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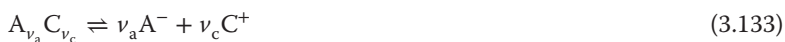
The Thermodynamics of Electrolytes

Electrolytes are substances that ionize when dissolved in certain solvents, such as water. Once the substance dissociates into ions in the solution, it has the capacity to conduct electricity or to create an electric potential energy gradient in the system [42, 81, 189]. When we consider a mixture of charged particles in the presence of an electrostatic potential ϕ , the definition of the chemical potential must be expanded to include the contribution to the energy required to add a particle with charge q to the mixture in the presence of the field. Let us assume there are N different kinds of charged particle in the mixture. Particles $j = 1, \dots, m$ are ions with charge $q_j = ez_j$, where z_j is the valency or charge of the ion and e is the charge of a proton. Particles $j = m + 1, \dots, N$ are neutral (uncharged). Then differential changes in the internal energy density (internal energy per unit volume $u = U/V$) can be written

$$du = T ds + \sum_{j=1}^m \mu_j^e dc_j + \sum_{j=m+1}^N \mu_j dc_j, \quad (3.132)$$

where $s = S/V$, $c_j = n_j/V$ is the molar concentration of type j particles, $\mu_j^e = \mu_j + z_j \phi F$ is the electrochemical potential, and F is the amount of charge in one mole of protons and is called a *Faraday* ($1 F = 96.485 C/mol$). For charged particles, equilibrium occurs when the electrochemical potentials of each species are equal.

A particularly important type of charged mixture (the type considered in this section) contains charged ions in an electrically neutral solution. Such systems are common in biological systems and form the basis for the construction of batteries. Let us consider the behavior of dilute solutions of a salt (the solute), such as NaCl, CaCl₂, AgNO₃, or Cu(NO₃)₂ in water (the solvent). If we denote the negative ion (the anion) as A⁻ and the positive ion (the cation) as C⁺, the dissociation of the salt into charged ions can be denoted



(e.g., CaCl₂ \rightleftharpoons 2Cl⁻ + Ca²⁺), where ν_a and ν_c are the stoichiometric coefficients for the dissociation. (We could also have Ag \rightarrow Ag⁺ + e⁻ in an aqueous solution.) The condition for equilibrium is

$$\mu_{ac} = \nu_a \mu_a^e + \nu_c \mu_c^e, \quad (3.134)$$

where $\mu_a^e(\mu_c^e)$ is the electrochemical potential of ion, A⁻(C⁺) and μ_{ac} is the chemical potential of the undissociated salt. Electrical neutrality of the fluid requires that $\nu_a z_a + \nu_c z_c = 0$, where $z_a e(z_c e)$ is the charge of the ion, A⁻(C⁺), and e is the proton charge.

The chemical potential of the salt in aqueous solution is extremely complicated, but experiments show that it can be written in the form

$$\mu_{ac}(P, T, x_{ac}) = \mu_{ac}^0(P, T) + RT \ln \alpha_{ac}, \quad (3.135)$$

where α_{ac} is called the *activity* and $\mu_{ac}^0(P, T)$ is the chemical potential of the salt in aqueous solution at temperature T and pressure P in the limit of infinite dilution ($\mu_{ac}^0(P, T)$ is *proportional* to the energy needed to add one salt molecule to pure water).

We can relate the activity, α_{ac} , for the salt molecule to activities for the ions. We define $\alpha_{ac} = \alpha_a^{\nu_a} \alpha_c^{\nu_c}$. Then

$$\ln(\alpha_{ac}) = \nu_a \ln(\alpha_a) + \nu_c \ln(\alpha_c). \quad (3.136)$$

The quantities α_a and α_c are defined to be the activities of the anion and cation, respectively. It is found experimentally that in the limit of infinite dilution, $\alpha_a = f_a c_a$ and $\alpha_c = f_c c_c$, where c_a and c_c are the concentrations (mol/volume) of the anions and cations, respectively. The quantities f_c and f_a are called *activity coefficients*. In the limit $c_i \rightarrow 0$, $f_i \rightarrow 1$ ($i = a, c$). Solutions for which $f_c = 1$ and $f_a = 1$ are said to be *ideal*.

The condition for equilibrium, Eq. (3.134), for *ideal solutions* is satisfied if we define the electrochemical potentials of the ions to be

$$\mu_j^e = \mu_j^0(P, T) + RT \ln c_j + z_j F \phi \quad (3.137)$$

where $j = \{a, c\}$. Two important applications of the thermodynamics of electrolytes concerns the functioning of batteries and biological cells. We first consider batteries and then biological cells.

3.11.1

Batteries and the Nernst Equation

A simple battery consists of two “half-cells.” Each half-cell contains a pure metal electrode immersed in a dilute aqueous solution of the corresponding salt (e. g., an Ag electrode with a dilute solution of AgNO_3 or a Cu electrode with a dilute solution of $\text{Cu}(\text{NO}_3)_2$).

For a half-cell with a silver (Ag) electrode, the salt dissociates into a dilute solution of Ag^+ and NO_3^- ions, and an equilibrium is set up between the silver ions on the electrode and those in the solution. Either silver ions dissolve from the electrode into the solution, leaving excess electrons on the electrode, or silver ions in the solution can attach to the electrode leaving it with a net positive charge. In either case, a charged bilayer is set up at the interface between the electrode and the solution causing an electric potential energy difference between the solution and the electrode.

For simplicity, consider two half-cells, with silver electrodes, which we label I and II . When the whole system is at equilibrium, the chemical potential of the silver ions in solution and silver ions on the electrode must be equal. The chemical potential on the electrode in I can be written $\mu_{\text{Ag}^+}^I(s) = \mu_{\text{Ag}^+}^{0,I}(s) + zF\phi_I$, since it is pure solid silver. The chemical potential of ions in the solution in I is $\mu_{\text{Ag}^+}^I(\ell) = \mu_{\text{Ag}^+}^{0,I}(\ell) + RT \ln[c_I] + zF\phi_I$. Similar expressions can be written for half-cell II . The quantities $\mu_{\text{Ag}^+}^{0,I}(s)$ and $\mu_{\text{Ag}^+}^{0,I}(\ell)$ are the energies required to add one

silver ion to the silver electrode and an infinitely dilute solution, respectively, Φ_I and ϕ_I are the electric potentials on the electrode and in the solution, respectively, and c_I is the concentration of silver ions in the solution.

The conditions for equilibrium between the silver ions on the electrode and the solution, in each of the half-cells, can be written

$$\mu_{\text{Ag}^+}^{0,I}(s) + zF\Phi_I = \mu_{\text{Ag}^+}^{0,I}(\ell) + RT \ln c_I + zF\phi_I, \quad (3.138)$$

$$\mu_{\text{Ag}^+}^{0,II}(s) + zF\Phi_{II} = \mu_{\text{Ag}^+}^{0,II}(\ell) + RT \ln c_{II} + zF\phi_{II}. \quad (3.139)$$

Now note that $\mu_{\text{Ag}^+}^{0,I}(s) = \mu_{\text{Ag}^+}^{0,II}(s)$, since they both apply to pure silver, and $\mu_{\text{Ag}^+}^{0,I}(\ell) = \mu_{\text{Ag}^+}^{0,II}(\ell)$ since they both apply to infinitely dilute solutions. Assume that electrical contact is made (via a salt-bridge for example) between the solutions in the two half-cells so that the electric potential energies of the solutions is the same. Then $\phi_I = \phi_{II}$, but the concentrations and temperatures need not be the same. We can now subtract Eqs. (3.138) and (3.139) and obtain

$$\Phi_I - \Phi_{II} = \frac{RT}{zF} \ln \left(\frac{c_I}{c_{II}} \right) = (0.0257 \text{ V}) \ln \left(\frac{c_I}{c_{II}} \right). \quad (3.140)$$

Equation (3.140) is the Nernst equation. It relates the difference in the electric potential energy of the electrodes to the difference in the concentrations of silver ions in the two solutions. This electric potential difference can be measured with a volt meter. For example, if $c_I = 2c_{II}$ then $\Phi_I - \Phi_{II} = 0.0178 \text{ V}$ and a small voltage difference has been created between the two electrodes when thermodynamic equilibrium exists between the two half-cells. Thus, we have created a battery, although a rather weak one.

There are a number of different metals that can be used for batteries. The absolute potential on an electrode cannot be measured without changing the chemistry of the half-cell, so all voltages have been standardized relative to a *standard hydrogen half-cell*. A standard hydrogen half-cell uses a porous platinum electrode that serves as a catalyst for the reaction $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$. The platinum electrode is partially submerged in a dilute sulfuric acid (H_2SO_4) solution at a temperature of $T = 298 \text{ K}$. Hydrogen gas (H_2), at a pressure of $P = 1.0 \text{ bar}$, flows over the porous platinum (see Figure 3.7) catalyzing the reaction. The concentration of hydrogen ions (H^+) in the solution is maintained at $c_{\text{H}} = 1.0 \text{ M} = 1.0 \text{ mol/dm}^3$. This standard hydrogen half-cell is connected to a half-cell containing a solid metal electrode and corresponding salt solution (e. g. Cu and Cu_2SO_4 or Zn and $\text{Zn}(\text{NO}_3)_2$). The connection between the solutions is made via a “salt-bridge,” so the potentials in the solutions can equilibrate. The concentration of the metal ion (let us assume Cu^{2+}) is also maintained at $c_{\text{Cu}} = 1.0 \text{ M} = 1.0 \text{ mol/dm}^3$. The potential energy difference between the “hydrogen” (platinum) electrode and the Cu electrode, $\Delta\Phi^0 = \Phi_{\text{Cu}}^0 - \Phi_{\text{H}}^0$, is measured. The potential $\Phi_{\text{H}}^0 \equiv 0$, by convention. In this way, the *standard electrode potential* Φ^0 of various metal half-cells can be determined and tabulated. Some *standard electrode potentials* include $\Phi_{\text{Li}}^0 = -3.03 \text{ V}$, $\Phi_{\text{Zn}}^0 = -0.76 \text{ V}$, $\Phi_{\text{Fe}}^0 = -0.44 \text{ V}$, $\Phi_{\text{H}}^0 = 0.0 \text{ V}$, $\Phi_{\text{Cu}}^0 = +0.34 \text{ V}$, $\Phi_{\text{Ag}}^0 = +0.80 \text{ V}$, and $\Phi_{\text{Au}}^0 = +1.50 \text{ V}$.

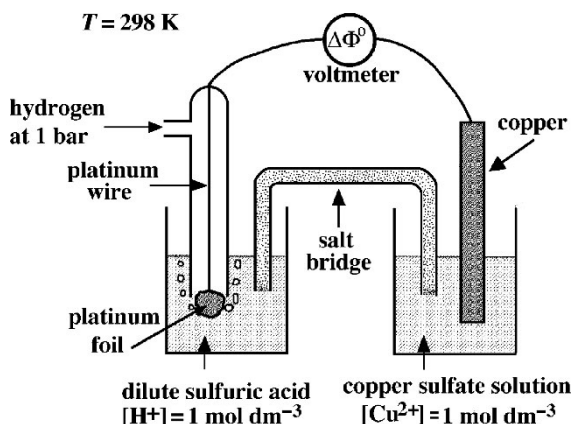


Figure 3.7 The standard hydrogen cell used to measure the *standard electrode potential* of various metals (in this case Cu).

The Nernst equation can also be used to determine the variation of a metal electrode potential from its *standard value* Φ^0 by an analysis similar to that in Eqs. (3.138)–(3.140). We compute equilibrium conditions between the standard metal half-cell (metal ion concentration $c = 1.0 \text{ M}$) and the standard hydrogen half-cell, and then we compute equilibrium conditions between the metal half-cell with metal ion concentration c and the standard hydrogen half-cell. If we then eliminate the parameters related to the standard hydrogen half-cell, we obtain

$$\Phi = \Phi^0 + \frac{RT}{zF} \ln[c], \quad (3.141)$$

where Φ is the potential of the metal electrode, for metal ion concentration c , and Φ^0 is the *standard electrode potential* of the metal.

The *standard electrode potentials* can be used to determine the potential difference of two different metal half-cells. For example, a battery consisting of a Cu half-cell connected to a Zn half-cell, under standard conditions, can generate a voltage $\Phi_{\text{Cu}}^0 - \Phi_{\text{Zn}}^0 = +0.34 \text{ V} - (-0.76 \text{ V}) = 1.10 \text{ V}$.

3.11.2

Cell Potentials and the Nernst Equation

Sports drinks contain electrolytes, such as potassium chloride KCl and sodium chloride NaCl, to help maintain the balance of cations (K^+ and Na^+) and anions (Cl^-) needed for proper cell function. All animal cells are surrounded by a lipid bilayer that is largely inert but contains embedded proteins that form selective ion channels. For example, potassium channels allow passage of potassium ions but effectively block passage of other types of ions. An aqueous solution of K^+ , Na^+ , and Cl^- ions outside a cell with potassium channels will allow the passage of 1000 potassium ions into the interior of the cell for every Na^+ ion allowed passage. As a

consequence of this selective flow of potassium ions, an electric potential energy difference is established across the cell wall. Lipid bilayers have a width of about $\Delta d = 8 \text{ nm}$ and have a capacitance of about $C = 2.0 \text{ } \mu\text{F}/\text{cm}^3$. They can sustain a potential energy difference of up to about 0.2 V before breaking down.

When the system is in equilibrium, the electrochemical potential of K^+ inside, $\mu_{\text{K}}^{\text{in}}$, and outside, $\mu_{\text{K}}^{\text{out}}$, the cell must be equal. This equilibrium condition allows us to derive a Nernst equation that relates the potassium concentrations inside and outside the cell to the potential energy difference across the cell wall. The chemical potential inside the cell is $\mu_{\text{K}}^{\text{in}} = \mu_{\text{K}}^{0,\text{in}} + RT \ln c_{\text{K}}^{\text{in}} + z_{\text{K}} F \phi_{\text{in}}$, where ϕ_{in} is the electric potential inside the cell and $z_{\text{K}} = 1$ is the charge of potassium ions. Outside the cell the chemical potential is $\mu_{\text{K}}^{\text{out}} = \mu_{\text{K}}^{0,\text{out}} + RT \ln c_{\text{K}}^{\text{out}} + z_{\text{K}} F \phi_{\text{out}}$. Since $\mu_{\text{K}}^{0,\text{out}} \approx \mu_{\text{K}}^{0,\text{in}}$ is the energy needed to add one potassium ion to an infinitely dilute solution, we can equate these equations and obtain

$$\Delta\phi = \phi_{\text{in}} - \phi_{\text{out}} = \frac{RT}{z_{\text{K}}F} \ln \left(\frac{c_{\text{K}}^{\text{out}}}{c_{\text{K}}^{\text{in}}} \right). \quad (3.142)$$

The potential energy difference, $\Delta\phi$, needed to maintain the potassium concentration difference is called the *Nernst potential* or *equilibrium potential*. For a body temperature of $T = 98 \text{ }^\circ\text{C} = 295.6 \text{ K}$ the potential difference across the walls of a cell with only potassium channels is $\Delta\phi \approx (0.0255 \text{ V}) \ln (c_{\text{K}}^{\text{out}}/c_{\text{K}}^{\text{in}})$.

The potassium channel is only one of several types of channels that exist in membranes. There are also sodium channels, calcium channels, and other types of ion channels. In addition, there are ion pumps, which play an active role in maintaining a potential difference across cell walls, and often these processes act together. The Nernst equation only applies when equilibrium exists between the intracellular and extracellular fluids.

3.12

Problems

Problem 3.1 Electromagnetic radiation in an evacuated vessel of volume V at equilibrium with the walls at temperature T (blackbody radiation) behaves like a gas of photons having internal energy $U = aVT^4$ and pressure $P = 1/3aT^4$, where a is Stefan's constant. (a) Plot the closed curve in the P - V plane for a Carnot cycle using blackbody radiation. (b) Derive *explicitly* the efficiency of a Carnot engine which uses blackbody radiation as its working substance.

Problem 3.2 A Carnot engine uses a paramagnetic substance as its working substance. The equation of state is $M = \mathfrak{n}DH/T$, where M is the magnetization, H is the magnetic field, \mathfrak{n} is the number of moles, D is a constant determined by the type of substance, and T is the temperature. (a) Show that the internal energy U , and therefore the heat capacity C_M , can only depend on the temperature and not the magnetization. Let us assume that $C_M = C = \text{constant}$. (b) Sketch a typical