

4

Equilibrium in chemical systems

4.1 Free energy

We have seen that for systems at constant energy the position of equilibrium can be defined by the condition of maximum entropy. Since a system and its surroundings taken together could be regarded as a new system whose energy is constant, the position which leads to the maximum entropy for system *and* surroundings is the equilibrium position. However, it is more convenient to have a definition of the position of equilibrium which can be expressed in terms of the properties of the system alone and which does not require a knowledge of changes taking place in the surroundings. To find such a condition we return to the concept of maximum work. In Section 3.2 we defined the position of equilibrium in terms of the capacity of a system to do work. When during a change a system does the maximum possible work, that change is reversible and the system is, at every stage, at equilibrium. We shall now introduce thermodynamic functions which are related to the maximum amount of work that can be obtained from a system at constant temperature. These provide a most useful definition of the position of equilibrium in chemical and physical systems. For reversible conditions, as $dU = dq_{\text{rev}} + \delta w_{\text{rev}}$ (Section 2.5) and $dS = dq_{\text{rev}}/T$ (Section 3.3), we have

$$dU = TdS + \delta w_{\text{rev}}$$

and

$$\delta w_{\text{rev}} = dU - TdS.$$

If we define a state function, the *Helmholtz free energy* A , such that

$$A = U - TS$$

then at constant temperature

$$dA = dU - TdS$$

and

$$\delta w_{\text{rev}} = dU - TdS = dA.$$

This is a condition that must be satisfied by a reversible process and hence $\delta w = dA$ is also a condition for the system to be at equilibrium. If during a reversible change the system does work, δw_{rev} will be negative. dA will also be

negative and A will decrease. A is the equivalent function, in this molecular system at constant T and V , to the energy U in a mechanical system; *it is a measure of the maximum amount of work the system can do on its surroundings.*

For a spontaneous process, the system may do work but the work will be less than for the equivalent reversible change: thus δw will be less negative than δw_{rev} .

$$\delta w > \delta w_{\text{rev}}$$

and

$$\delta w > dA.$$

For the spontaneous process both δw and dA will be negative but δw will be less negative than dA . The work done *by* the system ($-\delta w$) will be less than the decrease in A , thus only part of the system's change in free energy will be obtained as work.

If a system is not harnessed to do work $\delta w = 0$ and, as $\delta w_{\text{rev}} < \delta w$, $dA < 0$, and dA for a spontaneous process will again be negative. Eventually if the spontaneous change continues, A will reach a minimum value and no further work can be obtained from the system even under reversible conditions.

Then

$$\delta w_{\text{rev}} = 0$$

and

$$dA = 0.$$

Thus the condition of equilibrium in a system at constant temperature and volume which does no work is

$$dA = 0.$$

Spontaneous processes may occur in such a system when it is not at equilibrium with a consequent decrease in the free energy. When A is a minimum and $dA = 0$ no further spontaneous changes can occur and the system is at equilibrium. Again we see the parallel between the free energy A and the potential energy in a mechanical system. If the latter system is not harnessed to do work the position of equilibrium could be defined in terms of minimum energy.

4.2 Gibbs free energy

As chemists, we are often interested in systems at constant pressure and temperature rather than at constant volume. Under constant pressure conditions we can write

$$\delta w_{\text{rev}} = -PdV + \delta w_{\text{additional}},$$

where $\delta w_{\text{additional}}$ is the work other than PV work done on the system.

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Electrical work done on a solution being electrolysed would be an example of this additional work. At equilibrium

$$\dot{d}w_{\text{rev}} = dU - \dot{d}q_{\text{rev}} \quad (\text{Section 2.5})$$

and

$$\dot{d}q_{\text{rev}} = TdS \quad (\text{Section 3.3}),$$

thus

$$\dot{d}w_{\text{additional}} - PdV = dU - TdS.$$

We may define a further state function, the *Gibbs free energy* G , such that

$$G = U + PV - TS = H - TS.$$

At constant P and T

$$dG = dU + PdV - TdS.$$

As $\dot{d}w_{\text{additional}} = dU + PdV - TdS$ for a reversible change we have

$$\dot{d}w_{\text{additional}} = dG.$$

This is also the condition for equilibrium in a system at constant temperature and pressure. For a spontaneous process $\dot{d}w_{\text{additional}}$ will be less negative than for the corresponding reversible change and not all the decrease in G will be obtained as additional work.† If a system at constant T and P does no additional work then the condition for equilibrium is $dG = 0$. G will be at a minimum when the system is at equilibrium. In a molecular system at constant T and P , G is the measure of the maximum work (other than PV work) which may be obtained from the system. When the system is capable of doing no work and is at equilibrium, $dG = 0$ and G is a minimum. Again we can point to the analogy between free energy G in molecular systems and energy in mechanical systems (Fig. 4.1).

G is a state function and therefore ΔG has a definite value for any change. However it is equal to the maximum available work only for a change that is carried out at constant T and P .

In the equation

$$\Delta G = \Delta H - T\Delta S$$

we have found the proper balance at constant pressure and temperature between the tendencies of a system to maximize its entropy and to minimize its energy (or, at constant pressure, more strictly its enthalpy). At higher temperatures the contribution of entropy change to the free-energy change,

† As PdV is the same for a reversible or an irreversible change at constant pressure, the additional work will behave in the same way as the total work. Thus the system will do the maximum additional work in a reversible change.

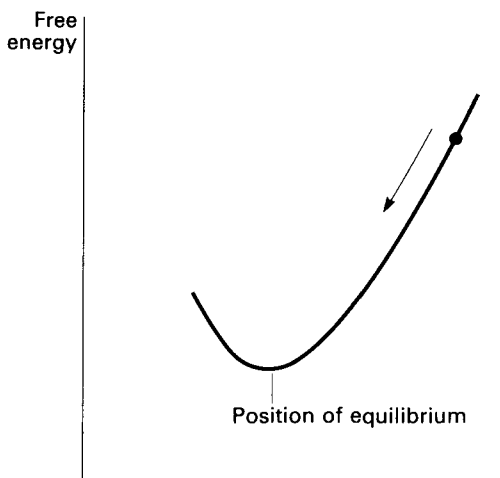
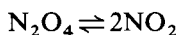


Fig. 4.1. Position of equilibrium in terms of Gibbs free energy for a system at constant pressure and temperature.

$-T\Delta S$, becomes relatively more important. As we have seen, for the reaction



ΔH is positive, since there is an energy that holds together the dimer, and ΔS is positive because the separated monomers have more freedom to move than when bound in dimers. At low temperatures ΔG is positive and little dissociation will occur. At high temperatures the favourable entropy term ($-T\Delta S < 0$) will dominate and increased dissociation will be observed.

Having found how the position of equilibrium can be defined at constant temperature and pressure we shall now restrict ourselves to these conditions. We shall investigate the properties of the Gibbs free energy G which provides our criterion of equilibrium.

As

$$G = U + PV - TS \quad (\text{Section 4.2}),$$

$$dG = dU + P dV + V dP - S dT - T dS.$$

But for a system that does only PV work,

$$\text{as } dU = dq_{\text{rev}} + dw_{\text{rev}} \quad (\text{Section 2.5}),$$

$$dU = T dS - P dV,$$

and

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

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This is a most important thermodynamic equation for chemists as it tells us how free energy, and hence equilibrium position, varies with pressure and temperature.

4.3 Pressure-dependence of free energy

At constant temperature $dT = 0$ and

$$dG = VdP, \quad \text{or} \quad \left(\frac{\partial G}{\partial P}\right)_T = V.$$

For n moles of a perfect gas $PV = nRT$ (Section 1.6), so

$$dG = nRT \frac{dP}{P}.$$

For a change in pressure from P_A to P_B ,

$$\Delta G = G_B - G_A = nRT \int_{P_A}^{P_B} \frac{dP}{P},$$

$$\Delta G = nRT \ln \frac{P_B}{P_A}. \dagger$$

We usually relate the free energy of a gas to the *standard free energy* G^0 . This is defined as the free energy of one mole of the gas at one atmosphere pressure.

Then

$$G = G^0 + RT \ln P/P^0.$$

As P^0 has the value 1 atmosphere,

$$G^0 = G^0 + RT \ln P/1 \text{ atm.}$$

We write

$$G = G^0 + RT \ln (P/\text{atm}).$$

This equation is sometimes expressed

$$G = G^0 + RT \ln P$$

† We could have obtained this equation from $\Delta G = \Delta H - T\Delta S$ as we have already established (Section 3.9) that $\Delta S = -nR \ln P_B/P_A$ and that ΔH is independent of pressure for a perfect gas (so that at constant temperature $\Delta H = 0$).

where P now represents a *dimensionless* ratio. This can lead to confusion when equations of this type are used.

Example

The standard free energy of nitrogen is defined as zero at 298 K and 1 atm pressure. Calculate its value at 10 atm and 0.20 atm at the same temperature.

For a perfect gas

At 10 atm

$$\begin{aligned} G &= G^{\circ} + RT \ln(P/\text{atm}) \\ &= 0 + 8.314 \times 298.2 \times \ln 10 \\ G &= 5710 \text{ J mol}^{-1}. \end{aligned}$$

At 0.2 atm

$$\begin{aligned} G &= 0 + 8.31 \times 298 \ln (0.2) \\ G &= - 3986 \text{ J mol}^{-1}. \end{aligned}$$

4.4 Temperature variation of free energy

Recalling the basic equation $dG = VdP - SdT$, at constant pressure $dP = 0$, therefore

$$dG = -SdT, \text{ and } \left(\frac{\partial G}{\partial T}\right)_P = -S.$$

But

$$G = H - TS;$$

therefore

$$G = H + T\left(\frac{\partial G}{\partial T}\right)_P.$$

If we divide throughout by T^2 we obtain

$$-\frac{G}{T^2} + \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P = -\frac{H}{T^2}.$$

Since

$$-\frac{G}{T^2} + \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P = \left[\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right]_P,$$

$$\left[\frac{\partial \left(\frac{G}{T} \right)}{\partial T} \right]_P = - \frac{H}{T^2},$$

and

$$\left[\frac{\partial \left(\frac{\Delta G}{T} \right)}{\partial T} \right]_P = - \frac{\Delta H}{T^2}.$$

These are the *Gibbs–Helmholtz equations*. They are very important because they relate the temperature dependence of free energy, and hence the position of equilibrium, to the enthalpy change. We shall illustrate their application in the next section.

4.5 Phase equilibria

Equilibrium between the states of matter can be understood in terms of the equation $G = H - TS$ (Section 4.2). The phase with the lowest free energy under any conditions is the most stable. For solids H is relatively large and negative† because of the strong binding forces in solids but S is small as the molecules have little freedom, so at low temperatures solids are the most stable phase.

For gases H is close to zero as there are no strong interactions between the molecules, but S is large because the molecules have a large amount of room in which to move. Thus gases are the stable phase at high temperatures. There is an intermediate region where liquids, which have a less negative H but larger S than solids, are stable. This is illustrated in Fig. 4.2 where the free energy is plotted as a function of temperature. The slopes of the lines reflect the entropy of the phases because $\left(\frac{\partial G}{\partial T} \right)_P = -S$ (Section 4.4).

The phase with the highest entropy, the gas phase, has the largest negative slope and its free energy is the lowest at high temperatures. Where the lines intersect, the free energies of the two phases represented by the lines are equal. As $\Delta G = 0$, and $\Delta G = \Delta H - T\Delta S$ we obtain for the transition between two phases in equilibrium $\Delta H = T\Delta S$. Thus

$$\Delta S_{\text{fus}} = \frac{\Delta H_{\text{fus}}}{T_{\text{fus}}} \quad \text{and} \quad \Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_{\text{vap}}}.$$

† Relative to the enthalpy of the substance in the perfect-gas state and under the same conditions.

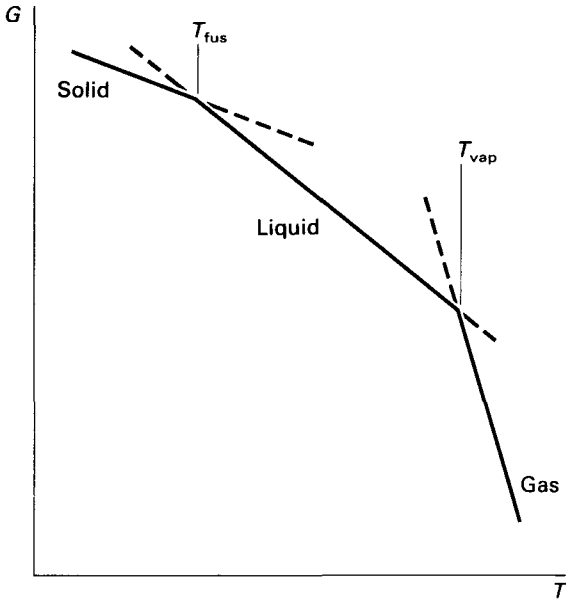


Fig. 4.2. Gibbs free energy as a function of temperature for a pure substance.

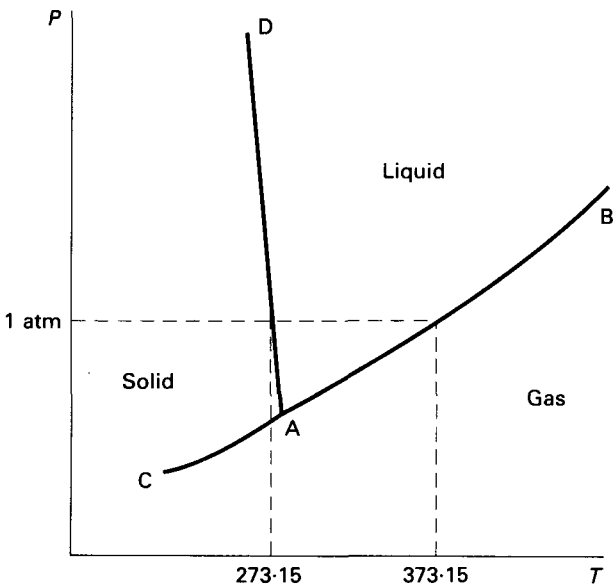


Fig. 4.3. Phase diagram for water (schematic: not to scale).

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The information from such diagrams, if available at a series of pressures, may be represented in *phase diagrams* such as Fig. 4.3. Line AB is the vapour pressure curve for water. AD is the melting curve. AC gives the vapour pressure of ice. Point A, at which all three lines meet, is called the *triple point* (for water it is at 273.16 K and 4.58 mmHg pressure, i.e. 0.61 kPa).

Whereas the temperature-dependence of the free energy of a phase is related to its entropy, the pressure dependence is related to its volume. As shown in Section 4.3, $(\partial G/\partial P)_T = V$, and the variation in the equilibrium position between phases (as represented by the lines in Fig. 4.3) depends on the volume change associated with the phase transition. Thus as ΔV for melting is small compared with the volume change associated with vaporization, the melting point is very much less sensitive to pressure than the boiling point.

4.6 Clapeyron equation

We can now apply the thermodynamic considerations of the previous section in a quantitative manner to obtain an important relation. Consider two phases, a liquid and its vapour, in equilibrium at temperature T and pressure P . If we alter the conditions to $T + dT$ and $P + dP$ then, as $dG = VdP - SdT$ (Section 4.2), we obtain for the liquid $dG(l) = V(l)dP - S(l)dT$, and for the vapour $dG(g) = V(g)dP - S(g)dT$. If under the new conditions the phases are still in equilibrium then $dG(l) = dG(g)$.

Equating the free-energy changes,

$$V(l)dP - S(l)dT = V(g)dP - S(g)dT,$$

and

$$\frac{dP}{dT} = \frac{S(g) - S(l)}{V(g) - V(l)} = \frac{\Delta S_{\text{vap}}}{\Delta V_{\text{vap}}}.$$

As the two phases are in equilibrium,

$$\Delta G_{\text{vap}} = \Delta H_{\text{vap}} - T\Delta S_{\text{vap}} = 0,$$

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T};$$

and

$$\frac{dP}{dT} = \frac{\Delta H_{\text{vap}}}{T\Delta V_{\text{vap}}}$$

where T is the boiling point at the pressure under consideration. The

equation

$$\left(\frac{dP}{dT}\right)_{\text{equil}} = \frac{\Delta H}{T\Delta V}$$

is known as the Clapeyron equation. It is exact and applies to equilibrium between any two phases, that is the melting process as well as vaporization and sublimation.

Example

At 273.16 K the enthalpy change on fusion of water is 6.0 kJ mol^{-1} and the corresponding volume change $-1.6 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$. Estimate the temperature at which ice will melt at 1000 atm pressure (take $1 \text{ atm} = 10^5 \text{ N m}^{-2}$).

We can write the Clapeyron equation

$$\frac{\Delta T}{\Delta P} = T \frac{\Delta V}{\Delta H}$$

and thus

$$\begin{aligned} \Delta T &= \frac{273 \times (-1.6 \times 10^{-6}) \times 10^3 \times 10^5}{6 \times 10^3} \text{ K} \\ &= -7.3 \text{ K}. \end{aligned}$$

Thus we estimate that ice will melt at $(273.16 - 7.3) \text{ K} = 265.9 \text{ K}$.

4.7 Clausius–Clapeyron equation

When applied to vaporization the Clapeyron equation can be modified to give another useful and important relation. We use the equation derived in Section 4.6,

$$\frac{dP}{dT} = \frac{\Delta H_{\text{vap}}}{T\Delta V_{\text{vap}}},$$

together with

$$\Delta V_{\text{vap}} = V(\text{g}) - V(\text{l}).$$

At room temperature and 1 atm pressure $V(\text{g}) \approx 24\,000 \text{ cm}^3$ and $V(\text{l}) \approx 100 \text{ cm}^3$ for one mole of substance, so that $V(\text{g}) \gg V(\text{l})$ and we can replace ΔV_{vap} by $V(\text{g})$. Again, if the vapour follows the perfect-gas equation, for one mole we have

$$V(\text{g}) = \frac{RT}{P} \quad (\text{Section 1.5}),$$

and

$$\frac{dP}{dT} = \frac{\Delta H_{\text{vap}}}{RT^2} P.$$

Thus

$$\frac{d \ln P}{dT} = \frac{\Delta H_{\text{vap}}}{RT^2}.$$

If ΔH is independent of temperature then

$$\ln P = -\frac{\Delta H_{\text{vap}}}{RT} + \text{const.}$$

These equations, which relate the temperature dependence of the vapour pressure of a liquid to ΔH_{vap} , its enthalpy change per mole on vaporization, are called the Clausius–Clapeyron equations. Unlike the Clapeyron equation, they are not exact, as a number of approximations were introduced in their derivation, but they are nevertheless extremely valuable.

4.8 The vapour pressure of liquids

Let us now consider the vaporization of a liquid from the standpoint of the free-energy change on vaporization. The free energy of one mole of perfect vapour is given by

$$G(\text{g}) = G^0(\text{g}) + RT \ln(P/\text{atm}) \quad (\text{Section 4.3}),$$

where P is the vapour pressure of the liquid. $G^0(\text{g})$ is the free energy of one mole of vapour at 1 atm pressure. The free energy of one mole of liquid will be simply $G^0(\text{l})$ as we can assume that the free energy of a condensed phase is virtually independent of pressure. The change in free energy when vaporization of one mole of liquid occurs producing one mole of vapour at its equilibrium pressure, P , is

$$\Delta G = G(\text{g}) - G(\text{l}) = G^0(\text{g}) - G^0(\text{l}) + RT \ln(P/\text{atm}).$$

As the liquid and its vapour are in equilibrium there is no change in free energy when a quantity of the liquid is vaporized. Thus $G(\text{g}) = G(\text{l})$ and

$$\Delta G_{\text{vap}}^0 = -RT \ln(P/\text{atm}).$$

This equation tells us that the vapour pressure of a liquid is determined by the free energy change when one mole of liquid is vaporized to produce one mole of vapour *at one atmosphere pressure*. At the normal boiling point where the liquid is in *equilibrium* with its vapour at one atmosphere pressure, $P = 1$ and $\Delta G_{\text{vap}}^0 = 0$. (At other temperatures ΔG_{vap}^0 represents a hypothetical process but is, none the less, a very useful function.)

To find the temperature variation of vapour pressure we use the Gibbs–Helmholtz equations derived earlier (Section 4.4).

$$\left[\frac{\partial \left(\frac{\Delta G}{T} \right)}{\partial T} \right]_P = - \frac{\Delta H}{T^2}$$

$$\frac{d \ln P}{dT} = - \frac{1}{R} \left[\frac{\partial \left(\frac{\Delta G_{\text{vap}}^0}{T} \right)}{\partial T} \right] = \frac{\Delta H_{\text{vap}}^0}{RT^2}; \ddagger$$

$$\frac{d \ln P}{dT} = \frac{\Delta H_{\text{vap}}^0}{RT^2} \cdot \ddagger$$

This is the Clausius–Clapeyron equation we derived in another way in the previous section.

The vapour pressure of n-butane has been measured, with the results given in Table 4.1.

We plot $\lg P$ against $1/T$ as in Fig. 4.4, and if ΔH_{vap}^0 is independent of temperature over the range of our data, we have $\lg P = -\Delta H_{\text{vap}}^0/2.3 RT + \text{const}$. The slope of the plot is $-\Delta H_{\text{vap}}^0/2.3 R$. The slope is found to be -1.3×10^3 therefore $\Delta H_{\text{vap}} = 24.8 \text{ kJ mol}^{-1}$ (an average value in the temperature range 200–270 K). Closer inspection shows the plot to be slightly curved, and more careful analysis of this data gives ΔH_{vap}^0 at the normal boiling point as $22.38 \text{ kJ mol}^{-1}$.

Table 4.1 The vapour pressure of n-butane

Experimental results†		Our calculation	
T/K	P/mmHg	10 ³ K/T	lg (P/mmHg)‡
195.12	9.90	5.125	0.9956
212.68	36.26	4.702	1.5595
226.29	85.59	4.419	1.9324
262.28	503.34	3.812	2.7019
272.82	764.50	3.665	2.8834

† Aston, J. G. and Messerly, G. H. (1940). *J. Am. Chem. Soc.*, **62**, 1917.

‡ We use the convention that $\lg x = \log_{10} x$, just as $\ln x = \log_e x$.

† The Gibbs–Helmholtz equation is strictly applicable only at constant pressure, but as the vapour pressure of a liquid is relatively insensitive to changes in the applied pressure we need not trouble with this restriction.

‡ Note: As $d \ln P = dP/P$ it is a dimensionless quantity.

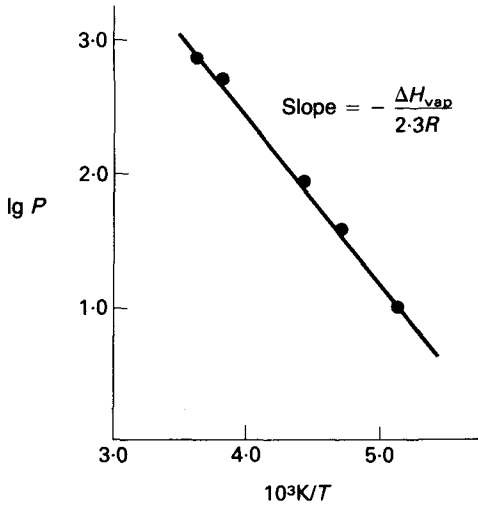


Fig. 4.4. Logarithm of the vapour pressure of liquid n-butane as a function of reciprocal temperature.

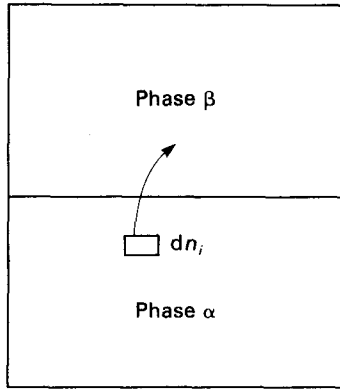


Fig. 4.5. A component in equilibrium between two phases α and β .

4.9 Chemical potential

In our discussion so far we have restricted ourselves to systems containing only one chemical component. We must now consider how we can treat many-component systems, in particular those systems in which the chemical composition changes, as in systems in which chemical reactions take place.

For a pure substance or a system of constant chemical composition

$$dG = VdP - SdT \quad (\text{Section 4.2}).$$

If the numbers of moles of various components of the system, n_1, \dots, n_i , vary we may add further terms to this equation:

$$dG = VdP - SdT + \left(\frac{\partial G}{\partial n_1}\right)_{T, P, n_j} dn_1 + \dots + \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j} dn_i,$$

where the subscript n_j indicates that the quantities of all components, except the one in the derivative, are kept constant. We may define the *chemical potential* μ_i of the i th component

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

then

$$dG = VdP - SdT + \sum_i \mu_i dn_i.$$

This is sometimes called the fundamental equation of chemical thermodynamics. μ_i may be thought of as the increase in the free energy of the system when one mole of component i is added to an infinitely large quantity of the mixture so that it does not significantly change the overall composition. Chemical potential is an intensive property and can be regarded as providing the force which drives chemical systems to equilibrium. Consider a chemical i distributed between two phases α and β as illustrated in Fig. 4.5. Let its chemical potential be $\mu_i(\alpha)$ and $\mu_i(\beta)$ in these phases. At constant T and P if we transfer dn_i moles of i from α to β ,

$$dG = [\mu_i(\beta) - \mu_i(\alpha)] dn_i.$$

At equilibrium $dG = 0$ and as we can always consider a small but non-zero value of dn_i this means that $\mu_i(\alpha) = \mu_i(\beta)$ is the condition for equilibrium. Thus for a system at constant pressure and temperature the chemical potential of each component must be equal in all parts of the system. Thus

$$\mu_i(\alpha) = \mu_i(\beta)$$

$$\mu_j(\alpha) = \mu_j(\beta) \quad \text{etc.}$$

This is a most useful definition of the position of chemical equilibrium.

4.10 Chemical potential and free energy

For a pure substance the chemical potential $\left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j}$ is simply the molar free energy G/n_i (Fig. 4.6). Thus for one mole of gas

$$G = G^0 + RT \ln (P/\text{atm}) \quad (\text{Section 4.3})$$

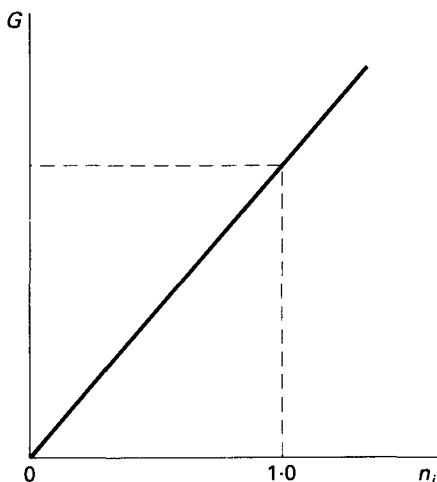


Fig. 4.6. Gibbs free energy as a function of the number of moles of a pure substance.

and $\mu = \mu^0 + RT \ln (P/\text{atm})$. Mixtures of perfect gases behave as if each gas were alone in the container. The thermodynamic properties of the gases making up such a mixture can be expressed in terms of their partial pressures, the pressures they would generate if alone in the container (Section 1.6). Thus

$$\mu_i = \mu_i^0 + RT \ln (P_i/\text{atm})$$

where P_i represents the numerical value of the partial pressure of component i when this is expressed in atmospheres.

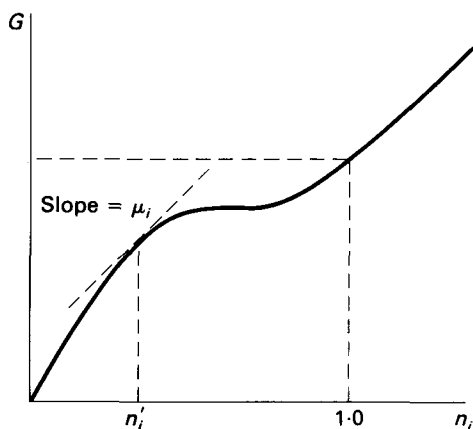


Fig. 4.7. Gibbs free energy as a function of the number of moles of substance i added to a mixture. The slope is the chemical potential of i , μ_i .

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moles of A are converted into dn_B moles of B at constant T and P we have $dG = (+\mu_A dn_A + \mu_B dn_B)$, where dn_A is negative and dn_B positive. We can define an *extent of reaction* ξ which is 0 when the reaction position is entirely to the left of the equation (i.e. only reactants present) and is 1 when one mole of reactant has gone over entirely to products. In our simple example we may write

$$d\xi = dn_B = -dn_A,$$

and

$$dG = (\mu_B - \mu_A)d\xi \quad \text{at constant } T \text{ and } P.$$

The reaction will proceed until G reaches a minimum value and $\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = 0$, as illustrated in Fig. 4.8. As $\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \mu_B - \mu_A$, this is the position where $\mu_A = \mu_B$.

If the components follow the perfect-gas laws,

$$\mu_i = \mu_i^0 + RT \ln(P_i/\text{atm}) \quad (\text{Section 4.10}).$$

Therefore

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \mu_B - \mu_A = \mu_B^0 - \mu_A^0 + RT \ln \frac{P_B}{P_A}.$$

$\mu_B^0 - \mu_A^0$ is ΔG^0 , the free-energy change if one mole of reaction takes place with both reactant and product remaining in their standard state (at 1 atm pressure).

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \Delta G^0 + RT \ln \frac{P_B}{P_A}.$$

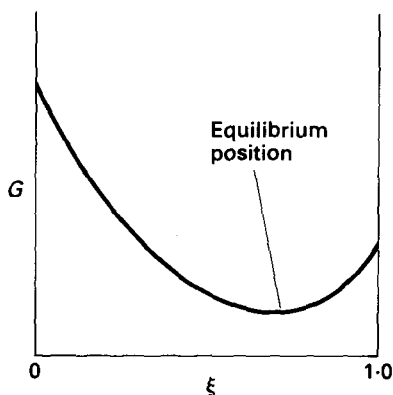


Fig. 4.8. The Gibbs free energy as a function of the extent of a chemical reaction (ξ).

$\left(\frac{\partial G}{\partial \xi}\right)_{T,P}$ is the change in free energy with the degree of advancement of the reaction under the conditions specified by P_A and P_B . It is equal to the free-energy change for one mole of reaction with A at partial pressure P_A going to B at partial pressure P_B , the partial pressures remaining constant. In modern treatments $-\left(\frac{\partial G}{\partial \xi}\right)_{T,P}$ is called the *affinity* of the reaction whereas in older or elementary texts $\left(\frac{\partial G}{\partial \xi}\right)_{T,P}$ is called the *reaction free energy* and written simply as ΔG . We will write it as $\Delta G'$, the prime reminding us that it is in reality a differential quantity and only corresponds to the free-energy change for a mole of reaction under precisely defined conditions.

At equilibrium

$$\Delta G' = \left(\frac{\partial G}{\partial \xi}\right)_{T,P} = 0,$$

and as

$$\Delta G' = \Delta G^0 + RT \ln \frac{P_B}{P_A},$$

$$\Delta G^0 = -RT \ln \left(\frac{P_B}{P_A}\right)_{\text{eq}}.$$

We call the value of $\left(\frac{P_B}{P_A}\right)$ at equilibrium the equilibrium constant of the reaction, K_p .

$$\Delta G^0 = -RT \ln K_p.$$

This important equation tells us how the position of chemical equilibrium can be defined in terms of the free energies of the reactants and products at 1 atm pressure. Such standard free energies can be determined experimentally and are tabulated for use in this way. We shall consider specific examples later. The equation is also valuable in a qualitative sense. If ΔG^0 is negative we know the equilibrium position will correspond to the presence of more product than reactants ($\ln K_p > 0$). If ΔG^0 is positive the reaction will not proceed to such an extent and reactants will predominate in the equilibrium mixture. With this result we have accomplished a major purpose of our study.

Had our reaction been more complicated we would have obtained essentially the same results. For example for the reaction

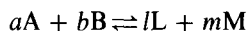


Table 4.2 Standard free energy changes and the corresponding values of the equilibrium constant at 298 K

$\Delta G^\circ/\text{kJ mol}^{-1}$	K	Composition of equilibrium mixture
- 50	6×10^8	negligible reactants
- 10	57	products dominate
- 5	7.5	
0	1.0	
+ 5	0.13	reactants dominate
+ 10	0.02	
+ 50	1.7×10^{-9}	negligible products

we would have

$$dG = \mu_L dn_L + \mu_M dn_M + \mu_A dn_A + \mu_B dn_B = \sum \mu_i dn_i.$$

The extent of reaction ξ would have to be defined in a more complicated manner so that

$$d\xi = \frac{dn_L}{l} = \frac{dn_M}{m} = -\frac{dn_A}{a} = -\frac{dn_B}{b} = \frac{dn_i}{v_i}$$

where v_i represents the stoichiometric coefficients $-a$, $-b$, m , and l . The v_i for the reactants are defined as negative and those for the products as positive. Thus

$$dG = (l\mu_L + m\mu_M - a\mu_A - b\mu_B)d\xi$$

and

$$\Delta G' = \left(\frac{\partial G}{\partial \xi} \right)_{T,P} = (l\mu_L + m\mu_M - a\mu_A - b\mu_B) = \sum_i v_i \mu_i.$$

As $\mu_A = \mu_A^\circ + RT \ln (P_A/\text{atm})$ etc., we obtain

$$\Delta G' = \Delta G^\circ + RT \ln \left[\frac{(P_L/\text{atm})^l (P_M/\text{atm})^m}{(P_A/\text{atm})^a (P_B/\text{atm})^b} \right]$$

which we can write in more concise notation

$$\Delta G' = \Delta G^\circ + RT \ln \prod_i (P_i/\text{atm})^{v_i}.$$

At equilibrium $\Delta G^\circ = -RT \ln K_p$, where

$$K_p = \left[\frac{(P_L/\text{atm})^l (P_M/\text{atm})^m}{(P_A/\text{atm})^a (P_B/\text{atm})^b} \right]_{\text{eq}} = \left[\prod_i (P_i/\text{atm})^{v_i} \right]_{\text{eq}}.$$

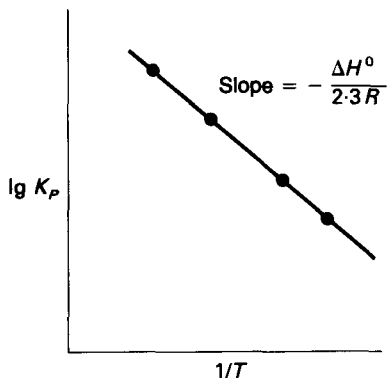


Fig. 4.9. The logarithm of an equilibrium constant as a function of reciprocal temperature (schematic).

and

$$\Delta G^0 = \sum_i \nu_i \mu_i^0,$$

the standard free-energy change for a mole of reaction.

These equations, though they look a little more complicated, are fundamentally the same as those we obtained in our simple illustrative example of butane isomerization. K_p is strictly dimensionless even if $(a + b) \neq (l + m)$, as all the pressures comprising it are themselves dimensionless ratios, i.e. $P(\text{atm})/(1 \text{ atm})$ (Section 4.3).

4.12 Temperature-dependence of equilibrium constants

We can use the thermodynamic relations we have obtained so far to find out how the position of equilibrium will change if we alter the temperature.

Remembering that using

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad (\text{Section 4.4}),$$

and

$$G = H - TS \quad (\text{Section 4.2}),$$

we obtained the Gibbs–Helmholtz equation (Section 4.4)

$$\left[\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right]_P = -\frac{\Delta H}{T^2},$$

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we can differentiate the equation $\Delta G^0 = -RT \ln K_p$ (Section 4.11) obtaining

$$\left(\frac{\partial \ln K_p}{\partial T}\right)_p = -\frac{1}{R} \left[\frac{\partial \left(\frac{\Delta G^0}{T}\right)}{\partial T} \right]_p = \frac{\Delta H^0}{RT^2}.$$

This important equation

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

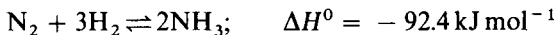
is called the Van't Hoff Isochore. As ΔG^0 and ΔH^0 are not functions of pressure (as they are by definition the values at 1 atm) we can write

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

If we assume ΔH^0 is independent of temperature (which is often a fair approximation) then integration gives

$$\ln \frac{K_p(T_2)}{K_p(T_1)} = -\frac{\Delta H^0}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right).$$

Plotting $\lg K_p$ against $1/T$, as illustrated in Fig. 4.9, the slope is $-\Delta H/2.3R$. For an exothermic reaction ($\Delta H < 0$) K_p must decrease as the temperature increases. Thus with the reaction



we predict and indeed obtain less ammonia in the equilibrium mixture at higher temperatures. For an endothermic reaction ($\Delta H > 0$) K_p increases with increasing temperature; so for the equilibrium



we predict and observe more dissociation at higher temperatures.

Example

The equilibrium constant K_p for the dissociation of bromine into atoms



is 6×10^{-12} at 600 K and 1×10^{-7} at 800 K. Calculate the standard free energy change for the reaction at these temperatures and the standard enthalpy change assuming this is constant in the temperature range 600–800 K.

At 600 K

$$\Delta G^0 = -RT \ln K_p \quad (\text{Section 4.11})$$

$$\Delta G^0 = -8.3 \times 600 \times \ln(6 \times 10^{-12}) \text{ J}$$

$$\Delta G^0 = 129 \text{ kJ mol}^{-1} \text{ at } 600 \text{ K.}$$

At 800 K

$$\Delta G^0 = -8.3 \times 800 \times 2.3 \times (-7) \text{ J}$$

$$\Delta G^0 = 107 \text{ kJ mol}^{-1} \text{ at } 800 \text{ K}$$

$$\frac{d \ln K_p}{dT} = \frac{\Delta H^0}{RT^2} \quad (\text{Section 4.12}).$$

Integrating

$$\ln \frac{K_p(T_2)}{K_p(T_1)} = \frac{\Delta H^0}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\frac{\Delta H^0}{8.3} \left(\frac{1}{600} - \frac{1}{800} \right) = \ln \left(\frac{10^{-7}}{6 \times 10^{-12}} \right)$$

$$\Delta H^0 = 194 \text{ kJ mol}^{-1}.$$

We can also calculate the standard entropy change associated with the reaction as $\Delta G^0 = \Delta H^0 - T\Delta S^0$.

At 600 K

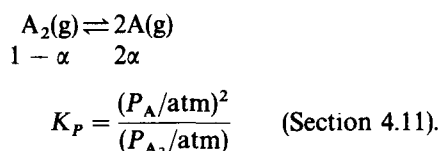
$$\Delta S^0 = \frac{(193 - 129)}{600} \times 10^3 \text{ J K}^{-1} \text{ mol}^{-1} = 107 \text{ J K}^{-1} \text{ mol}^{-1}.$$

As we would expect, the energy of the molecules is large and negative with respect to the constituent atoms, thus the enthalpy change on dissociation is positive and unfavourable to the dissociation process. However, the additional freedom acquired by the dissociated atoms leads to a positive entropy change. This favours dissociation, which becomes more significant as the temperature is increased.

4.13 Effect of pressure on equilibrium constants

As K_p may be defined in terms of the free energies of the participant substances in the *standard states*, i.e. at 1 atm pressure, it must be independent of pressure.

Consider the reaction



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If we express the partial pressures in terms of the degree of dissociation α ,

$$P_A = \frac{2\alpha}{1 + \alpha}P \quad (\text{Section 1.5})$$

and

$$P_{A_2} = \frac{1 - \alpha}{1 + \alpha}P$$

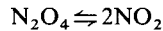
where P is the total pressure. Therefore

$$K_p = \frac{4\alpha^2(P/\text{atm})}{(1 - \alpha)(1 + \alpha)} = \frac{4\alpha^2(P/\text{atm})}{(1 - \alpha^2)}.$$

Thus as K_p is independent of the total pressure, the degree of dissociation α must in fact decrease as P increases.

Example

At 298 K the equilibrium constant for the dissociation



is 0.14. Calculate the fraction of N_2O_4 molecules dissociated at 1 atm and 10 atm pressure.

As

$$K_p = \frac{4\alpha^2(P/\text{atm})}{1 - \alpha^2}$$

we obtain

$$\alpha = \left(\frac{K_p}{4P + K_p} \right)^{\frac{1}{2}}.$$

Substituting $K_p = 0.14$ and $P = 1$ we obtain

$$\alpha = \left(\frac{0.14}{4.14} \right)^{\frac{1}{2}} = 0.18.$$

At 10 atm,

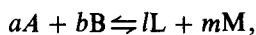
$$\alpha = \left(\frac{0.14}{40.14} \right)^{\frac{1}{2}} = 0.06.$$

If K_p is small compared with P/atm , α is approximately proportional to $(1/P)^{\frac{1}{2}}$.

If we can express the equilibrium constant in terms of mole fractions defined by

$$x_i = \frac{n_i}{n}$$

where n is the total number of moles in the system, then for the equilibrium



$$K_x = \frac{x_L^l x_M^m}{x_A^a x_B^b}.$$

As the partial pressure is proportional to the mole fraction for perfect-gas mixtures, $(P_i/\text{atm}) = x_i(P/\text{atm})$, and so

$$K_x = \frac{(P_L/\text{atm})^l (P_M/\text{atm})^m}{(P_A/\text{atm})^a (P_B/\text{atm})^b} \cdot (P/\text{atm})^{(a+b-l-m)}$$

or
$$K_x = K_p(P/\text{atm})^{-\Delta n}$$

where $\Delta n = l + m - a - b$ is the change in the number of moles of gaseous substances, as the reaction goes from left to right. Thus unless $\Delta n = 0$ the mole fractions of the components of the equilibrium mixture will depend on the total pressure even though K_p does not. If the reaction is such as to increase the number of moles of gas, an increase in pressure will reduce the mole fraction of products in the final equilibrium mixture. We can express the dependence of K_x on pressure more generally.

$$\left(\frac{\partial \ln K_x}{\partial P}\right)_T = \left(\frac{\partial \ln K_p}{\partial P}\right)_T - \Delta n \left(\frac{\partial \ln P}{\partial P}\right)_T.$$

For perfect gases $P\Delta V = \Delta nRT$. Therefore as $\left(\frac{\partial \ln K_p}{\partial P}\right)_T = 0$, we obtain

$$\left(\frac{\partial \ln K_x}{\partial P}\right)_T = -\frac{\Delta n}{P} = -\frac{\Delta V}{RT}.$$

This equation applies not only to equilibria involving gases but also to equilibria in solution, and indeed to any equilibrium when the equilibrium constant is expressed in terms of mole fractions rather than partial pressures. In these circumstances ΔV is the volume change accompanying one mole of reaction.†

4.14 Basic results of chemical thermodynamics

A famous physical chemist, G. N. Lewis, once stated: ‘Thermodynamics exhibits no curiosity’. By this he meant that the conclusions of thermo-

† Strictly, one mole of reaction with all substances in their standard states. These new standard states, to be discussed later, are defined at unit concentrations rather than at unit partial pressures and are not the standard states we have used up to the present.

dynamics are quite general. Thus if we apply thermodynamics to an equilibrium we will get the correct answer even if, for example, we have an entirely wrong idea of the nature of the molecules making up our system. For this reason there can be relatively few important thermodynamics equations and these must be of extremely wide applicability. You may have noticed that when studying both the vapour pressure of a liquid and a chemical reaction we obtained equations which, though known by different names, had exactly the same form. We shall now summarize these equations.

(i) For any system at equilibrium $\Delta G^\ominus = -RT \ln K$ (Section 4.11), where K is some quantity which characterizes the equilibrium position in terms of the amounts of materials present in the equilibrium mixture. Thus K could be an equilibrium constant, a vapour pressure, or a solubility. ΔG^\ominus is a standard free-energy change for one mole of reaction for the equation which describes the equilibrium. (In this general formulation the standard states are not necessarily those based on the 1 atm standard.)

(ii) The second type of equation is $\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta H^\ominus}{RT^2}$ (Section 4.12), where again K is a quantity which characterizes the position of equilibrium and ΔH^\ominus is the standard enthalpy change for one mole of reaction.

(iii) The effect of pressure on the position of equilibrium may be expressed as $\left(\frac{\partial \ln K_x}{\partial P}\right)_T = -\frac{\Delta V^\ominus}{RT}$ (Section 4.13), where ΔV^\ominus is the volume change accompanying a mole of reaction under standard conditions.

(iv) The final equation we recall, Section 4.11, can be written in the generalized form

$$\Delta G' = \left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \Delta G^\ominus + RT \ln \prod_i \left(\frac{c_i}{c^\ominus}\right)^{\nu_i}$$

where $\left(\frac{c_i}{c^\ominus}\right)$ is some measure of the quantity of the i th constituent of the reaction mixture relative to that in the standard state, c^\ominus .

These equations depend on the fact that

$$\mu_i = \mu_i^\ominus + RT \ln \left(\frac{c_i}{c^\ominus}\right)$$

where $\left(\frac{c_i}{c^\ominus}\right)$ represents some suitable measure of concentration of i , for example, (P_i/atm) or x_i . μ_i^\ominus is the chemical potential of the standard state, that is the state for which $c_i = c^\ominus$. If we select the one atmosphere standard state we used above when considering reactions in the gaseous phase, $\mu^\ominus = \mu^0$.

4.15 Le Chatelier's Principle

The direction of change in the position of equilibrium due to change in the external variables such as T and P may generally be found by the application of Le Chatelier's Principle which states: *Perturbation of a system at equilibrium will cause the equilibrium position to change in such a way as to tend to remove the perturbation.*

For instance, if heat is evolved in a reaction ($\Delta H < 0$), lowering the temperature will promote more reaction because moving the equilibrium toward the product side tends to raise the temperature of the system. If a reaction proceeds with a positive volume change, then application of pressure shifts the equilibrium in the direction of the reactants. These conclusions are given quantitative expression in the equations

$$\left(\frac{\partial \ln K}{\partial T}\right)_P = \frac{\Delta H^0}{RT^2} \quad (\text{Section 4.12});$$

$$\left(\frac{\partial \ln K_x}{\partial P}\right)_T = -\frac{\Delta V}{RT} \quad (\text{Section 4.13}).$$

Le Chatelier's Principle provides a good guide to the effects of pressure and temperature changes. To make it universally true however it would have to be stated in a more rigorous form, so it is wise to regard it as a useful guide or *aide memoire* rather than as a fundamental thermodynamic principle.

Problems

- 4.1. Naphthalene melts at 353 K at 1 atm pressure with an enthalpy change on fusion of 19 kJ mol^{-1} . The volume increase on fusion is $19 \times 10^{-6} \text{ m}^3$. What change in the melting temperature will be observed if the pressure is raised by 100 atm? ($1 \text{ atm} = 10^5 \text{ N m}^{-2}$.)
- 4.2. The vapour pressure of a liquid is

T/K	326.1	352.9	415.0	451.7
Vapour pressure/mm Hg	1.0	5.0	100	400

Calculate the enthalpy change on vaporization and the entropy of vaporization. Calculate the standard Gibbs free-energy change accompanying vaporization at 373 K.

- 4.3. Formic acid is partially associated into dimers in the vapour phase. The mole fraction present as monomer is 0.228 at 283 K and 10 mmHg pressure and 0.715 at 333 K and 16 mmHg. Calculate the enthalpy change on dimerization. ($760 \text{ mmHg} = 1 \text{ atm} = 10^5 \text{ N m}^{-2}$.)
- 4.4. In a mixture at 1 atm the partial pressure of CO in equilibrium with CO_2 and C was as follows:

T/K	1083	1173	1253
Partial pressure of CO/atm	0.931	0.978	0.991

Calculate the enthalpy change accompanying the reaction $\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$.

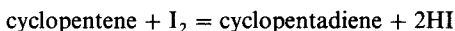
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- 4.5. The equilibrium constant for the reaction $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$ is 45.6 at 764 K and 60.8 at 667 K. Estimate the enthalpy change which accompanies one mole of the forward reaction.
- 4.6. The enthalpy of vaporization of water at 373 K and 1 atm is 40.7 kJ mol^{-1} . Estimate the vapour pressure of water at 368 K.
- 4.7. In the *Handbook of Chemistry and Physics* the following data are given for the vapour pressure of mercury

Temp/ $^{\circ}\text{C}$	0	4	8	12
Pressure/mm Hg	0.000185	0.000276	0.000406	0.000588

Calculate the entropy and enthalpy changes accompanying vaporization at 1 atm and the Gibbs free energy change accompanying vaporization at 273 K and at the boiling point of mercury.

- 4.8. For the gas phase reaction



$$\log K_p = 7.55 - 4817 T^{-1} \text{ in the temperature range } 450\text{--}690 \text{ K.}$$

Calculate the standard enthalpy, entropy, and Gibbs free-energy changes accompanying the reaction at 573 K.