{\text{Ca}}}{p_{\text{Ca}}^0}$ = 0.5.

Hence, $p_{\text{Ca}} = 0.5 \times 14.6 = \mathbf{7.3}$ **Pa**

$\Delta G = \Delta G^0 + RT \ln \frac{a_{\text{CaSi}}}{a_{\text{Ca}} \times a_{\text{Si}}} \rightarrow \Delta G = -172000 + 8.314 \times 1000 \times \ln \frac{0.8}{0.5 \times \mathbf{0.4}}$

$\Delta G = -160474 \text{ J} \equiv \mathbf{-160.5\ kJ.mol^{-1}}$

The negative sign of ΔG means that this reaction will proceed spontaneously at 1000K.

Example 2.4

Find the change in free energy for the following reaction at 1000K:

Ca $(a = 0.9) =$ Ca $(a = 0.5)$

(a) If the components are at their standard states.
(b) If the components have the activities shown above.

Solution:

(a) Since Ca is at its standard state, then $a_{\text{Ca}} = 1$ and $\Delta G^0 = -RT \ln \frac{1}{1} = \mathbf{0}$

(b) $\Delta G = \Delta G^0 + RT \ln \frac{0.5}{0.9} = 0 + 8.314 \times 1000 \ln \frac{0.5}{0.9} \rightarrow \Delta G = \mathbf{-4887}$ **J.mol^{-1}**

2.2.2 Testing the feasibility of a chemical reaction

Assume that in a chemical reaction all species are at their standard states, in which case the free energy change of the reaction = ΔG^0. For the reaction to occur, a necessary condition is that $\Delta G^0 < 0,$ as mentioned previously.

In general, the standard free energies of chemical reactions are expressed as function of temperature, sometimes in the form:

$$\Delta G^0 = a + bT + c\log T \qquad (2.10)$$

This can be used, together with equation (2.6) to decide about the feasibility of a chemical reaction at a given temperature, or to predict the critical temperature above (or below) which the reaction can take place. This is illustrated by the following example.

Example 2.5

The decomposition of manganese dioxide takes place according to the following equation:

MnO_2 (s) = Mn (s) + O_2 (g)

The standard free energy for that reaction (kJ.mol^{-1}) is related to temperature (K) through the following expression:

$$\Delta G^0 = 251.6 - 0.334T + 0.023\log T$$

What is the minimum temperature at which this reaction can take place under atmospheric conditions? And what would be the minimum oxygen partial pressure to carry out that reaction at 600 K?

Solution

Assuming both Mn and MnO_2 to be pure species, then their activities = 1. The activity of the gas is equal to its partial pressure, since its standard state is at 1 atm. Hence, from equation (2.6):

$$\Delta G^0 = -RT\ln p_{O_2}$$

$$251600 - 334T + 23\log T = -8.314T\ln 0.21 = 13T$$

$$347T - 23\log T = 251600$$

Solving, one gets $\boldsymbol{T = 725.3\ K}$

To carry out that reaction at 600 K, the value of ΔG^0 at that temperature is first determined.

$$\Delta G^0 = 251600 - 334 \times 600 + 23\log 600 = 51264$$

$$51264 = -8.314 \times 600\ln p_{O_2} \rightarrow p_{O_2} = \mathbf{3.44 \times 10^{-5}\ atm}$$

2.2.3 Effect of temperature on the equilibrium constant

Following equation (2.6):

$$\Delta G^0 = -RT\ln K_e \qquad (2.6)$$

While equation (1.44) can be written as:

$$\left(\frac{\partial\left(\frac{\Delta G^0}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right)_p = \Delta H^0 \qquad (1.44)$$

Hence, $\frac{\Delta G^0}{T} = -R \ln K_e$

Substituting in (1.44), one gets:

$$\left(\frac{\partial \ln K_e}{\partial\left(\frac{1}{T}\right)}\right)_p = -\frac{\Delta H^0}{R}$$

And since $d\left(\frac{1}{T}\right) = -\frac{1}{T^2}.dT$, one gets:

$$\left(\frac{\partial \ln K_e}{\partial T}\right)_p = \frac{\Delta H^0}{RT^2} \tag{2.10}$$

Upon integration, one gets:

$$\ln K_e = C - \frac{\Delta H^0}{RT} \tag{2.11}$$

This result implies that for endothermic reactions ($\Delta H^0 > 0$), the equilibrium constant will increase with increasing temperature, thus favoring the reaction to proceed in its positive direction. In exothermic reactions, an increase in temperature will negatively affect the yields of the products.

Example 2.5

If the standard enthalpy of the reaction Ca + Si = CaSi at 1000K is -185 kJ.mol^{-1}, and the equilibrium constant at that temperature = 9.65×10^8, estimate its value when temperature is increased to 1100K.

Solution:

Equation (2.10) takes the form:

$$\left(\frac{\partial \ln K_e}{\partial T}\right)_p = \frac{-185000}{8.314 \times T^2} = -22251.6T^{-2}$$

$$\int_{1000}^{1100} -22251.6T^{-2}.dT = \ln K_{e,1100} - \ln 9.65 \times 10^8$$

$$\ln K_{e,1100} = 20.687 + 22251.6 \times (1100^{-1} - 1000^{-1}) = 16.642 \rightarrow$$

$$\boldsymbol{K_{e,1100} = 1.69 \times 10^7}$$

This means that an increase of 10% in the reaction temperature has caused a corresponding decrease of about 57-fold in the value of K_e.

PROBLEMS

1. The densities of solid and liquid copper are 8.95 and 7.93 g.cm^{-3} respectively. The melting point of copper under atmospheric pressure = 1083°C. estimate the necessary pressure to apply to raise the melting point to 1090°C. (Enthalpy of melting = 13.59 kJ.mol^{-1}).

2. The following table indicates the vapor pressure of molten aluminum (in millibar) as function of temperature:

$\log p$	-7	-6	-5	-4	-3	-2	-1	0	1	2
T K	1020	1075	1172	1243	1374	1498	1669	1805	2023	2255

   Use these data to predict the normal boiling point of the metal and its enthalpy of sublimation.

3. Carbon is dissolved in molten iron at 1600 K at an activity = 0.0038. Determine the free energy change associated with an increase in its activity to 0.00572.

4. The vapor pressure of zinc (s) at 600°C is 975 Pa. When dissolved in molten copper, its vapor pressure = 0.03 mmHg at that temperature. Calculate the free energy change of zinc due to dissolution.

5. The vapor pressure of CO_2 (atm) varies with temperature (K) following the relation:

$$p_{CO_2} = 4.137 \times 10^7 e^{-\frac{20474}{T}}$$

   Deduce the minimum temperature of calcination of $CaCO_3$ in air, where the mol fraction of CO_2 = 0.0005. Also, deduce the standard entropy change at that temperature from the following data:

   - Enthalpy of formation of $CaCO_3$ at 298 K = -1205.6 kJ.mol^{-1}
   - Enthalpy of formation of CaO at 298 K = -635.5 kJ.mol^{-1}
   - Enthalpy of formation of CO_2 at 298 K = -394 kJ.mol^{-1}
   - Average heat capacities on the range 300 – 800 K:
     - $CaCO_3$ = 83.48 J.mol^{-1}.K^{-1}.
     - CaO = 47.5 J.mol^{-1}.K^{-1}.
     - CO_2 = 36 J.mol^{-1}.K^{-1}

6. The free energy of formation of $TiCl_4$ gas from the following reaction is related to temperature by the shown expression.

   Ti (s) + $2Cl_2$ (g, 1 atm) = $TiCl_4$ (g, 1 atm)

$$\Delta G^0 = -75.7 \times 10^4 - 7.5T.\log T + 145T \text{ J.mol}^{-1}$$

   Deduce the following:

   (a) The equilibrium constant of this reaction at 1500K.

   (b) The standard enthalpy of that reaction at that same temperature.

(c) The standard entropy of that reaction at that same temperature.

7. If the standard enthalpy of the reaction: 2Ti (s) + ⅓Fe_2O_3 (s) = 2TiO (s) + ⅔Fe (s) at 1500 K is -410 kJ and the equilibrium constant at that temperature = 8.903×10^{15}, estimate the value of the equilibrium constant at 1400 K.

8. The standard enthalpy of a certain reaction is related to temperature by the expression:

   $\Delta H_R = -1860 + 0.13T$ kJ.mol^{-1}.

   The standard free energy at 298K = -1705 kJ.mol^{-1}.

   Evaluate the standard free energy and entropy of reaction at 1000 K.

9. Draw a relation between $\ln p^0$ and T for copper metal from the following data:

	Cu
Normal Melting point K	1358
$\boldsymbol{\Delta H_m}$ **kJ.mol^{-1}**	13.26
Normal Boiling point K	2835
$\boldsymbol{\Delta H_v}$ **kJ.mol^{-1}**	300.4

Consider the heat of the sublimation reaction: Cu (*l*) = Cu (*v*) to be the sum of the heat of melting and vaporization.

Show on the figure the equilibrium regions where solid, liquid and vapor phases of copper are stable.

CHAPTER 3

Thermodynamics of Solutions

3.1 Partial molal quantities

3.1.1 Definitions

Assume a certain solution consists of two components (1) and (2). Let the volume of the solution = V. If 1 mole of the first component (1) is added to the solution at constant temperature and pressure, without varying the number of moles of (2), this will cause its volume to increase. The volume increase per mole of added (1) is termed the partial molal volume of component (1). In general, for a solution composed of N components (1), (2), …, (i), …, (N), the partial molal volume of component (i) is denoted by $\bar{V}_i$ and defined as:

$$\bar{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{p,T,n_1,n_2,\ldots} \tag{3.1}$$

Similar partial molal quantities can be written for enthalpy, entropy, free energy, etc. as an infinitesimal amount of component (i) is added (dn_i), the volume of the solution will increase by an infinitesimal amount dV. This can be expressed as a perfect differential is the following way:

$$dV = \left(\frac{\partial V}{\partial n_1}\right)_{p,T,n_2,n_3} dn_1 + \left(\frac{\partial V}{\partial n_2}\right)_{p,T,n_1,n_3} dn_1 + \cdots \tag{3.2}$$

From equations (3.1) and (3.2):

$$dV = \bar{V}_1 dn_1 + \bar{V}_2 dn_2 + \bar{V}_3 dn_3 + \cdots = \sum_{i=1}^{N} \bar{V}_i dn_i \tag{3.3}$$

Similarly, one may write:

$$dH = \sum_{i=1}^{N} \bar{H}_i dn_i \tag{3.4}$$

$$dG = \sum_{i=1}^{N} \bar{G}_i dn_i \tag{3.5}$$

On the other hand, if the solution contains n_1 mole of component (1), n_2 mole of component (2), etc., then one can write:

$$V = \bar{V}_1 n_1 + \bar{V}_2 n_2 + \bar{V}_3 n_3 + \cdots = \sum_{i=1}^{N} \bar{V}_i n_i \tag{3.6}$$

$$H = \bar{H}_1 n_1 + \bar{H}_2 n_2 + \bar{H}_3 n_3 + \cdots = \sum_{i=1}^{N} \bar{H}_i n_i \tag{3.7}$$

$$G = \bar{G}_1 n_1 + \bar{G}_2 n_2 + \bar{G}_3 n_3 + \cdots = \sum_{i=1}^{N} \bar{G}_i n_i \tag{3.8}$$

Differentiation of equation (3.6) yields:

$$dV = \sum_{i=1}^{N} \bar{V}_i dn_i + \sum_{i=1}^{N} n_i \, d\bar{V}_i \tag{3.9}$$

Comparing equations (3.3) and (3.9), we have the following results:

$$\sum_{i=1}^{N} n_i\, d\bar{V}_i = n_1 d\bar{V}_1 + n_2 d\bar{V}_2 + n_3 d\bar{V}_3 + \cdots = 0 \qquad (3.10)$$

$$\sum_{i=1}^{N} n_i\, d\bar{H}_i = n_1 d\bar{H}_1 + n_2 d\bar{H}_2 + n_3 d\bar{H}_3 + \cdots = 0 \qquad (3.11)$$

$$\sum_{i=1}^{N} n_i\, d\bar{G}_i = n_1 d\bar{G}_1 + n_2 d\bar{G}_2 + n_3 d\bar{G}_3 + \cdots = 0 \qquad (3.12)$$

The last equation being more of interest than the previous two equations, we define the molar fraction of a component (i) as:

$$X_i = \frac{n_i}{N} \qquad (3.13)$$

Dividing both sides of equation (3.12) by the total number of moles (N), one gets:

$$\sum_{i=1}^{N} X_i\, d\bar{G}_i = X_1 d\bar{G}_1 + X_2 d\bar{G}_2 + X_3 d\bar{G}_3 + \cdots = 0$$

This equation is known as the **Gibbs – Duhem equation**.

Using the definition in equation (3.13), equations (3.6) TO (3.8) may be expressed as:

$$V = \sum_{i=1}^{N} \bar{V}_i X_i = \bar{V}_1 X_1 + \bar{V}_2 X_2 + \bar{V}_3 X_3 + \cdots \qquad (3.14)$$

$$H = \sum_{i=1}^{N} \bar{H}_i X_i = \bar{H}_1 X_1 + \bar{H}_2 X_2 + \bar{H}_3 X_3 + \cdots \qquad (3.15)$$

$$G = \sum_{i=1}^{N} \bar{G}_i X_i = \bar{G}_1 X_1 + \bar{G}_2 X_2 + \bar{G}_3 X_3 + \cdots \qquad (3.16)$$

Also, (3.10) to (3.12) may be expressed in the same way:

$$\sum_{i=1}^{N} X_i\, d\bar{V}_i = X_1 d\bar{V}_1 + X_2 d\bar{V}_2 + X_3 d\bar{V}_3 + \cdots = 0 \qquad (3.17)$$

$$\sum_{i=1}^{N} X_i\, d\bar{H}_i = X_1 d\bar{H}_1 + X_2 d\bar{H}_2 + X_3 d\bar{H}_3 + \cdots = 0 \qquad (3.18)$$

$$\sum_{i=1}^{N} X_i\, d\bar{G}_i = X_1 d\bar{G}_1 + X_2 d\bar{G}_2 + X_3 d\bar{G}_3 + .. = 0 \qquad (3.19)$$

3.1.2 Determination of partial molal quantities

Consider a binary solution consisting of two components A and B. Figure (3.1) illustrates the relation between the volume of solution V and the mole fraction of B.

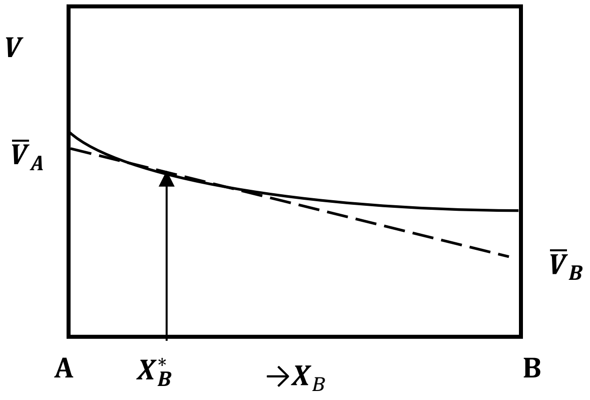


Fig (3.1): Effect of mole fraction B on the volume of solution

From equation (3.14):

$dV = \bar{V}_A dX_A + \bar{V}_B dX_B$

Since $X_A + X_B = 1$, then one gets: $dX_A = -dX_B$

Therefore:

$dV = (\bar{V}_B - \bar{V}_A) dX_B$

Dividing by dX_B yields:

$$\frac{dV}{dX_B} = (\bar{V}_B - \bar{V}_A) \rightarrow \bar{V}_A = \bar{V}_B - \frac{dV}{dX_B} \qquad (3.20)$$

On the other hand, from equation (3.14):

$V = \bar{V}_A X_A + \bar{V}_B X_B$

So that:

$$\bar{V}_A = \frac{V - \bar{V}_B X_B}{1 - x_B} \qquad (3.21)$$

Equating equations (3.20) and (3.21):

$$\bar{V}_B - \frac{dV}{dX_B} = \frac{V - \bar{V}_B X_B}{1 - x_B}$$

This reduces to:

$$\bar{V}_A = V - X_B \frac{dV}{dX_B} \qquad (3.22)$$

This is the equation of a straight line of slope $\frac{dV}{dX_B}$ and intercept V at $X_B = 0$, which is the equation of the tangent to the curve at a chosen value of X_B. We note that if $X_B = 0$, then the intercept of the tangent with the volume axis = $\bar{V}_A$.

Therefore, to obtain the partial molal volume of A for a specific value X_A^* of its mole fraction in the solution, a tangent is drawn to the curve at $X_B^* = 1 - X_A^*$ and the intercept. (Figure 3.1). The value of $\bar{V}_B$ is obtained from the intercept at $X_A = 0$.

Example 3.1

An equation for the variation of the free energy of a solution was established as function of the mole fraction of copper in a binary solid solution with gold in the form:

$\Delta G = 21540 X_{\mathrm{Cu}}^2 - 22651 X_{\mathrm{Cu}} + 807.6$ J.mol^{-1}

Estimate the partial molal values of free energy for both metals at $X_{\mathrm{Cu}} = 0.3$

Solution:

For $X_{\mathrm{Cu}} = 0.3, \Delta G = -4050$ (By substitution in the equation).

So, it is required to obtain the equation of the tangent to the curve at the point $(0.3; -4050)$

To that aim, the equation of the curve is differentiated:

$$\frac{d\Delta G}{dX_B} = 43080X_{\text{Cu}} - 22651 \rightarrow X_{\text{Cu}} = 0.3 \rightarrow \text{slope} = -9727$$

The equation of the tangent then takes the form:

$\Delta G = -9727X_{\text{Cu}} + C$

To get the value of C, we substitute with the coordinates of the point to get: $C = -1132$

Therefore, the equation of the tangent is:

$\Delta G = -9727X_{\text{Cu}} - 1132$

At $X_{\text{Cu}} = 0, \Delta\boldsymbol{\bar{G}}_{\textbf{Au}} = \boldsymbol{-1132}$ **J.mol^{-1}**

At $X_{\text{Cu}} = 1, \Delta\boldsymbol{\bar{G}}_{\textbf{Cu}} = \boldsymbol{-10859}$ **J.mol^{-1}**

3.1.3 Free energy of mixing

Consider a component (i) present in solution. At constant pressure and temperature, one may write:

$dG_I = dH_i - TdS_i$

Dividing by dn_i, while keeping all other mole fractions constant:

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

That is:

$\bar{G}_I = \bar{H}_i - T\bar{S}_i$

This means that the definition of free energy applies to the partial molal function as well. This way, equation (2.8) will also yield:

$$d\bar{G}_i = RTd\ln a_i \tag{3.24}$$

This equation can be integrated to give:

$\bar{G}_i = RT\ln a_i + C$

To obtain the value of the constant of integration C, we recall that for the pure component $(i), a_i = 1$. If $G_i^{\cdot}$ Represents the free energy of the pure component, then one gets:

$$\bar{G}_i - G_i^{\cdot} = RT\ln a_i \tag{3.25}$$

Consider now two solids A and B forming a solid solution as follows:

$X_AA(s) + X_BB(s) = S.S.$

The **free energy of mixing $\boldsymbol{\Delta G_m}$** is defined as the net free energy arising from mixing the two solids A and B in the molar ratios X_A and X_B respectively:

$$\Delta G_m = G_{ss} - (X_AG_A^{\cdot} + X_BG_B^{\cdot}) \tag{3.26}$$

From equation (3.16):

$G_{ss} = \bar{G}_AX_A + \bar{G}_BX_B$

Substituting in (3.25):

$\Delta G_m = (\bar{G}_A - G_A^{\cdot})X_A + (\bar{G}_B - G_B^{\cdot})X_B$

From equation (3.24), one gets:

$$\Delta G_m = RT(X_A \ln a_A + X_B \ln a_B) \qquad (3.27)$$

3.1.4 Ideal solutions

Ideal solid solutions represent a hypothetical case, seldom encountered in practice, such as Ni – Pt solid solution. These are defined by Raoult's law which states that the partial pressure of a component is proportional to its mole fraction in the solution:

$$p_i = p_i^0 X_i \qquad (3.28)$$

In section (2.2.1), the activity of a component was defined as:

$$a_i = \frac{p_i}{p^0}$$

Therefore, one may conclude that **in an ideal solution, the activity of any component is equal to its mole fraction: $a_i = X_i$**

Consequently, equation (3.26) can be written as follows:

$$\Delta G_m = RT(X_A \ln X_A + X_B \ln X_B) \qquad (3.29)$$

$$\Delta G_m = RT[(1 - X_B)\ln(1 - X_B) + X_B \ln X_B)]$$

Differentiating with respect to X_B and equating to 0:

$$\frac{d\Delta G_m}{dX_B} = RT\left[-\ln(1 - X_B) - (1 - X_B).\frac{1}{(1 - X_B)} + \ln X_B + X_B.\frac{1}{X_B}\right]$$

$$= RT[-\ln(1 - X_B) + \ln X_B] = 0 \rightarrow \ln\frac{X_B}{1-X_B} = 0 \rightarrow \frac{X_B}{1-X_B} = 1 \rightarrow X_B = 0.5$$

Hence, a plot of the free energy of mixing of an ideal solution should result in a curve possessing an extremum value at $X_A = X_B = 0.5$. It can be proved that this is a minimum value.

On the other hand, equation (3.29) can be written as:

$$\frac{\Delta G_m}{T} = R(X_A \ln X_A + X_B \ln X_B)$$

So that the LHS is no longer a function of temperature and hence:

$$\left(\frac{\partial\left(\frac{\Delta G_m}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right)_p = 0$$

From equation (1.44). This means that:

For ideal solutions: The enthalpy of mixing $\Delta H_m = 0$

This result is sometimes used to define ideal solutions.

On the other hand, since:

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

Then, in case of ideal solutions: $\Delta G_m = -T\Delta S_m$

And, from equation (3.29), one gets the expression for the entropy of mixing for ideal solutions:

$$\Delta S_m = -R(X_A \ln X_A + X_B \ln X_B) \qquad (3.30)$$

This is the same result achieved in chapter 1 (Equation 1.33), using a statistical approach.

Figure (3.2) represents the variation of free energy and entropy of mixing with the molar fraction of zinc in the zinc – gallium solid solution at 700K, after Novakovic et al **. The experimental points were taken from three different references available at the reference list of this paper.

It is clear from the figure that, while the free energy of mixing passes through a minimum value at $X_{Zn} \approx 0.5$, the entropy of mixing passes through a corresponding maximum value because of the (–) sign in equation (3.30).

** R. Novakovic, D. Giuranno, E. Ricci, T. Lanata "Surface and transport properties of In–Sn liquid alloys" Surface Science 602: 1957–1963 (2008).

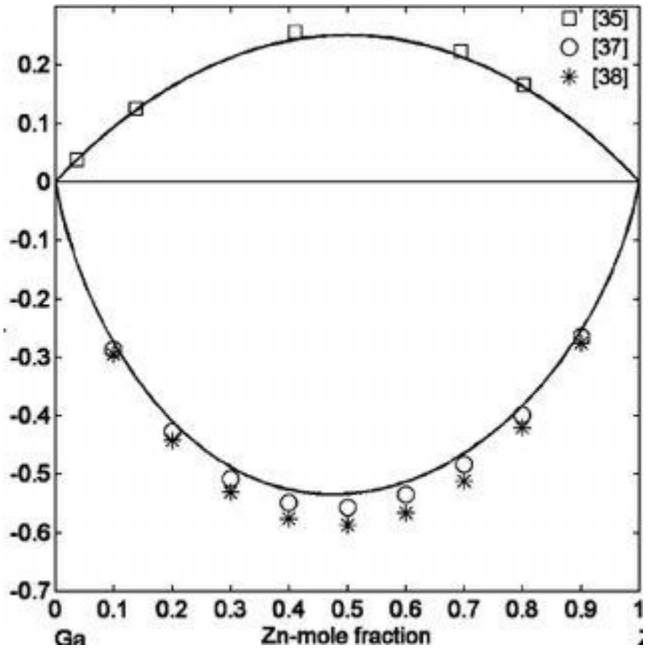


Fig (3.3): Free energy and entropy of mixing in the Ga – Zn system at 700K*

3.1.5 Non-ideal dilute solutions

Non-ideal dilute solutions are those where the solute is present in small amounts. For example, let A and B two components form a solid solution where the molar fraction of B is low ($< 10\%$). In that case, it is common for the dilute solute to follow **Henry's law**, according to which, the vapor pressure of the solute B is proportional to its molar fraction in solution:

$$p_B = H.X_B \qquad (3.31)$$

From the definition of activity (Page 18):

$$a_B = \frac{p_B}{p_B^0}$$

$$a_B = \frac{H.X_B}{p_B^0}$$

The constant H/p_B^0 is known as the activity coefficient γ_B so that:

$$a_B = \gamma_B X_B \qquad (3.32)$$

For ideal solutions, $\gamma_B = 1$. Otherwise, it is independent of concentration if the solute is present in small amounts.

Now, referring to equation (3.20):

$$X_A d\bar{G}_A + X_B d\bar{G}_B = 0$$

And from equation (3.24):

$$d\bar{G}_i = RTd\ln a_i$$

Hence:

$$X_A d\ln a_A + X_B d\ln a_B = 0 \qquad (3.33)$$

From equation (3.32):

$$\ln a_B = \ln \gamma_B + \ln X_B$$

$d\ln a_B = d\ln X_B$ (Since γ_B is constant)

From equation (3.33);

$$X_A d\ln a_A + X_B d\ln X_B = 0$$

Which can be written in the form:

$$d\ln a_A = -\frac{X_B.d\ln X_B}{X_A} = -\frac{X_B.dX_B}{X_A X_B} = -\frac{dX_B}{X_A} = -\frac{dX_B}{1-X_B}$$

Integration yields:

$$\ln a_A = \ln(1 - X_B) + C$$

Now, if $X_B = 0, X_A = 1 \rightarrow a_A = 1 \rightarrow \ln a_A = 0$ and hence $C = 0$

Hence,

$$\ln a_A = \ln(1 - X_B) = \ln X_A$$

And therefore:

$$a_A = X_A$$

Which means that the solute A behaves ideally, that is, obeys Raoult's law.

Hence, **for dilute solutions, the solute will obey Henry's law while the solvent obeys Raoult's law.**

Conversely, if A obeys Henry' law, then B will obey Raoult's law (Figure 3.4)

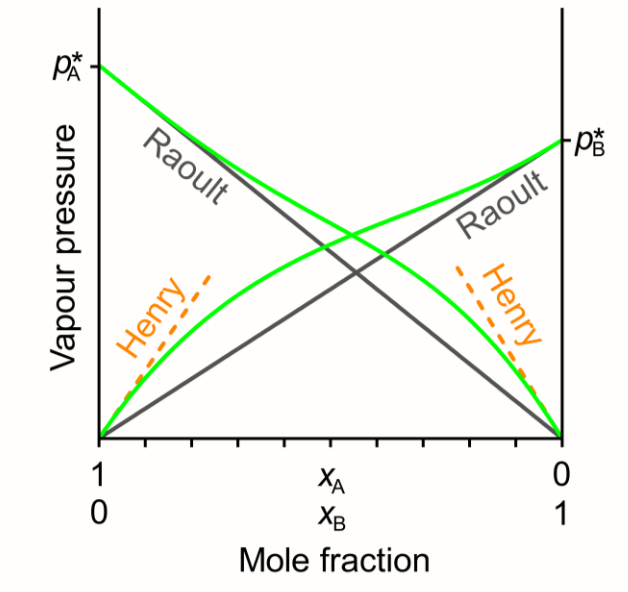


Fig (3.4): Application of Henry's and Raoult's laws

Example 3.2

In the CaO – MgO system, CaO can dissolve MgO in solid solution up to 16% MgO. A solution containing 5% molar MgO shows a total vapor pressure of 6.2×10^{-6} atm. at 2000ºC. The activity coefficient of MgO at that temperature = 0.88 and its vapor pressure = 1.12×10^{-4} atm. Estimate the vapor pressure of pure CaO at that temperature, considering the solution of MgO in CaO to be a dilute solution.

Solution:

$p^0_{\text{MgO}} = 1.12 \times 10^{-4}$ and $\gamma_{\text{MgO}} = 0.88$

Hence, from equation (3.33):

$a_{\text{MgO}} = 0.88 \times 0.05 = 0.044$

And, since $a_B = \frac{p_B}{p_B^0}$

Therefore: $p_{\text{MgO}} = 0.044 \times 1.12 \times 10^{-4} = 4.93 \times 10^{-6}$ atm.

Also, $a_{\text{CaO}} = X_{\text{CaO}} = 0.95$

$p_{\text{CaO}} = p^0_{\text{CaO}} X_{\text{CaO}}$

$p_{\text{CaO}} = 6.2 \times 10^{-6} - 4.93 \times 10^{-6} = 1.27 \times 10^{-6}$ atm

Hence: $1.27 \times 10^{-6} = p^0_{\text{CaO}} \times 0.95 \rightarrow p^0_{\text{CaO}} = \mathbf{1.336 \times 10^{-6}}$ **atm**.

- **An application: Depression in freezing point**

Consider a solute B added in small amounts to a solvent A so that $X_B \approx 0$. This way, the solvent will obey Raoult's law:

$p_A = p_A^0 X_A = p_A^0(1 - X_B)$

Applying equation (2.3):

$$\frac{d\ln p^0}{dT} = \frac{\Delta H_f}{RT^2}$$

Integrating between p_A^0 and p_A, and assuming the depression in freezing point to be ΔT_f

$$\ln\frac{p_A^0(1-X_B)}{p_A^0} = \frac{\Delta H_{fA}}{R}.\left(\frac{1}{T_f} - \frac{1}{T_f-\Delta T}\right) \rightarrow \ln(1-X_B) = -\frac{\Delta H_{fA}}{R}\frac{\Delta T_f}{T_f^2 - \Delta T_f T_f} \approx -\frac{\Delta H_f}{R}\frac{\Delta T_f}{T_f^2}$$

$\ln(1-X_B)$ can be expanded in Taylor's series:

$$\ln(1-X_B) = -X_B + \frac{X_B^2}{2} + \cdots \approx -X_B$$

One finally gets:

$$\Delta T_f \approx \frac{RT_f^2}{\Delta H_{fA}} X_B \qquad (3.34)$$

3.1.6 Regular solutions

These are solid solutions in which the entropy of mixing is still obtained from equation (3.30), while its enthalpy of mixing ≠ 0 and can be expressed as:

$$\Delta H_m = \Omega X_A X_B \qquad (3.35)$$

Ω is a constant directly proportional to temperature that considers the amount of interaction existing between the solute and the solvent atoms. Therefore, the expression for the free energy of mixing takes the form:

$$\Delta G_m = \Omega X_A X_B - RT(X_A \ln X_A + X_B \ln X_B) \qquad (3.36)$$

It can be proved that this function still goes through a minimum value at $X_A = X_B = 0.5$. The merit of using this expression is that it can be considered as a first approximation for predicting the free energy of mixing of a non-ideal concentrated solution. The only practical difficulty consists of finding experimentally the value of the interacting parameter Ω at different compositions and temperatures.

For concentrated non-regular solutions, it is no more possible to use any of the previously mentioned relations, and empirical expressions for the enthalpy and entropy of mixing are used in polynomial forms like: $\Delta H_m = a_0 + a_1 X_B + a_2 X_B^2 + a_3 X_B^3 + \cdots$

3.1.7 Excess thermodynamic properties

The excess thermodynamic quantity represents the difference between the actual value of that quantity and the corresponding value for an ideal solution.

For example,

$$d\bar{G}_i = RTd\ln a_i \qquad (3.24)$$

From equation (3.32):

$$d\bar{G}_i = RTd\ln\gamma_i X_i = RTd\ln\gamma_i + RTd\ln X_i$$

Since, for ideal solutions, $\gamma_i = 1$, then:

$(d\bar{G}_i)_{ideal} = RTd\ln X_i$

Therefore:

$d\bar{G}_i - (d\bar{G}_i)_{ideal} = d\bar{G}^{ex} = RTd\ln \gamma_i$

This can be integrated to read:

$$\Delta\bar{G}^{ex} = RT\ln \gamma_i \tag{3.37}$$

Similarly, the excess free energy of mixing is:

$$\Delta G_m^{ex} = RT\,(X_A\ln \gamma_A + X_B\ln \gamma_B) \tag{3.38}$$

As for the enthalpy of mixing: since the ideal enthalpy of mixing = 0, then the excess enthalpy of mixing will simply equal the heat of mixing of the concentrated solution.

$$\Delta H_m^{ex} = \Delta H_m \tag{3.39}$$

In ideal solutions, there is no interaction between the atoms of the two components. The excess quantities express the nature and the intensity of these interactions.

From equation (3.36), if $\gamma_i > 1,$ then $\Delta\bar{G}^{ex} > 0,$ while it will be negative if $\gamma_i < 1.$

The first case represents a positive deviation from Raoult's law where the actual activity is higher than that predicted by this law. On the other hand, the case $\gamma_i < 1$ represents a negative deviation from the law.

Example 3.3

The Au – Cu system is known to behave as a regular solution. At 775K, the enthalpy of mixing is related to the molar fraction of Cu by the following expression:

$\Delta H_m = 21540X_{Cu}^2 - 22651X_{Cu} + 808$ J.mol^{-1}.

Evaluate the following at that temperature for $X_{Cu} = 0.3$: $\Delta\bar{H}_{Cu}, \Delta\bar{H}_{Au}, \Delta\bar{G}_{Cu}$ and $\Delta\bar{G}_{Au}$.

Solution:

From equation (3.15):

$\Delta H_m = \Delta\bar{H}_{Cu}.X_{Cu} + \Delta\bar{H}_{Au}.X_{Au}$

$\Delta H_m = 0.3\Delta\bar{H}_{Cu} + 0.7\Delta\bar{H}_{Au}$

From section 3.1.2, one first gets the equation of the tangent line to the curve at $X_{Cu} = 0.3$:

$\frac{d\Delta H_m}{dX_{Cu}} = 43080X_{Cu} - 22651 \rightarrow X_{Cu} = 0.3 \rightarrow \text{slope} = -9727$

Therefore, the equation of tangent is:

$\Delta H = -9727 \times 0.3 + C = -2918 + C$

At $X_{Cu} = 0.3, \Delta H_m = 21540 \times 0.3^2 - 22651 \times 0.3 + 808 = -4049$

Hence: $-2918 + C = -4049 \rightarrow C = -1131$

The equation of the tangent at $X_{Cu} = 0.3$ is:

$\Delta H = -9727X_{Cu} - 1131$

Therefore, for $X_{Cu} = 1$: $\boldsymbol{\Delta\bar{H}_{Cu} = -10858}$ **J.mol^{-1}**

And, for $X_{Au} = 1 \rightarrow X_{Cu} = 0$: $\Delta\boldsymbol{\bar{H}_{Au}} = \mathbf{-1131}$ **J.mol^{-1}**

The same procedure adopted for the partial molar enthalpies can also be applied to obtain partial molar free energies. However, it is necessary first to obtain the entropy of mixing as function of X_{Cu}. For example, for $X_{Cu} = 0.3$:

$\Delta S_m = -R(X_A \ln X_A + X_B \ln X_B) = -8.314 \times (0.3 \ln 0.3 + 0.7 \ln 0.7)$
$= 5.079$ J.mol^{-1}.K^{-1}

The following table illustrates the values obtained by applying each time equation (3.30). The last row has been calculated from: $\Delta G_m = \Delta H_m - T\Delta S_m$ at $T = 775$K

$\boldsymbol{X_{Cu}}$	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
$\Delta\boldsymbol{H_m}$	-1242	-2861	-4049	-4806	-5133	-5028	-4493	-3527	-2131
$\Delta\boldsymbol{S_m}$	2.703	4.160	5.079	5.595	5.763	5.595	5.079	4.160	2.703
$\Delta\boldsymbol{G_m}$	-3337	-6085	-7985	-9142	-9599	-9364	-8429	-6751	-4225

Next, an expression for ΔG_m as function of X_{Cu} is deduced from the previous table:

$\Delta G_m = 36398X_{Cu}^2 - 37509X_{Cu} + 15.45$

At $X_{Cu} = 0.3, \Delta G_m = -7985$

$\frac{d\Delta G_m}{dX_{Cu}} = 72796X_{Cu} - 37509$

$X_{Cu} = 0.3 \rightarrow \text{slope} = -15670$

Therefore, the equation of tangent is:

$\Delta G = -15670X_{Cu} + C$

$-7985 = -15670 \times 0.3 + C$ Hence: $C = -3284$

The equation of the tangent at $X_{Cu} = 0.3$ is:

$\Delta G = -15670X_{Cu} - 3284$

Therefore, for $X_{Cu} = 1$: $\Delta\boldsymbol{\bar{G}_{Cu}} = \mathbf{-18954}$ **J.mol^{-1}**

And, for $X_{Au} = 1 \rightarrow X_{Cu} = 0$: $\Delta\boldsymbol{\bar{G}_{Au}} = \mathbf{-3284}$ **J.mol^{-1}**

The results are illustrated for the free energy values in Figure (3.5)

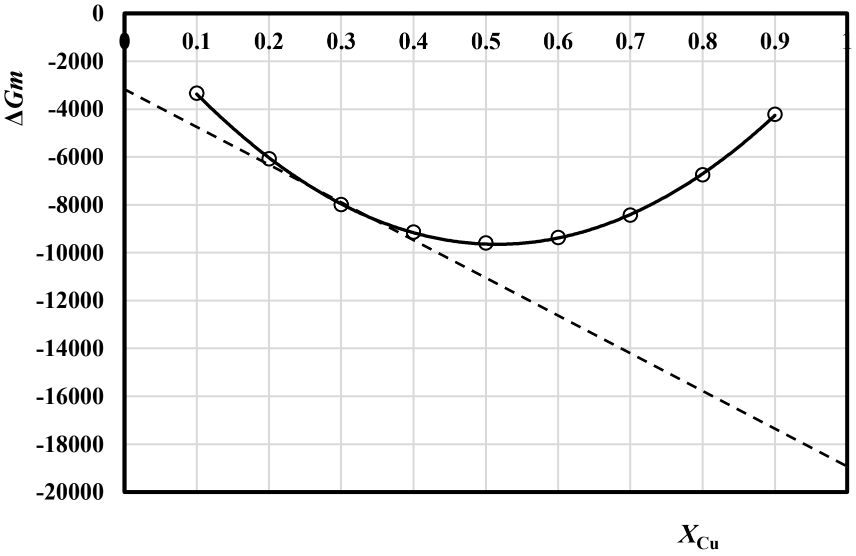


Fig (3.5): Free energy curve of solution in the Cu–Au system at 775K

3.1.8 An application to phase diagrams

(a) Free energy of binary systems with total solid solubility

The principles explained in the past sections will be used to predict the equation of the shapes of the liquidus curve in a simple diagram like the one shown in Figure (3.6). This figure depicts a binary system A – B where total solubility exists for all compositions of the two components.

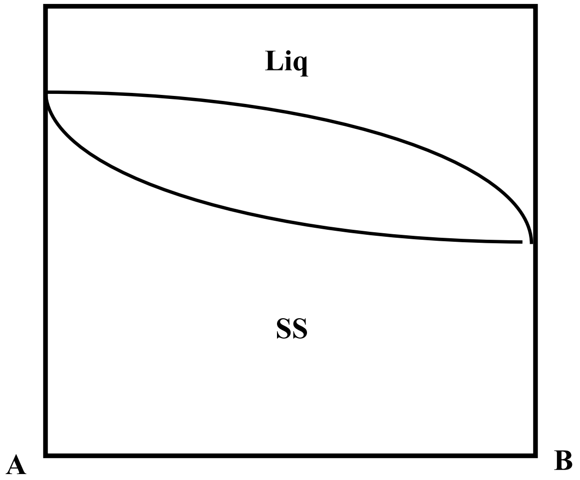


Fig (3.6): Phase diagram A – B

At any temperature T, for compositions with B content close to 1 with a liquid of molar fraction of B = X_L. The free energy of melting, according to the scheme:

B(s) ↔ B Liquid (of composition X_L) is, from equation (2.8):

$\Delta G_M = RT\ln a_{BL} - RT\ln a_{BS}$

$a_L = \gamma_L X_L$ and $a_S = \gamma_S X_S$

Therefore:

$$\Delta G_M = RT\ln\frac{\gamma_L X_L}{\gamma_S X_S}$$

From equation (1.43):

$$\left(\frac{\partial\left(\frac{\Delta G_M}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right)_p = \frac{\partial(R\ln\frac{\gamma_L X_L}{\gamma_S X_S})}{\partial\left(\frac{1}{T}\right)}$$

Assuming the activity coefficient to be constant, then $d(R\ln\gamma_L X_L) = R.(0 + d\ln X_L)$ and $d(R\ln\gamma_S X_S) = R.(0 + d\ln X_S)$,

$$\frac{\partial(R\ln\frac{\gamma_L X_L}{\gamma_S X_S})}{\partial\left(\frac{1}{T}\right)} = -R\frac{d\left(\ln\frac{X_L}{X_S}\right)}{dT}\times T^2 = \Delta H_M$$

$$\frac{d\left(\ln\frac{X_L}{X_S}\right)}{dT} = -\frac{\Delta H_M}{RT^2} \qquad (3.40)$$

Integration is performed in the neighborhood of B where $X_B \to 1$, and as $T \to T_B$, the composition of B in either liquid or solid phases are close enough to assume that $\frac{X_L}{X_S} \approx 1$, so that at $T \to T_B$, $\ln\frac{X_L}{X_S} \to 0$. Also, it can be proved that in that case, the enthalpy of mixing approaches that of melting of B. The result of integration produces the expression:

$$\ln\frac{X_{BL}}{X_{BS}} = \frac{\Delta H_B}{R}\left(\frac{1}{T_B} - \frac{1}{T}\right) \qquad (3.41)$$

This way, this equation can be used to predict the composition of the liquid associated with a solid composition at any temperature T.A similar expression that can be written on the A side:

$$\ln\frac{X_{AL}}{X_{AS}} = \frac{\Delta H_A}{R}\left(\frac{1}{T_A} - \frac{1}{T}\right) \qquad (3.42)$$

Where, $X_{AL} = 1 - X_{BL}$ and $X_{AS} = 1 - X_{BS}$

Solving these two equations together for chosen values of T can disclose the shapes of the liquidus and solidus curves.

Example 3.4

Silicon and germanium form a complete series of solid solutions. From the following data, draw the expected phase diagram.

	Si (A)	**Ge (B)**
Melting point K	1687	1211
ΔH_m **kJ.mol^{-1}**	50.2	31.8

Solution:

Temperatures are assumed between 1211 and 1687K, and each time $\frac{X_{BL}}{X_{BS}}$ and $\frac{1-X_{BL}}{1-X_{BS}}$ are computed to obtain the solid and liquid compositions of Ge at that temperature:

$\ln\frac{X_{BL}}{X_{BS}} = 3825\left(\frac{1}{1211} - \frac{1}{T}\right)$ and $\ln\frac{1-X_{BL}}{1-X_{BS}} = 6038\left(\frac{1}{1687} - \frac{1}{T}\right)$

T K	1211	1230	1270	1310	1350	1390	1430	1470	1510	1550	1590	1630	1680	1687
$\ln X_L/X_S$		0.049	0.147	0.239	0.325	0.407	0.484	0.557	0.625	0.691	0.753	0.812	0.882	
X_L/X_S		1.05	1.158	1.269	1.384	1.501	1.622	1.744	1.869	1.995	2.123	2.252	2.415	
$\ln(1-X_L)/(1-X_S)$		-1.329	-1.175	-1.030	-0.893	-0.764	-0.643	-0.528	-0.42	-0.316	-0.218	-0.125	-0.015	
$(1-X_L)/(1-X_S)$		0.265	0.309	0.356	0.409	0.465	0.526	0.59	0.657	0.729	0.804	0.882	0.985	
X_S	1	0.936	0.814	0.705	0.606	0.516	0.433	0.355	0.283	0.214	0.149	0.086	0.010	0
X_L	1	0.983	0.943	0.895	0.839	0.775	0.702	0.62	0.529	0.427	0.316	0.193	0.025	0

Fig (3.7) shows the diagram obtained (Closed circles) compared to experimental points (Open squares).

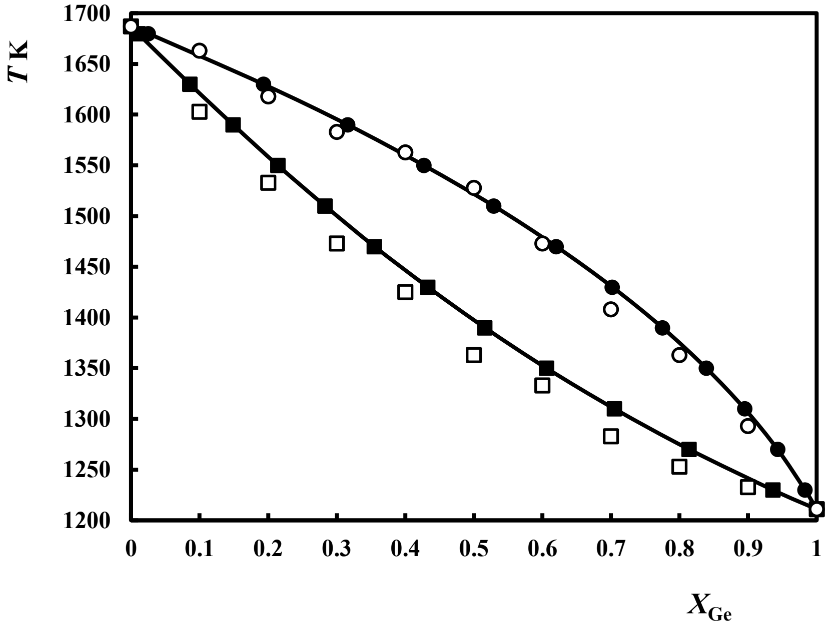


Fig 3.7: Calculated and experimental points in the system Si – Ge

(b) Free energy – composition diagrams

In section (3.1.4), it was explained that for ideal systems, the free energy – composition curve passes through a minimum value at 50 mol% of either component. In case the two components do not form an ideal solution, the situation gets more complicated. If the two components form a simple eutectic with solid solubility, then at a temperature above the liquidus temperature (T_1), the free energy of mixing will show a minimum value, not necessarily at 50% composition (Figure 3.8).

Consider now a temperature $T_{2,}$ above the solidus but below the liquidus curve. The free energy of mixing curves of both B in A and A in B take a parabolic shape with minimum values. Figure (3.8) show that the free energy of mixing of the two components in the liquid state shows as a parabolic curve with a minimum value lower than those of the two free energy curves for solid solubility. When common tangents are drawn to the solid solubility curves and the liquid curve, they show that the free energy of the coexistence of A and liquid, as denoted by the left tangent line, as well as that of coexistence of B and liquid (Right tangent line) are lower than that of mixing in the liquid state.

One can deduce that, at $T_{2,}$ if $a < X_B < c$, the phases A + liquid will be present, whereas if $d < X_B < b,$ the phases liquid + B will coexist. If $c < X_B < d,$ the free energy curve of mixing in the liquid state will be lower than the two tangents, and the only phase present is liquid.

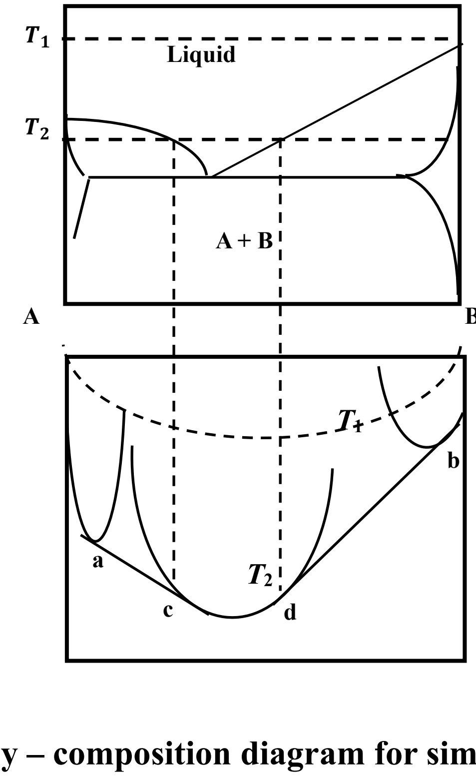


Fig (3.8): Free energy – composition diagram for simple eutectic system at T_2

Another interesting case is that where a solid compound dissociates upon cooling (or heating) to two solid phases.

Let A and B form an intermediate compound C = A_mB_n, which is stable at any temperature above T_e. Below that temperature, it dissociates to its initial components A and B:

C (s) = A(s) + B(s) $(T < T_e)$

This is known as **a eutectoid** reaction, and plays a major role in material engineering, particularly in the iron and steel industry.

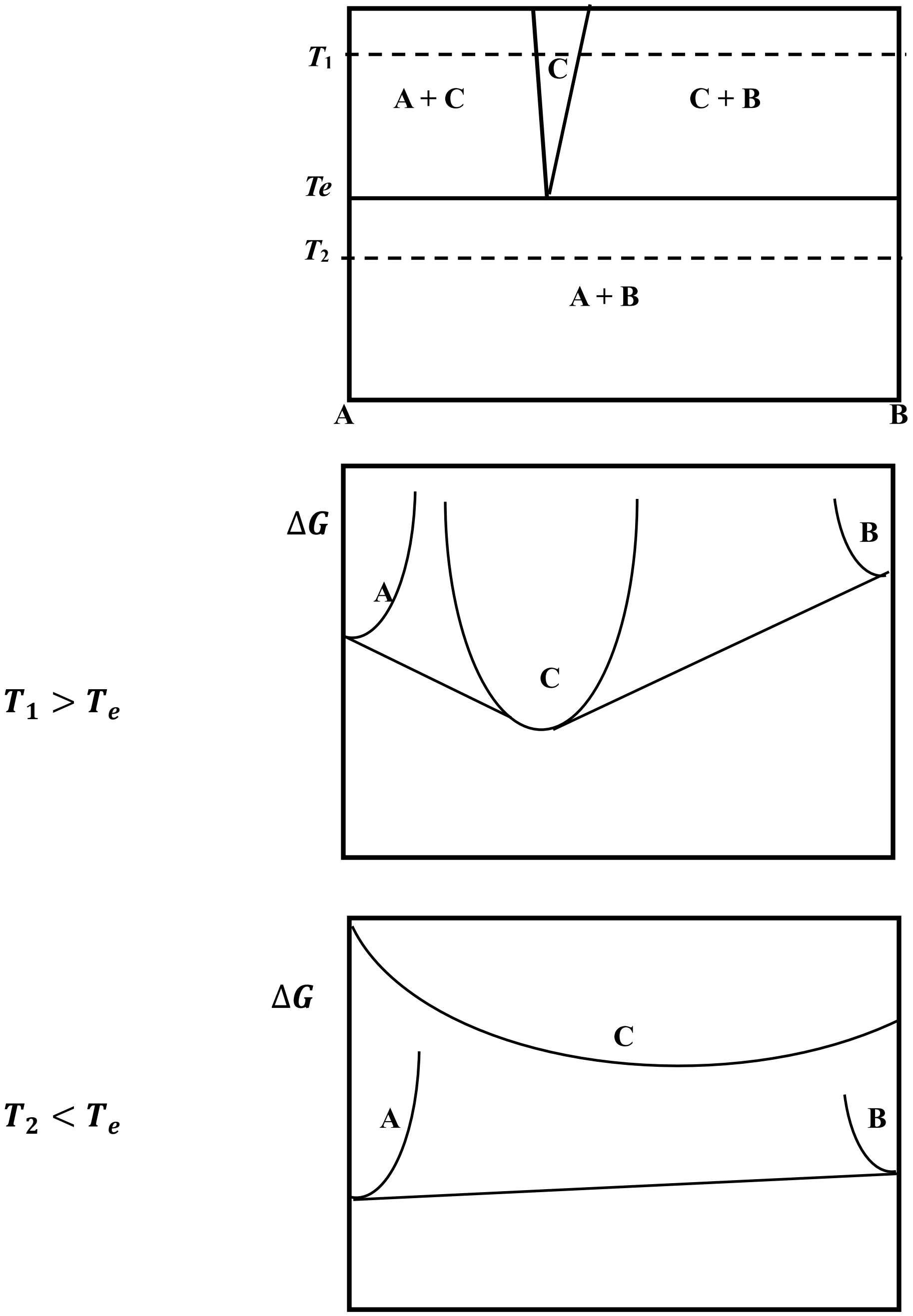


Fig (3.9): Free energy – composition diagram for a eutectoid system at T_e

Figure (3.9) shows that at temperatures above the eutectoid temperature T_e, the two common tangents drawn from the free energy curves of A and B to that of C, are situated at free energy values lower than those of the free energy curve of C. Hence, there will exist two two-phase regions: A + C and C + B, except at the small composition region where the temperature line at T_1 crosses the non-stoichiometric portion of C. Only in that limited region will C be present as a single phase.

On the other hand, at temperatures below the eutectoid temperature T_e, The free energy curve of C is well above the tangent line to the free energy curves of A and B, thus revealing the two phases A and B will be stable at these temperatures.

PROBLEMS

1. 40 g nickel is mixed with 100 g copper and the mixture heated to complete melting. When the melt solidifies, an ideal solution is formed. Estimate the following at 300K:
   (a) The entropy of mixing.
   (b) The enthalpy of mixing.
   (c) The free energy of mixing.

2 The following data give the free energy of a solution of zinc and gallium. Derive an equation for the variation of the free energy as function of the mole fraction of zinc in the binary solid solution in the form of a second-degree polynomial.

X_{Zn}	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1
ΔG kJ.mol^{-1}	0	-0.28	-0.43	-0.5	-0.57	-0.58	-0.55	-0.5	-0.4	-0.29	0

Estimate the partial molal values of free energy for both metals at $X_{\text{Zn}} = 0.4$

3. TiO_2 can dissolve BeO in solid solution for up to 8% molar BeO. In a solution containing 2% molar BeO, At 1800°C, the vapor pressure of BeO = 4.6×10^{-3}Pa, and the activity coefficient = 0.91. At that temperature, the vapor pressure of TiO_2 = 7.8×10^{-5} Pa. Estimate the total pressure of that solution at 1800°C.

4. Silicon is slightly soluble in aluminum. The melting point of Al = 660°C and its enthalpy of fusion = 10.8 kJ.mol^{-1}. What is the melting point at the maximum solubility limit of silicon = 2.3% mol?

5. MgO and NiO form a regular solution for all compositions. The enthalpy of mixing at 700K is given by the following expression:

   $\Delta H_m = 4510X_{\text{NiO}}^2 - 4510X_{\text{NiO}}$ J.mol^{-1}

   Estimate the following:
   (a) The entropy of mixing at $X_{\text{NiO}} = 0.4$
   (b) The free energy of mixing at that composition.
   (c) The partial molal enthalpy of MgO and NiO at $X_{\text{NiO}} = 0.4$.

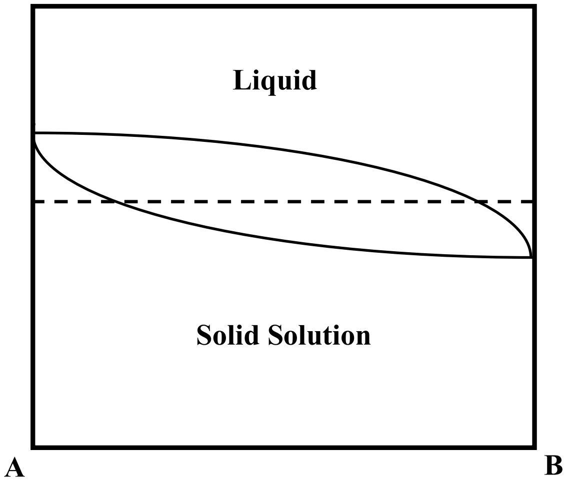
6. Nickel and copper form a complete series of solid solutions. Their melting points are 1728K and 1358K respectively. Their enthalpy of melting are 17.2 kJ.mol^{-1} and 13.6 kJ.mol^{-1}, respectively. Draw the corresponding phase diagram, assuming activity coefficients = 1.

7. At 1200K, the enthalpy of mixing of a solid B in another solid A is related to the mol fraction of B by the expression:

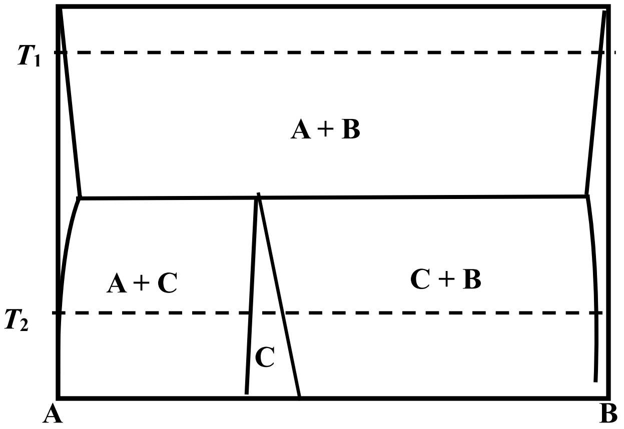
   $\Delta H_m = -20150 X_B(1 - X_B)$ J.mol^{-1}

   If the two solids form a regular solid solution, estimate the entropy and free energy of mixing when the enthalpy of mixing reaches its minimum value.

8. For the given phase diagram, draw the free energy of mixing – composition diagram at the temperature corresponding to the dashed line.



9. Draw the free energy – composition diagrams corresponding to the two temperatures T_1 and T_2 in the following diagram representing a non – stoichiometric compound C dissociating on heating to A and B (Peritectoid reaction).



CHAPTER 4

Phase Equilibrium Diagrams with variable pressure

4.1 Basic concepts

Consider the diagram RO_2 – RO where R is a metal that can have oxidation states 2 and 4. As the higher oxide decomposes to the lower form, the following reaction takes place:

$2\ RO_2\ (s) = 2\ RO\ (s) + O_2\ (g)$

The presence of three phases means that, at constant oxygen partial pressure: $F = 2 - 3 + 1 = 0$. That is, at constant partial pressure of oxygen, this reaction will take isothermally at a temperature that can be determined from Equation (2.6):

$$\Delta H^0 - T\Delta S^0 = -RT \ln p_{O_2}$$

If these two oxides form a simple eutectic, the situation will appear as in Figure (4.1). If RO_2 is heated at low oxygen partial pressure (p_1), then it will decompose to RO at a fixed temperature T_1 obtained from the above equation. As RO is formed, this will represent a single phase and one single component. At constant pressure, so that $F = 1 - 1 + 1 = 1$. This means that the temperature will not remain constant but rather increase until a certain value $T_1^*$where a liquid is formed. In that case, the value of $F = 0$ and the temperature will remain constant while an uptake of oxygen will take place until the isobar at p_1 intercepts the liquidus line. As one liquid phase remains, the value of $F = 1$ and temperature will go on increasing with oxygen loss.

As the partial pressure of oxygen is raised to p_2, the decomposition temperature will follow suit and will increase to T_2. The melting temperature (T_2^*) will be lower than T_1^* since melting is accompanied with a gain of oxygen. Here also, as the isobar intercepts the liquidus line, temperature will increase with loss of oxygen.

As the partial pressure is further increased to p_3, the decomposition temperature T_3 may exceed the eutectic temperature T_E and the drawn isotherm at T_3 will intersect the liquidus line with loss of oxygen with the high oxygen partial pressure suppressing reduction to RO. As the partial pressure is increased to p_4, the melting temperature will increase to T_4.

The temperature at which any of the above transformations take place is related to the oxygen partial pressure by equation (2.6). This can be rearranged to read:

$\frac{\Delta H^0}{T} - \Delta S^0 = -R \ln p_{O_2}$ which can be put in the form:

$$\ln p_{O_2} = A - \frac{B}{T} \qquad (4.1)$$

In this equation, the slope $B = -\Delta H^0/R$ and the intercept $A = \Delta S^0/R$

The standard values of enthalpy and entropy of reaction should be determined at the temperature of reaction. However, the heat capacities of the solids involved are usually close enough to use the standard values at 25°C.

Figure (4.2) represents the relation between p_{O_2} and T for the phase transformations appearing in Fig (4.1). The discussion above can be easily seen to apply to that figure.

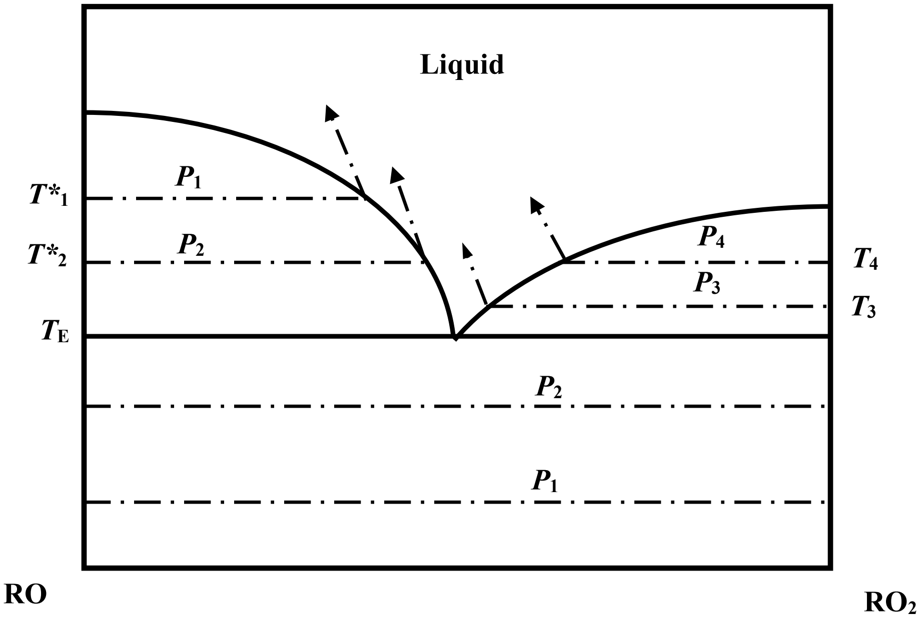


Fig 4.1: RO₂ – RO phase diagram with simple eutectic formation

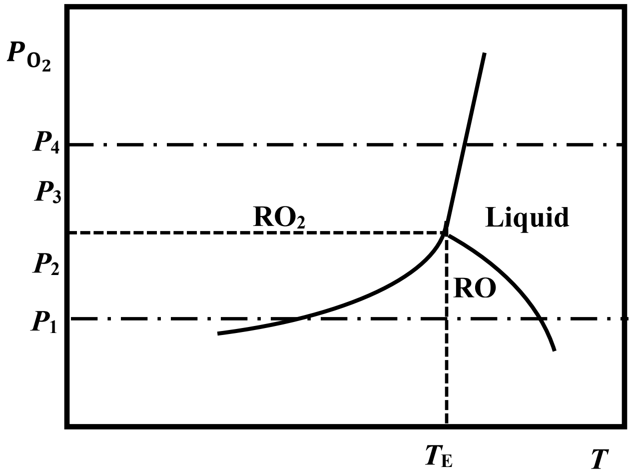


Fig 4.2: Oxygen partial pressure – Temperature diagram for the RO₂ – RO system

4.2 The case of complete solid solubility

If the two end members of a non – condensed oxide system are totally soluble in each other, then the corresponding phase diagram will appear as shown in Figure (4.3). We assume that when RO_2 is heated at low oxygen partial pressure p_1, it will gradually lose oxygen until the metal R is reached, following the reaction:

$RO_2\ (s) = R\ (s) + O_2\ (g)$

However, since the two solids are totally soluble in sold state, then the number of degrees of freedom at constant p_{O_2} will not be zero: $F = 2 - 2 + 1 = 1$. This means that this decomposition will not take place at constant temperature and the corresponding isobar will be a curve.

As the partial pressure of oxygen is raised to p_2, the corresponding rise in temperature will get the isobar to intercept with the solidus curve, at a temperature T_2. In the presence of three phases (Liquid + solid + oxygen), the number of degrees of freedom will drop to zero and melting will occur isothermally. Once the solid has totally melted, there will be only two phases (Liquid + O_2) and the isobar will move along a curve, losing oxygen towards the R end. At very high oxygen partial pressure p_3, RO_2 will melt first, then the liquid formed will lose oxygen along a curved isobar.

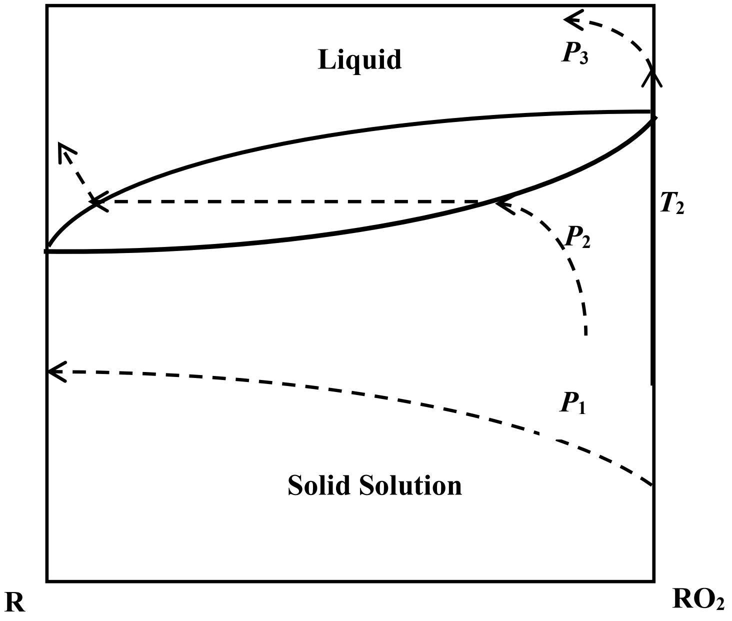


Fig 3: RO_2 – R phase diagram with total solubility in the solid state

However, the relation between p_{O_2} and T is not as simple as that predicted by Equation (4.1), since the activity of the oxide in solid solution ≠ 1, and the term p_{O_2} in that equation should be replaced by $\frac{p_{O_2} \times a_R^2}{a_{RO_2}^2}$. If the activity coefficients of the two solids = 1, then Equation (4.1) takes the form:

$$\ln \frac{p_{O_2} . X_R^2}{1 - X_R^2} = A - \frac{B}{T} \tag{4.2}$$

At constant oxygen partial pressure, assuming the pressure is too low for any melting to take place, the relation between temperature and composition takes the form:

$$T = \frac{B}{A - \ln\frac{p_{O_2} \cdot X_R^2}{1 - X_R^2}} \qquad (0 < X_R < 1) \tag{4.3}$$

This represents the equation of the dotted isobar at pressure p_1 in Figure (4.2).

It is to be noted that in that case, it is not possible to draw a diagram like that in Figure (4.2) representing the relation between oxygen partial pressure and temperature since, as can be seen from equation (4.3), this will require a three – dimensional representation since temperature will be a function of both oxygen partial pressure and molar composition.

It is also important to note that, in applying equations (4.1) and (4.2), care should be taken to use the values of p_{O_2} in atmosphere, since the standard state of gases is taken as 1 atm.

4.3 Formation of an intermediate compound

Consider now the case where the low valence oxide RO can be reduced to a lower oxide like R_2O or to metallic R. In that case, RO will be an intermediate compound between RO_2 and R_2O (or R). Figure (4.4) shows the case where RO_2 and RO are the only two oxides of the metal R. It will be assumed that no solid solubility will be exhibited by any of the oxides and that the oxide RO is congruently melting at temperature T_M.

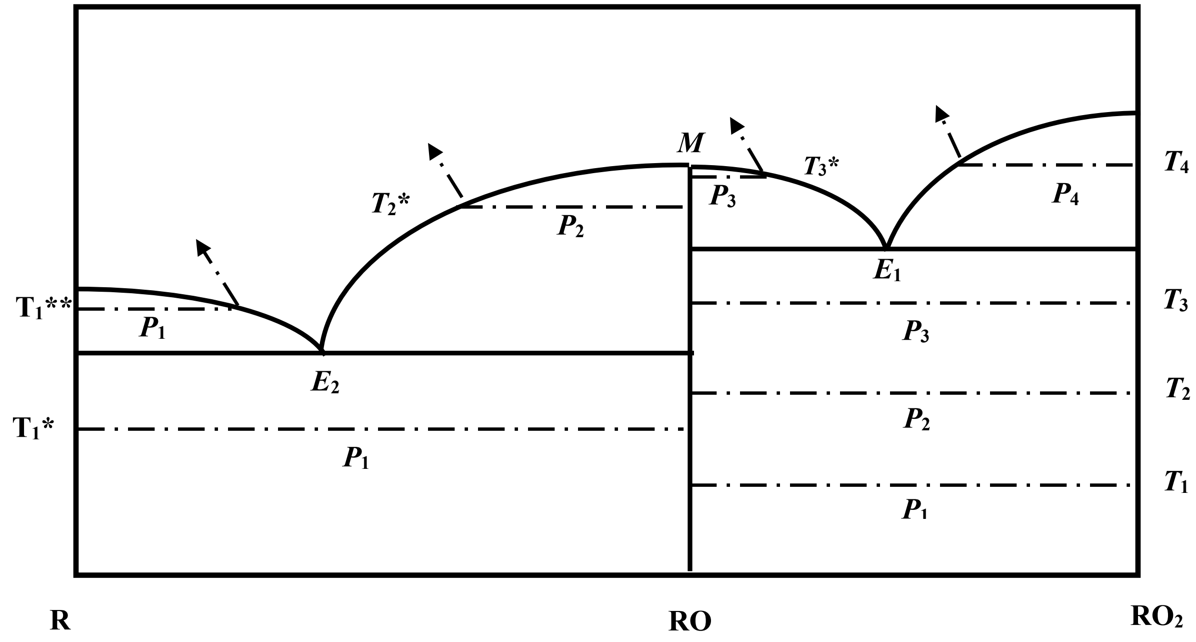


Fig 4.4: Formation of a congruently melting intermediate compound

At a low oxygen pressure p_1, RO_2 decomposes to RO at a temperature T_1. On raising temperature, RO will be reduced to the metallic form R at a temperature T_1^*. On further temperature rise, the metal will melt at fixed temperature T_1^{**} with partial gain of oxygen. Once full melting has taken place, a rise in temperature will cause the liquid melt to lose oxygen.

At a higher oxygen pressure p_2, RO_2 will decompose to RO at a higher temperature T_2. However, this oxide will not be reduced to the metal because of the higher oxygen level present. Rather, it will melt with oxygen loss at T_2^*.

Further increase in the oxygen pressure to p_3 will cause the oxide RO to form at a higher temperature T_3. However, this oxide will start melting isothermally at T_3^* with oxygen gain until total melting, after which raising the temperature will cause the melt to lose oxygen.

Finally, the application of a high pressure p_4 will suppress the reduction of RO_2 and this oxide will melt with oxygen loss at temperature T_4.

The corresponding $p_{O_2} - T$ diagram is shown in Figure (4.5).

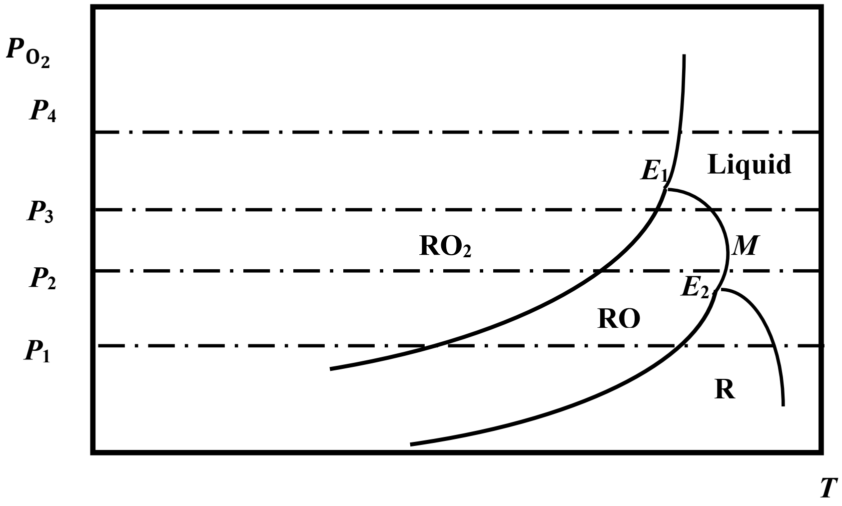


Fig 4.5: Oxygen partial pressure – Temperature diagram for the RO_2 – R system

In that figure, the boundary between RO and liquid possesses a turning point at M, corresponding to the congruently melting point of RO.

Such systems are very common when dealing with the thermal behavior of multivalent oxides. They may involve a series of oxides as is the case with the Mn – O system where the following degradation takes place:

$MnO_2 \rightarrow Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow MnO \rightarrow Mn$

The corresponding diagram is extremely useful in predicting the temperatures at which any of these transitions will take place and is of importance in the refining of manganese ores.

4.4 Application: The Fe – O system

The Fe – O diagram is a typical case of such systems of utmost importance in iron and steel manufacture. Its features are presented in Figure (4.6) which displays the partial system $FeO – Fe_2O_3$.

The higher oxide (Hematite Fe_2O_3) melts at about 1620°C at a partial oxygen pressure of about 10^4 atm. Under atmospheric pressure $p_{O_2} = 0.21$ atm, it converts to the spinel solid solution Fe_3O_4 (Magnetite) at about 1500°C. However, this temperature can be drastically reduced if the oxygen partial pressure is decreased. For example, at an oxygen partial pressure of 10^{-10} atm. This reduction will take place at 760°C.

The Fe_3O_4 spinel melts congruently at about 1600°C at an oxygen partial pressure of about 10^{-1} atm. It forms a eutectic with hematite at about 1550°C and 10 atm oxygen pressure.

Fe_3O_4 is reduced to wüstite solid solution (FeO) at temperatures increasing with increased oxygen partial pressures ranging from 610°C at $p_{O_2} = 10^{-24}$atm to 1340°C at $p_{O_2} = 10^{-6}$atm. Any further rise in oxygen pressure will cause the spinel (Fe_3O_4) to melt directly with loss of oxygen. As shown in Figure, at $p_{O_2} = 10^{-2}$atm, melting takes place at about 1515°C with loss of O_2.

Wüstite, on the other hand, covers a wide range of solid solutions having the iron deficit structure $Fe_{1-x}O$ with values of x ranging from 0.04 to 0.12. It melts incongruently at about 1415°C at an oxygen partial pressure of about 10^{-4} atm. The composition of the formed liquid, under these conditions, is 0.37 Fe_2O_3:($FeO + Fe_2O_3$). Wüstite forms a eutectic with metallic iron at about 1380°C and $p_{O_2} = 10^{-10}$atm. At lower oxygen partial pressures, wüstite will directly convert to metallic iron. Below 560°C, at an extremely low pressure, it decomposes to Fe_3O_4 and pure iron in a eutectoid reaction.

Finally, it is worth mentioning that a miscibility gap is present on the high iron side associated with a monotectic point formation, although this is not shown on the figure.

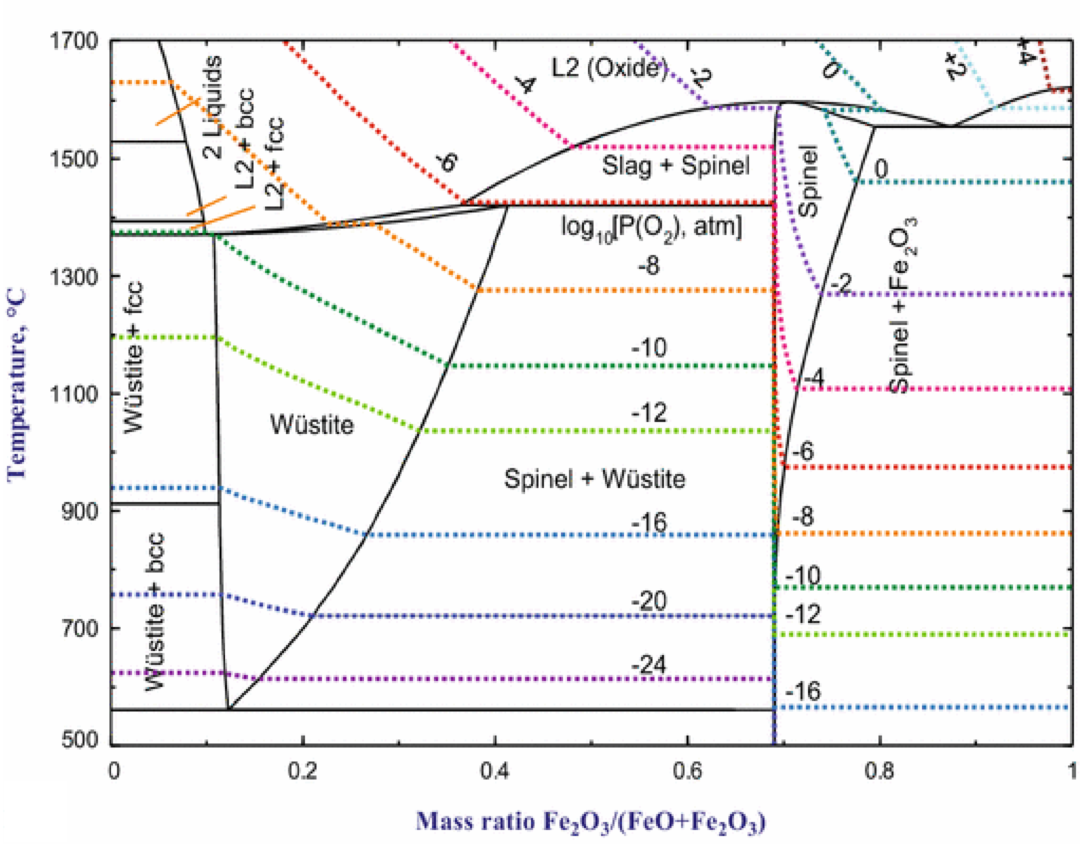


Fig 4.6: The Fe – O system

Example 4.1

The following figure refers to the Ni – NiO system under various oxygen partial pressures ranging from 1 to 10^4 Pa. Enumerate the invariant situations together with the corresponding temperature and composition.

Perform a plot between $\ln p_{O_2}$ and $1/T$ for the oxidation reaction and deduce the temperature at which the metal will oxidize under atmospheric conditions. Predict the decomposition temperature of NiO at oxygen partial pressures of 1 and 0.1 Pa.

Also deduce the enthalpy and entropy changes of the reduction of NiO to metallic Ni through the reaction: 2 NiO = 2 Ni + O_2. Compare with the published values: $\Delta H^o = 239.2$ kJmol^{-1} Ni and $\Delta S^o = 171$ J.mol^{-1} Ni. Give the reason for any discrepancies.

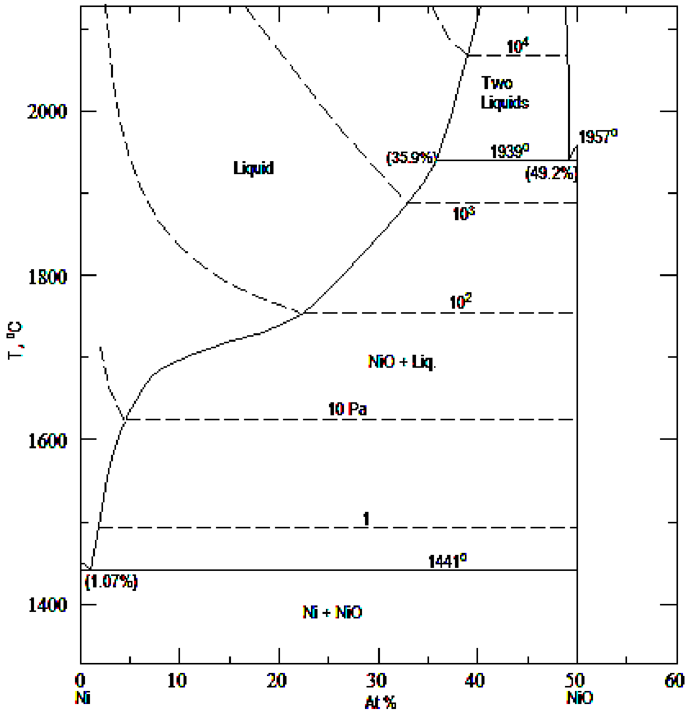


Fig 4.7: The NiO – Ni system

Solution:

The following table indicates the different invariant points, the corresponding temperature, reaction and composition of each.

Type of invariant point	O:NiO	Reaction on cooling	T°C
Monotectic	0.492	Liquid = 2 Liquids	1939
Eutectic	0.0107	Liquid = Ni + NiO	1441

The following table relates to the oxygen pressure – temperature plot.

T°C	p_{O_2} Pa	p_{O_2} atm	$1/T$ K^{-1}	$\ln p_{O_2}$ (atm)
1441	1	9.87E-06	0.000583	-11.526
1622	10	0.0000987	0.000528	-9.223
1755	10^2	0.000987	0.000493	-6.921
1888	10^3	0.00987	0.000463	-4.618
2064	10^4	0.0987	0.000428	-2.316

The requested $\ln p_{O_2}$ vs $1/T$ diagram is shown in Figure (4.8). Its equation takes the form:

$$\ln p_{O_2} = -\frac{60509}{T} + 23.27$$

$p_{O_2} = 0.21$ atm, $T = 2787.2\text{K} \equiv \mathbf{2514.2^oC}$

When $p_{O_2} = 0.1$ Pa $\equiv 9.87 \times 10^{-6}$ atm, $T = 1738.9\text{K} \equiv \mathbf{1465.9^oC}$

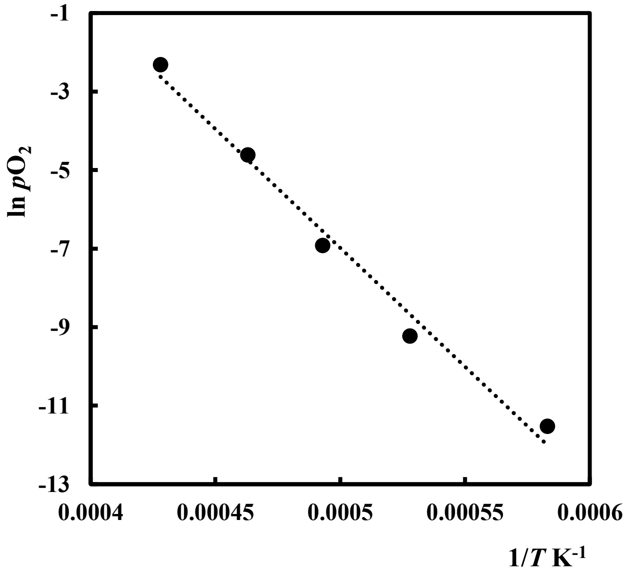


Fig 4.8: $\ln p_{O_2}$–$1/T$ diagram

The slope of the curve = $-\frac{\Delta H^0}{R} = -60509$, from which: $\Delta H^0 = 503071$ J.mol^{-1}, equivalent to 503.07 kJ.mol^{-1}.

This represents the enthalpy of the reaction 2NiO = 2Ni + O_2. Hence the enthalpy of the reaction per g atom Ni = 0.5 × 503.07 = $\mathbf{251.54}$ **kJ.mol^{-1}**

Similarly, the intercept $\frac{\Delta S^0}{R}$ = 23.27 J.mol^{-1}K^{-1} and hence $\Delta S^0 = 193.5$ J.mol^{-1}K^{-1}. Per g atom nickel, this figure is divided by 2 to give: $\mathbf{\Delta S^0 = 96.75}$ **J.mol^{-1}K^{-1}**.

The result for enthalpy fairly compares with the experimental: $\Delta \boldsymbol{H^o} = \mathbf{239.2}$ **kJ.mol^{-1}** However, $\Delta \boldsymbol{S^0} = \mathbf{171}$ **J.mol^{-1}K^{-1}**, and the difference in entropy is appreciable.

The difference in values is due that the reduction of NiO to Ni does not exactly follow the stoichiometric equation cited previously. The actual reaction is:

NiO (s) = NiO_{1-x} (liq) + $\frac{x}{2}$ O_2

Only when $x = 1$, would the two equations get alike. From Figure (4.7), this will only happen at extremely low pressures.

Example 4.2

Figure (4.9) represents the case of an oxide RO melting incongruently at temperature T_p according to the peritectic reaction: Liquid + R (s) = RO (s). Roughly plot the corresponding $\ln p_{O_2} - 1/T$ diagram.

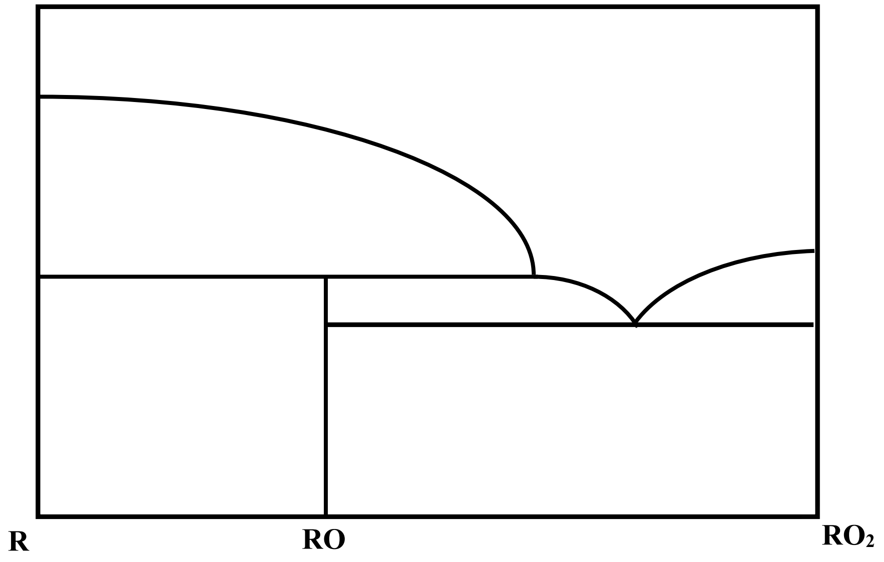


Fig (4.9): RO is incongruently melting

Solution:

The diagram is redrawn adding the phases in each region and the main isobars (Figure 4.10). the requested oxygen partial pressure – temperature diagram is shown in Figure (4.11).

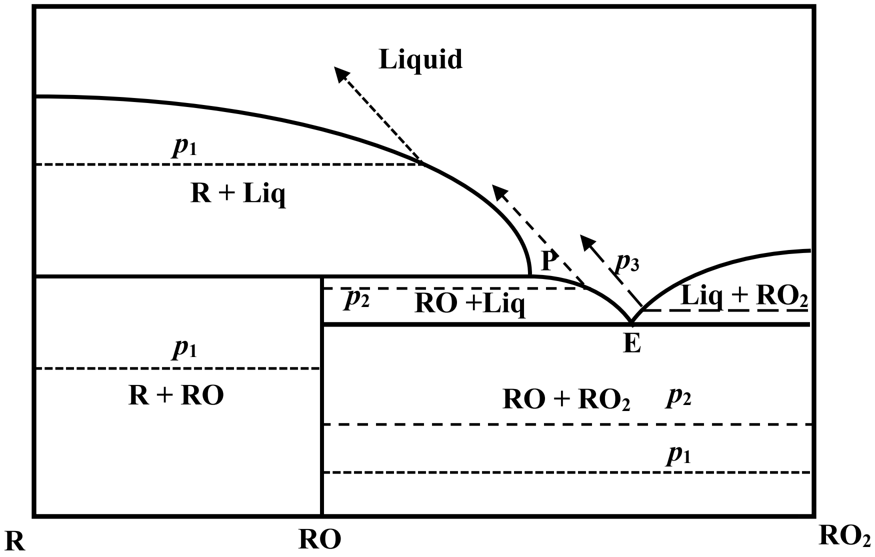


Fig 4.10: RO$_2$ – R Diagram with added data

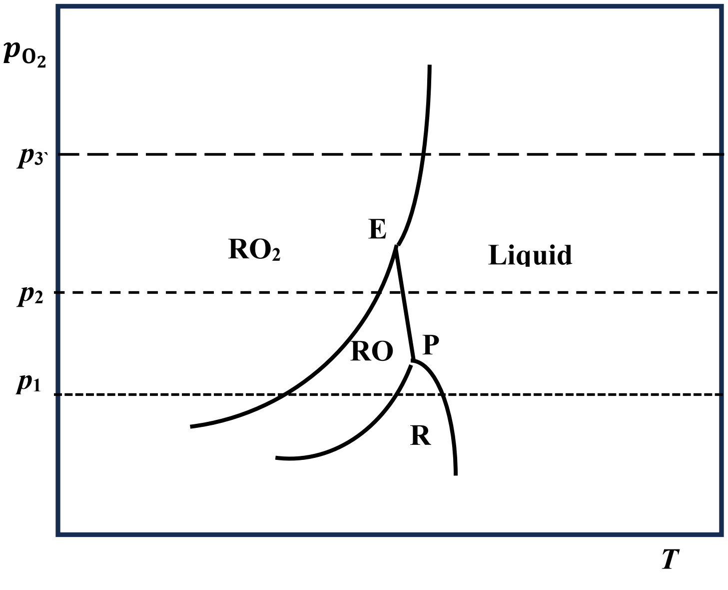


Fig 4.11: Oxygen partial pressure – Temperature diagram

Example 4.3

Figure (4.14) shows the U – O diagram with isobars drawn at oxygen partial pressures = 10^k Pa. Draw the $\ln p_{O_2} - 1/T$ diagram considering the formation of solid solutions and deduce from that diagram the enthalpy and entropy changes of the reaction:

UO_2 (s) = U (s) + O_2 (g) (Consider the activity coefficient = 1 in all cases)

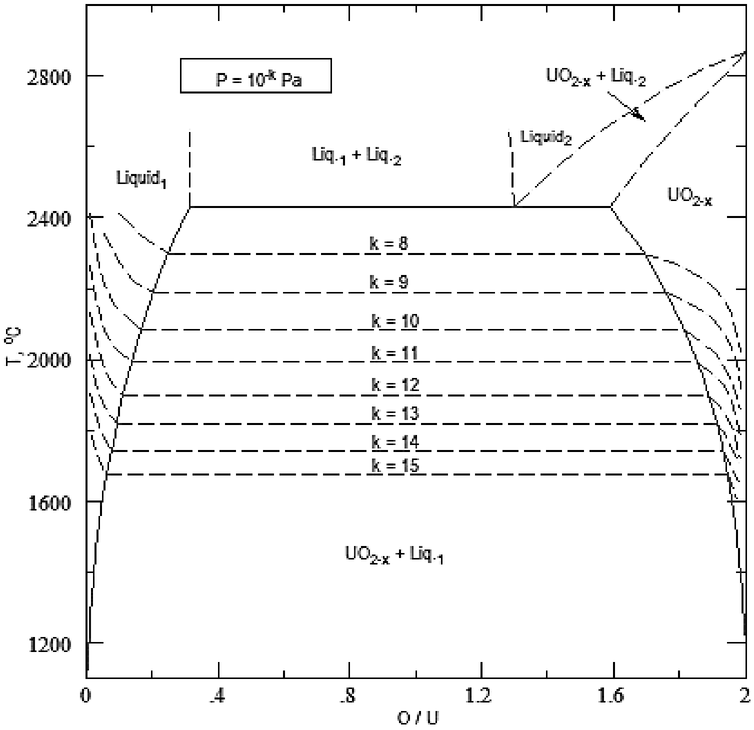


Fig 4.12: The U – O system

Solution:

Since activity coefficients are supposed to be equal to unity, then $a_i = X_i$. The following table was set from the isobars in the diagram:

The values of X_U are obtained from $X_U = 1 - 0.5 \times \left(\frac{O}{U}\right)$ and those of X_{UO_2} from $0.5 \times \frac{O}{U}$.

$\log p_{O_2}$	T °C	$1/T$ K^{-1}	p_{O_2} Pa	p_{O_2} atm	X_U(in liquid)	X_{UO_2}
-15	1680	0.00051	10^{-15}	9.8721×10^{-21}	0.975	0.9775
-14	1760	0.00049	10^{-14}	9.8721×10^{-20}	0.9625	0.965
-13	1820	0.00048	10^{-13}	9.8721×10^{-19}	0.954	0.9575
-12	1910	0.00046	10^{-12}	9.8721×10^{-18}	0.945	0.94
-11	1990	0.00044	10^{-11}	9.8721×10^{-17}	0.93	0.925
-10	2090	0.00042	10^{-10}	9.8721×10^{-16}	0.9135	0.905
-9	2210	0.0004	10^{-9}	9.8721×10^{-15}	0.9	0.88
-8	2320	0.00039	10^{-8}	9.8721×10^{-14}	0.8775	0.845

The reduction of the oxide to the metal being $UO_2 = U + O_2$, Equation (4.2) takes the form:

$$\ln\frac{p_{O_2}.X_U}{X_{UO_2}}=\frac{\Delta S^0}{R}-\frac{\Delta H^0}{RT}$$

The following table represents the values of the LHS and $1/T$ (Figure (4.13)).

$1/T$	0.000512	0.000492	0.000478	0.000458	0.000442	0.000423	0.000403	0.000386
LHS	-46.06	-43.76	-41.46	-39.16	-36.86	-34.56	-32.27	-29.98

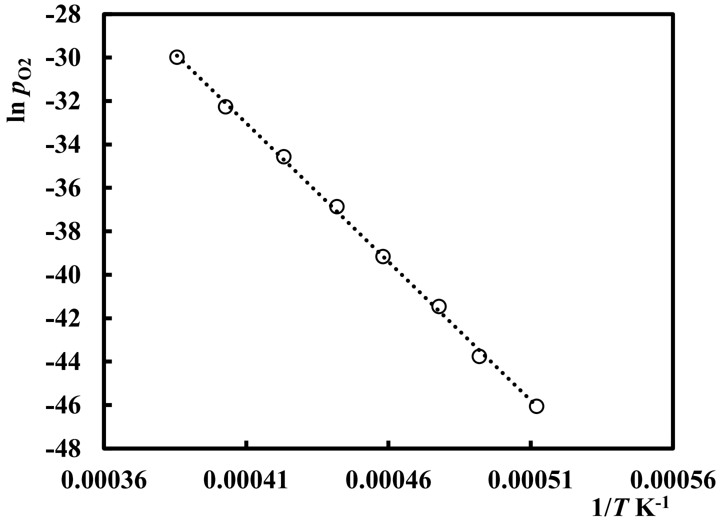


Fig 4.13: Plot of $\ln\frac{p_{O_2}.X_U}{X_{UO_2}}$ against $1/T$

From the slope $\Delta H^0 = 1061$ **kJ.mol^{-1}** and, from the intercept: $\Delta S^0 = 160.55$ **J.mol^{-1}K^{-1}.** (The actual value of $\Delta H^0 = 1084$ kJ.mol^{-1}).

PROBLEMS

1. The following table shows the heats of formation of two manganese oxides.

	ΔH^0 kJ.mol^{-1}	**ΔS^0 J.mol^{-1}.K^{-1}**
Mn_3O_4	-1386.3	186
MnO	-384.6	81.5

(a) Determine the enthalpy and entropy changes of the following decomposition reaction:

$2\ Mn_3O_4\ (s) = 6\ MnO\ (s) + O_2\ (g)$

Neglect the variation of enthalpies of formation due to variations in temperature.

(b) Plot the $\ln p_{O_2} - 1/T$ diagram for the previous reaction using the data of Figure (4.14), assuming solid activities = 1. (Oxygen partial pressures in atm.)

From this diagram, deduce the enthalpy and entropy changes of the reaction, then compare with the values obtained in (a).

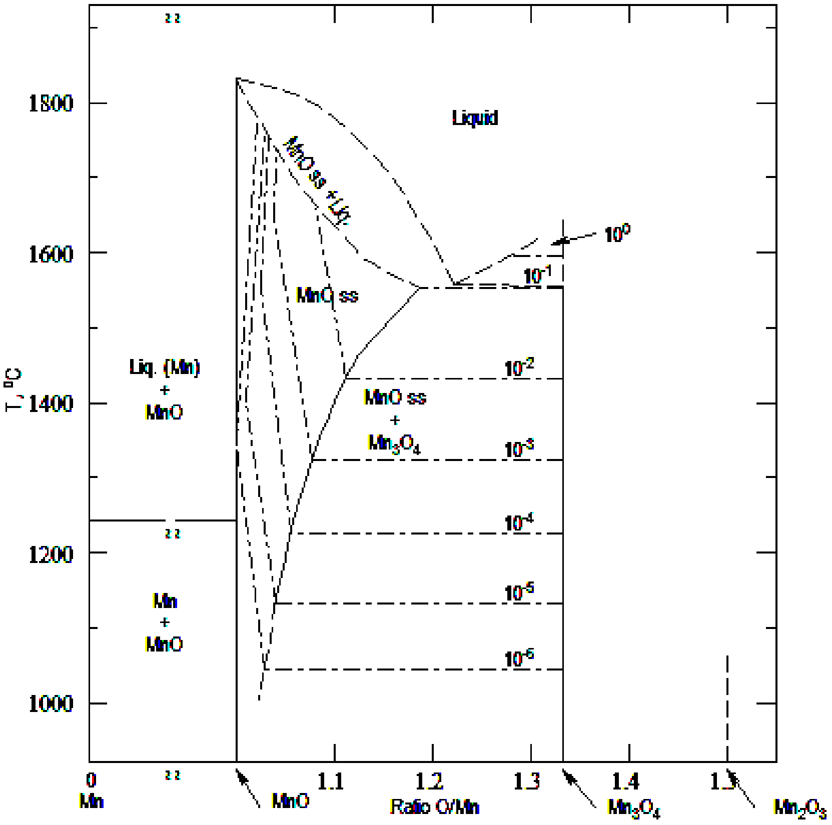


Fig 4.14: The Mn – O system

2. From the diagram in Figure (4.15), deduce the enthalpy and entropy for the reaction: $2\ CuO = Cu_2O + O_2$

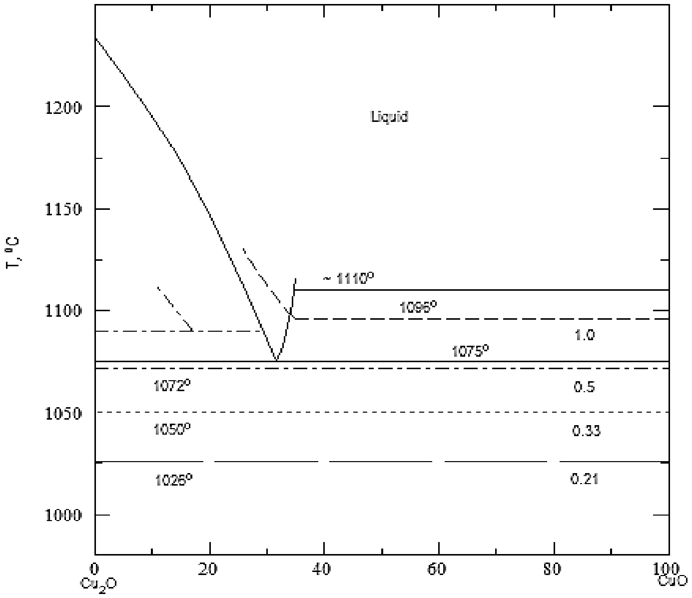


Fig 4.15: The Cu – O system

3. The phase diagram W – O is shown in Figure (4.16). Draw the $\ln p_{O_2} - 1/T$ for:

   WO_2 (s) = W (s) +O_2 (g) for $10^{-30} \leq p_{O_2} \leq 10^{-8}$ atm.

   Deduce the standard enthalpy and entropy of that reaction. Compare with the enthalpy of reaction calculated from an enthalpy of formation of $WO_2 = -564.3$ kJ.mol^{-1}

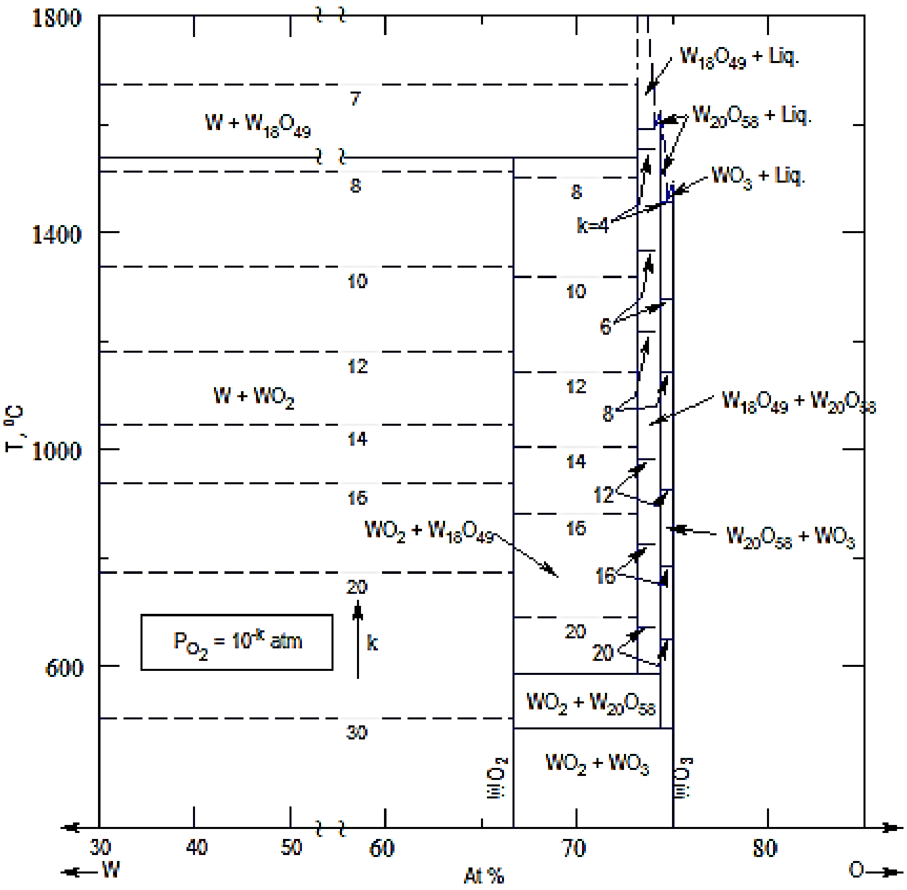


Fig 4.16: The W – O system

4. The following curves relate the equilibrium transformation temperature of TiO_2 to its lower oxides and, ultimately, to Ti metal. From this diagram, estimate the enthalpy and entropy changes for the following reactions:

   4 TiO_2 (s) = 2 Ti_2O_3 (s) + O_2 (g)

   2 TiO (s) = 2 Ti (s) + O_2 (g)

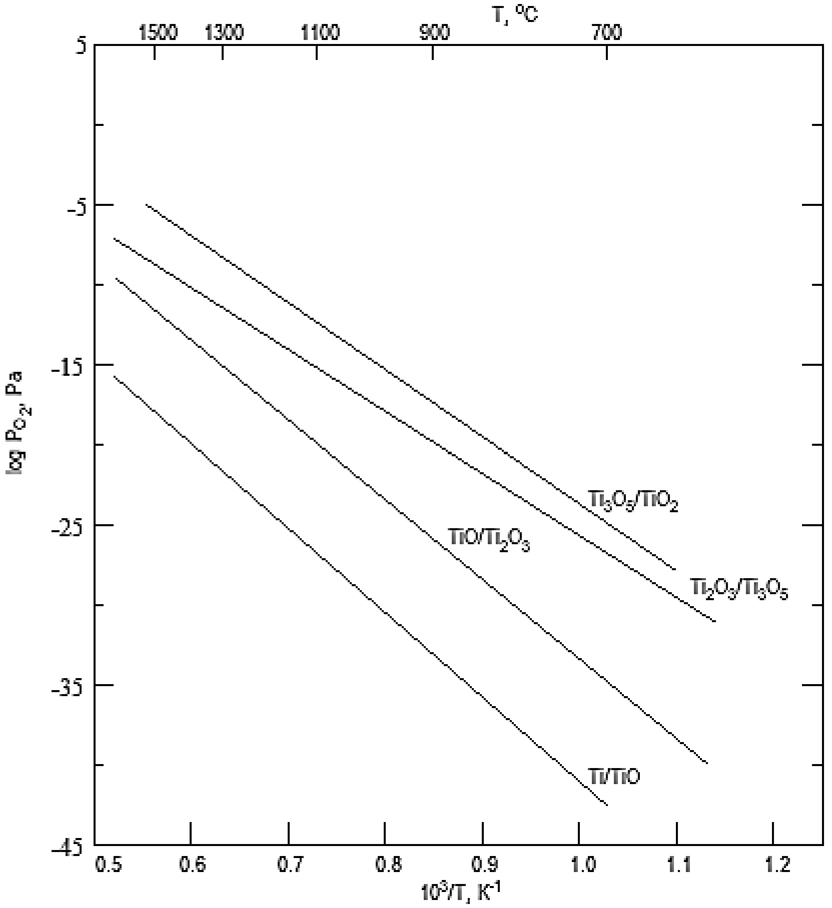


Fig 4.17: $\log p_{O_2} - \frac{1}{T}$ diagram at different temperatures (Ti – O system)

5. The enthalpy and entropy changes of the decomposition of MgO according to the reaction:

   $2MgO (s) = 2Mg (s) + O_2$

   are respectively: $-635\ \mathrm{kJ.mol^{-1}}$ and $38.1\ \mathrm{J.mol^{-1}K^{-1}}$. Use these data to plot $\ln p_{O_2}$ against $1/T$ for this reaction on the temperature range $[3000 - 4000](\mathrm{K})$

References:

R.A. Swalin “Thermodynamics of Solids”, 2nd Edition, Wiley – VCH (1972).

Q. Jiang, Z. Wen “Thermodynamics of Materials” 1st Edition, Springer-Nature (2011)