

Read Reichl's introductory remarks for §S2.D.

S2.D.1. The Affinity

Consider the chemical reaction



where the **stoichiometric coefficient** $|v_j|$ indicates the number of type j molecules required for a single reaction. For some reason to be made clear later [see (2.235)], we have used the convention

$$v_A, v_B \leq 0 \quad v_C, v_D \geq 0 \quad (2.227a)$$

Consider now the forward (left to right) reaction. Its occurrence implies a number $|v_A|$ of A molecules have collided with a number $|v_B|$ of B molecules and reacted. Let N_j be the number of type j molecules present. The probability of finding a type j molecule is therefore

$$p_j = \frac{N_j}{N} \quad N = \sum_j N_j$$

Since $N_j \gg |v_j|$, the probability of finding a cluster of molecules consisting of $|v_A|$ type A and $|v_B|$ type B molecules is approximately

$$C_{|v_A|+|v_B|}^{|v_A|+|v_B|} \left(\frac{N_A}{N}\right)^{|v_A|} \left(\frac{N_B}{N}\right)^{|v_B|}$$

where $C_k^n = \frac{n!}{(n-k)!k!}$ is the k -combination of n things.

Let r_1 be the **rate of the forward reaction** (number of forward reactions per unit time). By lumping all the kinetic effects of the reactions into a **rate constant** k_1 , we can write

$$r_1 = k_1 N_A^{|v_A|} N_B^{|v_B|} \quad (2.228a)$$

Similarly, for the backward (right to left) reaction,

$$r_2 = k_2 N_C^{|v_C|} N_D^{|v_D|} \quad (2.228b)$$

Now, in each forward reaction,

$$\begin{aligned} \Delta N_A &= -|v_A| = v_A & \Delta N_B &= -|v_B| = v_B \\ \Delta N_C &= |v_C| = v_C & \Delta N_D &= |v_D| = v_D \end{aligned}$$

while for each backward reaction,

$$\begin{aligned} \Delta N_A &= |v_A| = -v_A & \Delta N_B &= |v_B| = -v_B \\ \Delta N_C &= -|v_C| = -v_C & \Delta N_D &= -|v_D| = -v_D \end{aligned}$$

Therefore, the net reaction rate is

$$\begin{aligned} r_1 - r_2 &= k_1 N_A^{|v_A|} N_B^{|v_B|} - k_2 N_C^{|v_C|} N_D^{|v_D|} \\ &= -\frac{1}{|v_A|} \frac{dN_A}{dt} = -\frac{1}{|v_B|} \frac{dN_B}{dt} = \frac{1}{|v_C|} \frac{dN_C}{dt} = \frac{1}{|v_D|} \frac{dN_D}{dt} \end{aligned} \quad (2.228)$$

Dividing (2.228) by the Avogadro number \mathcal{N}_a , we get

$$\frac{dn_A}{v_A} = \frac{dn_B}{v_B} = \frac{dn_C}{v_C} = \frac{dn_D}{v_D} \equiv d\xi = \left(\frac{r_1 - r_2}{\mathcal{N}_a}\right) dt \quad (2.235)$$

where ξ is called the **degree of reaction**. Thus,

$$\begin{aligned} d\xi > 0 & \quad \text{if forward reaction prevails} \quad (r_1 > r_2) \\ d\xi < 0 & \quad \text{if backward reaction prevails} \quad (r_2 > r_1) \end{aligned} \quad (2.235a)$$

Consider now the case where there are excess type B & D molecules so that initially,

$$\begin{aligned} n_A &= |v_A| n_0 & n_B &= |v_B| n_0 + \tilde{n}_B \\ n_C &= |v_C| n_0' & n_D &= |v_D| n_0' + \tilde{n}_D \end{aligned} \quad (2.229a)$$

If the conditions are favorable to the forward reaction, then the system will reach equilibrium when all type A molecules are exhausted, leaving

$$\begin{aligned} n_A &= 0 & n_B &= \tilde{n}_B \\ n_C &= v_C(n_0 + n_0') & n_D &= v_D(n_0 + n_0') + \tilde{n}_D \end{aligned} \quad (2.229b)$$

In general, after $m \mathcal{N}_a$ forward reactions, we have

$$\begin{aligned} n_A &= -v_A n_0 + m v_A & n_B &= -v_B n_0 + \tilde{n}_B + m v_B \\ n_C &= v_C n_0' + m v_C & n_D &= v_D n_0' + \tilde{n}_D + m v_D \end{aligned} \quad (2.229c)$$

Comparing (2.229c) with (2.235) gives

$$\begin{aligned} dm &= d\xi \\ \rightarrow m &= \xi + c \quad [c = \text{const}] \end{aligned} \quad (2.229d)$$

(2.229c) thus becomes

$$\begin{aligned} n_A &= -v_A(n_0 - c) + \xi v_A & n_B &= -v_B(n_0 - c) + \tilde{n}_B + \xi v_B \\ n_C &= v_C(n_0' + c) + \xi v_C & n_D &= v_D(n_0' + c) + \tilde{n}_D + \xi v_D \end{aligned}$$

Setting $c = -n_0'$ then gives

$$\begin{aligned} n_A &= -v_A(n_0 + n_0') + \xi v_A & n_B &= -v_B(n_0 + n_0') + \tilde{n}_B + \xi v_B \\ n_C &= \xi v_C & n_D &= \tilde{n}_D + \xi v_D \end{aligned} \quad (2.230-3)$$

Solving (2.230) gives

$$\xi = \frac{n_A}{v_A} + (n_0 + n_0') \quad (2.229)$$

so that (2.229d) becomes

$$\begin{aligned} m &= \frac{n_A}{v_A} + n_0 & (2.229e) \\ &= \frac{n_A - n_{A0}}{v_A} \end{aligned}$$

where n_{A0} is the initial value of n_A [see (2.229b)].

Note that, like energies, only the difference $d\xi$ is physically significant.

Chemical reactions experiments are often carried out under constant T & P , which makes the Gibbs free energy G the natural choice of thermodynamic potential. Putting (2.235) into (2.108) of §2.F.4 gives

$$\begin{aligned} dG &= -SdT + VdP + \sum_{j=1}^m \mu_j n_j \\ &= -SdT + VdP + \mathcal{A}d\xi \end{aligned} \quad (2.236)$$

where

$$\mathcal{A} = \sum_{j=1}^m \mu_j \nu_j \quad (2.238)$$

is called the **affinity**. Hence,

$$\left(\frac{\partial G}{\partial \xi} \right)_{T,P} = \mathcal{A} = \sum_{j=1}^m \mu_j \nu_j \quad (2.237)$$

At chemical equilibrium, G is at a minimum so that

$$\left(\frac{\partial G}{\partial \xi} \right)_{T,P}^0 = \mathcal{A}^0 = 0 \quad (2.239)$$

By the same token, spontaneous approach towards equilibrium must satisfy

$$\begin{aligned} (dG)_{T,P} &= \left(\frac{\partial G}{\partial \xi} \right)_{T,P} d\xi = \mathcal{A} d\xi \\ &< 0 \end{aligned} \quad (2.240)$$

For the reaction (2.227), this means [see (2.235a)]

1. If the forward reaction prevails, i.e., $d\xi > 0$, then $\mathcal{A} < 0$.
2. If the backward reaction prevails, i.e., $d\xi < 0$, then $\mathcal{A} > 0$.

Generalization to the case where there are r chemical reactions in the system is straightforward. To begin, (2.235) becomes, for the k^{th} reaction

$$\frac{dn_j}{\nu_{jk}} = d\xi_k \quad j = 1, \dots, m \ \& \ k = 1, \dots, r$$

so that for the whole system

$$dn_j = \sum_{k=1}^r \nu_{jk} d\xi_k \quad (2.241)$$

We can derive some useful results by treating the reactants as ideal gases. To begin, using (2) of Ex.2.3 in §2.E gives

$$\mu_j(T, P_j) = -RT \ln \left[\frac{P_0}{P_j} \left(\frac{T}{T_0} \right)^{5/2} \right] + \mu_j^0 \quad (2.242)$$

where P_j is the partial pressure for type j molecules [see §S.2B] and

$$\mu_j^0 = \mu_j(T_0, P_0)$$

Hence,

$$\begin{aligned} G(T, P, \xi) &= \sum_{j=1}^m n_j \mu_j \\ &= \sum_{j=1}^m n_j \left\{ -RT \ln \left[\frac{P_0}{P_j} \left(\frac{T}{T_0} \right)^{5/2} \right] + \mu_j^0 \right\} \\ &= \sum_{j=1}^m n_j \left\{ -RT \ln \left[\frac{P_0}{P x_j} \left(\frac{T}{T_0} \right)^{5/2} \right] + \mu_j^0 \right\} \quad [(2.212) \ \S 2.B \text{ of used. }] \\ &= \sum_{j=1}^m n_j \left\{ -RT \ln \left[\frac{P_0}{P} \left(\frac{T}{T_0} \right)^{5/2} \right] + \mu_j^0 \right\} + RT \sum_{j=1}^m n_j \ln x_j \\ &= \sum_{j=1}^m n_j \left\{ -RT \ln \left[\frac{P_0}{P} \left(\frac{T}{T_0} \right)^{5/2} \right] + \mu_j^0 \right\} + RT \ln \left(\prod_{j=1}^m x_j^{n_j} \right) \end{aligned} \quad (2.243a)$$

For the reaction (2.227),

$$G(T, P, \xi) = \sum_{j=A,B,C,D} n_j \left\{ -RT \ln \left[\frac{P_0}{P} \left(\frac{T}{T_0} \right)^{5/2} \right] + \mu_j^0 \right\} + RT \ln (x_A^{n_A} x_B^{n_B} x_C^{n_C} x_D^{n_D}) \quad (2.243)$$

Similarly, (2.238) becomes

$$\begin{aligned} \mathcal{A}(T, P, \xi) &= \sum_{j=1}^m \nu_j \left\{ -RT \ln \left[\frac{P_0}{P_j} \left(\frac{T}{T_0} \right)^{5/2} \right] + \mu_j^0 \right\} \\ &= \sum_{j=1}^m \nu_j \left\{ -RT \ln \left[\frac{P_0}{P} \left(\frac{T}{T_0} \right)^{5/2} \right] + \mu_j^0 \right\} + RT \ln \left(\prod_{j=1}^m x_j^{\nu_j} \right) \end{aligned} \quad (2.244a)$$

For the reaction (2.227),

$$\mathcal{A}(T, P, \xi) = \sum_{j=A,B,C,D} \nu_j \left\{ -RT \ln \left[\frac{P_0}{P} \left(\frac{T}{T_0} \right)^{5/2} \right] + \mu_j^0 \right\} + RT \ln \left(\frac{x_C^{\nu_C} x_D^{\nu_D}}{x_A^{|\nu_A|} x_B^{|\nu_B|}} \right) \quad (2.244)$$

At equilibrium, $\mathcal{A} = 0$, and we have

$$\ln \left(\frac{x_C^{\nu_C} x_D^{\nu_D}}{x_A^{|\nu_A|} x_B^{|\nu_B|}} \right) = \sum_{j=A,B,C,D} \nu_j \left\{ \ln \left[\frac{P_0}{P} \left(\frac{T}{T_0} \right)^{5/2} \right] - \frac{\mu_j^0}{RT} \right\} \quad (2.245)$$

which is known as the **law of mass action**. See Ex 2.11 for its application.