

Chemical Equilibrium

1. *Equilibrium conditions*

In previous sections, the term “equilibrium” has been used with different connotations. The more familiar meaning is that a system resides at an “equilibrium” position, as defined by a mechanical

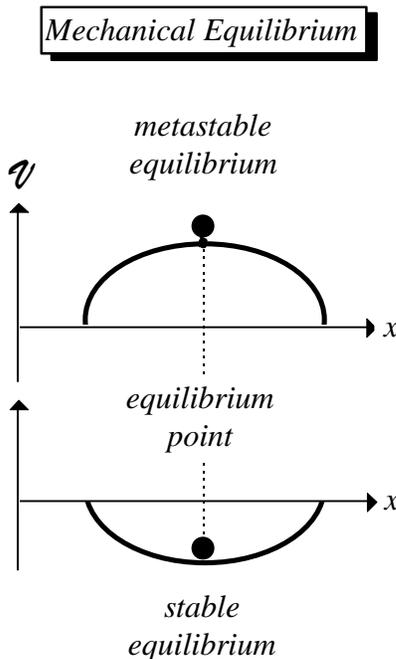


Figure 1: Equilibrium point of potentials

equilibrium point.

potential \mathcal{V} . This case is illustrated on the left, where a ball is shown in *metastable (unstable) mechanical equilibrium* (top part) or *stable mechanical equilibrium* (bottom part). In either case, the first derivative of the potential, the “*driving force*” $F = -d\mathcal{V}/dx$ vanishes, and the system does not undergo any spontaneous (irreversible) transitions. For an equilibrium to be stable against small influences on the system of interest, the potential has to be concave, like at the bottom of Fig.1. Therefore, a stable equilibrium requires the second derivative of the potential to be negative, $dF/dx = -d^2\mathcal{V}/dx^2 < 0$, at the

A second, different type of “*dynamical*” *equilibrium* was introduced in the *context of entropy* S , involving the *number or density of (micro-)states*, Ω , of the system (and its surroundings). It was shown, that it is the entropy, rather than a simple mechanical potential energy, that drives a system towards the ultimate state of *thermal equilibrium*. However, the energy always plays an important role. According to the First Law of Thermodynamics, the total energy (of system and surroundings) is conserved. Therefore,

the effect of the energy must reside in the prospects of its *redistribution between system and surroundings*.

How to find the situation of equilibrium of a thermodynamic system has been discussed previously. In these procedures, one needs to consider both, the system and its surroundings. For applications, it is important to know the properties of the surroundings, or better perhaps, it is important to know how to design the most appropriate surroundings of a system of interest, which may be an industrial reactor. For a detailed discussion of the important thermodynamic processes, however, it would be more desirable to be able to concentrate on the system and disregard the (well-understood) surroundings. This leads to the introduction of *thermodynamic potentials or free energies*.

2. Thermodynamic Potentials

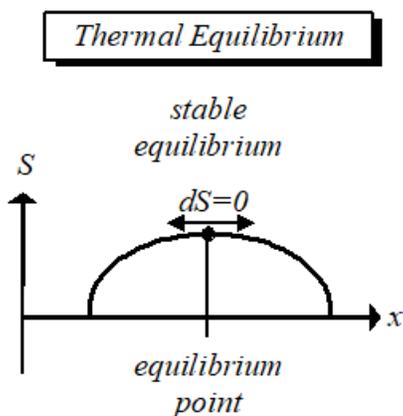


Figure 2: Entropy vs. extent of process, point of stable equilibrium is marked

Thermodynamic equilibrium is reached in a process when the system at interest reaches a point of maximum total entropy of both, the given system and its surroundings,

$$dS_{total} = dS_{sys} + dS_{surr} = 0 \quad (1)$$

The *combination of system and its surroundings can be considered to constitute an isolated, homogenous system, a system that has a uniform*

temperature $T \equiv const.$ For a reversible process involving such an isolated system, there is no net heat loss or gain. Hence,

$$dq_{total} = dq_{sys} + dq_{surr} = 0 \quad (2)$$

and

$$dS_{sys} = dq_{sys}/T = - dS_{surr} \quad (3)$$

Inserting this expression into Equ. 1 leads to the following *reformulation of the equilibrium condition* of system and surroundings,

$$dq_{sys}/T - dS_{sys} = 0 \quad (4)$$

or

$$dq_{sys} - T \cdot dS_{sys} = 0 \quad (4a)$$

But now the equilibrium condition *is expressed completely in terms of properties of the system*. The properties of the surroundings have been eliminated. In the following, the subscript ‘sys’ is, therefore, omitted.

For processes that occur under *conditions of constant pressure*, the process *heat dq evolved* is *given by the enthalpy dH*. In terms of the enthalpy, a system is in equilibrium, when

$$dH - T \cdot dS = 0 \quad (5)$$

Since the *temperature T* ($\equiv const.$) is *here just a constant parameter*, Equ.5 represents the differential of the “*Gibbs Free Energy*”

$$G = H - T \cdot S \quad (6)$$

Therefore, one can say that *a system exposed to a constant pressure (and constant temperature) is exactly then in equilibrium, when the Gibbs free energy is at its minimum*. Here, $dG = 0$ corresponds to $S = S_{max}$. As long as a system is not yet in equilibrium, one has $S < S_{max}$ and for a process $dS > dq/T$, i.e., the heat dq absorbed

($dq > 0$) by the system in the process is less than its maximum value $dq_{rev} = TdS$, or the heat released by the system ($dq < 0$) is smaller (larger in magnitude) than that, $dq_{rev} = TdS$, required by the entropy change. For such, obviously irreversible, processes,

$$dG = dH - TdS = dq - TdS < 0 \quad (7)$$

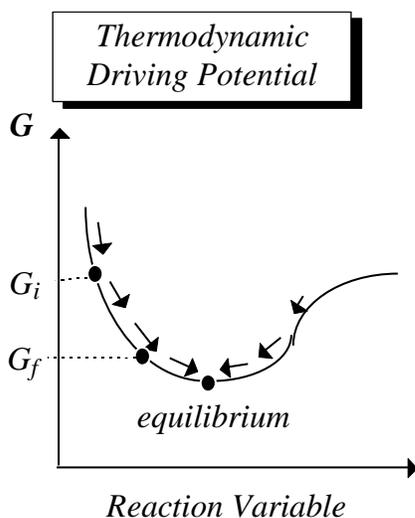


Figure 3: Gibbs free energy vs. extent of process.

As long as Equ. 7 holds, spontaneous (irreversible) processes can occur, which increase the total entropy of system and surroundings and, hence, drive the system towards equilibrium. The sketch illustrates irreversible processes a system will undergo spontaneously, if its initial state is situated somewhere on the slope of the G - function, either on the left or the right side of the minimum in G . The equilibrium of a thermodynamic system is reached by a system when its free energy is at its minimum value.

Gibbs free energy has, therefore, a function analogous to that of a driving potential of a mechanical system.

$$\begin{aligned} &\text{A system with } p=\text{const. and } T=\text{const.} \\ &\text{is at equilibrium, when} \\ &\quad G = G_{min} \text{ and } dG = 0 \\ &\text{For irreversible processes: } dG < 0 \end{aligned} \quad (8)$$

The term "system at equilibrium" really means "system at equilibrium with its surroundings".

For cases, where not the pressure, but the *volume as well as the temperature are held constant*, $V \equiv \text{const.}$, $T \equiv \text{const.}$, an argument is made in analogy to Equ. 5: For such systems and processes, *no work is done and dq is equal to a change dU in internal energy*. Therefore,

$$dA := dU - TdS = dq - TdS \leq 0 \quad (9)$$

Since $T (\equiv \text{const.})$ is here just a parameter, Equ. 9 represents the differential of the “*Helmholtz Free Energy*”

$$A = U - T \cdot S \quad (10)$$

In other words, as long as the $<$ sign in Equ. 9 holds, spontaneous (irreversible) processes can occur, which drive the system towards equilibrium. The *Helmholtz free energy has, therefore, a function analogous to that of a driving potential of a mechanical system*. The equilibrium of a thermodynamic system is reached by a system when its free energy is at its minimum value.

*A system with $V=\text{const.}$ and $T=\text{const.}$ is at equilibrium, when
 $A = A_{\min}$ and $dA = 0$
 For irreversible processes: $dA < 0$*

(11)

It is important to realize that: *As combinations of state functions, both free energies G and A are state functions.*

The quantities G and A are called “Free Energies”, because they characterize the total energy available to a system (under the conditions given by the surroundings).

For example, a transition $A \rightarrow B$ of a system from state A to state B may be energetically disallowed, as long as the system is isolated. However, it can occur if the system is *placed in a heat bath* of high temperature, such that it can *access enough additional energy* to proceed.

Consider as an illustration the *dissociation of hydrogen gas* molecules in a thermally insulated container:



Since H_2 is bound, it is obvious that the enthalpy increases for the dissociation, $\Delta H > 0$. Energy would have to be supplied to the system, i.e., the *process* would *not* be *spontaneous*. The equilibrium would be entirely on the left-hand side of the reaction. H_2 would not dissociate, and free H atoms would spontaneously combine to form H_2 , in the reverse of the reaction 12.

The situation is quite different, when the system is immersed in a heat bath and is held at a very high temperature T . Then, the net *free-energy balance for the dissociation reaction can be* negative:

$$\underline{\Delta G} = \Delta H (> 0) - T\Delta S (> 0) \underline{\leq 0} \quad (13)$$

With increasing temperature, the second term in Equ. 13, $-T\Delta S$, can be made extremely large and negative, such that any effect of $\Delta H > 0$ can be counterbalanced and overwhelmed at high enough temperatures. Then, dissociation of H_2 will occur spontaneously, because the energy is readily available to the system and delivered by the surroundings. *The temperature is a weighting factor that determines the relative weights of enthalpy and entropy for a given process $A \rightarrow B$.*

It is useful to inspect the *relation between the free energy* (Gibbs or Helmholtz) *and the useful work* that a system can provide. As discussed before, *it is important to consider work done in reversible processes*. For *irreversible processes, there is no unique relation between the entropy S and the work w* done on or by the system.

Consider first the case of *constant temperature*, $T = \text{const.}$, but possibly variable volume V and pressure p . For a reversible process,

$$\delta q_{\text{rev}} = T \cdot dS \quad (14)$$

Then, changes in internal energy can be expressed in terms of the entropy S and the reversible work δw_{rev} ,

$$dU = T \cdot dS + \delta w_{\text{rev}} \quad (15)$$

At constant temperature T , $d(T \cdot S) = T \cdot dS$, and one has

$$\delta w_{\text{rev}} = dU - T \cdot dS = d(U - T \cdot S) = dA \quad (16)$$

Therefore, a non-zero change in free (Helmholtz) energy indicates that the system performs some work. *The system does work, if $dA < 0$, it is being worked on if $dA > 0$.*

In other words: *The Helmholtz Free Energy of a system at $T = \text{const.}$ is a measure of the amount of the maximum reversible work that the system can do.* Of course, the reversible work is always smaller than the irreversible work,

$$dA = \delta w_{\text{rev}} < \delta w_{\text{irr}} \quad (17)$$

For example, if $dA < 0$ for a certain process, the system can do work during the process. The maximum work it can do is given by $dA = dw_{rev}$, any irreversible process connecting the same initial and final states of the system will lead to less work by the system,

$$|dw_{irr}| < |dw_{rev}| = |dA| \quad (18)$$

for the case $dA < 0$, i.e., when the system does the work on its surroundings.

For a spontaneous process $A \rightarrow B$ to occur, the condition

$$\Delta A_{A \rightarrow B} < 0 \quad (19)$$

has to be fulfilled, since $dw_{irr} = 0$ can be chosen as a possible path for the transition $A \rightarrow B$, and Equ.17 has still to be valid. Hence, as long as the free energy A is not yet at its minimum, spontaneous (irreversible) processes can occur. ***When the minimum of the Helmholtz Free Energy A is reached, no further work can be obtained from the system. This is quite analogous to the potential energy for a mechanical system.***

The ***Gibbs Free Energy $G = H - TS$ is also related to work for systems at constant temperature and pressure, $T = \text{const.}$ $p = \text{const.}$*** This, one can see from the differential

$$\begin{aligned} dG &= d(H - TS) = dH - TdS = d(U + pV) - TdS \\ &= d(U - TS) + pdV = dA + pdV \end{aligned} \quad (20)$$

Here, one recognizes the term $+pdV$ as ***the negative of the normal reversible pV - work done by or on gases.*** Hence, this trivial pV term cancels in the definition of the change in Gibbs' free energy.

However, in a general process $A \rightarrow B$, for example in a chemical reaction, in a process in an electrolytic cell, or in the stretching of an organic fiber, other types of work can also be done, for example, bond-breaking, ionizing work, or elastic-deformation work. These latter types of work are summarized by the notation δw_{non-pV} .

For example, in a gaseous dissociation reaction $AB \rightarrow A+B$, the number of moles of gas is changed, and pV work has to be done

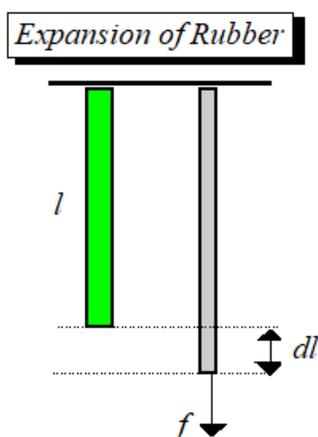


Figure 4: Stretching of a rubber band.

against atmospheric pressure. This work is not useful to the experimenter but has to be provided in the experiment. Gibbs Free Energy contains these trivial amounts already and is, therefore, very convenient in practice to use. The same is true for the *expansion of a piece of a rubber-like substance*. The rubber can transfer heat and do trivial pV -work. In addition, it performs work δw_{non-pV} *against an external force f in proportion to the elongation dl of the rubber*, such that the differential of the internal energy of the rubber can be written as,

$$dU = \delta q - pdV + fdl \quad (21)$$

Then, Equ. 20 yields (*for T, p constant*)

$$dG = \delta w_{non-pV} \quad (22)$$

and for the above example of the rubber expansion,

$$dG = f \cdot dl \quad (23)$$

In analogy to what has been discussed before in the case of the Helmholtz energy, spontaneous processes at constant p and T are characterized by negative changes in Gibbs' energy. Such processes occur, until the minimum of G is reached. Then, no further work can be performed by the system.

Thermodynamic relations of practical importance can be derived from the structure of the free-energy differentials

$$dA = d(U - TS) = dU - SdT - TdS = (dq_{rev} - pdV) - SdT - TdS$$

or

$$dA = -pdV - SdT \quad (24)$$

where use has been made of the relation $dq_{rev} - SdT = 0$. Equ. 24 also implies that the Helmholtz energy is a function of only two variables, V and T , i.e., $A = A(V, T)$.

On the other hand, the differential 24 can be expressed by definition as

$$dA(V, T) = \left(\frac{\partial A}{\partial V} \right)_T \cdot dV + \left(\frac{\partial A}{\partial T} \right)_V \cdot dT \quad (25)$$

Since Eqs. 24 and 25 have to give the same result, for any change dV or dT , one concludes that

$$p = - \left(\frac{\partial A}{\partial V} \right)_T \quad \text{and} \quad S = - \left(\frac{\partial A}{\partial T} \right)_V \quad (26)$$

if the system is in equilibrium with a heat bath of constant temperature T .

Similarly, from the two following expressions

$$dG = Vdp - SdT = \left(\frac{\partial G}{\partial p} \right)_T \cdot dp + \left(\frac{\partial G}{\partial T} \right)_p \cdot dT \quad (27)$$

for the differential dG , one derives the following relations

$$V = \left(\frac{\partial G}{\partial p} \right)_T \quad \text{and} \quad S = - \left(\frac{\partial G}{\partial T} \right)_p \quad (28)$$

valid for a system in equilibrium with a heat bath of constant temperature T and at constant pressure p , where the free energy is a function of p and T , $G = G(p, T)$.

For an isolated system at temperature T , a similar consideration for the internal energy $U = U(V, S)$ yields

$$p = - \left(\frac{\partial U}{\partial V} \right)_S \quad \text{and} \quad T = \left(\frac{\partial U}{\partial S} \right)_V \quad (29)$$

Since the variables describing a system, e.g., p and T for an isolated system, can be expressed in terms of partial derivatives of state functions, their partial derivatives are correlated according to the **Maxwell Relations**. For example,

$$\left(\frac{\partial p}{\partial S} \right)_V = - \left(\frac{\partial^2 U}{\partial S \partial V} \right)_S = - \left(\frac{\partial^2 U}{\partial V \partial S} \right)_V = - \left(\frac{\partial T}{\partial V} \right)_S \quad (30)$$

because a second-order derivative does not depend on the order of differentiation.

Such relations are of practical importance, since they allow one to derive quantities that are difficult to evaluate from those that are readily available. For example, it is easy to measure the expansion coefficient, or equivalently, $(\partial V/\partial T)_p$ of the volume of a system upon raising its temperature, while it is difficult to measure $(\partial S/\partial p)_T$. Fortunately, these two quantities are related by Equ. 30.

3. Free Energy in Chemical Reactions

A very important application of the concept of a free energy is in chemical reactions, many of which are *good examples of reversible processes*. For simplicity, assume that the system is in contact with a *large heat bath of constant temperature T* , i.e., consider an *isothermal and reversible process $A \rightarrow B$* . This latter assumption simplifies the case considerably for ideal gases, since *for ideal gases, the enthalpy H and the internal energy U depend only on temperature* and stay constant in an isothermal process. Then, the (Helmholtz or Gibbs) free energy is altered only by the *exchanged heat $q_{rev} = T\Delta S$* .

$$\Delta G = \Delta H - T \cdot \Delta S = \Delta U - T \cdot \Delta S = \Delta A = - T \cdot \Delta S \quad (31)$$

Using the equivalence between entropy and reversible heat, the free energy can be expressed as

$$\Delta G = - q_{rev} = nRT \ln(V_A/V_B) = nRT \ln(p_B/p_A) \quad (32)$$

Starting from the standard state at $p_A = 1$ bar, where $G := G^\circ(p=1\text{bar}, T)$, one calculates the free energy at a different pressure p from

$$G = G^\circ + nRT \ln(p/1\text{bar}) \quad (33)$$

or, *with the implicit understanding that p be given in units of 1 bar*,

$$G = G^\circ + nRT \ln(p) \quad (33a)$$

expressed per mole, the *molar free energy* is given by

$$\mu = \mu^\circ + RT \ln(p) \quad (33b)$$

where $\mu(p, T) := \partial G / \partial n$ (here $\mu := G/n$) is the *chemical potential* and $\mu^\circ(p, T) = \mu^\circ(p=1\text{bar}, T)$.

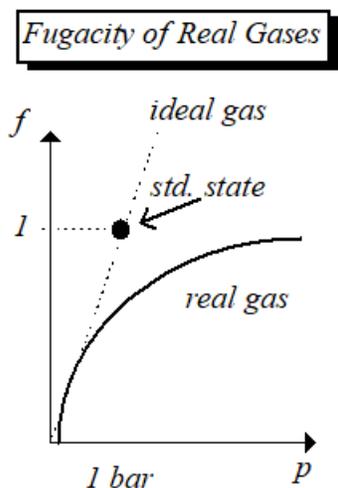


Figure 5: Effective pressure vs. actual pressure at fixed T . Note that standard state is not on fugacity curve.

An approximately *similar behavior of the free energy can be observed not only for ideal gases, but also for real gases*. This is trivial for low pressures, where interactions in the real gas are unimportant. For higher pressures, one can define an *effective pressure (the “fugacity” f)* for a real gas, correcting for the deviations of the real gas from an ideal gas. Obviously, if one defines the *fugacity* as

$$f = e^{\left\{ \frac{\mu - \mu^\circ}{RT} \right\}} (\text{bar}) \quad (34)$$

with the Gibbs energy per mole of $\mu := G/n$, n moles of the *real gas* obey the relation

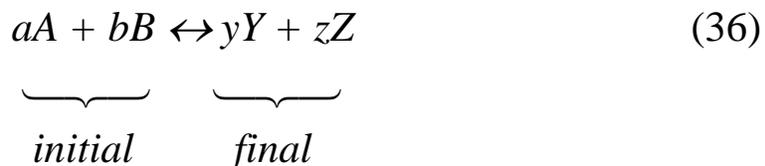
$$G = G^\circ + nRT \ln(f) \quad (33c)$$

Therefore, the fugacity can be understood as an effective pressure simulating ideal behavior of a real gas. **Replacing the pressure in a real-gas equation of state by the fugacity results in an EOS of the type obeyed by an ideal gas.**

This definition can be extended to substances other than gases. Here, the ratio $f / f(\text{standard state})$ of the fugacity to that in the standard state is called *activity*,

$$a = f / f(\text{standard state}) \quad (35)$$

With these results, it is straight-forward to *calculate the energy balance in chemical reactions*, allowing to make predictions about whether or not they will occur spontaneously, even if the substances are not in their standard states. Consider the *reversible* reaction



from initial to final state. *Energies are extensive variables*, hence, the free energy in the initial state is the sum of the free energies of both gases A and B. With μ_i defined as the *molar Gibbs energy of substance i*, one has

$$\begin{aligned}
 G_{\text{initial}} &= G_A + G_B = a\mu_A + b\mu_B = \\
 &= (a\mu_A + b\mu_B)^{\circ} + RT(a \ln p_A + b \ln p_B) \\
 G_{\text{initial}} &= G^{\circ}_{\text{initial}} + RT \cdot \ln[(p_A)^a \cdot (p_B)^b] \quad (37)
 \end{aligned}$$

and similarly for the final state of the products

$$\begin{aligned}
 G_{\text{final}} &= G_Y + G_Z = y\mu_Y + z\mu_Z = \\
 &= (y\mu_Y + z\mu_Z)^{\circ} + RT(y \ln p_Y + z \ln p_Z) \\
 G_{\text{final}} &= G^{\circ}_{\text{final}} + RT \cdot \ln[(p_Y)^y \cdot (p_Z)^z] \quad (38)
 \end{aligned}$$

Therefore, the change in Gibbs free energy is given by

$$\Delta G = G_{\text{final}} - G_{\text{initial}} = \Delta G^{\circ} + RT \cdot \{ \ln[(p_Y)^y \cdot (p_Z)^z] - \ln[(p_A)^a \cdot (p_B)^b] \}$$

or

$$\Delta G = \Delta G^0 + RT \cdot \ln \left(\frac{p_Y^y \cdot p_Z^z}{p_A^a \cdot p_B^b} \right) \quad (39)$$

According to Equ. 8, as long as $\Delta G < 0$, the reaction 36 will proceed to the right. If $\Delta G > 0$, the reaction will proceed to the left, until *reactants and products are present in a mixture for which exactly $\Delta G = 0$. This is the chemical equilibrium.* Since in equilibrium $\Delta G = 0$, Equ. 39 yields

$$\Delta G^0 = -RT \cdot \ln \left(\frac{p_Y^y \cdot p_Z^z}{p_A^a \cdot p_B^b} \right)_{equ} = -RT \cdot \ln K_p^0 \quad (40)$$

The ratio of the pressures of reactants and products defines the *equilibrium constant for the chemical reaction*

$$K_p^0 = \left(\frac{p_Y^y \cdot p_Z^z}{p_A^a \cdot p_B^b} \right)_{equ} \quad (41)$$

Using this *dimension-less equilibrium constant*, one can express the change in Gibbs' free energy for the more general case of Equ. 39, in which the pressures are not equal to the equilibrium pressures, as

$$\Delta G = -RT \ln K_p^0 + RT \ln \left(\frac{p_Y^y \cdot p_Z^z}{p_A^a \cdot p_B^b} \right) \quad (42)$$

Note that the ratio of pressures in Eqs. 40 and 41 is taken for *equilibrium pressures*, while in Eqs. 39 and 42, this ratio is calculated for the *actual pressures* (see Equ. 32). All pressures are expressed in units of *1 bar*.

Because of the close relationship between the equilibrium constant for a chemical reaction and the associated change ΔG° , one can predict whether a reaction will proceed spontaneously or not just from the magnitude of K_p^0 . From Equ. 8, one knows that the *reaction will be spontaneous, if $\Delta G < 0$* . then, according to Equ. 40,

$$\left. \begin{array}{l} \ln K_p^0 > 0 \\ K_p^0 > 1 \end{array} \right\} \hat{=} \left\{ \begin{array}{l} \Delta G^0 < 0 \\ \text{spontaneous reaction} \end{array} \right. \quad (43)$$

In equilibrium, $K_p^0 = 1$ and $\Delta G^0 = 0$

There are a number of formulations equivalent to Equ. 42, but for *concentrations or mole fractions*. At constant pressure, the free energy can then be expressed as

$$\Delta G = -q_{rev} = nRT \ln(p_B/p_A) = nRT \ln(c_A/c_B) \quad (44)$$

Starting from the standard state at $c_A^0 := [A]^0 = 1 \text{ mole/dm}^3$, where $G := G^0$, one calculates the free energy at a different concentration from

$$G = G^0 + nRT \ln(c_A/c_A^0) \quad (45)$$

or, *with the implicit understanding that $c_A = [A]$ be given in units of 1 mole/dm^3 ,*

$$G = G^o + nRT \ln(c_A) \quad (45a)$$

For the reaction IV.36, one derives then in a fashion very similar to the above procedure for pressure,

$$\Delta G = -RT \ln K_c^0 + RT \ln \left(\frac{[Y]^y \cdot [Z]^z}{[A]^a \cdot [B]^b} \right) \quad (46)$$

for the *change in free energy when a moles of A react with b moles of B, to give y moles of Y and z moles of Z, at the various concentrations [i]*. Here, the first term is again the free energy change with the substances in standard states and in concentrations leading to equilibrium,

$$\Delta G^0 = -RT \cdot \ln \left(\frac{[Y]^y \cdot [Z]^z}{[A]^a \cdot [B]^b} \right)_{equ} = -RT \cdot \ln K_c^0 \quad (47)$$

Yet another alternative formulation makes use of *partial pressures or mole fractions x_i* . Here, the partial pressure of substance i is given in terms of the total pressure p :

$$p_i = x_i p \quad (48)$$

However, the total pressure cancels in the corresponding equilibrium constant, if its derivation follows the above scheme:

$$K_x^0 = \left(\frac{x_Y^y \cdot x_Z^z}{x_A^a \cdot x_B^b} \right)_{equ} \quad (49)$$

As before, the total change in free energy is given by

$$\Delta G = -RT \ln K_x^0 + RT \ln \left(\frac{x_Y^y \cdot x_Z^z}{x_A^a \cdot x_B^b} \right) \quad (50)$$

with

$$\Delta G^0 = -RT \cdot \ln \left(\frac{x_Y^y \cdot x_Z^z}{x_A^a \cdot x_B^b} \right)_{equ} = -RT \cdot \ln K_x^0 \quad (51)$$

similar to the other notations discussed earlier.

A similar formulation can be derived for *chemical reactions in solutions*. Here, one has to use *fugacities or activities a* (see *Equ.35*) *instead of pressures or concentrations*.

$$\Delta G = -RT \ln K_a^0 + RT \ln \left(\frac{a_Y^y \cdot a_Z^z}{a_A^a \cdot a_B^b} \right) \quad (52)$$

The various equilibrium constants discussed above are all related to each other, e.g., they can all be expressed in terms of K_p , multiplied by a power of the total pressure p or of pV .

Heterogeneous equilibria require special attention. Here, *different phases of substances* are involved. An example is the reaction



The equilibrium constant for concentrations for this process is calculated from

$$K'_c = \frac{[\text{CaO}] \cdot [\text{CO}_2]}{[\text{CaCO}_3]} \quad (54)$$

For pure liquids and pure solids, the activities or concentrations are taken as $a_i = 1$ and $[i] = 1$, respectively, which drop out of any of the expressions for equilibrium constants and free energy changes, since their activities and concentrations (mole per volume) do not change in a process. Then, the equilibrium constant for the reaction 53 is simply given by the CO_2 concentration:

$$K_c = [CO_2] \quad (55)$$

An important application of these concepts is the description of the *equilibrium of a solid salt and its saturated solution*. Consider, for example, the solution of *silver chloride*



Here, the concentration $[AgCl]$ and its activity a_{AgCl} are constant. Therefore, one combines them with the equilibrium constant to give the *solubility product*

$$K_{sp} = [Ag^+][Cl^-] = a_{Ag^+} \cdot a_{Cl^-} \quad (57)$$

expressed either in concentrations or activities.

4 Temperature Dependence of Chemical Equilibrium

In the preceding section, it has been shown how the equilibrium “constant” K_p^0 determines the outcome of a chemical reaction. This constant, in turn, is given by changes ΔG^0 in the free energy of reactants and products involved in the reaction. Of course, K_p^0 is not really a constant. Already Equ. 40 suggests an exponential dependence on the temperature. However, the free energy change ΔG^0

is itself dependent on temperature and pressure. Therefore, the evaluation of temperature and pressure dependencies of the equilibrium constant of a chemical reaction has to be done in careful detail. In the following, the *temperature dependence (at constant pressure)* will be considered first.

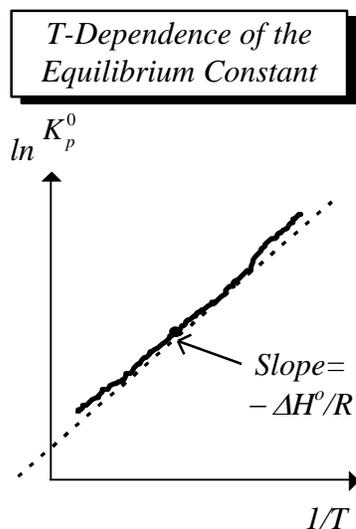


Figure 6:

According to Equ. 40, one needs the T dependence of the combined function $\Delta G^0/RT = -\ln K_p^0$, i.e., **one needs** $\partial (G/T)/\partial T$. According to Equ. IV.28, one already has an expression for the rate of change of G with temperature:

$$S = -\left(\frac{\partial G}{\partial T}\right)_p \quad (58)$$

Since (cf. Equ. 6), $G = H - TS$, one can then write

$$G = H + T \cdot \left(\frac{\partial G}{\partial T}\right)_p \quad (59)$$

which is equivalent to (dividing Equ. 59 by T^2)

$$-\frac{H}{T^2} = -\frac{G}{T^2} + \frac{1}{T} \left(\frac{\partial G}{\partial T}\right)_p \quad (60)$$

According to the product rule for differentiation applied to the product $G \cdot (1/T)$, the *r.h.s.* of this equation is equal to the desired partial derivative $\partial (G/T)/\partial T$. Therefore, one also concludes that

$$\left(\frac{\partial(\Delta G/T)}{\partial T} \right)_p = -\frac{\Delta H}{T^2} \quad (61)$$

This equation is usually called the **Gibbs-Helmholtz Equation**. With this result, one can calculate the T dependence of the function $\Delta G^\circ/RT = -\ln K_p^0$ as

$$\frac{\partial \ln K_p^0}{\partial T} = \frac{\Delta H^0}{RT^2} \quad (62)$$

This latter relation defines the **Van't Hoff Isochor**. Since $d(1/T) = -(1/T^2)$, it is equivalent to

$$\frac{\partial \ln K_p^0}{\partial(1/T)} = -\frac{\Delta H^0}{R} \quad (63)$$

As discussed in earlier sections, the enthalpy and therefore its change ΔH^0 is in general T -dependent. According to **Kirchoff's Equation**, it is related to the difference ΔC_p in heat capacities of products and reactants,

$$\left(\frac{\partial(\Delta H)}{\partial T} \right)_p = \Delta C_p \quad (64)$$

This difference depends on the number of moles of products minus that of the reactants and is therefore in general non-zero even for ideal gases. Thus, Equ. 63 is easily integrated only in certain cases. However, one expects a characteristic dependence of the function $\ln K_p^0$ on the inverse temperature $1/T$. If $\Delta H^0 \approx \text{const}$, this function

should be approximately a straight line, with a slope of $-\Delta H^0/R$, as shown in the plot on the left.

If ΔH^0 were approximately independent of T , then one could integrate Equ. 63 resulting in

$$\ln K_p^0 = -\frac{\Delta H^0}{RT} + \text{const.} \quad (65)$$

The integration constant for this case can be read off Equ. 40, such that

$$\ln K_p^0 = -\frac{\Delta G^0}{RT} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (66)$$

Then, the intercept of the experimental curve with the *ordinate axis* in the above plot indicates directly the quantity $\Delta S^0/R$.

In the simple case of a ***T-independent enthalpy change ΔH^0 in a reaction***, these thermodynamic properties can be deduced from a measurement of the equilibrium constants at two temperatures. Consider, for example, the dissociation of bromine into atoms:



The experimental equilibrium constants are

$$K_p^0 = \begin{cases} 6 \cdot 10^{-12} & T = 600\text{K} \\ 1 \cdot 10^{-7} & T = 800\text{K} \end{cases} \quad (68)$$

From Equ. 40, it is easy to obtain the two values of the Gibbs Free Energy

$$\Delta G^0 = -RT \ln K_p^0 = \begin{cases} -8.3 \frac{J}{Kmol} \cdot 600K \cdot \ln(6 \cdot 10^{-12}) = 129kJ / mol \\ -8.3 \frac{J}{Kmol} \cdot 800K \cdot \ln(1 \cdot 10^{-7}) = 107kJ / mol \end{cases} \quad (69)$$

for $T = 600$ (top) and 800 K (bottom). From Equ. 65, one obtains a value for ΔH^0 :

$$\begin{aligned} \Delta H^0 &= R \cdot \ln \left(\frac{K_p^0(T_2 = 800K)}{K_p^0(T_1 = 600K)} \right) = \\ &= 8.3 \frac{J}{Kmol} \cdot \ln \left(\frac{10^{-7}}{6 \cdot 10^{-12}} \right) \cdot \left(\frac{480000}{800 - 600} \right) K = 193kJ / mol \end{aligned} \quad (70)$$

Using the relation $\Delta S^0 = (\Delta H^0 - \Delta G^0)/T$ (cf Equ. 6), and the above result for ΔH^0 and ΔG^0 , one calculates

$$\Delta S^0 = \frac{193 - 129}{600} \frac{J}{Kmol} = 107 J / Kmol \quad (71)$$

One observes that the energy change ΔH^0 is large and positive, i.e., dissociation of Br_2 is energetically unfavorable. Therefore, the reaction would not proceed spontaneously, if the reaction vessel were completely isolated from any surroundings. On the other hand, the dissociated atoms have more degrees of freedom and more accessible states, such that the entropy would be larger than for the molecule Br_2 . Giving the system access to the energy pool of a heat bath of sufficiently high temperature, the dissociation reaction will proceed, driven by the entropy increase.

However, it should be emphasized again, that *in general*, ΔH^0 is a function of temperature. Then, from Eqs. 63 and 64, one would have to calculate

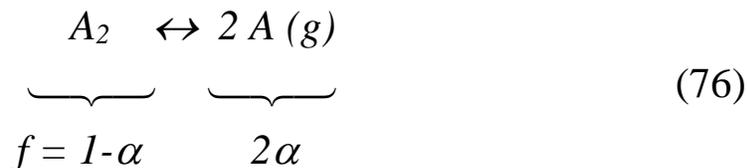
$$\ln K_p(T) = \ln K_p(T_1) + \frac{1}{R} \int_{T_1}^T dT' \frac{1}{T'^2} (\Delta H^0(T_1) + \Delta C_p(T')) \quad (72)$$

from the changes in the heat capacities of products and reactants which all would have to be known.

5 Pressure Dependence of Chemical Equilibrium

So far, only the temperature dependence of the equilibrium constant K_p^0 has been discussed. As far as any *pressure dependence* of this constant is concerned, one *expects none, essentially by definition*. After all, the equilibrium constant is *defined in terms of the constant standard-state pressures ($p = 1\text{bar}$)*. However, this statement *applies to partial pressures of the individual substances, not to the total pressure of the reactive system*. As a result, the relative magnitudes of the partial pressures at equilibrium can and usually do change with the applied total pressure, *although the equilibrium constant remains unchanged*.

Consider, for example, the dissociation reaction



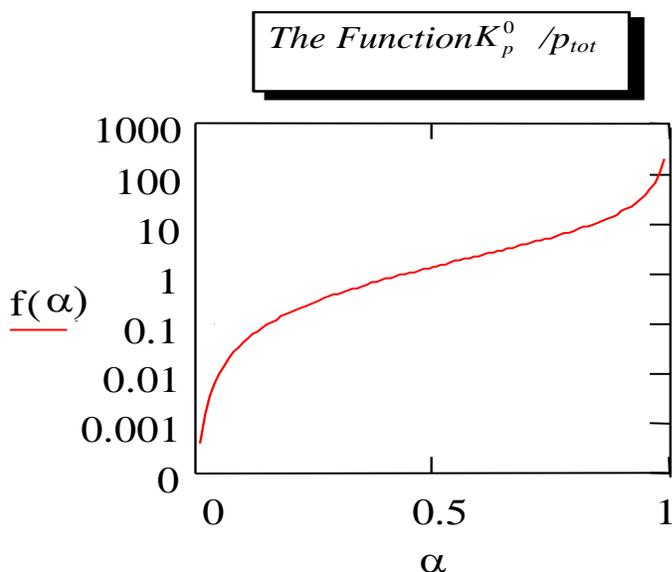
i.e., a *fraction $f = \alpha$ of the A_2 molecules has dissociated*, making an additional pressure proportional to 2α . With a total pressure of p_{tot} , the partial pressures are calculated as

$$p_A = \frac{2\alpha}{1 + \alpha} \cdot p_{tot} \quad \text{and} \quad p_{A_2} = \frac{1 - \alpha}{1 + \alpha} \cdot p_{tot} \tag{77}$$

with the two partial pressures adding up to p_{tot} . According to Equ. IV.41, the pressure equilibrium constant for this dissociation reaction reads

$$K_p^0 = \frac{p_A^2}{p_{A_2}} = \frac{4\alpha^2}{(1 - \alpha^2)} \cdot p_{tot} \tag{78}$$

This equilibrium constant must not depend on the total pressure p_{tot} . Therefore, a change in this pressure results in a change of the degree of dissociation α . The figure shows on a logarithmic scale



the dependence of the quantity K_p^0 / p_{tot} on the degree of dissociation α . It is obvious that a ***raise in total pressure p_{tot} must lead to a decrease in α , in order to keep K_p^0 constant.*** Fewer molecules dissociate at higher pressures, thus keeping the number of moles of the gas mixture in the system at the value

required by the *EOS*.

This pressure dependence of the equilibrium constant K_x^0 can be quantified, using Equ. IV.60 with the quantity $\Delta n = (y+z)-(a+b)$ defined as the difference in the number of moles of products and reactants. It is

$$0 = \left(\frac{\partial \ln K_p^0}{\partial p_{tot}} \right)_T = \left(\frac{\partial \ln K_x^0}{\partial p_{tot}} \right)_T + \Delta n \left(\frac{\partial \ln p_{tot}}{\partial p_{tot}} \right)_T \quad (79)$$

because of the independence of K_p^0 on the total pressure p_{tot} . Using the ideal-gas *EOS*, it follows that

$$\left(\frac{\partial \ln K_x^0}{\partial p_{tot}}\right)_T = -\Delta n \left(\frac{\partial \ln p_{tot}}{\partial p_{tot}}\right)_T = -\frac{\Delta n}{p_{tot}} = -\frac{\Delta V}{RT} \quad (80)$$

This result is easy to interpret: If the reaction leads to an increase in volume, i.e., *if the volume of the products is greater than that of the reactants by $\Delta V > 0$, then the equilibrium constant decreases with increasing total pressure p_{tot} .* The reaction becomes less likely at higher pressures. According to the *EOS*, an *increase in pressure is equivalent to a decrease in the volume available to the gas mixture*. The gas mixture reacts to this change by reducing the total number of particles in recombining some of the *A* atoms, in order to retain equilibrium conditions. The inverse reaction, associated with a change in volume $\Delta V < 0$ becomes more likely.

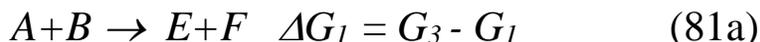
It seems as if the system retracts from changes in the externally imposed conditions and readjusts and counteracts these changes (Principle of LeChatelier).

6 Additivity of Chemical Reactions

According to a discussion of *Hess' Law*, elsewhere, *one can "add", more generally, linearly combine reactions and their energetics*, obtaining new a "sum", "composite" or "chain" reaction. This is a principle that is very important for the analysis of biological systems, where enzymatic or catalytic reactions proceed via intermediate steps.

As in this earlier discussion, consider the reactions $A+B \rightarrow E+F$ and $E+F \rightarrow C+D$ connecting the initial state ($A+B$) of the (gaseous) system with the final state ($C+D$), with known free energies G_i . To obtain the free energy for the overall "sum" process $A+B \rightarrow C+D$, one just has to add up the equations and the corresponding energies of the individual reactions.

"Adding" formally the two stoichiometric equations representing chemical reactions



results in



and accordingly for the particularly interesting case involving all substances in their standard states, when all energies G in Eqs. 81 have to be replaced by the respective standard-state values G° . For each partial reaction 81a and 81b, as well as for the sum reaction 81c, the associated equilibrium constants can be calculated according to Equ. 40:

$$\Delta G_i^0 = -RT \ln(K_p^0)_i \quad (82)$$

and therefore,

$$\Delta G^0 = \sum_i \Delta G_i^0 = -RT \sum_i \ln(K_p^0)_i \quad (83)$$

This is equivalent to the decomposition of the equilibrium constant for the overall reaction in terms of the individual constants:

$$K_p^0 = \prod_i (K_p^0)_i = (K_p^0)_1 \cdot (K_p^0)_2 \cdots \quad (84)$$

For practical applications, *it is important to realize that only the overall reaction constant needs to be large ($K_p^0 > 1$) in order to have a spontaneous process. It is not necessary that all individual reactions in a chain are spontaneous!*

The *multiplicativity of equilibrium constants is often used to influence (shift) the equilibrium of a reactive system.* For example, if a reaction



leads to a desired end product C and a useless by-product D , one can *couple* the above reaction with one, e.g.,



Reaction 2 converts D into something else (E) very efficiently, implying that $[E] \gg [D]$, and, hence, takes D out of the equilibrium. According to Equ. 84,

$$(K_p^0)_3 = (K_p^0)_1 \cdot (K_p^0)_2 = \left(\frac{[C] \cdot [D]}{[A] \cdot [B]} \right)_{equ} \cdot \left(\frac{[E]}{[D]} \right)_{equ} = \left(\frac{[C] \cdot [E]}{[A] \cdot [B]} \right)_{equ} \quad (87)$$

and therefore,

$$(K_p^0)_3 \gg (K_p^0)_1 \quad (88)$$

Consequently, component *C* is produced with a much higher yield than in the original reaction (1), which is the desired result.