Physical chemistry

Chemical equilibrium including ionic equilibrium

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CONTENTS

Chemical equilibrium: Equilibrium constant and free energy

Consider a system having a number of chemical species reacting according to the equation given by

$$0=\sum_i \nu_i A_i \qquad \text{(Eq.11.1.1)}$$

Where the A_i represent the chemical species of the reaction and ν_is are the corresponding stoichiometric coefficients, negative for reactants and positive for products. The change in the amount of reactant or a product during the progress of a reaction may be given in terms of the extent of reaction (ξ) defined as

$$n_t(A_i) = n_o(A_i)+\nu_i \xi \qquad \text{(Eq. 11.1.2)}$$

where $n_o(A_i)$ is the amount of A_i at t=o. The unit of the extent of reaction, ξ is that of the amount of a substance, i.e. mol. The change in the amount of a reactant or a product with change in the extent of reaction is

$$\frac{dn(Ai)}{d\xi}=\nu_i \qquad \text{(Eq. 11.1.3)}$$

the stoichiometric coefficient of the species A_i in the chemical equation.

If we consider a simple reaction consisting of only two reactants and two products, then we write the chemical equation as:

$$\nu_1A_1+\nu_2A_2 \rightarrow \nu_3A_3+\nu_4A_4 \qquad \text{(Eq.11.1.4)}$$

If the amounts of reactants at the start of the reaction are $n_o(A_1)$ and $n_o(A_2)$ and ξ is the extent of reaction; then

$$n(A_1) = n_o(A_1)+\nu_1 \xi$$
$$n(A_2) = n_o(A_2)+\nu_2 \xi$$
$$n(A_3) = \nu_3 \xi$$
$$n(A_4) = \nu_4 \xi$$

As the νs are negative for reactants and positive for products, the amounts of reactants decrease and that of products increase as the reaction progresses.

Reaction potential and criterion for chemical equilibrium

The change of Gibbs function due to either chemical reaction or variation in temperature and pressure is given by

$$dG = -SdT+Vdp+\sum_i \mu_{A_i}\, dn_{A_i} \qquad \text{(Eq.11.1.5)}$$

Substituting for dn_{Ai} from equation 11.1.3, we write

$$dG=-SdT+Vdp+\sum_i (\nu_i \mu_{A_i})d\xi \qquad \text{(Eq.11.1.6)}$$

The term $\sum_i \nu_i \mu_{A_i}$ is called the reaction potential and is given by ΔrG

$$\sum_i \nu_i \mu_{A_i} = \Delta rG \qquad \text{(Eq.11.1.7)}$$

As the reaction advances at constant T and P, the change in Gibbs energy is given by:

$$dG=(\sum_i \nu_i \mu_{A_i})\, d\xi \qquad \text{(Eq.11.1.8)}$$

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \sum_i \nu_i \mu_{A_i} = \Delta rG \qquad \text{(Eq.11.1.9)}$$

The reaction potential is equal to the rate of change of total free energy with extent of reaction at constant temperature and pressure. The reaction potential is identical to the free energy change of a reaction, ΔrG. A reaction will take place spontaneously or not depends on the value of dG. At constant T and P, we can write from equation 11.1.9:

$$dG = \Delta rG\, d\xi \qquad \text{(Eq.11.1.10)}$$

A reaction proceeds spontaneously if there is a free energy decrease, that is, $dG<0$, $\Delta rG d\xi<0$. On the other hand, if, as the reaction advances, there is an increase in free energy, $dG>0$, $\Delta rG d\xi>0$, the reaction will not proceed in the forward direction. The reaction goes spontaneously in the opposite direction with a decrease in free energy. Thus reaction goes spontaneously in the direction of free energy decrease but only until the free energy of the

system reaches a minimum value. When the free energy of the system is a minimum, the reaction is at equilibrium, that is, dG=0, $\Delta rG d\xi = 0$.

As $\Delta rG d\xi < 0$ for a spontaneous reaction and $d\xi$ is positive for the forward reaction,

$\Delta rG < 0$ can be taken as a criterion for a spontaneous reaction.

$$\Delta rG = \nu_3\mu_3 + \nu_4\mu_4 - \nu_1\mu_1 - \nu_2\mu_2 \qquad \text{(Eq.11.1.11)}$$

ΔrG is given by the equation 11.1.11 for the reaction given by the equation 11.1.4. In equation 11.1.11, μ_{A_i} is being given as μ_i for the sake of convenience.

$\Delta rG > 0$ shows a non spontaneous forward reaction, but the back reaction will be spontaneous, products will be converted to reactants.

$\Delta rG = 0$ can be taken as a criterion for a reaction to be at equilibrium as a infinitesimal change in ξ produces dG=0. This happens when

$$\nu_1\mu_I + \nu_2\mu_2 = \nu_3\mu_3 + \nu_4\mu_4 \qquad \text{(Eq.11.1.12)}$$

Equation 11.1.12 is the requirement for the reaction at equilibrium. As the variables in this equation are intensive variables, it is independent of the relative amounts of the various species involved in the reaction.

The equilibrium condition for any chemical reaction can be written as:

$$\Delta rG = \sum_i \nu_i\mu_i = 0 \qquad \text{(Eq.11.1.13)}$$

The chemical potential of an ideal gas is given by:

$$\mu_i = \mu_i^0 + RT\ln(p_i/p^0) \qquad \text{(Eq.11.1.14)}$$

Where μ_i^0 = standard chemical potential,

p_i = Partial pressure of the gas,

p^o = standard-state pressure, 1 bar

The reaction potential can then be written as :

$$\Delta rG = \sum_i \nu_i\mu_i = \Delta rG^o + RT\sum_i \nu_i\ln(p_i/p^0)$$

$$\Delta rG = \Delta rG^o + RT\ln\left[\pi_i (p_i/p^o)^{\nu_i}\right]$$

(Eq.11.1.15)

Where standard reaction potential, $\Delta rG^o = \sum_i \nu_i \mu_i^0$ and

$\prod_i$ = is the multiplication symbol.

$$\Delta rG = \Delta rG^o + RT\ln\frac{\prod_{\text{i products}} (p_i/p^o)^{\nu_i}}{\prod_{\text{i reactants}} (p_i/p^o)^{\nu_i}} \qquad \text{(Eq.11.1.16)}$$

The value of the reaction potential of a reaction which has just started, the extent of reaction ξ is almost zero, the system has only reactants and products have not formed as yet, due to the second term of equation 11.1.16, is negative and very large. The reaction because ΔrG is negative and very large, proceeds spontaneously in the forward direction.

If we have a reaction mixture rich in products with almost no reactants, ξ nearly one, then the value of the reaction potential ΔrG will be positive and large. The reaction then proceeds spontaneously in the reverse direction and the products decompose to give reactants. For a particular composition of the reaction mixture containing both products and reactants, ΔrG=0. The reaction has no tendency to form either products or reactants. The reaction is at equilibrium.

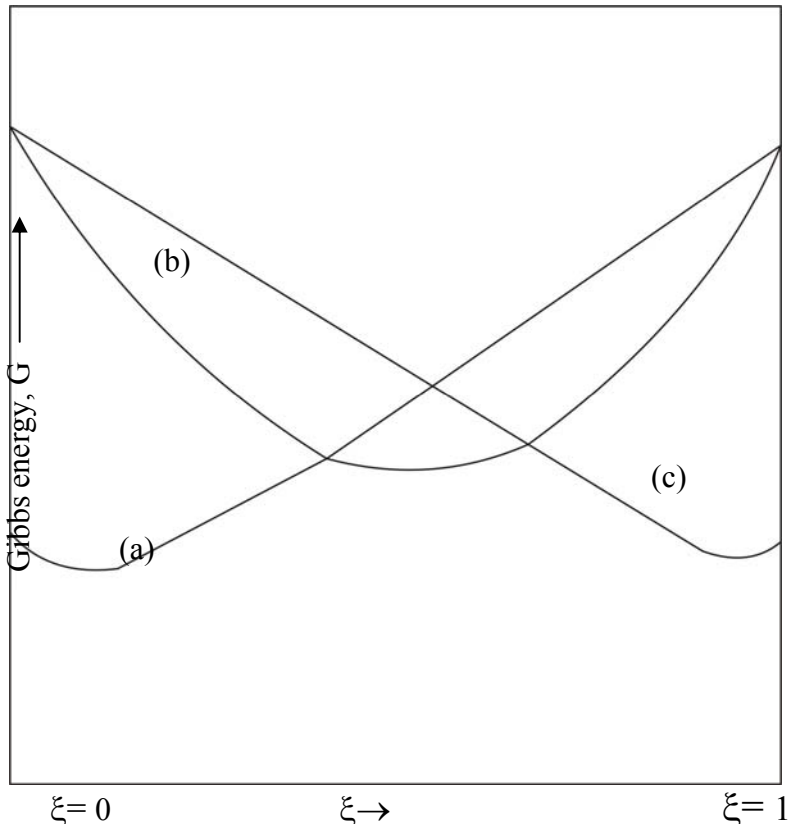

Figure 11.1.1: Gibbs energy variation with extent of reaction at constant T and p.

Figure 11.1.1 shows how (Gibbs) free energy, G varies with the extent of reaction. The curve (a) depicts a reaction which proceeds very little in the forward direction, the minimum in the Gibbs energy occurs very close to ξ=O. Curve (b) represents a reaction which has approximately equal amounts of reactants and products present in the reaction mixture. The curve (c) shows a reaction that has proceeded to near completion, the minimum in Gibbs energy is very near ξ=1.

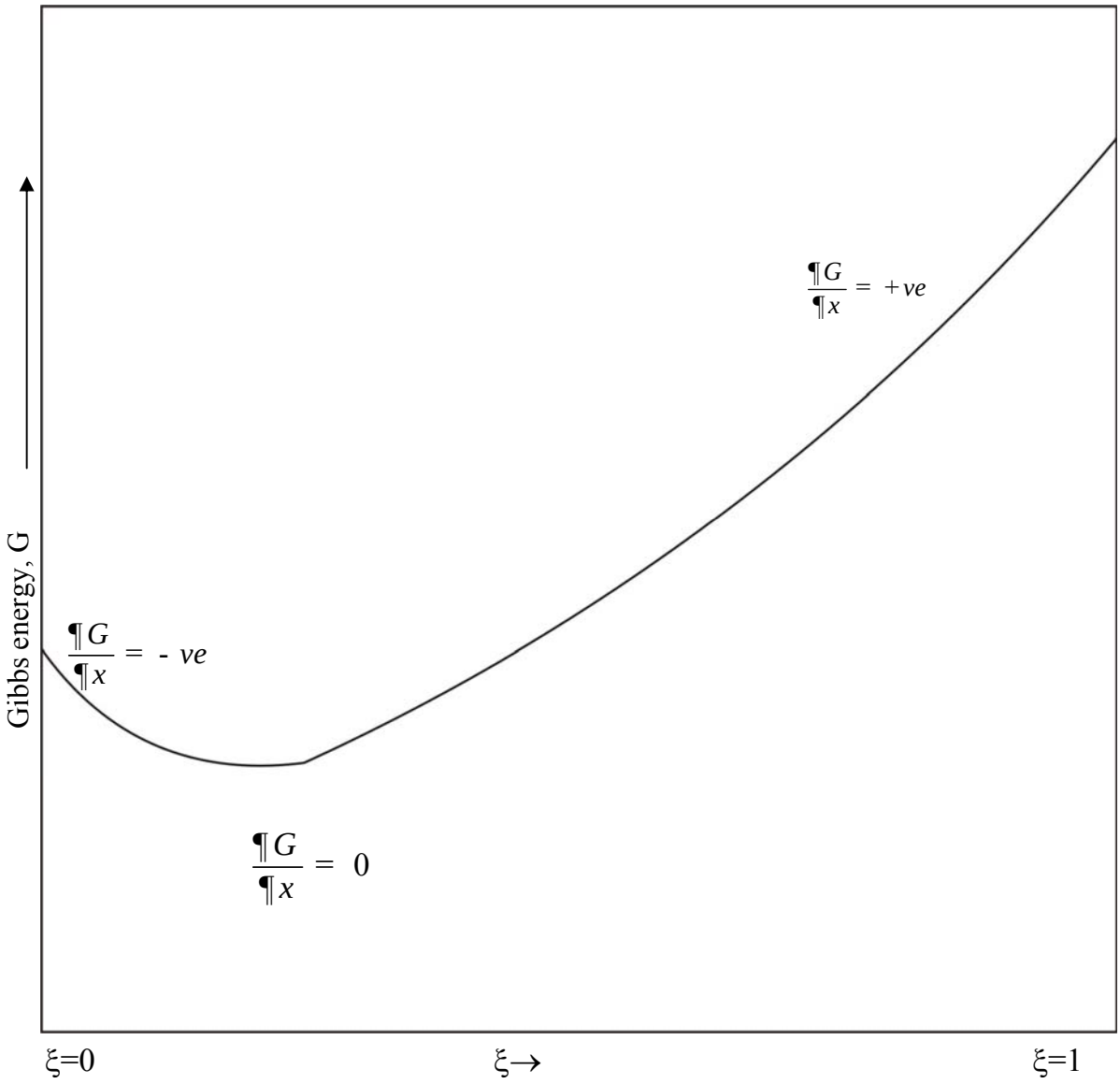

Figure 11.1.2: Gibbs energy variation with extent of reaction at constant T and p

The reaction potential, ΔrG is the slope of G plotted against extent of reaction, ξ (equation 11.1.9). We see from the graph of G versus ξ (Figure 11.1.2), for values of ξ close to zero, $\frac{\partial G}{\partial \xi}$ is negative, ΔrG<0, the reaction is spontaneous and moves in the forward direction. For values of ξ close to one, $\frac{\partial G}{\partial \xi}$ is positive, ΔrG>0, which indicates spontaneity in the reverse direction. At some intermediate value of ξ, G passes through a minimum, $\frac{\partial G}{\partial \xi}$=0, ΔrG=0, and the reaction is at equilibrium.

The term $\prod_i (p_i/p^o)^{\upsilon_i}$ in equation 11.1.15 is known as the standard reaction quotient Q_p^0. At equilibrium,

$$\prod_i \left\{ \left(p_i / p^o \right)^{\nu_i} \right\}_{eq} = (Q_p^0)_{eq} = K_p^0 \qquad \text{(Eq. 11.1.17)}$$

Where K_p^0 is called the standard equilibrium constant. Writing equation 11.1.15 at equilibrium and substituting from equation 11.1.17, we get

$$0 = \Delta rG^o + RT\ln K_p^0$$

$$\Delta rG^o = -RT\ln K_p^0 = -2.303RT\log K_p^0 \qquad \text{(Eq.11.1.18)}$$

Equation 11.1.18 is a very important equation in chemical thermodynamics. Standard reaction potential ΔrG^o, as defined earlier is given by

$$\Delta rG^o = \sum_i \nu_i \mu_i^0$$

Where μ_i^o s are standard chemical potentials, each is a function of temperature only. Hence ΔrG^o is a function of only temperature and so is K_p^0, the standard equilibrium constant. This equation helps to predict the value of K_p^0 of any reaction from tables of thermodynamic data. Alternatively, ΔrG^o can be calculated for any reaction from a measurement of its equilibrium constant.

Writing equation 11.1.15 in terms of K_p^0 and Q_p^0, we have

$$\Delta rG = RT\ln K_p^0 + RT\ln Q_p^0$$

$$\Delta rG = RT\ln (Q_p^0 / K_p^0) \qquad \text{(Eq.11.1.19)}$$

If for a reaction $Q_p^0 < K_p^0$, then ΔrG=-ve, dG=-ve. The reaction will proceed spontaneously. As the reaction progresses, concentration of the products increases, that of the reactants decreases, Q_p^0 increases. When Q_p^0 becomes equal to K_p^0, ΔrG=O, the reaction is in a state of equilibrium. If, on the other hand, for a reaction $Q_p^0 > K_p^0$, then ΔrG=+ve, dG=+ve, the reaction will not proceed in the forward direction, but has a tendency to proceed in the reverse direction.

Example 11.1.1. Calculating ΔrG^o from K_p^0

The equilibrium constant for the reaction

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$$

is 6.59×10^{-3} at 450°C. Calculate the standard reaction potential.

$$\Delta rG^o = -RT\ln K_p^0$$

$$= -(8.314 J/Kmol)(723K)\ln(6.59 \times 10^{-3})$$

$= 30.2\text{kJ mol}^{-1}$

$\Delta rG^o = \sum_i \nu_i \mu_i^o$

Writing ΔrG^o for this reaction, we have

$\Delta rG^o = \mu^o_{NH_3} - \frac{1}{2}\mu^o_{N_2} - \frac{3}{2}\mu^o_{H_2}$

$= 30.2\text{kJmol}^{-1}$

As this is the formation reaction for ammonia, 30.2kJmol^{-1} is the standard Gibbs energy of formation of ammonia at 450^oC.

Example 11.1.2 Calculating K_p^0 from ΔrG^o value

Calculate the equilibrium constant for the reaction

$COCl_2(g) \rightleftharpoons CO(g)+Cl_2(g)$ at 724K

Given $\Delta rG^o=8.68\text{ kJ mol}^{-1}$

$\Delta rG^o= -RT\ln K_p^0$

$\ln K_p^0 = -\frac{\Delta rG^o}{RT}$

$\ln K_p^0 = -\frac{8.68\times10^3\text{Jmol}^{-1}}{8.314\text{JK}^{-1}\text{mol}^{-1}\times724\text{K}}$

$\ln K_p^0 = -1.4420$

$K_p^0 = 0.2364$

The standard equilibrium constant for the reaction works out to 0.2364 at 724K.

Example 11.1.3

The decomposition of $H_2O(g)$ was studied at 2155^oC taking 1.0mol of water. At equilibrium the extent of reaction was found to be 0.012mol for a total pressure of 1 bar. Calculate K_p^0 and ΔrG^o for the reaction. The reaction is :

$2H_2O(g) \rightleftharpoons 2H_2(g)+O_2(g)$

t=0	1.0 mol	0	0
$t=t_{eq}$	(1.0-0.012)mol	0.012mol	0.006mol

Total amount of substances at equilibrium= 1.006 mol

Partial pressures $p_{H_2O}, p_{H_2}, p_{O_2}$, at equilibrium are :

$p_{H_2O}=\frac{0.988}{1.006}\times1\text{bar}=0.982\text{ bar}$

$p_{H_2}=\frac{0.012}{1.006}\times1\text{bar}=0.0119\text{ bar}$

$p_{O_2} = \frac{0.006}{1.006} \times 1\text{bar} = 0.006 \text{ bar}$

$K_p^o = \prod_i (p_i/p^0)^{vi} = (p_{H_2}/p^o)^2 (pO_{2/}p^0)(p_{H_2O}/p^0)^{-2}$

$K_p^0 = \left(\frac{0.0119 \text{ bar}}{1 \text{ bar}}\right)^2 \left(\frac{0.006 \text{ bar}}{1 \text{ bar}}\right) \left(\frac{0.982 \text{ bar}}{1 \text{ bar}}\right)^{-2}$

$K_p^0 = 8.811 \times 10^{-7}$

$\Delta rG^o = -RT\ln K_p^o = -(8.314 JK^{-1}mol^{-1})(2428K) \times \ln(8.811 \times 10^{-7})$

$\Delta rG^o = +281.440 kJ\ mol^{-1}$

Expressions of K_p^0 for heterogeneous equilibria

Equilibria in which substances are in the same phase are called homogeneous and those in which substances are in more than one phase are called heterogeneous equilibria. The examples we have discussed so far are all homogeneous equilibria. Some examples of heterogeneous equilibria are:

$C(s) + O_2(g) \rightleftharpoons CO_2(g)$

$H_2(g) + I_2(s) \rightleftharpoons 2HI(g)$

$PCl_3(s) + Cl_2(g) \rightleftharpoons PCl_5(s)$

We will see how an expression for K_p^0 is written for a heterogeneous equilibrium taking as an example the reaction:

$C(\text{graphite}) + CO_2(g) \rightleftharpoons 2CO(g)$

$\Delta rG = \sum_i \nu_i \mu_{Ai}$

$\Delta rG = 2\,\mu(CO,g) - \mu(CO_2,g) - \mu(C, gr)$

For an ideal gas, the expression for μ is given by:

$\mu_g(T, p) = \mu_g^o(T) + RT\ln(p/po)$ where $\mu_g^o(T)$ is the standard chemical potential of the gas at temperature T and p is the pressure of the gas.

The chemical potential of a condensed phase is given by $\mu_s(T,p) = \mu_s^o(T)$

$\Delta rG = 2\left\{\mu_{CO(g)}^o + RT\ln(p_{CO}/p^o)\right\} - \left\{\mu_{CO_2(g)}^o + RT\ln\left(\frac{p_{CO_2}}{p^0}\right)\right\} - \mu_{C(gr)}^o$

$\Delta rG = (2\mu_{CO(g)}^0 - \mu_{CO_2(g)}^0 - \mu_{C(g_r)}^0) + RT\ln\frac{(p_{CO}/p^0)^2}{(p_{CO_2}/p^0)}$

$\Delta rG = \Delta rG^o + RT\ln\frac{(p_{CO}/p^0)^2}{(p_{CO_2}/p^0)}$

At equilibrium, $\Delta rG = 0$

$\Delta rG^o = -RT\ln\frac{(p_{CO}/p^0)^2_{eq}}{(p_{CO_2}/p^0)_{eq}}$

$\Delta rG^o = -RT\ln K_p^0$

$\Delta rG^o = 2\mu_{CO(g)}^0 - \mu_{CO_2(g)}^0 - \mu_{C(gr)}^0$

ΔrG^o contains the standard chemical potentials of all the reactants and products.

$$K_p^0 = \frac{(p_{CO}/p^0)^2_{eq}}{(p_{CO_2}/p^0)_{eq}}$$

K_p^0, the standard equilibrium constant, has for a heterogeneous equilibrium only the partial pressures of gaseous substances involved in the equilibrium.

Example 11.1.4

NH_4HS dissociates as follows:

$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$

At 25°C the dissociation pressure of the pure gas is 0.66 bar. Calculate K_p^0 and ΔrG^o of the reaction.

At equilibrium, $p_{NH_3} = p_{H_2S}$

$p_{NH_3} + p_{H_2S} = 0.66$ bar

$p_{NH_3} = p_{H_2S} = 0.66$ bar/2 = 0.33 bar

$$K_p^0 = \prod_i (p_i/p^0)^{v_i} = (p_{NH_3}/p^0)\left(p_{H_2S}/p^0\right) = \left(\frac{0.33\text{bar}}{1\text{ bar}}\right)^2$$

$K_p^0 = 0.109$

$\Delta rG^o = -RT\ln K_p^0 = -(8.314 JK^{-1}mol^{-1})(298K)\times\ln(0.109)$

$\Delta rG^0 = 5491.3\ Jmol^{-1}$

Law of mass action

The law of mass action due to C.M. Guldberg and Peter Waage states:

The rate of a reaction is proportional to the product of effective concentrations of the reacting species, each raised to a power given by the stoichiometric coefficient of the species in the balanced chemical equation.

Recognizing the dynamic nature of chemical equilibria, Guldberg and Waage applied the law of mass action to both the forward and back reactions saying that both reactions continue to take place, only that at equilibrium their rates are equal.

Let us consider the reaction:

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

as an example. Applying the law of mass action to both the forward and reverse reactions, we write

$$-\frac{d[N_2]}{dt} = k_f[N_2][H_2]^3$$

$$-\frac{1}{2}\frac{d[NH_3]}{dt} = k_b[NH_3]^2$$

Where k_f and k_b are proportionality constants. At equilibrium, the rates of the forward and reverse reactions are equal.

$k_f [N_2]_{eq} [H_2]^3_{eq} = k_b [NH_3]^2_{eq}$

$$\frac{k_f}{k_b} = \frac{[NH_3]^2_{eq}}{[N_2]_{eq}[H_2]^3_{eq}}$$

$$\frac{k_f}{k_b} = K_{eq} = \prod_i (C_i)_{eq}^{\upsilon_i}$$

(Eq.11.1.20)

If we consider the gases as ideal, then K_{eq} can be written in terms of partial pressures as these are proportional to concentrations.

$$K_{eq} = \prod_i (p_i)_{eq}^{\nu_i} \qquad \text{(Eq. 11.1.21)}$$

In the case of heterogeneous equilibria, the effective concentrations of solids and liquids remain constant, these are merged with the constant K_{eq} and hence the form of K_{eq} remains the same as that given by equation 11.1.21.

Equation 11.1.20 is a statement of Guldberg and Waage's Law of chemical equilibrium and the constant K_{eq}, the equilibrium constant of the reaction. We have already derived the equilibrium law from thermodynamic principles via equations 11.1.5 to 11.1.19. Equation 11.1.18 relates the standard equilibrium constant K_p^0 to the standard reaction potential ΔrG^o.

Equilibrium constants K_c^0, K_x, K_n

It is convenient in some equilibria to express the composition of the reaction mixture in terms of molar concentration or mole fraction or amount of species instead of partial pressures. Hence let us develop equilibrium constant expressions in these units.

a) In terms of molar concentrations:

$$\kappa_p^0 = \prod_i (p_i/p^0)^{\nu i} \qquad \text{(Eq.11.1.22)}$$

$$\kappa_c^0 = \prod_i (C_i/C^0)^{\nu i} \qquad \text{(Eq. 11.1.23)}$$

Where p^o and c^o are the standard units of pressure and concentration, respectively. The ideal gas equation may be written as

$$Pv = nRT$$

$$p = (n/v)\,RT$$

$$p = CRT \qquad \text{(Eq.11.1.24)}$$

where C is the concentration in terms of mole per unit volume. Substituting for p from equation 11.1.24 into equation 11.1.22, we write

$$\kappa_p^o = \prod_i (C_i RT/p^o)^{\nu i}$$

$$\kappa_p^o = \prod_i \left((C_i/C^o)(C^o RT/p^o\right)^{\nu i}$$

$$\kappa_p^o = \kappa_c^o\,(C^o RT/p^o)^{\Delta \nu g} \qquad \text{(Eq.11.1.25)}$$

Where $\Delta\nu_g$ is the difference between the stoichiometric number of gaseous product molecules and gaseous reactant molecules.

$\Delta\nu_g = \Sigma\nu_g(\text{product}) - \Sigma\nu_g(\text{reactant})$

b) In terms of mole fractions:

The equilibrium constant expressed in terms of mole fractions, K_x is:

$$K_x = \prod_i (x_i)^{\nu i} \qquad \text{(Eq.11.1.26)}$$

The mole fraction of a gas in a gaseous mixture is related to its partial pressure as

$$p_i = Px_i \qquad \text{(Eq.11.1.27)}$$

Where P is the total pressure of the gaseous mixture.

$$K_p^o = \prod_i (p_i/p^0)^{vi} \qquad \text{(Eq.11.1.22)}$$

Substituting for p_i from equation 11.1.27 into equation 11.1.22, we have

$$K_p^o = \prod_i (Px_{i_i}/p^0)^{v_i}$$

$$K_p^o = \prod_i \{(x_i)(p/p^o)\}^{vi}$$

$$K_p^o = K_x (p/p^0)^{\Delta vg}$$

$$K_x = K_p^o (p/p^0)^{-\Delta vg} \qquad \text{(Eq.11.1.28)}$$

c) In terms of amount of substances:
The equilibrium constant expressed in terms of amounts is:

$$k_n = \prod_i (n_i)^{vi} \qquad \text{(Eq.11.1.29)}$$

$$p_i = x_i P \qquad \text{(Eq.11.1.27)}$$

$$p_i = (n_i/n_{total}) \times P \qquad \text{(Eq. 11.1.30)}$$

where n_i is the amount of substance i and n_{total} is the total amount of gases in the system.

$$K_p^o = \prod_i (pi/po)^{v_i} \qquad \text{(Eq.11.1.22)}$$

Substituting from equation 11.1.30 for p_i into equation 11.1.22, we get

$$K_p^o = \prod_i \left(\frac{n_i}{n_{total}} \times \frac{P}{p^0}\right)^{v_i}$$

$$= \prod_i \left(\frac{n_i}{n^0} \times \frac{n^0}{n_{total}} \times \frac{P}{p^0}\right)^{v_i}$$

$$= \left\{\prod_i \left(\frac{n_i}{n^0}\right)^{v_i}\right\} \left(\frac{n^o}{n_{total}}\right)^{\Delta vg} \left(\frac{p}{p^o}\right)^{\Delta vg}$$

$$= K_n^o \times \left(\frac{n^o}{n_{total}}\right)^{\Delta vg} \left(\frac{p}{p_0}\right)^{\Delta vg} \qquad \text{(Eq. 11.1.31)}$$

Where n^o = 1 mol.

We have seen earlier that K_p^o depends only on temperature and is independent of the total pressure of the system. K_c^o also depends only on temperature and independent of pressure. But K_x and K_n depend on both pressure and temperature.

Example 11.1.5

For the reaction:

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

The value of $K_p^o = 5.8 \times 10^{-5}$ at 298 K. Calculate K_p^o and K_c^o at this temperature for the reactions:

(i) $\frac{1}{2}\ N_2\ (g) + \frac{3}{2}\ H_2(g) \rightleftharpoons NH_3\ (g)$

(ii) $NH_3\ (g) \rightleftharpoons \frac{1}{2}\ N_2(g) + \frac{3}{2} H_2\ (g)$

(i) (a) $N_2(g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g)$

$$K_p^0 = \frac{(p_{NH_3}/p^0)^2}{(p_{N_2}/p^0)(p_{H_2}/p^0)^3} = 5.8\times10^{-5}$$

$\frac{1}{2}\ N_2(g) + \frac{3}{2} H_2(g) \rightleftharpoons NH_3\ (g)$

$$K_{p,1}^0 = \frac{(p_{NH3}/p^0)}{(p_{N_2}/p^o)^{\frac{1}{2}}(p_{H_2}/p^0)^{\frac{3}{2}}} = (K_p^o)^{1/2}$$

$K_{p,1}^0 = (5.8 \text{ x } 10^{-5})^{½} = 7.6 \text{ x } 10^{-3}$

$K_{p,1}^0$ for the reaction 1 is 7.6×10^{-3}

b) Calculating $K_{c,1}^0$ for reaction 1

$$K_p^o = K_c^o\left(\frac{c^oRT}{p^o}\right)^{\Delta\ vg}$$

$$K_{p,1}^o = K_{c,1}^o\left(\frac{1\text{moldm}^{-3}\times8.314\text{kPadm}^3\text{K}^{-1}\text{mol}^{-1}\times298\text{K}}{101.325\text{kPa}}\right)^{\Delta vg}$$

$\Delta vg = 1 - \frac{1}{2} - \frac{3}{2} = -1$

$$K_{c,1}^0 = K_{p,1}^0\left(\frac{8.314\times298}{101.325}\right)$$

$K_{c,1}^0 = 7.6\times10^{-3}\times24.45$

$K_{c,1}^0 = 1.9 \times 10^{-1}$

$K_{c,1}^0$ for reaction 1 is 0.19

ii) a) $NH_3(g) \rightleftharpoons \frac{1}{2} N_2\ (g) + \frac{3}{2}\ H_2\ (g)$

$$K_{p,2}^0 = \frac{(p_{N_2}/p^0)^{\frac{1}{2}}(p_{H_2}/p^0)^{\frac{3}{2}}}{(p_{NH_3}/p^0)} = \frac{1}{K_{p,1}^0}$$

$$K_{p,2}^0 = \frac{1}{7.6\times10^{-3}} = 1.3\times10^2$$

$K_{p,2}^0$ for reaction 2 = 1.3×10^2

b) Calculating $K_{c,2}^0$ for reaction 2

$$K_{p,2}^0 = K_{c,2}^0 \times \left(\frac{1\text{moldm}^{-3}\times8.314\text{kPadm}^3\text{K}^{-1}\text{mol}^{-1}\times298\text{K}}{101.325\text{kPa}}\right)^{\Delta vg}$$

$\Delta vg = \frac{1}{2} + \frac{3}{2} - 1 = 1$

$$K_{C,2}^0 = K_{p,2}^0 \times \left(\frac{8.314\times298}{101.325}\right)^{-1}$$

$K_{C,2}^0 = 1.3 \times 10^2\ (24.45)^{-1}$

$K_{C,2}^0 = 5.3$

$K^0_{C,2}$ for reaction 2 is 5.3

Example 11.1.6

The standard equilibrium constants for the following reactions are given at 1362K.

(i) $H_2(g) + ½\ S_2(g) = H_2S(g)$ $\quad K^0_{p,1} = 0.80$

(ii) $3H_2(g) + SO_2(g) = H_2S(g)+2H_2O(g)$ $\quad K^0_{p,2} = 1.8 \times 10^4$

Calculate K^0_p for the reaction given below at 1362 K.

$4H_2(g) + 2SO_2(g) = S_2(g)+4H_2O(g)$

We multiply equation (i) by 2.

(iii) $2H_2(g) + S_2(g) = 2H_2S(g)$

$$K^0_{p,3} = \frac{p^2_{H_2S}(p^0)}{p^2_{H_2} p_{S_2}} = (K^0_{p,1})^2 = 0.64$$

We multiply equation (ii) by 2 to get equation (iv)

(iv) $6H_2(g) + 2SO_2(g) = 2H_2S(g)+4H_2O(g)$

$$K^0_{p,4} = \frac{p^2_{H_2S} p^4_{H_2O} (p^0)^2}{p^6_{H_2} p^2_{SO_2}} = (K^0_{p,2})^2 = 3.24 \times 10^8$$

Subtracting equation (iii) from equation (iv) we get

(v) $4H_2(g) + 2SO_2(g) = S_2(g)+4H_2O(g)$

$$K^0_{p,5} = \frac{p_{S_2} \times p^4_{H_2O} \times (p^0)}{p^4_{H_2} \times p^2_{so_2}}$$

$$\frac{K^0_{p,4}}{K^0_{p,3}} = \frac{p^2_{H_2S} p^4_{H_2O} (p^0)^2}{p^6_{H_2} . p^2_{SO_2}} \times \frac{p^2_{H_2} \times p_{S_2}}{p^2_{H_2S}(p^0)} = \frac{p_{S_2} \times p^4_{H_2O} p^0}{p^4_{H_2} \times p^2_{SO_2}} = K^0_{p,5}$$

$$K^0_{p,5} = \frac{K^0_{p,4}}{K^0_{p,3}} = \frac{3.24 \times 10^8}{0.64} = 5.06 \times 10^8$$

The standard equilibrium constant, K^0_p for the given reaction is 5.06×10^8

LeChatelier-Braun Principle

LeChatelier-Braun Principle predicts qualitatively the effect of variation in pressure, temperature and concentration on a system under equilibrium. The principle states:

When a system in a state of equilibrium is subjected to a disturbance, the composition of the system changes to minimize the effect of the disturbance.

For example, if a system in a state of equilibrium is compressed, then according to the principle, the equilibrium shifts in a direction that has less number of molecules in the gas phase. If instead the system is heated, the system moves in a direction where heat is absorbed. On the other hand, say, one of the constituents is added, then the system proceeds in a direction that consumes this constituent.

The reason for a reaction responding in the way it is doing on the introduction of a disturbance, as predicted by LeChatelier-Braun principle, and the composition of the new equilibrium to which the system moves are provided by thermodynamics. We also need to keep this aspect in mind that a change of temperature of a system under equilibrium affects the value of ΔrG^0 and therefore the value of the equilibrium constant whereas a change in

pressure or amount of a constitutent affects only the equilibrium composition and not the value of the constant.

Effect of temperature and pressure variation on the equilibrium ξ value of a reaction

We have already seen earlier in this chapter that the reaction potential, ΔrG is equal to the rate of change of total free energy with extent of reaction at constant T and p. Thus ΔrG is a function of T, p and ξ

$$\Delta rG = \left(\frac{\partial G}{\partial \xi}\right)_{T,p}$$

$$d(\Delta rG) = \left(\frac{\partial}{\partial T}\Delta rG\right)_{p,\xi} dT + \left(\frac{\partial}{\partial P}\Delta rG\right)_{T,\xi} dp + \left(\frac{\partial}{\partial \xi}\Delta rG\right)_{T,p} d\xi \qquad \text{(Eq.11.1.32)}$$

$$dG = Vdp - SdT$$

$$\left(\frac{\partial G}{\partial p}\right)_T = V \text{ and } \left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$\left(\frac{\partial}{\partial P}\Delta rG\right)_T = \Delta rV \text{ and } \left(\frac{\partial}{\partial T}\Delta rG\right)_P = -\Delta rS \qquad \text{(Eq.11.1.33)}$$

Substituting from equation 11.1.33 into equation 11.1.32, we have

$$d(\Delta rG) = -\Delta rSdT + \Delta rVdp + G''d\xi \qquad \text{(Eq.11.1.34)}$$

Where ΔrS is the entropy change, ΔrV is the volume change for the reaction and G'' is

$$G'' = \left(\frac{\partial}{\partial \xi}\Delta rG\right)_{T,p} = \left(\frac{\partial}{\partial \xi}\left(\frac{\partial G}{\partial \xi}\right)_{T,p}\right)_{T,p}$$

We say that imposition of change in temperature, pressure and extent of reaction are done keeping the reaction at equilibrium. Then ΔrG = 0 and hence d(ΔrG)=0. We also have at equilibrium, ΔrS = ΔrH/T where ΔrH is the enthalpy change of the reaction.

$$0 = -\left(\frac{\Delta rH}{T}\right)(\partial T)_{eq} + \Delta rV(\partial p)_{eq} + G''_{eq}(\partial \xi)_{eq} \qquad \text{(Eq.11.1.35)}$$

Where G''_{eq} is the value of G'' at equilibrium. G has minimum value at equilibrium and hence G''_{eq} must be positive. We can write from equation 11.1.35:

$$\left(\frac{\partial \xi_{eq}}{\partial T}\right)_p = \frac{\Delta rH}{TG''_{eq}} \qquad \text{(Eq.11.1.36)}$$

$$\left(\frac{\partial \xi_{eq}}{\partial P}\right)_T = -\frac{\Delta rV}{G''_{eq}} \qquad \text{(Eq.11.1.37)}$$

If we assume that the reaction mixture gases obey the ideal gas equation, then

$$\Delta rV = \frac{\Delta vgRT}{p} \qquad \text{(Eq.11.1.38)}$$

$$\left(\frac{\partial \xi_{eq}}{\partial p}\right)_T = -\frac{(\Delta vg)RT}{p\, G''_{eq}} \qquad \text{(Eq.11.1.39)}$$

Equations 11.1.36 and 11.1.39 give the variation in extent of reaction at equilibrium, ξ_{eq} with change in T and p respectively.

a) Temperature dependence of ξ_{eq}

$$\left(\frac{\partial \xi_{eq}}{\partial T}\right)_p = \frac{\Delta rH}{T\, G''_{eq}} \qquad \text{(Eq.11.1.36)}$$

Since G''_{eq} is positive, the sign of $(\partial \xi_{eq}/\partial T)_p$ depends on the sign of ΔH. If ΔH is positive, an endothermic reaction, then $(\partial \xi_{eq}/\partial T)_p$ is positive. An increase in temperature increases the extent of reaction at equilibrium, that is, the equilibrium shifts in the forward direction. For an exothermic reaction, ΔH is negative, hence $(\partial \xi_{eq}/\partial T)_p$ is negative. An increase in temperature will decrease the extent of reaction at equilibrium, that is, the equilibrium shifts in the reverse direction. In other words we can say that an increase in temperature shifts, the equilibrium to the high-enthalpy side while a decrease in temperature shifts it to the low-enthalpy side.

For example, in the exothermic reaction:

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, $\Delta H^o = -11$kJ/mol; an increase in temperature will shift the equilibrium in the reverse direction while cooling will shift the equilibrium composition in the direction of the product.

b) Pressure dependence of ξ_{eq}

$$\left(\frac{\partial \xi_{eq}}{\partial p}\right)_T = -\frac{\Delta rV}{G''_{eq}} = \frac{-\Delta vgRT}{pG''_{eq}} \qquad \text{(Eq.11.1.37 and 39)}$$

The sign of $(\partial \xi_{eq}/\partial p)_T$ depends on the sign of ΔrV. If ΔrV is negative, then $\left(\frac{\partial \xi_{eq}}{\partial p}\right)_T$ is +ve, that is, if the product volume is less than the reactant volume, then ΔrV is –ve and $\left(\frac{\partial \xi_{eq}}{\partial p}\right)_T$ is +ve. Increase in pressure results in an increase in the extent of reaction at equilibrium, equilibrium shifts in the forward

direction. If on the other hand volume of the products is more than that of the reactants, that is , ΔrV is +ve, $\left(\frac{\partial \xi_{eq}}{\partial p}\right)_T$ is –ve. An increase in pressure decreases the extent of reaction at equilibrium, there is a shift towards the reactants of the equilibrium. In other words, an

increase in pressure shifts the equilibrium to the low- volume side of the reaction while a decrease in pressure shifts the equilibrium to the high-volume side.

Expressing in terms of $\Delta\nu_g$, we can say that an increase in pressure shifts the equilibrium to that side of the reaction which has the sum of stoichiometric numbers of gaseous molecules lower and a decrease in pressure to that side which has more molecules. For example, in the synthesis of ammonia,

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$$

increase in pressure favours the formation of ammonia whereas a decrease in pressure would shift the equilibrium to the reactant side.

A change in pressure has no effect on the composition when the number of gaseous molecules is the same in the reactants as in the products. In the hydrogen and iodine combination reaction,

$$H_2(g)+I_2(g) \rightleftharpoons 2HI(g)$$

a change in pressure has no effect on the equilibrium composition.

c) The presence of a catalyst

We know that a catalyst accelerates a reaction by providing an alternative, lower energy path for the conversion of reactants to products. ΔrG^o, the difference between the standard molar Gibbs energies of the products and reactants, is independent of the path linking the two. It follows that an alternative path between reactants and products leaves ΔrG^o and therefore K unchanged. That is, the equilibrium constant of a reaction remains unaffected by the presence of a catalyst.

d) Presence of an inert gas

If an inert gas is added to a reaction mixture in a vessel of constant volume, the overall pressure increases, but the partial pressures of the reactants and products remain unchanged, hence also the equilibrium composition. On the other hand, if an inert gas is added keeping the pressure of the reaction system constant, then the equilibrium composition is affected in the case of reactions for which $\Delta\nu g \neq 0$. A detailed discussion is given later.

Temperature dependence of K_p^0

We have seen earlier that the standard equilibrium constant K_p^0 depends only on temperature. The quantitative relation between K_p^0 and T is obtained by using the Gibbs-Helmholtz equation. We know that

$$\Delta rG^0 = -RT\ln K_p^0 \qquad \text{(Eq. 11.1.40)}$$

$$\ln K_p^0 = \frac{-\Delta rG^0}{RT}$$

Differentiating w.r.t T we get

$$\frac{d\ln K_p^0}{dT} = -\frac{1}{R}\frac{d(\Delta rG^0/T)}{dT} \qquad \text{(Eq. 11.1.41)}$$

$$\Delta rG^0 = \sum_i \nu_i \mu_i^0 \qquad \text{(Eq. 11.1.42)}$$

Dividing by T, we write

$$\frac{\Delta rG^0}{T} = \sum_i \nu_i (\mu_i^0/T) \qquad \text{(Eq.11.1.43)}$$

Differentiating w.r.t T, we get

$$\frac{d(\Delta rG^0/T)}{dT} = \sum_i \nu_i \frac{d(\mu_i^0/T)}{dT} \qquad \text{(Eq. 11.1.44)}$$

Where μ_i^0 are standard molar Gibbs energies of pure substances. Writing Gibbs-Helmholtz equation taking molar values, we have

$$\frac{d(\mu_i^0/T)}{dT} = -\bar{H}_i/T^2 \qquad \text{(Eq.11.1.45)}$$

Substituting from equation 11.1.45 into 11.1.44, we get

$$\frac{d(\Delta rG^0/T)}{dT} = \frac{-1}{T^2}\sum_i \nu_i \bar{H}_i^0 = \frac{-\Delta rH^0}{T^2} \qquad \text{(Eq.11.1.46)}$$

Substituting from equation 11.1.46 into 11.1.41,

$$\frac{d\ln K_p^0}{dt} = \frac{\Delta rH^0}{RT^2} \qquad \text{(Eq.11.1.47)}$$

Equation 11.1.47 is known as van't Hoff equation.

If a reaction is exothermic, ΔrH^0 is negative and the standard equilibrium constant K_p^0 decreases with increase in temperature. On the other hand, if a reaction is endothermic, ΔrH^0 is positive and K_p^0 increases with increase in temperature. An increase in K_p^0 means an increase in the concentration of the products, an increase in the extent of reaction at equilibrium with increase in temperature, as predicted by the Le Chatelier-Braun principle. Equation 11.1.47 can be modified to:

$$d\ln K_p^0 = \frac{\Delta rH^0 dT}{RT^2}$$

Integrating the above equation, we have

$$\ln K_p^0 = \frac{-\Delta rH^0}{RT} + I \qquad \text{(Eq.11.1.48)}$$

Where I is the integration constant. We have assumed in the above integration that ΔrH^o is constant, atleast over moderate ranges of temperature. A plot $\ln K_p^0$ vs $\frac{1}{T}$, which is often linear, has a slope equal to $-\Delta rH^0/R$. Hence this gives us a method of determining enthalpy of reaction, ΔrH^0 by measuring K_p^0 over a range of temperature. Calorimetric methods give more precise values of ΔrH^0.

Measuring K_p^0 at various temperatures, ΔrG^0 can be calculated using equation 11.1.40 and ΔrH^0 can be obtained from the slope of $\ln K_p^0$ vs $\frac{1}{T}$ plot. ΔrS^0 values at each temperature can be calculated using the equation:

$$\Delta rG^0 = \Delta rH^0 - T\,\Delta rS^0 \qquad \text{(Eq. 11.1.49)}$$

Standard equilibrium constant, K_p^0 can be written as an explicit function of temperature by integrating equation 11.1.47 between the limits: $(K_p^0)_1$ at temperature T_1 and $(K_p^0)_2$ at temperature T_2.

$$\int_{(K_p^0)_1}^{(K_p^0)_2} d\ln K_p^0 = \int_{T_1}^{T_2} \frac{\Delta rH^0}{RT^2} dT \qquad \text{(Eq.11.1.50)}$$

We assume that ΔrH^o is independent of T in the range T_1-T_2.

$$\int_{(K_p^0)_1}^{(K_p^0)_2} d\ln K_p^0 = \frac{\Delta rH^0}{R} \int_{T_1}^{T_2} \frac{dT}{T^2} \qquad \text{(Eq.11.1.51)}$$

$$\ln \frac{(K_p^0)_2}{(K_p^0)_1} = \frac{\Delta rH^0}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad \text{(Eq.11.1.52)}$$

$$\ln \frac{(K_p^0)_2}{(K_p^0)_1} = \frac{\Delta rH^0}{R}\left(\frac{T_2 - T_1}{T_1 \times T_2}\right) \qquad \text{(Eq.11.1.53)}$$

If we know $(K_p^0)_1$ at temperature T_1 and ΔrH^0, we can calculate K_p^0 at any other temperature using equations 11.1.52 and 11.1.53.

If ΔrH^0 is not a constant, it can ordinarily be expressed as a power series in temperature T:

$$\Delta rH^0 = \Delta rH^0 + a'T + b'T^2 + c'T^3 + \ldots\ldots\ldots\ldots$$

Using this expression for ΔrH^o in the equation 11.1.50 and integrating, we obtain

$$ln\frac{(K_p^0)_2}{(K_p^0)_1} = \frac{\Delta rH^0}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + \frac{a'}{R}\ln\frac{T_2}{T_1} + \frac{b'}{R}(T_2 - T_1) + \frac{c'}{R}(T_2^2 - T_1^2)\ldots \qquad \text{(Eq.11.1.54)}$$

which has the general functional form

$$\ln K_p^0 = \frac{a}{T} + b + c\ln T + dT + eT^2 + \ldots\ldots\ldots\ldots\ldots \qquad \text{(Eq.11.1.55)}$$

in which a,b,c,d and e are constants. Equations of the form given by 11.1.55 are generally used to calculate K_p^o at 25°C (in order to include in a table) from a value of K_p^0 at some other temperature. The constants can be evaluated if ΔrH^0 and heat capacities of all the reactants and products are known.

Variation of K_c^0 with temperature

An equation similar to equation 11.1.47 may be derived for the variation of K_c^0 of a gaseous reaction with temperature, namely,

$$\frac{d\ln K_c^0}{dT}=\frac{\Delta rU^0}{RT^2}$$

Where ΔrU^0 is the energy of reaction at constant volume

$$\frac{d\ln K_p^0}{dT}=\frac{\Delta rH^0}{RT^2} \qquad \text{(Eq.11.1.47)}$$

$$K_p^0 = K_c^0\left(\frac{C^0RT}{p^0}\right)^{\Delta\, vg} \qquad \text{(Eq.11.1.25)}$$

We know that

$$\Delta rH^0 = \Delta rU^0 + \Delta vgRT \qquad \text{(Eq.11.1.56)}$$

Substituting from equations 11.1.25 and 11.1.56 into equation 11.1.47, we get

$$\frac{d}{dT}\ln\left(K_c^0\left(C^0RT/p^0\right)^{\Delta\, vg}\right)=\frac{\Delta rU^0+\Delta vgRT}{RT^2}$$

$$\frac{d}{dT}\ln K_c^0+\Delta vg\frac{d\ln(C^0RT/p^0)}{dT}=\frac{\Delta rU^0}{RT^2}+\frac{\Delta vg}{T}$$

$$\frac{d}{dT}\ln K_c^0+\Delta vg\frac{(C^0R/p^0)}{(C^0RT/p^0)}=\frac{\Delta rU^0}{RT^2}+\frac{\Delta vg}{T}$$

$$\frac{d}{dT}\ln K_c^0=\frac{\Delta rU^0}{RT^2} \qquad \text{(Eq.11.1.57)}$$

This equation is integrated and handled in exactly the same manner as equation 11.1.47. when $\Delta vg=0$, $\Delta rH^o=\Delta rU^0$, $K_p^0 = K_c^0$ and the equations 11.1.47 and 11.1.57 become identical.

Example 11.1.7

The equilibrium constant for the dissociation

$2H_2S(g) \rightleftharpoons 2H_2(g)+S_2(g)$

Is $K_p^0 = 0.0118$ at 1338K while the enthalpy of dissociation is $\Delta rH^o=177.40$ KJ mol^{-1}. Find the standard equilibrium constant of the reaction at 1473K.

$$\ln\frac{(K_p^0)_2}{(K_p^0)_1}=\frac{\Delta rH^0}{R}\left(\frac{T_2-T_1}{T_1\times T_2}\right)$$

$$\ln\frac{(K_p^0)_2}{(K_p^0)_1}=\frac{177.40\times10^3 J\ mol^{-1}}{8.314JK^{-1}mol^{-1}}\left(\frac{135}{1473\times1338K}\right)$$

$$\ln(K_p^0)_2=\ln(0.0118)+\frac{1.7740\times10^5\times1.35\times10^2}{8.314\times1.473\times1.338\times10^6}$$

$$\ln(K_p^0)_2=-4.4397+1.4616$$

$$\ln(K_p^0)_2=-2.9781$$

$$(K_p^0)_2=0.0509$$

The standard equilibrium constant of the reaction at 1473K=0.0509

Example 11.1.8

For the reaction

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

$K_c^0 = 50.0$ at 721K and $K_c^0 = 66.9$ at 623 K.

Calculate ΔrU^0 and ΔrH^0 for the reaction.

$$\ln\frac{(K_c^0)_2}{(K_c^0)_1} = \frac{\Delta rU^0}{R}\left(\frac{T_2 - T_1}{T_1 \times T_2}\right)$$

$$\ln\left(\frac{50.0}{66.9}\right) = \frac{\Delta rU^0}{8.314} \times \frac{98}{6.23\times7.21\times10^4} \times \frac{K}{JK^{-1}mol^{-1}\times K^2}$$

$$\Delta rU^0 = \left(\ln\frac{50.0}{66.9}\right) \times \frac{8.314\times6.23\times7.21\times10^4}{98} J\ mol^{-1}$$

$$\Delta rU^0 = \frac{-0.2912\times8.314\times6.23\times7.21\times10^4}{98} J\ mol^{-1}$$

$\Delta rU^0 = -11.1 kJ\ mol^{-1}$

As $\Delta vg=0$ for this reaction, $\Delta rU^0 = \Delta rH^0$

$\Delta rU^0 = \Delta rH^0 = -11.1 kJ\ mol^{-1}$.

Effect of an inert gas on equilibrium-a detailed treatment

Let us consider a general reaction

$\nu_1A_1 + \nu_2A_2 \rightleftharpoons \nu_3A_3 + \nu_4A_4$ (Eq.11.1.58)

The equilibrium is achieved by taking only the reactants, with initial amounts of A_1 and A_2 as n_1 and n_2 respectively.

Let the extent of reaction at equilibrium be $\xi_{eq.}$

ν_1A_1	+	ν_2A_2	$\rightleftharpoons$	ν_3A_3 +	ν_4A_4
$\xi=0$	n_1	n_2		o	o
$\xi=\xi_{eq}$	$n_1-\nu_1\xi_{eq}$	$n_2-\nu_2\xi_{eq}$		$\nu_3\xi_{eq}$	$\nu_4\xi_{eq}$

Total amount of gases at equilibrium

$$n_{total} = (n_1-\nu_1\xi_{eq}) + (n_2-\nu_2\xi_{eq}) + \nu_3\xi_{eq} + \nu_4\xi_{eq}$$

The partial pressures of the various constituents are:

$$p_{A_1} = \frac{n_1-\nu_1\xi_{eq}}{n_{total}} \times p_{total}\ ;\ p_{A_2} = \frac{n_2-\nu_2\xi_{eq}}{n_{total}} \times p_{total}$$

$$p_{A_3} = \frac{\nu_3\xi_{eq}}{n_{total}} \times p_{total}\ ;\ p_{A_4} = \frac{\nu_4\xi_{eq}}{n_{total}} \times p_{total}$$

$$K_p = \frac{p_{A_3}^{\nu_3} . p_{A_4}^{\nu_4}}{p_{A_1}^{\nu_1} . p_{A_2}^{\nu_2}}$$ (Eq.11.1.59)

Substituting for the partial pressures and simplifying, we get

$$K_p = \frac{(\nu_3\xi_{eq})^{\nu_3}(\nu_4\xi_{eq})^{\nu_4}}{(n_1-\nu_1\xi_{eq})^{\nu_1}(n_2-\nu_2\xi_{eq})^{\nu_2}} \times \left(\frac{p_{total}}{n_{total}}\right)^{\Delta\nu g} \qquad \text{(Eq.11.1.60)}$$

On the addition of amount n of inert gas, let the extent of reaction at equilibrium shift from a value ξ_{eq} to ξ'_{eq} and the total amount of gases at equilibrium from n_{total} to n'_{total}.

$n'_{total}=n+(n_1-\nu_1\xi'_{eq})+(n_2-\nu_2\xi'_{eq})+\nu_3\xi'_{eq}+\nu_4\xi'_{eq}$

The mole fractions of the various constituents will decrease because n'_{total} is more than n_{total}. Substituting the new partial pressures and simplifying, we write K_p.

$$K_p = \frac{(\nu_3\xi'_{eq})^{\nu_3}(\nu_4\xi'_{eq})^{\nu_4}}{\left(n_1-\nu_1\xi'_{eq}\right)^{\nu_1}(n_2-\nu_2\xi'_{eq})^{\nu_2}} \left(\frac{p'_{total}}{n'_{total}}\right)^{\Delta\nu g} \qquad \text{(Eq.11.1.61)}$$

Reactions involving no change in number of gaseous species, $\Delta\nu g=0$ and since K_p remains unchanged,

$$\xi_{eq}=\xi'_{eq}$$

There is no change in the equilibrium position on the addition of an inert gas.

In the case of reactions with an increase in the number of gaseous species, $\Delta\nu g>0$, two cases need to be considered. The inert gas addition is done keeping pressure constant in one case and the other, addition done keeping volume constant.

a) Keeping pressure of the system constant

In this case the denominator of the equation 11.1.61 is greater than that of the equation 11.1.60. As K_p remains constant, the numerator of equation 11.1.61 must increase. This means, the extent of reaction ξ_{eq} must increase or $\xi'_{eq}>\xi_{eq}$. Thus the reaction is shifted to the products side.

b) Keeping volume of the system constant.
According to the ideal gas equation, we have
$p/n = RT/V$

In the equations 11.1.60 and 11.1.61, we substitute

$$\left(\frac{p_{total}}{n_{total}}\right)^{\Delta\nu g} = \left(\frac{p'_{total}}{n'_{total}}\right)^{\Delta\nu g} = \left(\frac{RT}{V}\right)^{\Delta\nu g}$$

As K_p remains constant and volume is being maintained constant, $\xi_{eq}=\xi'_{eq}$. There is no change in the equilibrium composition of the reaction.

In the case of reactions with a decrease in number of gaseous species, $\Delta\nu g <0$, we consider again two cases.

a) Addition of inert gas keeping pressure of the system constant. Arguing along the same lines as in the case of $\Delta\nu g>0$, we conclude that the extent of reaction, ξ_{eq} must decrease or $\xi'_{eq}<\xi_{eq}$. The equilibrium is shifted to the reactant side of the reaction.

b) Addition of inert gas keeping volume of the system constant.
Discussing along the same lines as in the case of $\Delta\nu g>0$, we get $\xi_{eq}=\xi'_{eq}$, that is, there is no effect on the equilibrium position of the reaction.

Example 11.1.9

a) Two moles of PCl_5 are heated at 502K till equilibrium is reached at a total pressure of 101.325kPa. Calculate the composition at equilibrium and also the percentage of PCl_5 decomposed (K_p^0 =0.4661).

PCl_5 decomposes according to the equation.

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

If we take the initial amount of PCl_5 as "a" and the extent of reaction at equilibrium is ξ, then the amount and partial pressures of the various species at equilibrium are:

	PCl_5	$\rightleftharpoons$	PCl_3	+	Cl_2	Total amount
At t=0	a		o		o	a
At equilibrium	a-ξ		ξ		ξ	a+ξ
Partial pressures	$\frac{a-\xi}{a+\xi}p$		$\frac{\xi}{a+\xi}p$		$\frac{\xi}{a+\xi}p$	

$$K_p = \frac{p_{PCl_3} \cdot p_{Cl_2}}{p_{PCl_5}} = \frac{\frac{\xi}{a+\xi}P \times \frac{\xi}{a+\xi}P}{\frac{a-\xi}{a+\xi}P} = \frac{\xi^2 P}{a^2-\xi^2}$$

$$K_p^0 = \frac{\xi^2}{a^2-\xi^2} \text{ (p/1 bar)}$$

a=2 mol, p=101.325 kPa = 1.01325bar, K_p^o = 0.4661

$$\frac{\xi^2}{4-\xi^2} = \frac{0.4661}{1.01325}$$

Solving this quadratic equation for ξ, we get ξ=1.12 mol.

Composition of the reaction mixture at equilibrium:

Amount of PCl_5 = 2.0 mol – 1.12 mol = 0.88 mol

Amount of PCl_3 or Cl_2 = 1.12 mol

Percentage of PCl_5 decomposed = $\frac{1.12}{2} \times 100 = 56$

b) If the pressure of the system is increased ten times to a value 1013.25 kPa keeping the temperature constant at 502K, calculate the percentage of PCl_5 decomposed.

K_p^0 =0.4661, p=1013.25 kPa=10.1325 bar.

$$K_p^0 = \frac{\xi^2}{4-\xi^2} \times 10.1325 = 0.4661$$

Solving this quadratic equation for ξ, we get ξ=0.42 mol.

Percentage of PCl_5 decomposed = $\frac{0.42}{2} \times 100 = 21$

c) If at the start of the reaction, the vessel contained apart from 2 moles of PCl_5, also 1 mole of chlorine, calculate the percentage of PCl_5 decomposed. The equilibrium pressure is 101.325kPa.

	PCl_5	$\rightleftharpoons$	PCl_3	+	Cl_2
At t=0	2 mol		0		1 mol
At equilibrium	2 mol-ξ		ξ		1 mol + ξ

Total amount at equilibrium = 3mol+ξ

The partial pressures are:

$p_{PCl_5}=\frac{2-\xi}{3+\xi}P, p_{PCl_3}=\frac{\xi}{3+\xi}P, p_{Cl_2}=\frac{1+\xi}{3+\xi}P$

$K_p^0 = \frac{(p_{PCl_3}/p^0)(p_{Cl_2}/p^0)}{p_{PCl_5}/p^0)}=\frac{\xi\times(1+\xi)}{(2-\xi)(3+\xi)}(p/p^0)$

$K_p^0 = \frac{\xi(1+\xi)}{(2-\xi)(3+\xi)}\times 1.01325=0.4661$

Solving the equation for ξ, we get ξ=0.96 mol

The percentage of PCl_5 decomposed = $\frac{0.96}{2}\times 100=48$

Example 11.1.10

a) NH_4HS dissociates as follows:

$NH_4HS(S) \rightleftharpoons NH_3(g) + H_2S(g)$

At 25°C, the dissociation pressure of the pure solid is 66.87 kPa. Calculate (i) K_p^o for the reaction and (ii) the total pressure at equilibrium when 40kPa of NH_3 are introduced into a flask containing solid NH_4HS.

(i) Dissociation pressure = 66.87 kPa

As NH_3 and H_2S are present in equal amounts,

$p_{NH_3}=p_{H_2S} = \frac{66.87kPa}{2}=33.435kPa$

$K_p^0 = (p_{NH_3}/p^0)(p_{H_2S}/p^0)$

$K_p^0 = \left(\frac{33.435kPa}{100kPa}\right)^2=0.111$

K_p^0 for the reaction = 0.111

(ii) When 40kPa of NH_3 are introduced, the equilibrium shifts towards the reactant side according to LeChatelier-Braun principle. Let the new partial pressure of H_2S be xkPa. The new partial pressure of NH_3 is then (x+40) kPa.

$K_p^0 = \frac{(x+40)kPa}{100kPa}\times\frac{xkPa}{100kPa}$

$0.111 = \frac{x+40}{100}\times\frac{x}{100}$

$1.11 \times 10^3 = 40x + x^2$

$x^2+40x - 1.11\times10^3 = 0$

Solving this quadratic, we get x = 18.86kPa

$p_{NH_3}=(40+x)kPa=58.86kPa$

$p_{H_2S}=xkPa=18.86kPa$

Total pressure at equilibrium = $p_{NH_3}+p_{H_2S}$ = 77.72 kPa

b) What fraction of the solid will dissociate when 0.1 mol of NH_4HS is introduced into a 1 dm^3 flask at 298K?

Let α be the degree of dissociation.

	NH_4HS (S) $\rightleftharpoons$	NH_3 (g) +	H_2S (g)	
At the start	0.1	0	0	mol
At the equilibrium	0.1(1-α)	0.1α	0.1α	mol

$p_{NH_3} = p_{H_2S} = \frac{nRT}{V}=\frac{0.1\alpha\times8.314\times298}{1}kPa$

$p_{NH_3} = p_{H_2S} = (247.76\alpha)kPa$

$K_p^0 = 0.111 = \left(\frac{p_{NH_3}}{p^0}\right) \times \left(\frac{p_{H_2S}}{p^0}\right)$

$0.111 = \left(\frac{247.76\alpha}{100}\right)^2$

$0.111 = (2.4776\alpha)^2$

Solving for α, we get α=0.134

The fraction of solid NH_4HS that dissociates = 0.134

The Reaction Isotherm

The Gibbs free energy of a substance is defined in terms of the standard Gibbs free energy, G_i^0 and the activity of the substance, a_i as

$$G_i = G_i^0 + nRT\ln a_i \qquad \text{(Eq.11.1.62)}$$

Dividing this equation by n, the number of mole, we get

$$\mu_i = \mu_i^0 + RT\ln a_i \qquad \text{(Eq.11.1.63)}$$

Where μ_i is the chemical potential, μ_i^o is the standard chemical potential (chemical potential at unit activity of the substance) and a_i is the activity of substance. We will write an expression for the change in free energy involved in any type of transformation, physical or chemical. Consider first a simple reaction consisting of only two reactants and two products. The chemical equation is:

$$\nu_1 A_1 + \nu_2 A_2 \rightarrow \nu_3 A_3 + \nu_4 A_4 \qquad \text{(Eq.11.1.64)}$$

The Gibbs energy change for the reaction (the reaction potential) is given by:

$$\Delta rG = \nu_3\mu_3 + \nu_4\mu_4 - \nu_1\mu_1 - \nu_2\mu_2 \qquad \text{(Eq.11.1.65)}$$

We write the chemical potential of the reactants and products using equation 11.1.63

$\mu_1 = \mu_1^0 + RT\ln a_1$

$\mu_2 = \mu_2^0 + RT\ln a_2$

$\mu_3 = \mu_3^0 + RT\ln a_3$

$\mu_4 = \mu_4^0 + RT\ln a_4$

$\Delta rG = (\nu_3\mu_3^0 + \nu_4\mu_4^0 - \nu_1\mu_1^0 - \nu_2\mu_2^0) + RT(\nu_3\ln a_3 + \nu_4\ln a_4 - \nu_1\ln a_1 - \nu_2\ln a_2)$

$$\Delta rG = \Delta rG^0 + RT\ln \frac{a_3^{\nu_3} a_4^{\nu_4}}{a_1^{\nu_1} a_2^{\nu_2}} \qquad \text{(Eq.11.1.66)}$$

When the activities of the substances, reactants and products, are all one, the second term of the equation 11.1.66 is zero and $\Delta rG = \Delta rG^o$. ΔrG^o, the free energy change of a reaction in the standard state (standard reaction potential) is constant at any given temperature and completely independent of pressure.

In general for a reaction given by

$$0 = \sum_i \nu_i A_i$$

(Eq.11.1.67)

the A_i represent the chemical species of the reaction and ν_is are the corresponding stoichiometric coefficients, negative for reactants and positive for products. The free energy change of the reaction is given by:

$$\Delta rG = \Delta rG^0 + RT \ln \prod_i (a_i)^{vi} \qquad \text{(Eq.11.1.68a)}$$

$$\Delta rG = \Delta rG^0 + RT \ln \frac{\prod_{products} (a_i)^{vi}}{\prod_{reactants} (a_i)^{vi}} \qquad \text{(Eq11.1.68b)}$$

This most fundamental thermodynamic equation (Eq.11.1.68) is referred to as the reaction isotherm. Reaction quotient Q is:

$$Q = \prod_i (a_i)^{vi}$$

(Eq.11.1.69)

$$\Delta rG = \Delta rG^o + RT\ln Q$$

(Eq.11.1.70)

Pure solids and liquids do not make any contribution to Q even though they may appear in the chemical equation because their activities are one. The term a_i is interpreted as a fugacity f_i, if A_i is a gas, activities of gaseous species are replaced by fugacities, by using

$$a_i = f_i/p^0$$

At equilibrium, $\Delta rG = 0$. The activities have their equilibrium values. The reaction quotient, Q at equilibrium is K, the thermodynamic equilibrium constant

$$K = \left(\prod_i (a_i)^{vi}\right)_{eq} \qquad \text{(Eq.11.1.71)}$$

While writing K, equilibrium values of activities would be used and for Q, the values at the specified stage of the reaction. Equation 11.1.70 reduces to

$$\Delta rG^0 = -RT\ln K \qquad \text{(Eq.11.1.72)}$$

at equilibrium. As activities are dimensionless numbers, the thermodynamic equilibrium constant is also dimensionless.

In elementary applications, the activities that occur in equation 11.1.71 are often substituted by molalities or molarities and fugacities by partial pressures. Expressions obtained by substituting are approximate and in the case of ionic solutions, even when they are very dilute, substantial approximation gets introduced.

The standard free energy change of reaction, ΔrG^0 can be evaluated from standard free energies of formation at the temperature of the reaction which are given in literature.

The Reaction Isochore

$$\frac{d\ln K_p^0}{dT} = \frac{\Delta rH^0}{RT^2} \qquad \text{(Eq.11.1.47)}$$

and

$$\frac{d\ln K_c^0}{dT} = \frac{\Delta rU^0}{RT^2} \qquad \text{(Eq.11.1.57)}$$

Equations 11.1.47,known as the van't Hoff reaction isobar and 11.1.57, known as the van't Hoff reaction isochore have already been discussed under temperature dependence of K_p^0 and K_c^0.

The Clapeyron equation

A system consists of a pure substance present in two phases A and B. The two phases may be:

Solid ⇌ liquid
Solid ⇌ vapour
Liquid ⇌ vapour

At equilibrium, the chemical potential of the substance in the two phases is the same.

$$\mu^A(T,p)=\mu^B(T,p) \qquad \text{(Eq.11.1.73)}$$

If the temperature of the system is changed by an infinitestimal amount, the system moves to a new equilibrium. The pressure also changes by an infinitesimal amount. Under these conditions, the chemical potential μ^A and μ^B also change by infinitesimal amounts $d\mu^A$ and $d\mu^B$, respectively. As the system has attained equilibrium again, μ^A (T, p) + $d\mu^A$ = $\mu^B(T,p)+d\mu^B$ (Eq.11.1.74)

Subtracting equation 11.1.73 from equation 11.1.74, we get

$$d\mu^A=d\mu^B \qquad \text{(Eq.11.1.75)}$$

$dG=-SdT+Vdp$

writing for 1 mole of the substance, we have

$$d\mu=-S_m dT+V_m dp \qquad \text{(Eq.11.1.76)}$$

Applying the equation 11.1.76 for the two phases, we get

$$d\mu^A = -S_m^A dT+V_m^A dp$$
$$d\mu^B = -S_m^B dT+V_m^B dp \qquad \text{(Eq.11.1.77)}$$

Where S_m^A and S_m^B are the molar entropies in phases A and B respectively and V_m^A and V_m^B are the respective molar volumes. Substituting from equation 11.1.77 into 11.1.75, we write

$-S_m^A dT+V_m^A dP = -S_m^B dT+V_m^B dp$

Rearranging, we have

$$\frac{dp}{dT}=\frac{S_m^B-S_m^A}{V_m^B-V_m^A}=\frac{\Delta S_{m,trans}}{\Delta V_{m,trans}} \qquad \text{(Eq.11.1.78)}$$

Where $\Delta S_{m,trans}$ and $\Delta V_{m,trans}$ are the changes in entropy and volume of the system respectively when 1 mole of a pure substance is transferred from phase A to phase B.

Equation 11.1.78 is known as the Clapeyron equation.

Application of Clapeyron equation; Clausius – Clapeyron equation

(i) Solid-liquid equilibrium

If one mole of a substance is transformed from the solid to the liquid phase, then

$$\Delta S_{m,trans}=S_{m,l}-S_{m,s}=\Delta S_{m,\,fus}$$
$$\Delta V_{m,trans}=V_{m,l}-V_{m,s}=\Delta V_{m,\,fus} \qquad \text{(Eq.11.1.79)}$$

Where fus stands for fusion.

$$\Delta S_{m,fus}=\frac{\Delta H_{m,fus}}{T} \qquad \text{(Eq.11.1.80)}$$

Where $\Delta H_{m,fus}$ is the molar enthalpy of fusion and the solid to liquid transformation is reversible at the equilibrium temperature.

$$\frac{dp}{dT}=\frac{\Delta S_{m,fus}}{\Delta V_{m,fus}}=\frac{\Delta H_{m,fus}}{T\Delta V_{m,fus}} \qquad \text{(Eq.11.1.81)}$$

The slope of the p versus T graph, $\frac{dp}{dT}$ depends on the sign of $\Delta H_{m,fus}$ and $\Delta V_{m,fus}$. The solid to liquid transformation is always an endothermic process and hence $\Delta H_{m,fus}$ is positive. $\Delta V_{m,\,fus}$ may be positive or negative depending upon the densities of the solid and liquid phases. For most substances, ρ_{solid} is greater than ρ_{liquid} and hence $\Delta V_{m,fus}$ is positive. For some substances, example water, $\Delta V_{m,\,fus}$ is negative as the $\rho s<\rho l$. For a typical value of 20 JK^{-1} for $\Delta S_{m,fus}$ and $\pm$ 5cm^3 for $\Delta V_{m,fus}$, we get $\frac{dp}{dT}=\pm 4 JK^{-1}cm^{-3}$

Converting this into atm K^{-1} units, we have

$\frac{dp}{dT}=\pm 39.45$ atm K^{-1}

Thus, we see that the slope of the pressure versus temperature graph for solid-liquid equilibrium has a large value. The almost vertical line is slightly tilted towards the pressure axis (negative slope) If $\Delta V_{m,fus}$ is negative (Figure 11.1.3) and away from the pressure axis (positive slope) if $\Delta V_{m,fus}$ is positive (Figure 11.1.4)

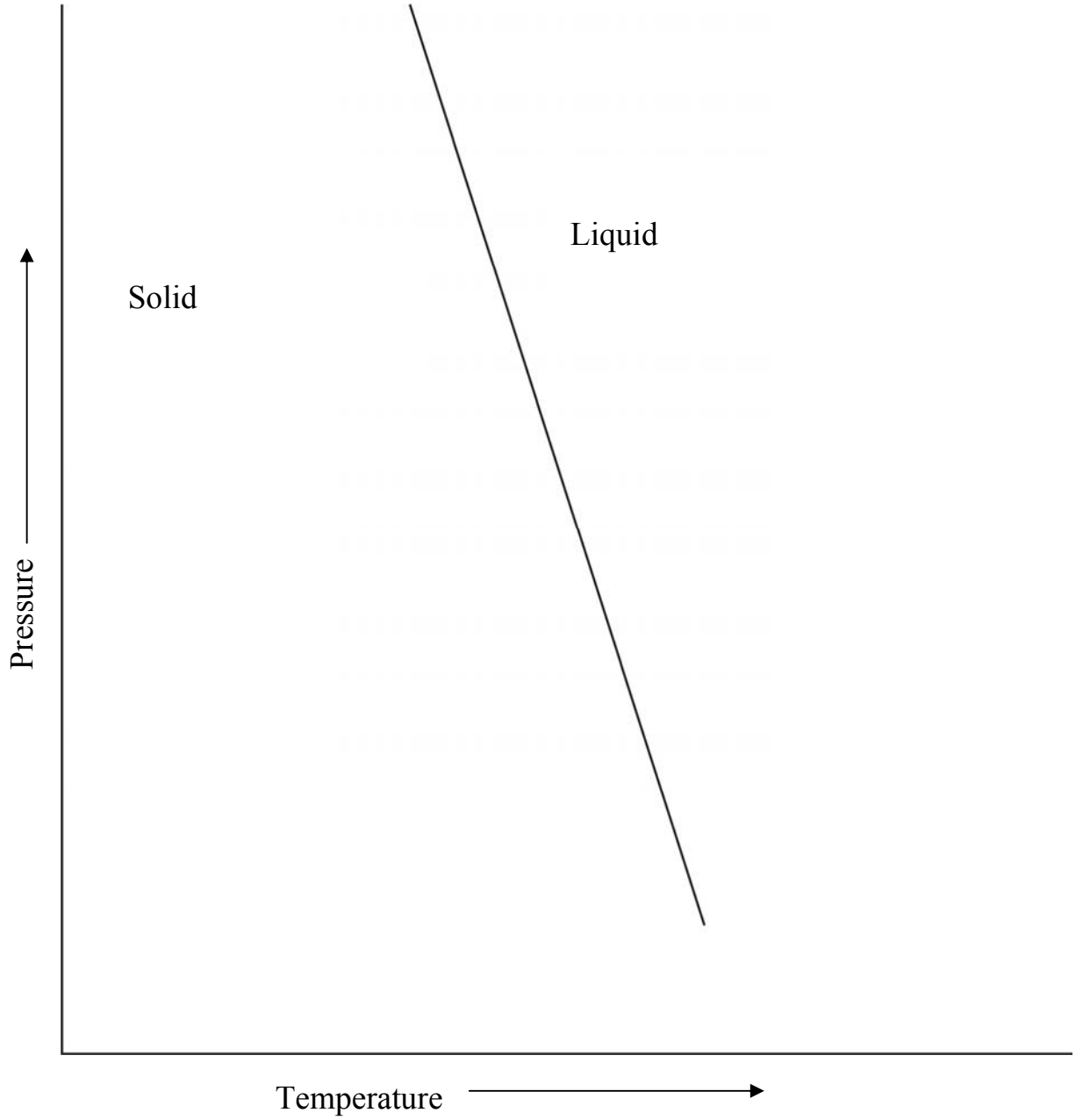

Figure 11.1.3: Plot of p vs T for solid liquid, $\Delta V_{m,fus}$=-ve

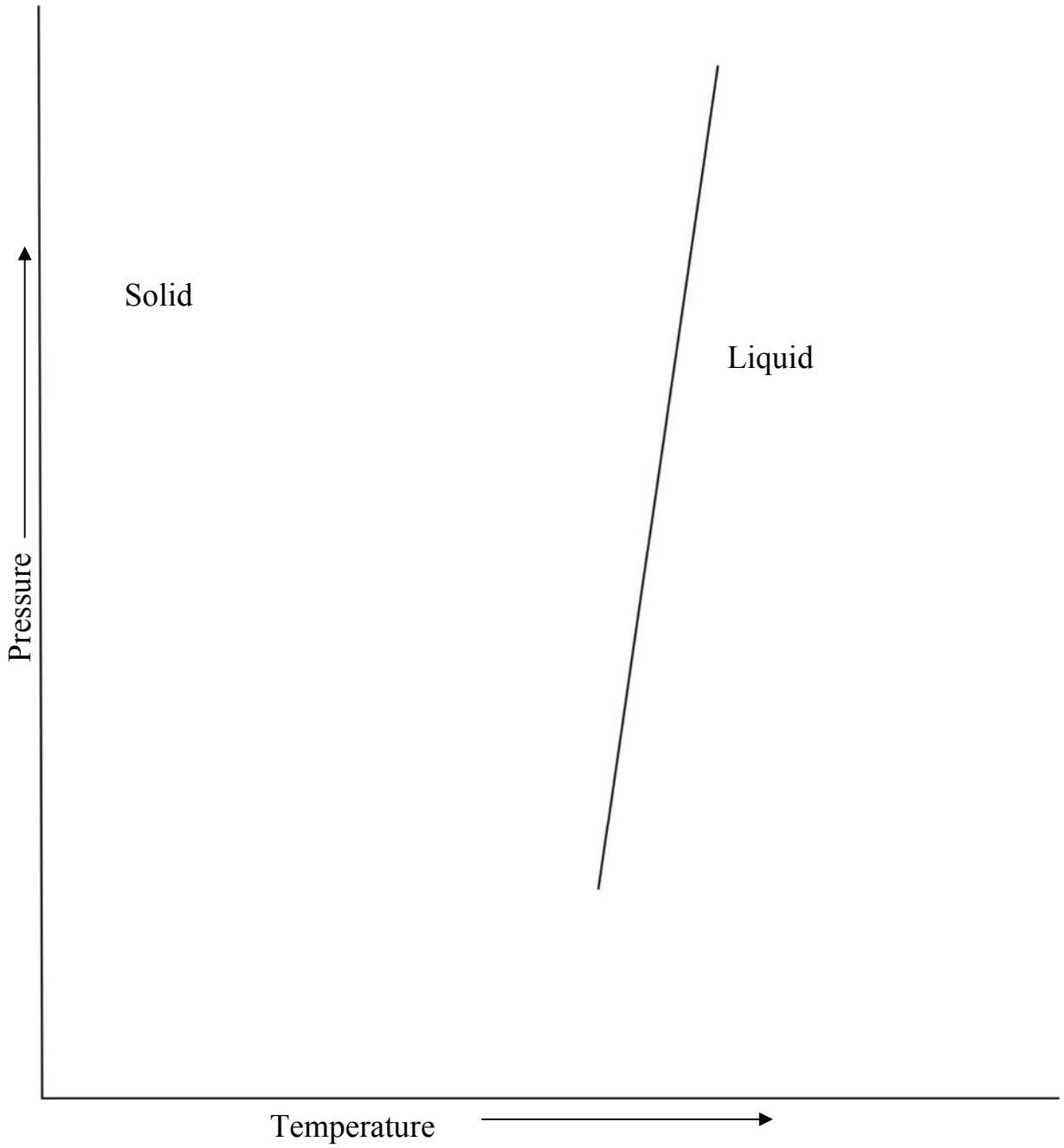

Figure 11.1.4: Plot of p vs T for solid liquid, $\Delta V_{m,fus}$=+ve

In figures 11.1.3 and 11.1.4, points on the lines represent states of the system in which solid and liquid coexist in equilibrium with each other. These points represent melting points of the system at different pressures or the variation of melting point with pressure. To the left of the line are temperatures less than the melting point and hence the region to the left of the line represents solid phase and to the right, liquid phase.

$$\frac{dT}{dp} = \frac{1}{dp/dT} = \pm\frac{1}{39.45}\ K\ atm^{-1} = \pm 0.025 K atm^{-1}$$

The value of dT/dp shows that the change in the melting point with variation in external pressure is very small. Substances which show an increase in volume on melting have $\frac{dT}{dp}$ =+0.025 Katm^{-1} and those which show a decrease in volume on melting have $\frac{dT}{dp}$ = -0.025 K atm^{-1}. For most substances, as ρs>ρl, $\Delta V_{m,fus}$ is positive, there is an increase in melting point with increase in external pressure. But for those that have ρs<ρl, $\Delta V_{m,fus}$ is –ve, there is a decrease in melting point with increase in external pressure.

The Clapeyron equation on integration gives:

$$dp=\frac{\Delta H_{m,fus}}{\Delta V_{m,fus}}\frac{dT}{T} \qquad \text{(Eq.11.1.82)}$$

$$\int_{p1}^{p2} dp=\int_{T_{m,1}}^{T_{m,2}} \frac{\Delta H_{m,fus}}{\Delta V_{m,fus}}\frac{dT}{T} \qquad \text{(Eq.11.1.83)}$$

$$p_2-p_1=\frac{\Delta H_{m,fus}}{\Delta V_{m,fus}}\ln\left(\frac{T_{m,2}}{T_{m,1}}\right) \qquad \text{(Eq.11.1.84)}$$

where the melting points are $T_{m,1}$ at pressure p_1 and $T_{m,2}$ at pressure p_2. $\Delta H_{m,fus}$ and $\Delta V_{m,fus}$ are assumed to remain constant in the temperature range $T_{m,1}$-$T_{m,2}$.

$$\ln\left(\frac{T_{m,2}}{T_{m,1}}\right)\cong\frac{T_{m,2}-T_{m,1}}{T_{m,1}}=\frac{\Delta T}{T_{m,1}} \qquad \text{(Eq.11.1.85)}$$

As $T_{m,2}$- $T_{m,1}$ = ΔT is usually small, the logarithmic term can be approximated to $\Delta T/T_{m,1}$. With this, we modify equation 11.1.84 to

$$p_2-p_1=\Delta p=\frac{\Delta H_{m,fus}}{\Delta V_{m,fus}}\times\frac{\Delta T}{T_{m,1}} \qquad \text{(Eq.11.1.86)}$$

This equation 11.1.86 is identical with the equation 11.1.82 except for the infinitestimal changes dT and dp which have been replaced by finite changes ΔT and Δp. The same arguments hold good here too. If $\Delta V_{m,fus}$ is +ve, ΔT is positive and if $\Delta V_{m,fus}$ is negative, ΔT is negative.

ii) Condensed phase – vapor equilibrium

a) Liquid – vapor equilibrium

$$\Delta S_{m,vap} = S_{m,v}-S_{m,l} = \frac{\Delta H_{m,vap}}{T} \qquad \text{(Eq.11.1.87)}$$

$$\Delta V_{m,vap} = V_{m,v}-V_{m,l} \qquad \text{(Eq.11.1.88)}$$

$$\frac{dp}{dT}=\frac{\Delta S_{m,vap}}{\Delta V_{m,vap}}=\frac{\Delta H_{m,vap}}{T\Delta V_{m,vap}} \qquad \text{(Eq.11.1.89)}$$

$\Delta S_{m,vap}$, $\Delta H_{m,vap}$ and $\Delta V_{m,vap}$ are the respective changes in entropy, enthalpy and volume during vaporization of one mole of liquid at its boiling point T. dp/dT is always positive as $\Delta H_{m,vap}$ and $\Delta V_{m,vap}$ are always positive and hence the slope of the p versus T curve for vaporization is always positive.

According to Trouton's rule, for most substances, $\Delta S_{m,vap}$ 90JK^{-1} and $\Delta V_{m,vap}$=24.0dm^3, $\frac{dp}{dT}=\frac{90JK^{-1}}{24.0dm^3mol^{-1}}$ =3.75JK^{-1}dm^{-3}

Converting it into atm K^{-1}unit,we get

$\frac{dp}{dT}$ =0.037 atm K^{-1}

This value is smaller than that for the solid-liquid equilibrium
For integrating the Clapeyron equation, we write

$$\frac{dp}{dT} = \frac{\Delta S_{m,vap}}{\Delta V_{m,vap}} = \frac{\Delta H_{m,vap}}{T(V_{m,v} - V_{m,l})} \qquad \text{(Eq.11.1.90)}$$

Where $\Delta H_{m,vap}$ is the molar heat of vaporization of the liquid, $V_{m,v}$ and $V_{m,l}$ are the molar volumes of the vapor and liquid respectively.

Equation 11.1.90 was simplified by Clausius as follows:

(i) $V_{m,v} - V_{m,l} \simeq V_{m,v}$ since $V_{m,v} >> V_{m,l}$

(ii) Assuming the vapor to be ideal, $V_{m,v}$ is replaced by $\frac{RT}{p}$

Putting in these simplifications, we modify equation 11.1.90 to

$$\frac{dp}{dT} = \frac{\Delta H_{m,vap}}{RT^2} p \qquad \text{(Eq.11.1.91)}$$

Separating the variables, we write

$$\frac{dp}{p} = \frac{\Delta H_{m,vap}}{R} \frac{dT}{T^2} \qquad \text{(Eq.11.1.92)}$$

Equation 11.1.92 is known as the Clausius-Clapeyron equation. On integrating, we get

$$\int_{p_1}^{p_2} \frac{dp}{p} = \frac{\Delta H_{m,vap}}{R} \int_{T_1}^{T_2} \frac{dT}{T^2} \qquad \text{(Eq.11.1.93)}$$

Where p_1 is the vapor pressure at temperature T_1 and p_2 is at T_2. Assuming $\Delta H_{m,vap}$ to remain constant in the temperature range T_1 to T_2, we have

$$\ln \frac{p_2}{p_1} = \frac{\Delta H_{m,vap}}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \qquad \text{(Eq.11.1.94)}$$

If p_1=1 atm, then T_1 is the normal boiling point, T_b. Then we have,

$$\ln\left(\frac{p_2}{atm} \right) = \frac{\Delta H_{m,vap}}{R} \left[\frac{1}{T_b} - \frac{1}{T_2} \right]$$

If we drop the subscript 2, we have

$$\ln(p/atm) = \frac{\Delta H_{m,vap}}{R} \left[\frac{1}{T_b} - \frac{1}{T} \right] \qquad \text{(Eq.11.1.95)}$$

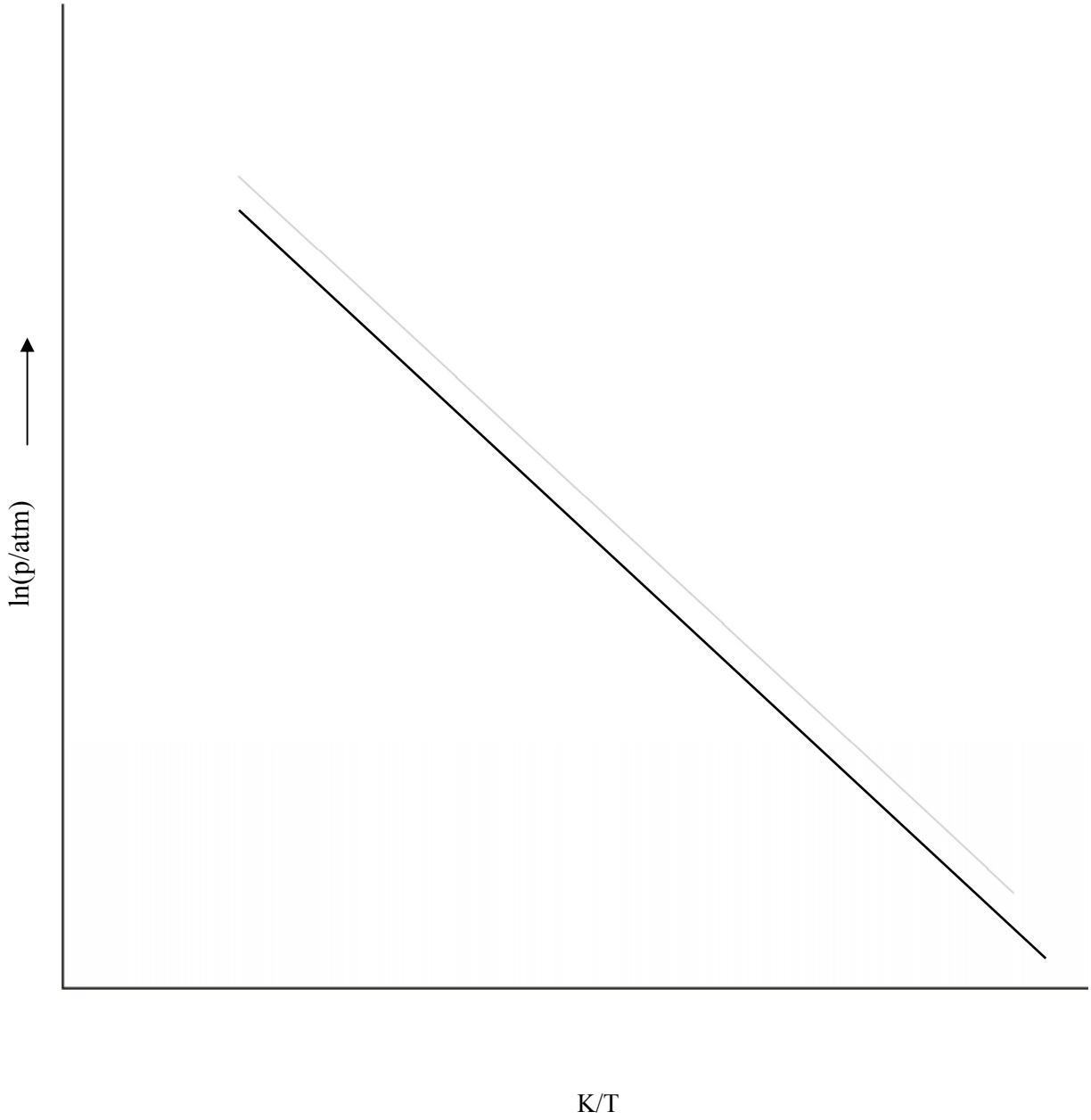

Figure 11.1.5: Plot of ln (p/atm) vs K/T for the liquid – vapor equilibrium

If we plot ln (p/atm) versus 1/T, we get a straight line graph wih slope to $-\Delta H_{m,vap}/R$ as shown in the figure 11.1.5. The intercept at 1/T=0 yields $\frac{\Delta H_{m,vap}}{RT_b}$. Thus from the slope and the intercept, both $\Delta H_{m,vap}$ and T_b of the substance can be determined.

b) Solid-vapor equilibrium

$$\Delta S_{m,subl} = S_{m,v} - S_{m,s} = \frac{\Delta H_{m,subl}}{T}$$

where T is the sublimation temperature

$$\Delta V_{m,subl} = V_{m,v} - V_{m,s} \qquad \text{(Eq.11.1.96)}$$

Where subl stands for sublimation. $\Delta S_{m,subl}$ and $\Delta V_{m,subl}$ are positive. Hence dp/dT (equation 11.1.97) is also positive.

$$\frac{dp}{dT} = \frac{\Delta S_{m,subl}}{\Delta V_{m,subl}} = \frac{\Delta H_{m,subl}}{T\Delta V_{m,subl}} \qquad \text{(Eq.11.1.97)}$$

At the triple point, where the three curves, solid-liquid, solid-vapor and liquid-vapor, meet, the slope of the solid-vapor curve is steeper than that of the liquid-vapor curve. At the triple point, we have $\Delta H_{m,subl} = \Delta H_{m,fus} + \Delta H_{m,vap}$ and hence

$$\Delta H_{m,subl} > \Delta H_{m,vap}$$

From equations 11.1.89 and 11.1.97, it is clear that

$$\left(\frac{dp}{dT}\right)_{s\text{-}v} > \left(\frac{dp}{dT}\right)_{l\text{-}v}$$ at the triple point.

Applying the Clausius-Clapeyron equation to the process of sublimation (Approximations introduced by Clausius hold good for sublimation as well), we write

$$\frac{dp}{p} = \frac{\Delta H_{m,subl}}{R}\frac{dT}{T^2} \qquad \text{(Eq.11.1.98)}$$

Integrating this equation between the limits: vapor pressures p_1 at temperature T_1 and p_2 at T_2.

$$\int_{p_1}^{p_2}\frac{dp}{p} = \frac{\Delta H_{m,subl}}{R}\int_{T_1}^{T_2}\frac{dT}{T^2}$$

$$\ln\frac{p_2}{p_1} = \frac{\Delta H_{m,subl}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad \text{(Eq.11.1.99)}$$

If p_1=1atm, then T_1 is the normal sublimation temperature T_S and we write

$$\ln(p_2/\text{atm}) = \frac{\Delta H_{m,subl}}{R}\left[\frac{1}{T_S} - \frac{1}{T_2}\right] \qquad \text{(Eq.11.1.100)}$$

Dropping the subscript 2, we write

$$\ln(p/\text{atm}) = \frac{\Delta H_{m,subl}}{R}\left[\frac{1}{T_S} - \frac{1}{T}\right] \qquad \text{(Eq.11.1.101)}$$

Using equation 11.1.101, the enthalpy of sublimation of any substance can be calculated knowing T at p atm and T_S at 1 atm. Alternatively, a plot of ln (p/atm) versus I/T enables us to calculate from the slope and intercept both $\Delta H_{m,\,subl}$ and T_S.

(iii) Solid-Solid equilibrium

If a substance exists in more than one polymorphic form, then equilibria between different polymorphic forms are observed. The slope of the curve representing the transformation from one form to the other is given by the Clapeyron equation.

Solid 1 ⇌ solid 2

Where Solids1 and 2 are the two polymorphic forms of the solid.

For the solid 1- solid 2 equilibrium, we write

$$\Delta S_{m,trans} = S_{m,solid2} - S_{m,solid1} = \frac{\Delta H_{m,trans}}{T}$$

$$\Delta V_{m,trans} = V_{m,solid2} - V_{m,solid1} \qquad \text{(Eq.11.1.102)}$$

Where trans stands for transformation.

$$\frac{dp}{dT} = \frac{\Delta S_{m,trans}}{\Delta V_{m,trans}} = \frac{\Delta H_{m,trans}}{T\Delta V_{m,trans}}$$

Where T is the equilibrium temperature.

Suggested readings and significant keywords

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2. Physical chemistry G.W.Castellan
3. A textbook of physical chemistry (Vol.3) K.L.Kapoor
4. The phase rule Alexander Findlay
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Robert A. Alberty
7. Physical chemistry Ira N. Levine