

### 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  $\mu^\circ(p, T) = \mu^\circ(p=1\text{bar}, T)$ .

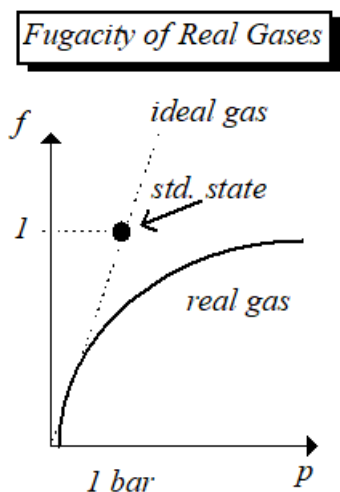


Figure 5: Effective pressure vs. actual pressure at fixed  $T$ . Note that standard state is not on fugacity curve.

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

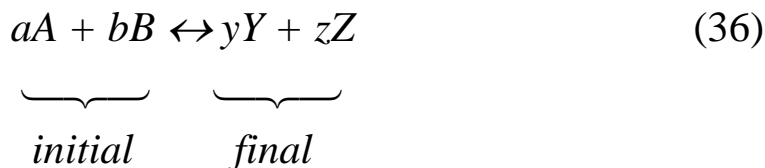
$$G = G^\circ + nRT \ln(f) \quad (33c)$$

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  $\mu_i$  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  $\Delta G^\circ$ , 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  $1 \text{ mole/dm}^3$ ,*

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

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

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

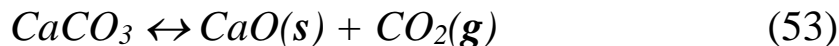
similar to the other notations discussed earlier.

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  $\Delta G^0$  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  $\Delta G^0$



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.

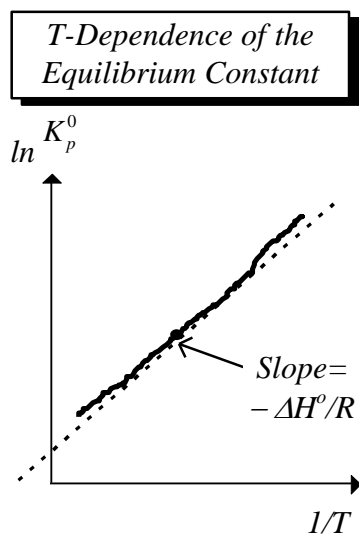


Figure 6:

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  $\Delta H^0$  is in general  $T$ -dependent. According to *Kirchoff's Equation*, it is related to the difference  $\Delta C_p$  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  $\Delta H^0$  were approximately independent of  $T$ , then one could integrate Equ. 63 resulting in

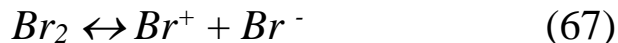
$$\ln K_p^0 = -\frac{\Delta H^0}{RT} + \text{const.} \quad (65)$$

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  $\Delta H^0$  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

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

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

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

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

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

One observes that the energy change  $\Delta H^0$  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*,  $\Delta H^0$  is a function of temperature. Then, from Eqs. 63 and 64, one would have to calculate

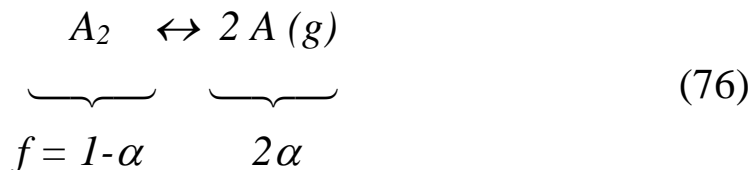
$$\ln K_p(T) = \ln K_p(T_1) + \frac{1}{R} \int_{T_1}^T dT' \frac{1}{T'^2} (\Delta H^0(T_1) + \Delta C_p(T')) \quad (72)$$

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



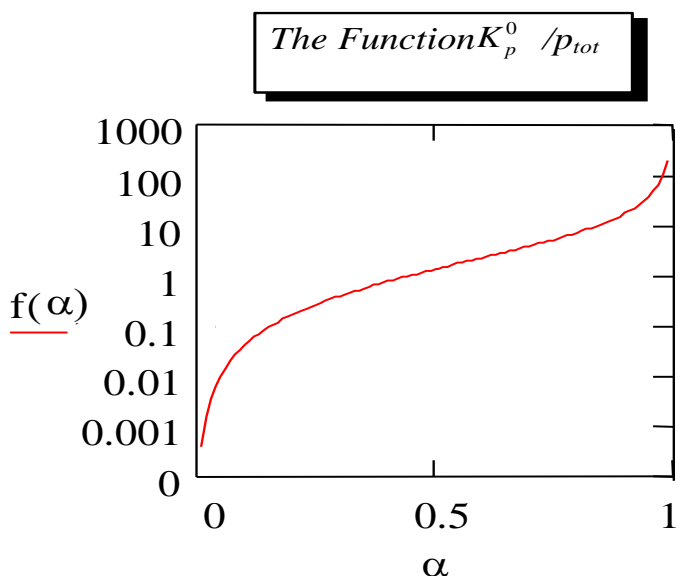
i.e., a *fraction  $f = \alpha$  of the  $A_2$  molecules has dissociated*, making an additional pressure proportional to  $2\alpha$ . With a total pressure of  $p_{tot}$ , the partial pressures are calculated as

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

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  $\alpha$ .*** The figure shows on a logarithmic scale



the dependence of the quantity  $K_p^0 / p_{tot}$  on the degree of dissociation  $\alpha$ . It is obvious that a ***raise in total pressure  $p_{tot}$  must lead to a decrease in  $\alpha$ , 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).*

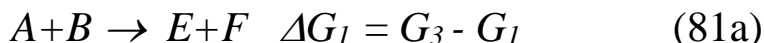


## 6 Additivity of Chemical Reactions

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  $G^\circ$ . 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.