

Chapter 2

Thermodynamics and Equilibrium

The concept of the equilibrium state of a system is of utmost importance in analytical chemistry. To illustrate this assertion briefly, recall that numerous chemical reactions are performed with analytical goals in mind. The conclusions they provide can be easily reached if and only if the reactions proceed through to their natural completion, that is, reach their equilibrium state.

The equilibrium concept cannot be separated from that of the free enthalpy change during the process of concern. In turn, the free enthalpy concept comes directly from the second principle of thermodynamics. In actuality, the free enthalpy concept is nothing more than the second principle expressed in a form that is particularly easy for chemists to handle, at least in some well-defined experimental conditions. These are the reasons why in this chapter we recall some general conclusions stemming from the thermodynamics framework.

The link between thermodynamics and analytical chemistry is strikingly apparent when we consider the work performed by electrochemical cells. This is done with the help of Nernst's law. Due to its importance, we will review it in detail. It will be particularly useful for the study of redox phenomena.

2.1 Chemical Potential

The *chemical potential* μ_i of a substance i is expressed in term of its activity a_i . The relationship between them is as follows:

$$\mu_i = \mu_i^\circ + RT \ln a_i. \quad (2.1)$$

μ_i° is the chemical potential of i in its standard state. More simply, it is its standard chemical potential. The definition of the standard state is given below. Of importance now is the fact that μ_i° is a constant characteristic of i for a given temperature. (In the case of solutions, it depends only weakly on pressure.) R is the ideal gas constant and T the absolute temperature of the system. a_i is the activity of species i in the experimental conditions, more clearly in the thermodynamic state of the system (see below). For this brief recall, it is sufficient to visualize an activity as a kind of

concentration. We must also know that in the case of solutes, the numerical value of a_i tends toward its concentration value C_i when the solution becomes more and more diluted. The differences between the numerical values of the activities and those of the corresponding concentrations are more pronounced for ions than for uncharged compounds. Finally, to terminate temporarily with the activity concept (see Chap. 3), let's note that an activity is quantified by a dimensionless number. Coming back to relation (2.1), we notice that the chemical potential of a substance is equal to its standard potential when its activity is unity (see Chap. 3).

A chemical potential is an intensive partial molar quantity. Its value does not depend on the sample mass since, by definition, a molar quantity concerns one mole. The chemical potential is also called the *partial molar free enthalpy* G_i :

$$\mu_i = G_i.$$

In order to grasp the very deep meaning of the chemical potential, consider that G. N. Lewis¹ described it as the “escaping tendency” of the species. The escaping tendency is the tendency of the substance to leave its thermodynamic state by either a physical or chemical process. A simple example taken in the realm of physical processes involves the partitioning of a solute i between two immiscible phases α and β . In the initial state (which is not the equilibrium state of the system), the solute is supposed to be wholly present in phase α . Its chemical potential in this phase is $\mu_{i\alpha}$, while it is $\mu_{i\beta} = 0$ in the other:

$$\mu_{i\alpha} \neq \mu_{i\beta}$$

and

$$\mu_{i\alpha} > \mu_{i\beta}.$$

By the mechanical stirring of both phases, the system is equilibrated. A fraction of the solute goes into phase β . The state of equilibrium partitioning is attained when the solute concentrations in both phases no longer change with time. Then the chemical potentials of the solute in both phases are equal:

$$\mu_{i\alpha} = \mu_{i\beta}.$$

This is the condition of *equilibrium partitioning*.

Partitioning occurred because the chemical potentials in both phases were different in the initial state. Therefore, it appears that the chemical and electrical potentials play analogous parts. There is a displacement of electrons because of the electrical potential difference between two points of a circuit. Likewise, a chemical reaction takes place because, at a given moment, a linear combination of the chemical potentials of the reactants and products differs from zero (see below).

¹ Gilbert Newton Lewis: American physicist and chemist (1875–1946), especially well known for his works concerning covalency and one definition of acids and bases.

- For a solution of n components including the solvent, the Gibbs free energy of the whole chemical system (solvent plus solutes) is given by the relationship

$$G_{\text{syst}} = n_1\mu_1 + n_2\mu_2 + \dots ; n_i\mu_i + \dots + n_n\mu_n \quad (2.2)$$

or

$$G_{\text{syst}} = \sum n_i\mu_i,$$

where the n_i are the numbers of moles of each component. In a binary solution composed of the solvent and the solute only, the Gibbs free energy is given by

$$G_{\text{syst}} = n_0\mu_0 + n_1\mu_1,$$

where the subscript 0 is usually related to the solvent. Contrarily to the case of chemical potentials, the Gibbs free enthalpy G is an extensive property since, quite evidently, it depends on the components' mole numbers.

- The chemical potentials or partial molar free enthalpies are defined by the following partial derivative:

$$\mu_i = G_i = (\partial G_{\text{syst}}/\partial n_i)_{T,P,n_j} (i \neq j). \quad (2.3)$$

The chemical potential is the partial derivative of the free enthalpy of the whole system with respect to the mole number of i ; the other variable values (temperature, pressure, and other species mole number n_j) remain constant. It is also the change in the system free enthalpy when the mole number n_i is varied by an infinitely small amount, while other variables defining the thermodynamic state remain constant. Most of the time, partial molar quantities do vary with the system composition. This is the case with chemical potentials. A familiar example is given by methanol/water mixtures. The total volume V_{syst} of the mixture is given by the relationship

$$V_{\text{syst}} = n_w V_w + n_m V_m,$$

where V_w and V_m are the partial molar volumes of water and methanol in the solution. They are defined by the relationships

$$V_w = (\partial V_{\text{syst}}/\partial n_w)_{T,P,n_m} \quad \text{and} \quad V_m = (\partial V_{\text{syst}}/\partial n_m)_{T,P,n_w}.$$

It is a well known fact that V_w and V_m change with the mixture composition. Hence, if the percentage in mass of methanol is 40%, $V_m = 39.0 \text{ cm}^3/\text{mol}$ and $V_w = 17.5 \text{ cm}^3/\text{mol}$. If it is 60%, $V_m = 39.8 \text{ cm}^3/\text{mol}$ and $V_w = 16.8 \text{ cm}^3/\text{mol}$. The molar volumes of the pure components are $V_m = 40 \text{ cm}^3/\text{mol}$, $V_w = 18 \text{ cm}^3/\text{mol}$ ($T = 298.15 \text{ K}$ and $P = 1 \text{ bar}$).

In some exceptional cases, the partial molar quantities do not change with the composition. Their values are then purely and simply equal to those of the molar quantities of the components in their pure state.

The absolute values of some partial molar quantities, such as the volume, can be determined experimentally. Other absolute values, however, cannot be; these include partial molar enthalpies, free enthalpies, and free entropies. However, their changes are measurable.

2.2 Gibbs Free Energy Change ΔG_{syst} and Useful Work Available from the Process

Let's consider a closed system in which the studied process takes place and examine its surroundings. According to the definition of a closed system, the system exchanges work and heat with its surroundings but does not exchange matter. If the initial and final temperatures are equal and also equal to the constant temperature of surroundings (heat bath) and the surroundings are displaced at constant pressure, the maximum work W' that can be done by the system of interest is equal to its Gibbs free energy decrease:

$$W'_{\text{max}} = \Delta G_{\text{syst}} \quad (\text{reversible process}).$$

W' does not include the work of displacement. W' is the useful work. It can be, for example, an electrical work. This is the maximum work obtained from a galvanic cell (see Sect. 2.8). The preceding relationship holds only in the case of a reversible process. Let's examine the concept of reversibility in some depth. The reversibility conditions are approached when the process takes place very slowly. In practice, a galvanic cell is an interesting device to obtain quasi-reversibility. When the process is irreversible, the following inequality holds:

$$|W'| < |\Delta G_{\text{syst}}| \quad (\text{irreversible process}).$$

In this case, the work done is less than the decrease of the Gibbs free energy of the system.

All the preceding considerations are quite general provided that only closed systems are under consideration. The processes can be physical, chemical, or biological, and they can be applied to the case of chemical reactions. In the usual experimental conditions in which the latter are performed, the variables that define the thermodynamic state of the system are its temperature, pressure, and composition. The thermodynamic system itself can be defined by the reactants and the products of the reaction. Its Gibbs free energy change during the process is given by

$$dG_{\text{syst}} = -S dT + V dP + \sum_{i=1}^n \mu_i dn_i. \quad (2.4)$$

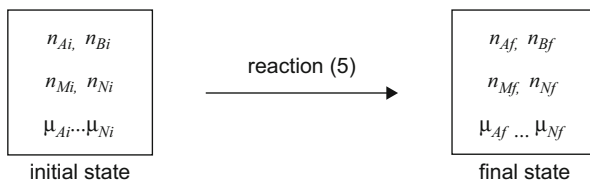
This relationship comes from general considerations. S and V are the entropy and the volume of the system, respectively, while n_i and μ_i are, respectively, the mole numbers and the chemical potentials of the species. Let's consider the following reaction:



which is often written as

$$\sum v_J R_J = 0.$$

Fig. 2.1 Definition of the initial and final states of reaction (2.5)



For the reactants (A, B), the stoichiometric coefficients are preceded by the minus sign because of the decrease in their concentrations during the reaction.

At the beginning of the process, the system consists of species A and B and possibly of species M and N , which can already be present in the reactor. Suppose that the reaction takes place at a constant pressure and temperature. The mole numbers of ions facing each other are n_{Ai} , n_{Bi} , n_{Mi} , and n_{Ni} and their chemical potentials are μ_{Ai} , μ_{Bi} , μ_{Mi} , and μ_{Ni} (i : initial). The initial state of the system is fully defined since the composition, temperature, and pressure are known. In the final state, the mole numbers of species have changed. They have become n_{Af} , n_{Bf} , n_{Mf} , and n_{Nf} (f : final), and the corresponding chemical potentials are μ_{Af} , μ_{Bf} , μ_{Mf} , and μ_{Nf} . The latter have changed quite evidently since the composition has changed (Fig. 2.1). (Incidentally, it is interesting to note that the final state can be chosen arbitrarily. For example, it can be realized experimentally by abruptly stopping the reaction at a given moment. Of course, the final state may also be the state in which equilibrium is achieved.)

The Gibbs free energy change during the process is

$$\Delta G_{\text{syst}} = [n_{Af}\mu_{Af} + n_{Bf}\mu_{Bf} + n_{Mf}\mu_{Mf} + n_{Nf}\mu_{Nf}] - [n_{Ai}\mu_{Ai} + n_{Bi}\mu_{Bi} + n_{Mi}\mu_{Mi} + n_{Ni}\mu_{Ni}]. \quad (2.6)$$

Equation (2.6) gives the maximum useful work available from the chemical reaction.

An inconsistency between Eqs. (2.4) and (2.6) appears at first sight. In fact, let's write Eq. (2.6) in its compact form:

$$\Delta G_{\text{syst}} = \sum n_j \mu_j$$

and differentiate it. We find

$$dG_{\text{syst}} = \sum n_j d\mu_j + \sum \mu_j dn_j.$$

By differentiation, Eq. (2.4) gives

$$dG_{\text{syst}} = \sum \mu_j dn_j;$$

both relationships were obtained at a constant pressure and temperature. The inconsistency comes from the fact that in the last equation, the term $\sum n_j d\mu_j$ is missing. This inconsistency is merely apparent.

The missing term, $\sum n_j d\mu_j$, indeed, is null; that is, the chemical potentials of a mixture's components cannot change independently of each other at constant pressure and temperature. The relationship

$$\sum n_i d\mu_i = 0 \quad (dT = 0, dP = 0)$$

is called Gibbs–Duhem's² equation. It originates in the mathematical nature of free enthalpy. The free enthalpy is a first-degree homogeneous function with respect to the mole number of each constituent.³

2.3 Molar Reaction Gibbs Function

The solute mole numbers change during a chemical reaction. They are linked by the equalities

$$(dn_A/v_A) = (dn_B/v_B) = (dn_M/v_M) = (dn_N/v_N) = d\xi.$$

ξ is called the *extent reaction*. In these equations, the changes dn_A and dn_B are negative because *A* and *B* disappear during the reaction, dn_M and dn_N being positive. When taking these equalities into account, the free enthalpy change accompanying reaction (2.5), given by Eq. (2.4) at constant temperature and pressure, becomes

$$dG_{\text{syst}} = (-v_A\mu_A - v_B\mu_B + v_M\mu_M + v_N\mu_N) d\xi \quad (dT = 0, dP = 0). \quad (2.7)$$

The entire term within parentheses in Eq. (2.7) is called the *molar reaction Gibbs function*, $\Delta_r G$. More precisely, it is the molar free enthalpy change accompanying the reaction at a given instant of its evolution, that is, for an extent ξ for which the instantaneous chemical potentials are μ_i :

$$\Delta_r G = -v_A\mu_A - v_B\mu_B + v_M\mu_M + v_N\mu_N. \quad (2.8)$$

The molar reaction Gibbs function varies with respect to the extent reaction. After Eq. (2.7), it is the partial derivative of the system free enthalpy with respect to ξ at constant pressure and temperature.

We must not confuse the free enthalpy change ΔG_{syst} accompanying a chemical reaction and the molar reaction Gibbs function change $\Delta_r G$. They do not have the same mathematical status. The former change is a difference, the latter a partial derivative. They no longer have the same physical status. The former is an extensive quantity, the latter an intensive one.

² Pierre Duhem: French mathematician, physicist, and philosopher (1861–1916).

³ See Euler's theorem in mathematics.

The change dG_{syst} is negative when the process is spontaneous. As a result, at constant pressure and temperature, the molar reaction Gibbs function $\Delta_r G$ must be negative in the case of a spontaneous process:

$$\Delta_r G < 0 \quad (\text{spontaneous process}).$$

In the case of reaction (2.5), we can write

$$\nu_A \mu_A + \nu_B \mu_B > \nu_M \mu_M + \nu_N \mu_N \quad (dT = 0, dP = 0).$$

The molar reaction Gibbs function $\Delta_r G$ quantity, whose algebraic sign has been inversed, is called the *chemical affinity* (de Donder's definition). It is positive for a spontaneous process:

$$A = -\Delta_r G,$$

where A is the chemical affinity.

2.4 Evolving Reactions and Equilibrium Conditions

According to the meaning of the free enthalpy function, the equilibrium state is obtained when

$$dG_{\text{syst}} = 0 \quad (\text{equilibrium}).$$

Then the system free enthalpy G_{syst} exhibits its minimum value. When the evolving system consists of reactants together with their reaction products, the equilibrium state is obtained for the extent ξ' such as

$$\left(\partial G_{\text{syst}} / \partial \xi\right)_{T, P, \xi=\xi'} = 0 \quad (\text{equilibrium; } dT = 0, dP = 0).$$

Then Eq. (2.7) shows that

$$\nu_A \mu_A + \nu_B \mu_B = \nu_M \mu_M + \nu_N \mu_N.$$

or

$$\Delta_r G = 0 \text{ or } A = 0.$$

As a result, for a spontaneous chemical change starting from the sole reactants A and B , the molar reaction Gibbs function $\Delta_r G$ becomes increasingly less negative when the extent of the reaction increases. Likewise, the reaction course starting from the sole reaction products is such that the molar reaction Gibbs function is increasingly less positive. Each point of the G/ξ curve can represent either the initial or the final instant of the reaction. Except for the farthest points, each curve point represents a state where the reactants and products A , B , M , and N are all present in the mixture.

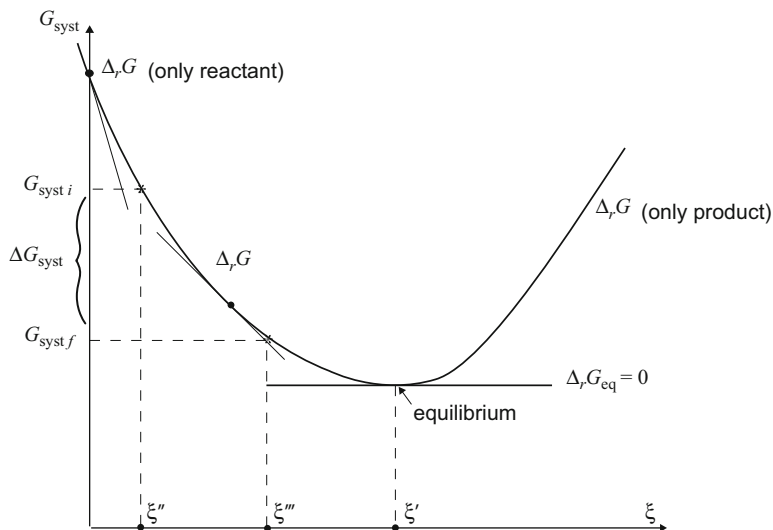


Fig. 2.2 Difference between the molar reaction Gibbs function and the free enthalpy change during a chemical reaction

Their chemical potentials are related to each other through Eq. (2.8). For example, the reaction can be initiated for $\xi = \xi''$ and stopped for $\xi = \xi'''$.

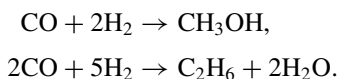
The extreme points represent the cases in which only reactants and only product are present in the mixture.

The system free enthalpy change is then (f : final, i : initial)

$$\Delta G_{\text{syst}} = G_{\text{syst}f} - G_{\text{syst}i}.$$

Figure 2.2 shows that $\Delta_r G$ also changes all along the process. At $\xi = \xi'''$, the reaction equilibrium is not obtained since the slope $\Delta_r G$ is not null. Slopes are maximal when the sole reactants or products are present in the reaction mixture (extreme points).

A question unavoidably comes to mind: What the equilibrium conditions must be respected when several chemical reactions simultaneously evolve? This is a problem encountered in chemical analysis when, for example, we titrate a mixture of two compounds and when they can react simultaneously with the common titrant. The answer to the question comes from the general criterion $dG_{\text{syst}} = 0$. It is inferred from this condition that the molar reaction Gibbs functions $\Delta_r G$ of each reaction must be simultaneously null provided that the different reactions are independent of each other. For example, in a system containing the compounds CO, H₂, H₂O, CH₃OH, and C₂H₆, all in gaseous state, only two independent reactions exist:



The general equilibrium conditions results in the simultaneous occurrence of the two equalities

$$\begin{aligned}\mu_{\text{CH}_3\text{OH}} - \mu_{\text{CO}} - 2\mu_{\text{H}_2} &= 0, \\ \mu_{\text{C}_2\text{H}_6} + 2\mu_{\text{H}_2\text{O}} - 2\mu_{\text{CO}} - 5\mu_{\text{H}_2} &= 0 \quad (\text{equilibrium}).\end{aligned}$$

The problem is to recognize the independent reactions.

2.5 Equilibrium Conditions and Mass Law

The expression of the molar reaction Gibbs function $\Delta_r G$ given by Eq. (2.8) is valid for each extent value ξ . After introducing the chemical potentials expressions (2.1) into it, we find

$$\begin{aligned}\Delta_r G &= (v_M \mu_M^\circ + v_N \mu_N^\circ - v_A \mu_A^\circ - v_B \mu_B^\circ) \\ &\quad + RT \ln \{ [a_M^{vM} \cdot a_N^{vN}] / [a_A^{vA} \cdot a_B^{vB}] \}. \end{aligned} \quad (2.9)$$

The activities in the logarithm argument can take any value. They depend only on the initial concentrations and on the reaction extent. The expression that constitutes the logarithm argument is called the *quotient reaction*, Q :

$$Q = [a_M^{vM} \cdot a_N^{vN}] / [a_A^{vA} \cdot a_B^{vB}],$$

or

$$Q = \Pi_i a_i^{v_i}.$$

Equation (2.9) can be written as

$$\Delta_r G = (v_M \mu_M^\circ + v_N \mu_N^\circ - v_A \mu_A^\circ - v_B \mu_B^\circ) + RT \ln Q, \quad (2.10)$$

or, with the introduction of the chemical affinity, as

$$\begin{aligned}A^\circ &= (v_A \mu_A^\circ + v_B \mu_B^\circ - v_M \mu_M^\circ - v_N \mu_N^\circ), \\ \Delta_r G &= -A^\circ + RT \ln Q. \end{aligned} \quad (2.11)$$

The terms enclosed within parentheses in Eqs. (2.10) and (2.11) are respectively called the standard molar reaction Gibbs function change $\Delta_r G^\circ$ ⁴ and the standard chemical affinity A° . By setting up

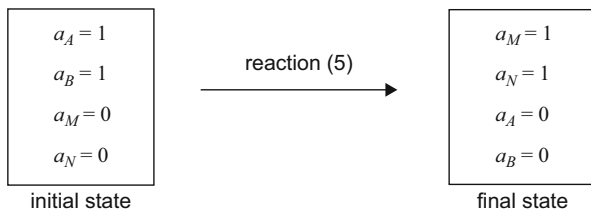
$$\Delta_r G^\circ = (v_M \mu_M^\circ + v_N \mu_N^\circ - v_A \mu_A^\circ - v_B \mu_B^\circ),$$

it is quite evident that

$$A^\circ = -\Delta_r G^\circ.$$

⁴ Or, more quickly, standard molar reaction free enthalpy. This denomination is misleading because it is a measurable quantity, whereas a free enthalpy cannot be measured.

Fig. 2.3 Initial and final states of reaction (2.5) defining $\Delta_r G^\circ$ and A°



Equation (2.9) then becomes

$$\Delta_r G = \Delta_r G^\circ + RT \ln [a_M^{vM} \cdot a_N^{vN}] / [a_A^{vA} \cdot a_B^{vB}]. \quad (2.12)$$

A° and $\Delta_r G^\circ$ are both constant quantities at a constant temperature since the standard chemical potentials are constant in these conditions (see Sect. 2.1). Both quantities can be determined. They are equal (in absolute values) to the *useful work*, or the maximum work available. Such is the case when the chemical reaction takes place reversibly and when the initial and final states are the standard ones. They are described in Fig. 2.3.

By introducing these activities of unit value (which, in fact, characterize the standard states of species A , B , M , and N —see Sect. 2.1) in Eqs. (2.9)–(2.11), we find $Q = 1$ and

$$\Delta_r G = \Delta_r G^\circ \quad (A = A^\circ).$$

It is interesting to note that the standard molar reaction Gibbs function $\Delta_r G^\circ$ does not have the same mathematical status as $\Delta_r G$ at each extent ξ value. $\Delta_r G^\circ$, indeed, is not a derivative, unlike $\Delta_r G$. $\Delta_r G$ is simply the system free enthalpy change ΔG_{sys} between two particular states, which happen to be the standard ones.

The fact that the standard molar reaction Gibbs function change $\Delta_r G^\circ$ and the standard chemical affinity A° are constant at a given temperature is of utmost importance. Its major outcome is the mass law. Indeed, the equilibrium condition $\Delta_r G = 0$ introduced into Eq. (2.9) gives

$$-RT \ln \{ [a_M^{vM} \text{eq} \cdot a_N^{vN} \text{eq}] / [a_A^{vA} \text{eq} \cdot a_B^{vB} \text{eq}] \} = \Delta_r G^\circ.$$

Since $\Delta_r G^\circ$ is constant, the term enclosed within brackets is also a constant. By definition, it is the thermodynamic constant K° of reaction (2.5):

$$K^\circ = [a_M^{vM} \text{eq} \cdot a_N^{vN} \text{eq}] / [a_A^{vA} \text{eq} \cdot a_B^{vB} \text{eq}], \quad (2.13)$$

$$-RT \ln K^\circ = \Delta_r G^\circ. \quad (2.14)$$

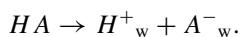
The adjective “thermodynamic” obligatorily implicates that the mass law is expressed in activity terms. Other kinds of equilibrium constants are also used (see Chap. 3). The

thermodynamic equilibrium constant is a dimensionless number since all activities are dimensionless.

It is important to note that the activities in Eq. (2.13) cannot have any value. They can have only the values at equilibrium. They are related to each other by Eq. (2.13).

Equilibrium constants are systematically used in general analytical chemistry. They are of huge importance. Their values permit us to calculate the concentrations of the reaction species, once the equilibria have been attained. Some equilibrium constants bear a particular name according to the kind of chemical reaction they quantify. For example,

- In the case of acid–base phenomena, the dissociation constant K_a is introduced. It quantifies the strength of the acid. An acid HA dissociates in aqueous solution and gives a hydrated proton H^+ and the conjugated base A^- (see the Part II) according to



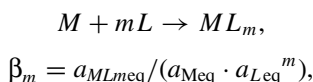
K_a is defined by the equation

$$K_a = (a_{H^+ \text{eq}} \cdot a_{A^- \text{eq}}) / a_{HA \text{eq}}.$$

The molar reaction Gibbs function of acid ionization is given by the equation

$$\Delta_r G^\circ = -RT \ln K_a.$$

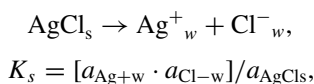
- For complexation phenomena, stability constants are used, in particular the overall stability constants β_n (see Part IV). In brief, a complexation reaction can be defined as resulting from the action of a ligand (an electrically neutral or negatively charged species) with a metallic ion, according to the equations



where L is the ligand and M the metallic ion (electrical charges are missing for the sakes of both generality and simplicity). The molar reaction Gibbs function of the overall complexation is given by the equation

$$\Delta_r G^\circ = -RT \ln \beta_m.$$

- For precipitation phenomena, equilibrium considerations introduce the concept of the solubility product K_s . This constant concerns the heterogeneous equilibrium between a precipitated compound and its constituent ions in solution (see Part V). For example, for silver chloride, one of the satisfied equilibria is



which, due to the conventions upon activities (see Chap. 3), reduces to

$$K_s = a_{\text{Ag}^+ + \text{w}} \cdot a_{\text{Cl}^- - \text{w}}.$$

The molar reaction Gibbs function of dissolution is

$$\Delta_r G^\circ = -RT \ln K_s.$$

2.6 Chemical Potentials and Standard States

Relation (2.1) involves the standard chemical potential μ° of a species. Definitively, it cannot be determined experimentally, nor is its chemical potential μ_i . However, we noticed when we were on the subject of mass law that a judicious linear combination of standard chemical potentials is experimentally accessible. In truth, it is impossible to know the absolute value of a chemical potential because it is a free enthalpy and because the absolute value of any free enthalpy itself cannot be known. However, the fact that an absolute value of a quantity cannot be determined is not rare. An example that is more common than those of enthalpies, free enthalpies, and free entropies is provided by an altitude point. The difference in altitude between two points is measurable. It is not the case for their absolute altitude. Numerous other quantities also follow suit.

In order to determine the standard molar reaction Gibbs function change $\Delta_r G^\circ$, the standard states of the reaction reactants and products must be defined. They must be chosen or, at a minimum, they must correspond to physical states, such as the physical property differences between them being endowed with an unambiguous physical meaning. As an example, a possible standard state of a solute is the state in which its concentration is 1 mol/L and in which the solution it forms with the solvent is an ideal one. Standard states are chosen conventionally for practical reasons. Fortunately, the conventions are universally agreed upon.

The fact that standard states are conventional may be somewhat troublesome. Indeed, the question immediately arises about equilibrium constant values with different arbitrarily chosen standard states. Quite evidently, when standard states other than the usual ones are chosen, the value of the standard molar reaction Gibbs function change $\Delta_r G^\circ$ is different; according to Eq. (2.14), it is also the case with K° . However, this is not the case with $\Delta_r G$ and ΔG_{sys} , which remain constant for a given process regardless of the adopted conventions. Actually, in Eq. (2.12),

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q.$$

If $\Delta_r G^\circ$ possesses different numerical values (due to the different choices of standard states), the reaction quotient Q is endowed with a different value, but the $\Delta_r G$ value remains the same as before. There exists a very subtle compensation between $\Delta_r G^\circ$ and the numerical values of the activities that depend on the chosen standard states. $\Delta_r G$ and ΔG_{sys} are the true invariants of the thermodynamic process. This subtle compensation takes its roots in the depth of the thermodynamics framework.

Let us give, incidentally, the important methods of $\Delta_r G$ and more precisely of $\Delta_r G^\circ$ determinations. They are grounded on the following bases:

- equilibrium constants' measurements. They themselves involve the determination of reactants and products concentrations at equilibrium;
- the use of thermodynamic tables. The literature contains numerous data that are the standard molar enthalpies and entropies of formation $\Delta_f H^\circ$ and $\Delta_f S^\circ$ of compounds and ions. They permit, in a first step, the calculation of the standard enthalpy and entropy of the reaction of concern via the following equations:

$$\Delta_r H^\circ = \sum v_p \Delta_f H_p^\circ - \sum v_r \Delta_f H_r^\circ,$$

$$\Delta_r S^\circ = \sum v_p S_p^\circ - \sum v_r S_r^\circ,$$

where the indices r and p are related to the reactants and products. In the second step, the following relationship is used to calculate $\Delta_r G^\circ$:

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ.$$

(The data mentioned in the tables are not absolute. They are relative but self-coherent. As a result, the calculations of changes in thermodynamic functions are accurate.);

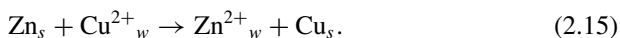
- calculations of statistical thermodynamics. They necessitate the knowledge of the molecular energy levels' differences, which can be accessible by spectroscopy;
- the use of the third law of thermodynamics;
- the determination of the electromotive force (EMF.) of galvanic cells. The methodology is detailed in the next section.

The relationship between the equilibrium constant of a redox reaction and the EMF of the corresponding galvanic cell (potential cell) is the subject of Nernst's law. It is of tremendous interest in analytical chemistry from both theoretical and practical points of view.

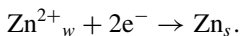
2.7 Redox Reaction: Redox Couples

The preceding considerations are quite general. As a result, they apply to redox reactions. The relationship between the equilibrium constant of a redox reaction and the EMF of the corresponding electrochemical cell mentioned just above necessitates the brief introduction of redox reactions (they will be studied further in Part III).

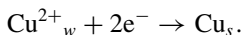
Let's consider the spontaneous chemical reaction



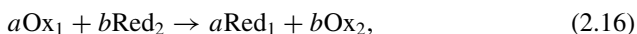
It involves an electron exchange between Zn_s and Cu^{2+} . We say that zinc is oxidized by cupric copper while this last one is reduced by zinc in copper. Zn_s and Zn^{2+}_w form a redox couple. Both species are interrelated by the half redox reaction:



It is the same state of affairs for the couple $\text{Cu}^{2+}/\text{Cu}_s$, the two elements of which are interrelated by the redox half-reaction



Reaction (2.15), which results from the exchange of electrons between the two pairs $\text{Zn}^{2+}_w/\text{Zn}_s$ and $\text{Cu}^{2+}_w/\text{Cu}_s$, is a redox reaction. Some redox reactions are more complicated than (2.15). Let's take a look, for example, at the following reaction:



where the different stoichiometric coefficient a and b values result from the different electron numbers exchanged in each redox half-reaction Ox_1/Red_1 and Ox_2/Red_2 .

The molar reaction Gibbs functions of reactions (2.15) and (2.16) are given by the following equations:

$$\Delta_r G = -\mu_{\text{Zn}} - \mu_{\text{Cu}^{2+}} + \mu_{\text{Zn}^{2+}} + \mu_{\text{Cu}}, \quad (2.17)$$

$$\Delta_r G = -a\mu_{\text{Ox}_1} - b\mu_{\text{Red}_2} + a\mu_{\text{Red}_1} + b\mu_{\text{Ox}_2}. \quad (2.18)$$

As stated previously, the value of these reactions does change with the extent reaction value ξ . In the case of reaction (2.16), Eq. (2.12) becomes

$$\Delta_r G = \Delta_r G^\circ + RT \ln \left\{ \frac{[a_{\text{Red}_1}]^a \cdot [a_{\text{Ox}_2}]^b}{[a_{\text{Ox}_1}]^a \cdot [a_{\text{Red}_2}]^b} \right\}. \quad (2.19)$$

2.8 Brief Description of an Electrochemical Cell: Daniell's Galvanic Cell

Let's consider the electrochemical cell represented in Fig. 2.4. It contains two compartments. One consists of a zinc strip dipping into a zinc sulfate solution, and the other is a copper strip dipping into cupric copper sulfate. The two metallic conductors are called the *electrodes*. Both electrode compartments are linked by a conducting *bridge*. An *electrolyte solution* completes the full circuit. The bridge precludes the mixing of the two electrolyte solutions. Moreover, the two electrodes dip into two electrolyte solutions. Finally, the two electrodes are in mutual electrical contact through a metallic thread, for example, a platinum thread. One galvanometer and possibly an electrical motor are inserted into the circuit. A millivoltmeter is connected in parallel between the two platinum threads. When the circuit is closed, a spontaneous current passes through it until equilibrium has been attained. Two kinds of electrical current exist in the cell. In the external circuitry, the electrical current is nothing more than the electrons' displacement. It exists through the electrodes and the metallic threads. In the electrolytic solutions, the current is due to the ions' displacements. It is an ionic current. The same current also exists in the conducting bridge. What happens at the interface of both kinds of current, that is, on the electrode's surfaces, is particularly interesting. According to Kirchhoff's law, the current

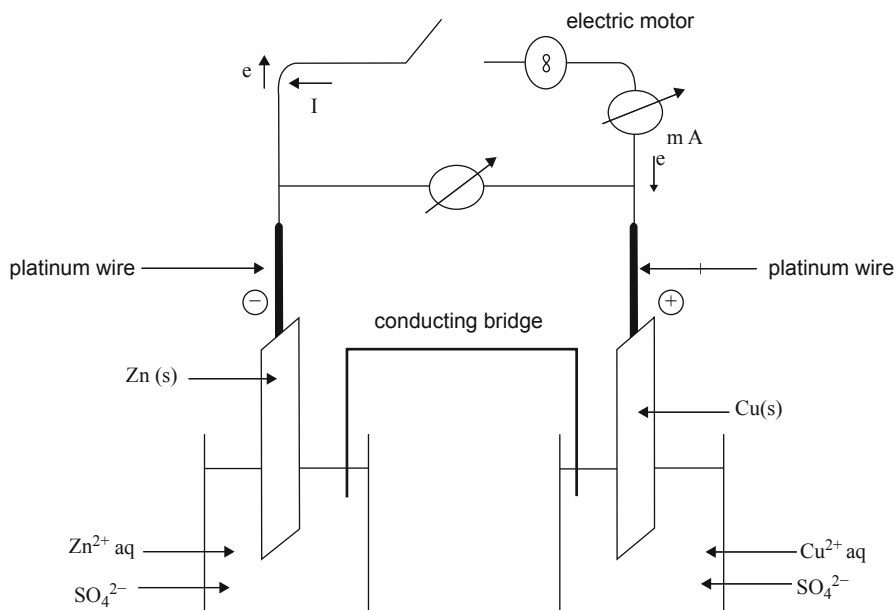
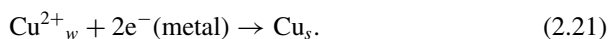
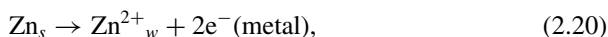


Fig. 2.4 Daniell's galvanic cell

continuity must exist. It can be realized only if the two following reactions take place simultaneously and separately:



The zinc strip loses electrons. The formed Zn^{2+} ions at the surface of the electrode go into the solution to give the hydrated Zn^{2+}_w ions. Thus, they contribute to the ionic current. The electrons liberated simultaneously (at the same electrode) go into the electric conductor, where they circulate toward the copper strip. At the surface of the copper electrode, the cupric Cu^{2+}_w ions capture these electrons brought by the metallic conductor. They also contribute, as do the Zn^{2+} and SO_4^{2-} ions, to the ionic current. The full circuitry is then ensured.

Reactions (2.20) and (2.21), which take place at the two interfaces, are called *electrochemical reactions*. The chemical reaction, which formally corresponds to the sum of the two preceding electrochemical reactions, is called the *cell reaction*. It is reaction (2.15) in the chosen example. When the cell reaction is equivalent to a spontaneous chemical reaction (under the same conditions of composition, temperature, and pressure), the electrochemical cell is called a *galvanic cell*. It is an energy-producing device.

In Daniell's galvanic cell, electrons spontaneously go from the zinc strip to the copper one. This indicates that, spontaneously, the copper strip is more positive than the zinc strip. The electrode signs indicated in Fig. 2.4 follow this conclusion.

Remark A potential difference can be measured only between two threads of the same chemical nature in order to be endowed with a physical meaning (see the two platinum threads in Fig. 2.4).

2.9 Electromotive Force of a Galvanic Cell, Cell Potential Difference, Maximum Work Available from a Chemical Reaction, and Nernst's Equation⁵

It is an experimental fact that reaction (2.15) performed by purely chemical means leads to the same final state as the same reaction performed by electrochemical means through the two half-reactions (2.20) and (2.21). This is the case, of course, provided that the initial states and the temperature and pressure are the same in both experiences. It is also the case if, moreover, no work is recuperated in the electrochemical experience. The galvanic cell must be short-circuited. More precisely, initial identical states mean that concentrations $[\text{Cu}^{2+}_w]_i$ and $[\text{Zn}^{2+}_w]_i$ (i : initial) are identical in the chemical reactor and in both electrode compartments of the cell together with identical temperature and pressure. This must be the same state of affairs for the final states. When the galvanic cell is definitely used, its concentrations $[\text{Cu}^{2+}_w]_f$ and $[\text{Zn}^{2+}_w]_f$ (f : final) are identical to those existing in the equivalent chemical reactor at the end of the chemical reaction.

Since the final and initial states are identical in both experiences, the free enthalpy change ΔG_{syst} is the same in the two processes. This result is general and applies to all redox reactions. A galvanic cell discharge is equivalent to a chemical process that can be decomposed into two electrochemical half-reactions that take place simultaneously but separately, the thermodynamic evaluations of both processes being identical.

Nernst's equation results from the equality of the work furnished by the electrochemical system under conditions of reversibility and free enthalpy decrease. The work performed in the cell is that of the transport of the Cu^{2+}_w and Zn^{2+}_w ions in both compartments against the electrical field since the copper electrode is positively charged. The charge q brought by dn mol/L of the Cu^{2+}_w and Zn^{2+}_w ions of valence two crossing the cell during a very brief time interval dt from the left to the right is

$$dq = 2F \, dn,$$

where F is the faraday. Since the interval dt is very brief, the potential difference between both electrodes can be considered constant. If its value is E , the work done

⁵ Hermann Walther Nernst: a German physicochemist (1864–1941); received Nobel Prize in chemistry (1920). Nernst's equation was published in 1889 in terms of concentrations. Some authors consider Nernst as the father of modern electrochemistry.

by the system for the displacement of positive ions is in absolute value:

$$|dw'| = |E dq|$$

or

$$|dw'| = |2 FE dn|.$$

This results from law of electrostatics. Since it is evolved by the system, we find

$|dw'| = -2FE dn$. From that, we have

$$dG_{\text{syst}} = -2FE dn. \quad (2.22)$$

The free enthalpy change accompanying reaction (2.15) is

$$dG_{\text{syst}} = (-\mu_{\text{Cu}^{2+}} - \mu_{\text{Zn}} + \mu_{\text{Cu}} + \mu_{\text{Zn}^{2+}})d\xi;$$

by comparison with (2.22), we obtain

$$\mu_{\text{Cu}} + \mu_{\text{Zn}^{2+}} - \mu_{\text{Cu}^{2+}} - \mu_{\text{Zn}} = -2FE \quad (2.23)$$

since $d\xi = dn$ with $\nu_{\text{Cu}}^{2+} = \nu_{\text{Zn}}^{2+}$. The left-hand term in Eq. (2.23) is the molar reaction Gibbs function change of the chemical reaction equivalent to the reaction cell. Relation (2.23) can be generalized. For reaction (2.16) performed via electrochemical means, we can write

$$\Delta_r G = -nFE, \quad (2.24)$$

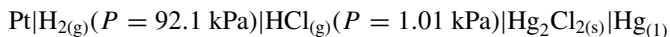
$$(-a\mu_{\text{Ox}_1} - b\mu_{\text{Red}_2} + a\mu_{\text{Red}_1} + b\mu_{\text{Ox}_2}) = -nFE, \quad (2.25)$$

where $n = ab$ is the number of electrons exchanged by the two pairs Ox_1/Red_1 and Ox_2/Red_2 .

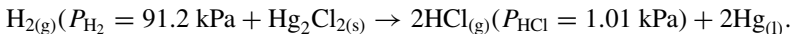
Relations (2.24) and (2.25) are the basis of Nernst's law. They are of enormous interest in physical and analytical chemistries. Among other features, they permit us to predict the redox reactions, at least from the thermodynamic standpoint, by introducing the concept of the standard electrode potential.

We must emphasize two points. The first one has already been mentioned. The molar reaction Gibbs function change is endowed with an instantaneous value. It depends on the reaction extent and, of course, on the initial reactants' and products' concentrations. As a result, the potential difference E is also instantaneous. This is the reason why the above reasoning involved differential quantities.

This is also the reason why the reversible potential difference of a cell is mentioned with the system composition. Formerly, the reversible potential difference was named the "electromotive force" of the cell. (For the meaning of the word "reversible," see immediately below). For example, the following galvanic cell (see Chap. 13 for the electrochemical cell representations)



exhibits the electromotive force $E = 0.011 \text{ V}$ ($T = 298 \text{ K}$). The chemical process is



The molar reaction Gibbs function change is

$$\Delta_r G = -\mu_{\text{H}_2}(g : P = 91.2 \text{ kPa}) - \mu_{\text{Hg}_2\text{Cl}_2(\text{s})} + 2\mu_{\text{HCl}}(g : P = 1.01 \text{ kPa}) + 2\mu_{\text{Hg}(\text{l})}.$$

The second point to emphasize is that the electromotive forces mentioned above are measured at null current. They are the zero cell potentials. This is a reversibility condition. In Daniell's galvanic cell experiment, electrical current can drive an electrical motor, for example. There is then an electrical energy recovery from the free enthalpy initially contained in the chemical system. Due to the current's occurrence, there are thus a release of heat due to the Joule effect as well as an entropy creation. The process is irreversible. However, the current can be very weak with the use of an opposition montage. In this condition, by avoiding any other irreversibility source, the free enthalpy decrease can be fully converted into electrical energy. Then the process becomes reversible. (The opposition montage even permits the reaction course to be inverted in some cases. The cell is then called a reversible one; see Chap. 13.)

An important particular case is that in which the system is in standard conditions. Then

$$\Delta_r G^\circ = -nFE^\circ, \quad (2.26)$$

where E° is the electromotive force of the galvanic cell in standard conditions or the standard potential cell. Equation (2.19) becomes

$$E = E^\circ - (RT/nF) \ln \left[(a_{\text{Red1}}^a \cdot a_{\text{Ox2}}^b) / (a_{\text{Ox1}}^a \cdot a_{\text{Red2}}^b) \right]. \quad (2.27)$$

This equation expresses Nernst's law written in activity terms.

2.10 Electrode Potentials

Relation (2.27) can be written equivalently as

$$E = E^\circ - (RT/nF) \ln [(a_{\text{Red1}}^a)/(a_{\text{Ox1}}^a)] + (RT/nF) \ln [(a_{\text{Red2}}^b)/(a_{\text{Ox2}}^b)].$$

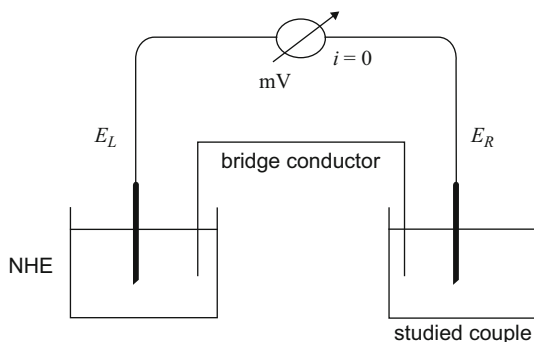
It is possible to set the standard potential E° , which is a constant equal to a difference of two constants, temporarily called E°_1 and E°_2 ; that is,

$$E^\circ = E^\circ_1 - E^\circ_2.$$

Next, two submembers appear on the right-hand side of the preceding equation, written in brackets:

$$E = \left\{ E^\circ_1 - (RT/nF) \ln [(a_{\text{Red1}}^a)/(a_{\text{Ox1}}^a)] \right\} - \left\{ E^\circ_2 - (RT/nF) \ln [(a_{\text{Red2}}^b)/(a_{\text{Ox2}}^b)] \right\}.$$

Fig. 2.5 Schematic representation of a cell permitting the determination of standard potentials of redox couples



Since the measured cell potential difference is actually the potential difference between two electrodes, it immediately comes to mind to assimilate each of the bracketed terms into the potential of each of the electrodes. They are called *electrode potentials*, E°_1 and E°_2 , which are in the two subgroups, exhibit characteristic values of both couples Ox_1/Red_1 and Ox_2/Red_2 . These constants are called *standard potentials* of both couples and are symbolized $E^\circ(\text{Ox}_1/\text{Red}_1)$ and $E^\circ(\text{Ox}_2/\text{Red}_2)$. Assigning numerical values to E°_1 and E°_2 has been a problem since the experimental determination of absolute electrode potentials; hence, assigning those to standard electrode potentials is impossible (see the electrochemistry part). It was solved by assigning relative values to them. The strategy was based on the fact that if absolute electrode potentials are not measurable, the difference between them can be. Thus, an electrode standard potential has been chosen conventionally for the couple $\text{H}^+_{\text{w}}/\text{H}_{2(\text{g})}$ (hydrogen electrode). Its standard electrode has been set definitively to the value 0.0000 V at every temperature:

$$E^\circ(\text{H}^+_{\text{w}}/\text{H}_{2(\text{g})}) = 0.0000 \text{ V}$$

(the standard conditions for the members of both couples being $P_{\text{H}_2} = 1$ bar and $a(\text{H}^+_{\text{w}}) = 1$: this is the *normal hydrogen electrode*, or *NHE*). The electromotive force of a cell that consists of the couple under study and by the couple $\text{H}_{2(\text{g})}/\text{H}^+_{\text{w}}$ in these conditions is, by definition, the standard potential electrode of the first couple. Standard electrode potentials have been established according to this principle (see Chap. 13). Note that cells that permit such determinations must be built so that the hydrogen electrode is on the left and that studied on the right (Fig. 2.5).

The accepted value $E^\circ(\text{Ox}/\text{Red})$ is

$$E^\circ(\text{Ox}/\text{Red}) = E_R - E_L$$

(R : right and L : left). It can be positive or negative. In the first case, the Ox form of the studied couple is more oxidant than H^+_{w} . In the second case, it is the opposite: $E^\circ = E_R - E_L$. Hence, $E^\circ(\text{Ox}/\text{Red})$ values are determined under reversibility conditions, that is, for a null intensity.

Remarks

- There are other kinds of electrodes in addition to those described above. However, the preceding considerations can be applied to all kinds of electrodes.
- It is not obligatory to be under standard conditions in order to determine the standard electrode potentials with the help of the preceding general cell (Fig. 2.5). Successive measurements in experimental conditions such as the activity coefficients of the couple members approaching unity permit their determination.
- From a theoretical standpoint, there is another way to introduce the electrode potential concept. This can be done by the use of electrochemical potentials (see a general course on electrochemistry).

Finally, let us point out that the absolute standard electrode potential value of the couple $\text{H}^+_{\text{w}}/\text{H}_{2(\text{g})}$ is actually about 4.5 V. This value cannot be verified since we cannot measure an absolute potential. It was obtained by using thermodynamic cycles, taking into account some thermodynamic data such as the proton hydration enthalpy and entropy. These last ones have been approached by considering the quadrupole model of water (see Chap. 1). It is quite evident that the value of 4.5 V differs considerably from the conventional one (0.00 V). However, it does not change the redox phenomena provision since only the standard electrode potential differences are taken into account.

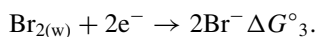
The reason why it is not possible to measure electrode potentials is of an operational nature. An absolute electrode potential is the potential difference settled at equilibrium between the electrode metal and the ionic solution where it dips. The measurement necessitates introducing another electrode into the solution. As a result, a supplementary electrode potential exists. The measurement with the help of a voltmeter cannot give another value than that of an electrode potential difference.

2.11 Addition of Free Enthalpies and Calculation of Standard Electrode Potentials from Other Standard Electrode Potentials

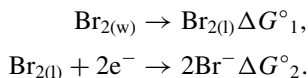
Free enthalpy is a state function. Its change does not depend on the stages through which the process takes place. It is equal to the sum of the free enthalpies of each stage. It is the same for the standard free enthalpy. This fundamental property is interesting because of the equivalence $\Delta_r G^\circ/E^\circ$, which permits the calculation of standard potentials of some redox couples that are difficult to obtain (see examples below). The principle of the calculation of the free enthalpy change of a redox process is to sum the already known free enthalpies of each stage. We will give some examples here.

The standard potential of the couple $\text{Br}_{2(\text{l})}/\text{Br}^-$ symbolized by $E^\circ(\text{Br}_{2(\text{l})}/\text{Br}^-)$. The problem is to calculate the standard potential of the couple $\text{Br}_{2(\text{w})}/\text{Br}^-$ from the

former one. The half-reaction under study is



It can be considered as resulting from the sum of the following two processes:



We can write

$$\Delta G^\circ_3 = \Delta G^\circ_1 + \Delta G^\circ_2.$$

ΔG°_1 is given by the equation

$$\Delta G^\circ_1 = RT \ln (s/C^\circ),$$

where s is the dibrome's solubility in water and C° its solution concentration in its standard state. Otherwise,

$$\Delta G^\circ_2 = -2FE^\circ(\text{Br}_{2(\text{l})}/\text{Br}^-).$$

Finally, by applying Nernst's law to the system $\text{Br}_{2(\text{w})}/\text{Br}^-$, we find

$$\Delta G^\circ_3 = -2FE^\circ(\text{Br}_{2(\text{w})}/\text{Br}^-).$$

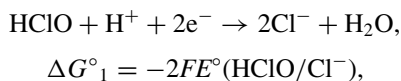
Remark The above equation giving ΔG°_1 comes from the equality of the dibrome's chemical potentials in a liquid state and in its saturated solution (see Part V):

$$\mu^\circ_{\text{Br}_{2(\text{l})}} = \mu^\circ_{\text{Br}_{2(\text{w})}} + RT \ln (s/C^\circ).$$

Now, let's consider the examples given by the pairs $I_{2(\text{w})}/I^-$ and $I_{2(\text{s})}/I^-$. Both are of analytical interest. How do we calculate the standard potential of one using the other's?

$$\begin{aligned}I_{2(\text{w})} + 2\text{e}^- &\rightarrow 2I^- \\ \Delta G^\circ_1 &= -2FE^\circ(I_{2(\text{w})}/I^-); \\ I_{2(\text{s})} &\rightarrow I_{2(\text{w})} \\ \Delta G^\circ_2 &= -RT \ln(s/C^\circ); \\ I_{2(\text{s})} + 2\text{e}^- &\rightarrow 2I^- \\ \Delta G^\circ_3 &= \Delta G^\circ_1 + \Delta G^\circ_2 \\ \Delta G^\circ_3 &= -2FE^\circ(I_{2(\text{s})}/I^-).\end{aligned}$$

Now, consider now the redox pairs HClO/Cl^- and ClO^-/Cl^- :



$$\begin{aligned}
\text{ClO}^- + \text{H}^+ &\rightarrow \text{HClO} \\
\Delta G^\circ_2 &= -RT \ln \left\{ 1 / [K_a(\text{HClO}, \text{ClO}^-)] \right\} \\
\text{ClO}^- + 2\text{H}^+ + 2\text{e}^- &\rightarrow \text{Cl}^- + \text{H}_2\text{O} \\
\Delta G^\circ_3 &= \Delta G^\circ_1 + \Delta G^\circ_2 \\
\Delta G^\circ_3 &= -2FE^\circ(\text{ClO}^- / \text{Cl}^-).
\end{aligned}$$

Remark $K_a(\text{HClO}, \text{ClO}^-)$ is the acid dissociation constant of hypochlorous acid:

$$K_a(\text{HClO}, \text{ClO}^-) = (a_{\text{H}^+} \cdot a_{\text{ClO}^-}) / a_{\text{HClO}}.$$

Redox pairs $\text{BrO}_3^- / \text{Br}^-$ in acidic medium and $\text{BrO}_3^- / \text{Br}^-$ in basic medium:

$$\begin{aligned}
\text{BrO}_3^- + 6\text{H}^+ + 6\text{e}^- &\rightarrow \text{Br}^- + 3\text{H}_2\text{O} \\
\Delta G^\circ_1 &= -6FE^\circ(\text{BrO}_3^- / \text{Br}^-; \text{H}^+); \\
6\text{H}_2\text{O} &\rightarrow 6\text{H}^+ + 6\text{OH}^- \\
\Delta G^\circ_1 &= -6RT \ln k_w; \\
\text{BrO}_3^- + 2\text{H}_2\text{O} + 6\text{e}^- &\rightarrow \text{Br}^- + 6\text{OH}^- \\
\Delta G^\circ_3 &= -\Delta G^\circ_1 + \Delta G^\circ_2, \\
\Delta G^\circ_3 &= -6FE^\circ(\text{BrO}_3^- / \text{Br}^-; \text{OH}^-).
\end{aligned}$$

Remark K_w is the ionic product of water: $K_w = (\text{H}^+)(\text{OH}^-)$.

Redox couples $\text{Au}^{3+} / \text{Au}_{(\text{s})}$ and $\text{AuCl}_4^- / \text{Au}_{(\text{s})}$:

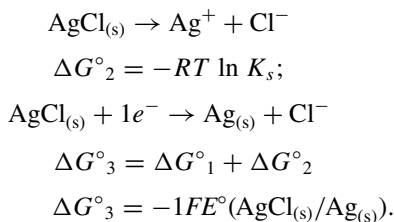
$$\begin{aligned}
\text{Au}^{3+} + 3\text{e}^- &\rightarrow \text{Au}_{(\text{s})} \\
\Delta G^\circ_1 &= -3FE^\circ(\text{Au}^{3+} / \text{Au}_{(\text{s})}); \\
\text{AuCl}_4^- &\rightarrow \text{Au}^{3+} + 4\text{Cl}^- \\
\Delta G^\circ_2 &= -RT \ln(1/\beta_4); \\
\text{AuCl}_4^- + 3\text{e}^- &\rightarrow \text{Au}_{(\text{s})} + 4\text{Cl}^- \\
\Delta G^\circ_3 &= -\Delta G^\circ_1 + \Delta G^\circ_2 \\
\Delta G^\circ_3 &= -3FE^\circ(\text{AuCl}_4^- / \text{Au}_{(\text{s})}).
\end{aligned}$$

Remark β_4 is the overall stability constant of the ultimate complex $[\text{AuCl}_4^-]$, (see the Part IV):

$$\beta_4 = (\text{AuCl}_4^-) / [(\text{Au}^{3+})(\text{Cl}^-)^4].$$

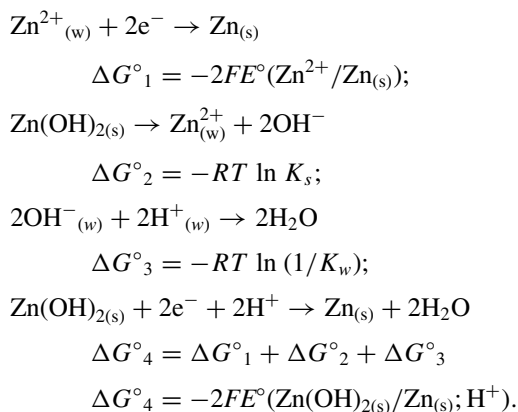
Redox couples $\text{Ag}^+ / \text{Ag}_{(\text{s})}$ and $\text{AgCl}_{(\text{s})} / \text{Ag}_{(\text{s})}$:

$$\begin{aligned}
\text{Ag}^+ + \text{Ie}^- &\rightarrow \text{Ag}_{(\text{s})} \\
\Delta G^\circ_1 &= -1FE^\circ(\text{Ag}^+ / \text{Ag}_{(\text{s})});
\end{aligned}$$



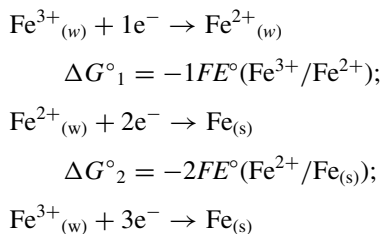
Remark K_s is the solubility product of the silver chloride: $K_s = (\text{Ag}^+)(\text{Cl}^-)$ (see Part V).

Pairs $\text{Zn}^{2+}_{(w)}/\text{Zn}_{(s)}$ and $\text{Zn}(\text{OH})_{2(s)}/\text{Zn}_{(s)}$:



This is an example in which the standard potential E° can be determined only by calculation. $\text{Zn}(\text{OH})_2$, indeed, cannot exist at a pH equal to 0.

The so-called Latimer⁶–Luther’s rule, which is frequently used in these calculations, is a particular case of the free enthalpy addition principle. It applies to the calculation of the standard potential of every redox pair once the potentials of other pairs where the same element is involved are already known. Let’s consider, for example, the iron pairs $\text{Fe}^{3+}/\text{Fe}^{2+}$ ($E^\circ = 0.77$ V) and $\text{Fe}^{2+}/\text{Fe}_{(s)}$ ($E^\circ = -0.44$ V). What is the standard potential of the pair $\text{Fe}^{3+}/\text{Fe}_{(s)}$? The free enthalpy addition principle leads to the following relationships:



⁶ Wendell Mitchell Latimer: American physicochemist, at the—University of California at Berkeley (1893–1955).

$$\begin{aligned}\Delta G^\circ_3 &= -3FE^\circ(\text{Fe}^{3+}/\text{Fe}_{(\text{s})}); \\ -3FE^\circ(\text{Fe}^{3+}/\text{Fe}_{(\text{s})}) &= -1FE^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) - 2FE^\circ(\text{Fe}^{2+}/\text{Fe}_{(\text{s})}).\end{aligned}$$

From the above, we have

$$\begin{aligned}E^\circ(\text{Fe}^{3+}/\text{Fe}_{(\text{s})}) &= [1E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) + 2E^\circ(\text{Fe}^{2+}/\text{Fe}_{(\text{s})})]/3, \\ E^\circ(\text{Fe}^{3+}/\text{Fe}_{(\text{s})}) &= -0.037\text{V}.\end{aligned}$$

This mathematical relationship expresses Latimer–Luther’s rule. We infer from it the fact that it is unnecessary to calculate the standard molar free enthalpy changes, but this result is not general. The rule is valid only for processes that involve only redox phenomena. This was not the case in the examples given before.



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