ECS@UW Notes on Bard's Electrochemical Methods Chapter 2: Potentials and Thermodynamics of Cells

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Reversibility in Electrochemical Thermodynamics

Definitions of Reversibility

1. **Chemical Reversibility** requires that the reversal of cell current merely reverses the cell reaction (no new reactions appear).
2. **Thermodynamic Reversibility** is a theoretical construct requiring that an infinitesimal reversal in a driving force causes the process to reverse direction. This requires that the system is always at equilibrium and means that traversing a reversible path between two states would require an infinite length of time.
3. **Practical Reversibility** refers to a process which in practice is carried out in a manner under which thermodynamic equations apply to a desired level of accuracy. Whether a process appears reversible or not depends on the ability to detect signs of disequilibrium. Consequently, systems where any change in the driving force is small or the equilibrium is reached rapidly enough compared to measurement time will appear to follow thermodynamic relations.

A cell that is chemically irreversible cannot behave thermodynamically reversibly; however, chemical reversibility does not necessarily imply thermodynamic or practical reversibility

Connection to Gibbs Free Energy and Cell emf

For a reversible (equilibrium) reaction, the maximum net work obtainable from the cell (the Gibbs free energy, ΔG) is given by,

$$|\Delta G| = \text{charge passed} \times \text{reversible potential difference} \tag{2.1.20}$$

$$|\Delta G| = nF|E| \tag{2.1.21}$$

where n is the moles of electrons passed per mole of reactant and F is the charge per mole of electrons (Faraday's constant, F = 96487 C/mol).

To account for the fact that ΔG is a direction-sensitive quantity (i.e., $\Delta G < 0$ is spontaneous) while E is a direction insensitive observation, the construct of the *emf of the cell reaction* is introduced. The cell reaction emf, E_{rxn} is defined as the electrostatic potential of the right electrode with respect to the potential of the left electrode. For the cell, [1]

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[1] Formally, a given chemical reaction can be associated with the cell schematic such that reduction takes place at the right electrode while oxidation occurs at the left electrode.

$$Zn/Zn^{2+}, Cl^-/AgCl/Ag \tag{2.1.17}$$

the potential across the cell is 0.985 V with the Zn as the more negative electrode. Thus, the emf for (2.1.17) is $+0.985V$ and the spontaneous reaction is given by,

$$Zn + 2AgCl \rightarrow Zn^{2+} + 2Ag + 2Cl^- \tag{2.1.22}$$

This convention implies that the emf is positive for a spontaneous reaction such that,

$$\Delta G = -nFE_{rxn} \tag{2.1.24}$$

Half-Reactions and Reduction Potentials

By choosing a well defined reference electrode (typically the *normal hydrogen electrode (NHE)*), a set of half-cell potentials can be defined for different electrochemical reactions.

These standard electrode potentials are tabulated with the half-reactions written as reductions,

$$Ag^+ + e \rightleftarrows Ag \qquad E^0_{Ag^+/Ag} = +0.799\text{V } vs. \text{ NHE} \tag{2.1.33}$$

Appendix C or other books[2] are full of tabulated values.

Concentration Dependence and Formal Potentials

For a general half reaction,

$$\nu_0 O + ne \rightleftarrows \nu_R R \tag{2.1.36}$$

the free energy of the cell reaction is given by,

$$\Delta G = \Delta G^0 + RT \ln \frac{a_R^{\nu_R} a_H^{\nu_{H^+}}}{a_O^{\nu_O} a_{H_2}^{\nu_{H_2}}} \tag{2.1.38}$$

which since $\Delta G = -nFE_{rxn}$ and $a_{H^+} = a_{H_2} = 1$ becomes,

$$E = E^0 + \frac{RT}{nF} \ln \frac{a_R^{\nu_R}}{a_O^{\nu_O}}. \tag{2.1.40}$$

This expression is called the *Nernst Equation*.

This relation can be simplified by introducing the *formal potential*, $E^{0'}$, since it is often inconvenient to deal with activities ($a_R = \gamma_R[R]$ where γ_R is the activity coefficient for R).[3] This results in,

$$E = E^{0'} + \frac{RT}{nF} \ln \frac{[R]}{[O]} \tag{2.1.44}$$

where

$$E^{0'} = E^0 + \frac{RT}{nF} \ln \frac{\gamma_R}{\gamma_O} \tag{2.1.45}$$

[2] Allen J Bard, Roger Parsons, Joseph Jordan, and International Union of Pure and Applied Chemistry. *Standard potentials in aqueous solution*. New York : M. Dekker, 1985

[3] The values for standard potentials for half-reactions are actually determined by measuring formal potentials at different ionic strengths and extrapolating to unit activity (zero ionic strength)

A More Detailed View of Interfacial Potential Differences

Inner Potentials and Charge Distribution in a Conductor

The potential at any point within a phase is defined as the work required to bring a unit positive charge from an infinite distance to the point (x,y,z),

$$\phi(x,y,z) = \int_{\infty}^{x,y,z} -\mathbf{E}\cdot d\mathbf{l} \tag{2.2.1}$$

where **E** is the electric field strength and **l** is tangent to the direction of movement.

For a conducting phase, the mobility of charge carriers ensures that (when no net current flows through the conductor) there is no net movement of charge carriers. This means that the electric field at all interior points is necessarily zero. The potential of this phase is known as the *inner potential*.

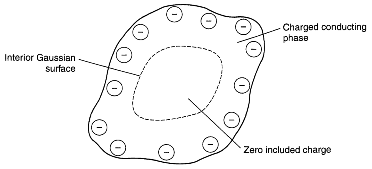

Figure 2.2.1 Gauss' law means that the net charge in the interior of a conductor is zero implying that any excess charge must reside on the surface.

Interactions Between Conducting Phases

The interface between two conductors - a metal particle in an electrolyte, for example - introduces a more complex charge distribution where changes in the charge of one phase affect the potential of the neighboring phase as well.

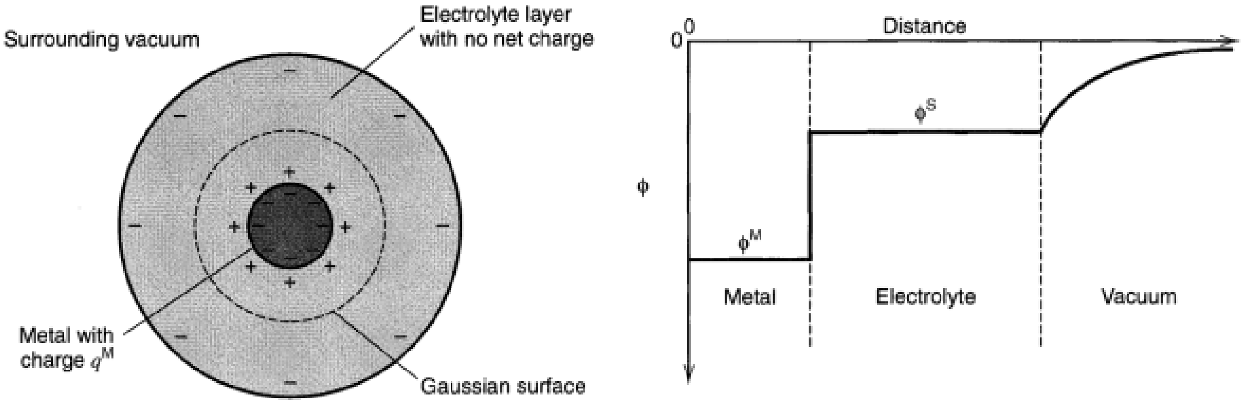

Figure 2.2.2 and 2.2.3 We know from Gauss' Law that the excess metal charge q^M lies on the surface of the metal particle. Extending the Gaussian surface to just inside the electrolyte phase, we determine that the excess positive charge in the electrolyte must be distributed at the electrolyte-electrode interface such that $q^M = -q^S$ is balanced (called an *electrochemical double layer*). This means the excess negative charge is distributed at the outer electrolyte surface.

The interfacial potential difference, $\Delta\phi = \phi^M - \phi^S$, depends on the charge density at the interface and can affect the kinetics of a reaction at the surface. We can study the effects of individual $\Delta\phi$'s by using a constant potential reference electrode.

Electrochemical Potentials

The electrochemical potential, $\bar{\mu}_i^\alpha$, of a species, i, in phase, α, represents the energy state of that species. It differs from the chemical potential, μ_i^α, by the inclusion of the potential, ϕ, surrounding the species,

$$\bar{\mu}_i^\alpha = \mu_i^\alpha + z_i F \phi^\alpha \tag{2.2.6}$$

Important properties of the Electrochemical Potential [4]

1. For an uncharged species: $\bar{\mu}_i^\alpha = \mu_i^\alpha$
2. For any substance: $\mu_i^\alpha = \mu_i^{0\alpha} + RT \ln a_i^\alpha$ where $\mu_i^{0\alpha}$ is the standard chemical potential, and a_i^α is the activity of species i in phase α.
3. For a pure phase at unit activity (e.g., solid Zn, AgCl, Ag, or H_2 at unit fugacity): $\bar{\mu}_i^\alpha = \mu_i^{0\alpha}$.
4. For electrons in a metal ($z = -1$): $\bar{\mu}_e^\alpha = \mu_e^{0\alpha} - F\phi^\alpha$. Activity effects can be disregarded because the electron concentration never changes appreciably.
5. For equilibrium of species i between phases α and β: $\bar{\mu}_i^\alpha = \bar{\mu}_i^\beta$.

These properties result in a few interesting observations:

For reactions in a single, conducting phase, ϕ is constant everywhere so only the chemical potentials remain. For reactions without charge transfer, the ϕ terms again cancel out and the final result depends only on the chemical potentials.

In general, however, the ϕ terms will not cancel and calculations of the cell potential will require using the electrochemical potential. For an example of how to do this, see (2.2.20 - 2.2.27) or Problem 2.8 at the end of this document.

Liquid Junction Potentials

A liquid junction potential occurs when two solutions with different concentrations are in contact. At the junction between the two solutions a concentration gradient drives the movement of ions which is in balance with the electric field. This results in a steady state potential which is not an equilibrium process sometimes referred to as the *diffusion potential*.

[4] Found on Electrochemical Methods Page 61

Three Types of Liquid Junctions [5]

1. Two solutions of the same electrolye at different concentrations
2. Two solutions at the same concentration with different electrolytes having an ion in common
3. Two solutions not satisfying conditions 1 or 2.

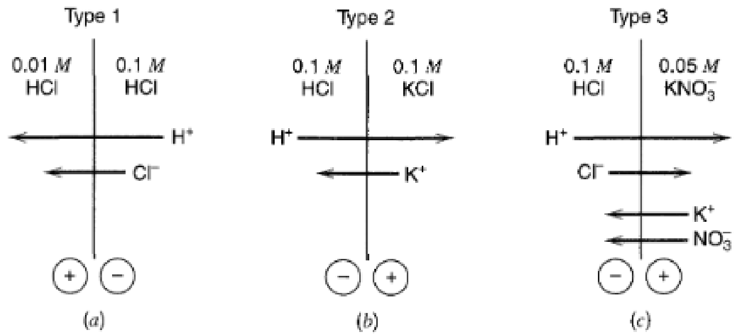

Figure 2.3.2 Various types of liquid junctions. Direction and relative magnitude of the ionic flow for each species is indicated by the arrows. Circled signs identify the polarity of the liquid junction potential in each type.

Ionic Current, Conductivity, and Transference Numbers

The movement of ions through solution is key to any electrochemical system and the measurements of the solution resistance (or its inverse, the conductance, L) can be related to the *conductivity*, κ of the solution,

$$L = \kappa \frac{A}{l} \tag{2.3.8}$$

where A is the cross sectional area and l is the length of the segment.

κ is a combination of each of the different species in the solution, where the ionic charge, concentration, and mobility all affect its resistance to movement,

$$\kappa = F \sum_i |z_i| u_i C_i \tag{2.3.10}$$

where $|z_i|$ is the magnitude of the charge, u_i is the mobility, and C_i is the concentration of each species i. Mobility is the terminal velocity of an ionic species in response to an electric field of unit magnitude. When the electric field is applied, the ion will accelerate until drag forces equal that of the imposed electrical forces. As such, it is intuitive that this will depend on the charge and radius of the ion, as well

[5] Found on Electrochemical Methods Page 64

as the viscosity of the medium through which it is travelling, as seen below.

$$u_i = \frac{v}{\xi} = \frac{|z_i|e}{6\pi\eta r} \tag{2.3.9}$$

The *transference number*, t_i, is defined as the amount of current carried by an individual species i in an electrolyte solution.[6]

$$t_i = \frac{|z_i|u_i C_i}{\sum_j |z_j|u_j C_j} \tag{2.3.11}$$

In a simple solution with just one positive and one negative ionic species (KCl, $CaCl_2$, HNO_3, etc.) an equivalent conductivity can be defined as

$$\Lambda = \frac{\kappa}{C_{eq}} \tag{2.3.12}$$

where C_{eq} is the concentration of the positive or negative charges. For these simple solutions, the transference number can be written as

$$t_i = \frac{u_i}{u_+ + u_-} \tag{2.3.17}$$

Calculating Liquid Junction Potentials

Junctions potentials, when they are significant enough for consideration, can be found by separating the charge transport at the junction from the reactions occuring at each electrode. A concentration cell will be considered in this section, such as 2.2.3.

$(-)Pt/H_2(1atm)/H^+, Cl^-(\alpha)/H^+, Cl^-(\beta)/H_2(1atm)/Pt'(+)$

Although the reactions may be at equilibrium, and have a null Gibbs free energy, transport through the junction is not at equilibrium, despite also having a null Gibbs free energy. A cell potential can be written generally as,

$$E_{cell} = E_{Nernst} + E_j \tag{2.3.26}$$

As an example, let us treat a Type 1 junction with a 1:1 electrolyte, such as HCl. Since activity coefficients for single ions cannot be rigorously determined, *mean ionic activity coefficients* are used as follows, $a^{\alpha}_{H^+} = a^{\alpha}_{Cl^-} = a_1 and a^{\beta}_{H^+} = a^{\beta}_{Cl^-} = a_2$. Through which E_j can be found by:

$$E_j = (\phi^{\beta} - \phi^{\alpha}) = (t_+ - t_-)\frac{RT}{F} ln\frac{a_1}{a_2} \tag{2.3.30}$$

[7]

Type 2 and 3 junctions must be treated as having smoothly varying compositions over an infinite number of volume elements, where each mole of charge passed is counterbalanced by $t_i/|z_i|$ moles of

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[6] Transference numbers are typically measured by quantifying the concentration changes caused by electrolysis (in a $Pt/H_2/H^+ \underset{a_1}{,} Cl^-/H^+ \underset{a_2}{,} Cl^-/H_2/Pt'$ cell for example). See Problem 2.11

[7] Here it was assumed that transference numbers were constant throughout the junction, which is generally valid for Type 1 junctions.

species i. If the standard chemical potential, μ_i^0 is the same in both α and β, then the junction potential is given by:

$$E_j = \phi^\beta - \phi^\alpha = \frac{-RT}{F} \sum_i \int_\alpha^\beta \frac{t_i}{z_i} dlna_i \tag{2.3.36}$$

Under assumptions that (a) ionic species act ideally and (b) species follow a linear concentration profile, the junction potential can be estimated by the *Henderson equation*

$$E_j = \frac{\sum_i \frac{|z_i|u_i}{z_i}[C_i(\beta) - C_i(\alpha)]}{\sum_i \frac{|z_i|u_i}{z_i}[C_i(\beta) - C_i(\alpha)]} \frac{RT}{F} ln \frac{\sum_i |z_i|u_i C_i(\alpha)}{\sum_i |z_i|u_i C_i(\beta)} \tag{2.3.39}$$

Liquid junction potentials can be minimized by including a high ionic strength section, or salt bridge. The salt bridge is often made with KCl, KNO_3, or CsCl. Junctions with immiscible fluids are also interesting for their applications as models for biological membranes. The expression for cell potential then becomes

$$\phi^\beta - \phi^\alpha = -[\delta G^0_{transfer,i} \alpha - > \beta \tag{2.3.47}$$

Chem

Add Section

Selective Electrodes

At an interface where only a single ion can penetrate, such as a selective membrane, all current is carried by that one species. If the activity of a species is held constant on one side of the membrane, then the potential across the membrane will be Nernstian in nature. This feature is often levereged for electrochemical sensors. This effect was first studied using thin glass membranes, where current in the bulk is carried by alkali ions, like Na^+, but there is an interfacial region of the glass that is hydrated where transfer is facilitated by swelling that comes with glass hydration.

Problems!

Problem 2.2

Several hydrocarbons and carbon monoxide have been studied as possible fuels for use in fuel cells. From thermodynamic data (see below), derive E^0s for the following reactions at 25^{o}C:

(a) $CO(g) + H_2O(l) \rightarrow CO_2(g) + 2H^+ + 2e$

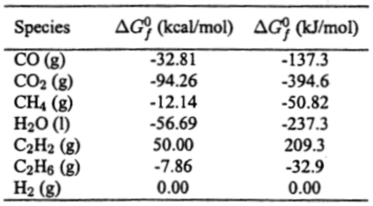
(b) $CH_4(g) + 2H_2O(l) \rightarrow CO_2(g) + 8H^+ + 8e$

(c) C_2H_6(g) + $4H_2O$(l) $\rightarrow$ $2CO_2$(g) + $14H^+$ + 14e

(d) C_2H_2(g) + $4H_2O$(l) $\rightarrow$ $2CO_2$(g) + $10H^+$ + 10e

Even though a reversible emf could not be established (Why not?), which half-cell would ideally yield the highest cell voltage when coupled with the standard oxygen half-cell in acid solution? Which of the above fuels could yield the highest net work per mole of fuel oxidized? Which would give the most per gram?

Note: The free energies needed to solve this problem are tabulated here.



Species	ΔG_f^0 (kcal/mol)	ΔG_f^0 (kJ/mol)
CO (g)	-32.81	-137.3
CO_2 (g)	-94.26	-394.6
CH_4 (g)	-12.14	-50.82
H_2O (l)	-56.69	-237.3
C_2H_2 (g)	50.00	209.3
C_2H_6 (g)	-7.86	-32.9
H_2 (g)	0.00	0.00

Answer:

Combining the half-reactions with the hydrogen reduction half-reaction (H^+ + e^- $\rightarrow$ H_2(g)) allows us to calculate the free energy change for the full reaction. This gives us E^0_{rxn} and E^0 through,

$$E^0_{rxn} = -\frac{\Delta G^0}{nF}$$

(a) CO(g) + H_2O(l) $\rightarrow$ CO_2(g) + $2H^+$ + 2e

$$\begin{aligned}
&\mathrm{CO(g) + H_2O(l) \rightarrow CO_2(g) + H_2(g)} \\
&\Delta G^0 = \Delta G^0_{\mathrm{CO_2}} + \Delta G^0_{\mathrm{H_2}} - \Delta G^0_{\mathrm{CO}} - \Delta G^0_{\mathrm{H_2O}} \\
&\Delta G^0 = -394.6 - 0 + 137.3 + 237.3 = -20\mathrm{kJ/mol} \\
&E^0_{rxn} = -\frac{-20\mathrm{kJ/mol}}{2 \times 96487\mathrm{C/mol}} = 0.104V = E^0_{H^+/H_2} - E^0_{CO_2/CO}
\end{aligned}$$

$$E^0_{CO_2/CO} = -0.104V$$

(b) CH_4(g) + $2H_2O$(l) $\rightarrow$ CO_2(g) + $8H^+$ + 8e

$$\begin{aligned}
&\mathrm{CH_4(g) + 2H_2O(l) \rightarrow CO_2(g) + 4H_2(g)} \\
&\Delta G^0 = \Delta G^0_{\mathrm{CO_2}} + 4\Delta G^0_{\mathrm{H_2}} - \Delta G^0_{\mathrm{CH_4}} - 2\Delta G^0_{\mathrm{H_2O}} \\
&\Delta G^0 = -394.6 - 0 + 50.82 + (2 \times 237.3) = 130.82\mathrm{kJ/mol} \\
&E^0_{rxn} = -\frac{130.82\mathrm{kJ/mol}}{8 \times 96487\mathrm{C/mol}} = -0.169V = E^0_{H^+/H_2} - E^0_{CO_2/CH_4}
\end{aligned}$$

$$E^0_{CO_2/CH_4} = 0.169V$$

(c) C_2H_6(g) + $4H_2O$(l) $\rightarrow$ $2CO_2$(g) + $14H^+$ + 14e

$$\begin{aligned}
&\mathrm{C_2H_6(g) + 4H_2O(l) \rightarrow 2CO_2(g) + 7H_2(g)} \\
&\Delta G^0 = 2\Delta G^0_{\mathrm{CO_2}} + 7\Delta G^0_{\mathrm{H_2}} - \Delta G^0_{\mathrm{C_2H_6}} - 4\Delta G^0_{\mathrm{H_2O}} \\
&\Delta G^0 = (2 \times -394.6) - 0 + 32.9 + (7 \times 237.3) = 904.8\mathrm{kJ/mol} \\
&E^0_{rxn} = -\frac{904.8\mathrm{kJ/mol}}{14 \times 96487\mathrm{C/mol}} = -0.669V = E^0_{H^+/H_2} - E^0_{CO_2/C_2H_6}
\end{aligned}$$

$$E^0_{CO_2/C_2H_6} = 0.669V$$

(d) $C_2H_2(g) + 4H_2O(l) \rightarrow 2CO_2(g) + 10H^+ + 10e$

$$C_2H_2(g) + 4H_2O(l) \rightarrow 2CO_2(g) + 5H_2(g)$$
$$\Delta G^0 = 2\Delta G^0_{CO_2} + 5\Delta G^0_{H_2} - \Delta G^0_{C_2H_2} - 4\Delta G^0_{H_2O}$$
$$\Delta G^0 = (2 \times -394.6) + 0 - 209.3 + (5 \times 237.3) = 188\text{kJ/mol}$$
$$E^0_{rxn} = -\frac{188\text{kJ/mol}}{10 \times 96487\text{C/mol}} = 0.195V = E^0_{H^+/H_2} - E^0_{CO_2/C_2H_2}$$

$$E^0_{CO_2/C_2H_2} = -0.195V$$

Problem 2.4

What are the cell reactions and their emfs in the following systems?
Are the reactions spontaneous? Assume that all systems are aqueous.

(a) $Ag/AgCl/K^+, Cl^-(1\text{ M})/Hg_2Cl_2/Hg$

(b) $Pt/Fe^{3+}(0.01\text{ M}), Fe^{2+}(0.1\text{ M}), HCl(1\text{ M})//Cu^{2+}(0.1\text{ M}), HCl(1\text{ M})/Cu$

(c) $Pt/H_2(1\text{ atm})/H^+, Cl^-(0.1\text{ M})//H^+, C, l^-(0.1\text{ M})/O_2(0.2\text{ atm})/Pt$

(d) $Pt/H_2(1\text{ atm})/Na^+, OH^-(0.1\text{ M})//Na^+, OH^-(0.1\text{ M})/O_2(0.2\text{ atm})/Pt$

(e) $Ag/AgCl/K^+, Cl^-(1\text{ M})//K^+, Cl^-(0.1\text{ M})/AgCl/Ag$

(f) $Pt/Ce^{3+}(0.01\text{ M}), Ce^{4+}(0.1\text{ M}), H_2SO_4(1\text{ M})//Fe^{2+}(0.01\text{ M}), Fe^{3+}(0.1\text{ M}), HCl(1\text{ M})/Pt$

Answer:

(a) $Ag/AgCl/K^+, Cl^-(1M)/Hg_2Cl_2/Hg$

$$\begin{array}{lr} Hg_2Cl_2 + 2e^- \rightleftarrows 2Hg + 2AgCl & E^o_c = 0.268V \\ \underline{AgCl + e^- \rightleftarrows Ag + Cl^-} & \underline{E^o_a = 0.222V} \\ Hg_2Cl_2 + 2Ag \rightleftarrows 2Hg + 2AgCl & E^o_{rxn} = E^o_c - E^o_a = 0.0456V \\ & \delta G < 0; \textbf{reaction is spontaneous} \end{array}$$

(b) $Pt/Fe^{3+}(0.01\text{ M}), Fe^{2+}(0.1\text{ M}), HCl(1\text{ M})//Cu^{2+}(0.1\text{ M}), HCl(1\text{ M})/Cu$

$$\begin{array}{ll} Cu^{2+} + 2e^- \rightleftarrows Cu & E^o_c = 0.340V \\ Fe^{3+} + e^- \rightleftarrows Fe^{2+} & E^o_a = 0.769V \end{array}$$

Adjusting for conditions:

$$E_c = 0.340 + \frac{0.0257}{2}\ln[Cu^{2+}] = 0.310V$$
$$E_a = 0.769 + \frac{0.0257}{1}\ln\frac{[Fe^{3+}]}{[Fe^{2+}]} = 0.710V$$

$E_{rxn} = E_c - E_a = -.40V$ $\quad\delta G < 0;$ **reaction is not spontaneous**

(c) $Pt/H_2(1\text{ atm})/H^+,Cl^-(0.1\text{ M})//H^+,Cl^-(0.1\text{ M})/O_2(0.2\text{ atm})/Pt$

$$4H^+ + O_2 + 4e^- \rightleftarrows 2H_2O \qquad E_c^o = 1.229V$$
$$2H^+ + 2e^- \rightleftarrows H_2 \qquad E_a^o = 0.000V$$

Adjusting for conditions:

$$E_c = 1.229 + \frac{0.0257}{4}\ln(P_{O_2}[H^+]^4) = 1.159V$$
$$E_a = 0.000 + \frac{0.0257}{2}\ln\frac{[H^+]^2}{P_{H2}} = -0.059V$$

$E_{rxn} = E_c - E_a = 1.219V$ $\qquad \delta G < 0;$ **reaction is spontaneous**

(d) $Pt/H_2(1\text{ atm})/Na^+,OH^-(0.1\text{ M})//Na^+,OH^-(0.1\text{ M})/O_2(0.2\text{ atm})/Pt$

$$O_2 + 2H_2O + 4e^- \rightleftarrows 4OH^- \qquad E_c^o = 0.401V$$
$$2H_2O + 2e^- \rightleftarrows H_2 + 2OH^- \qquad E_a^o = 0.828V$$

Adjusting for conditions:

$$E_c = 0.401 + \frac{0.0591}{4}\log\frac{1}{P_{H2}^2[OH^-]^4} = 0.45V$$
$$E_a = -0.828 + \frac{0.0591}{2}\log\frac{1}{P_{H2}[OH^-]^2} = -0.769V$$

$E_{rxn} = E_c - E_a = 1.219V$ $\qquad \delta G < 0;$ **reaction is spontaneous**

(e) $Ag/AgCl/K^+,Cl^-(1\text{ M})//K^+,Cl^-(0.1\text{ M})/AgCl/Ag$

$$AgCl + e^- \rightleftarrows Ag + Cl^- \qquad E_c^o = E_a^0 0.2223V$$

Adjusting for conditions:

$$E_c = 0.222 + 0.0257\ln\frac{1}{[Cl^-]} = 0.281V$$
$$E_a = 0.222 + 0.0257\ln\frac{1}{[Cl^-]} = 0.222V$$

$E_{rxn} = E_c - E_a = 0.059V$ $\qquad \delta G < 0;$ **reaction is spontaneous**

(f) $Pt/Ce^{3+}(0.01\text{ M}), Ce^{4+}(0.1\text{ M}), H_2SO_4(1\text{ M})//Fe^{2+}(0.01\text{ M}), Fe^{3+}(0.1\text{ M}), HCl(1\text{ M})/Pt$

$$Fe^{3+} + e^- \rightleftarrows Fe^{2+} \qquad E_c^o = 0.77V$$
$$Ce^{4+} + e^- \rightleftarrows Ce^{3+} \qquad E_a^o = 1.61V$$

Adjusting for conditions:

$$E_c = 0.77 + 0.0257\ln\frac{[Fe^{3+}]}{[Fe^{2+}]} = 0.829V$$
$$E_a = 1.61 + 0.0257\ln\frac{[Ce^{4+}]}{[Ce^{3+}]} = 1.669V$$

$E_{rxn} = E_c - E_a = -0.84V$ $\qquad \delta G > 0;$ **reaction is not spontaneous**

Problem 2.8

Consider the cell:

$$Cu/M/Fe^{2+}, Fe^{3+}, H^{+}//Cl^{-}/AgCl/Ag/Cu'$$

Would the cell potential be independent of the identity of M (e.g. graphite, gold, platinum) as long as M is chemically inert?

Answer:

Combining the two half-reactions on the right electrode ($AgCl + e(Cu') \rightleftarrows Ag + Cl^{-}$) and the left electrode ($Fe^{2+} \rightleftarrows Fe^{3+} + e(Cu)$, the overall reaction is given by,

$$AgCl + Fe^{2+} + e(Cu') \rightleftarrows Ag + Cl^{-} + Fe^{3+} + e(Cu) \tag{1}$$

At equilibrium, the electrochemical potentials of species in neighboring phases must be equal.

$$\bar{\mu}_e^{Cu} = \bar{\mu}_e^{M} \tag{2}$$

$$\bar{\mu}_{Cl^-}^{AgCl} = \bar{\mu}_{Cl^-}^{s} \tag{3}$$

$$\bar{\mu}_e^{Ag} = \bar{\mu}_e^{Cu'} \tag{4}$$

And the half-reactions must be in equilibrium,

$$\bar{\mu}_{Fe^{2+}}^{s} = \bar{\mu}_{Fe^{3+}}^{s} + \bar{\mu}_e^{M} \tag{5}$$

$$\bar{\mu}_{Ag^+}^{AgCl} + \bar{\mu}_e^{Ag} = \bar{\mu}_{Ag}^{Ag} \tag{6}$$

Combining these equalities gives,

$$\begin{aligned}
\bar{\mu}_{Cl^-}^{AgCl} + \bar{\mu}_{Fe^{2+}}^{s} + \bar{\mu}_{Ag^+}^{AgCl} + \bar{\mu}_e^{Ag} &= \bar{\mu}_{Cl^-}^{s} + \bar{\mu}_{Fe^{3+}}^{s} + \bar{\mu}_e^{M} + \bar{\mu}_{Ag}^{Ag} \\
\bar{\mu}_{Fe^{2+}}^{s} + \bar{\mu}_{AgCl}^{AgCl} + \bar{\mu}_e^{Cu'} &= \bar{\mu}_{Cl^-}^{s} + \bar{\mu}_{Fe^{3+}}^{s} + \bar{\mu}_e^{Cu} + \bar{\mu}_{Ag}^{Ag}
\end{aligned} \tag{7}$$

Solving for the cell potential gives,

$$\begin{aligned}
\bar{\mu}_e^{Cu'} - \bar{\mu}_e^{Cu} &= -FE \\
&= -\bar{\mu}_{Fe^{2+}}^{0s} - RT\ln a_{Fe^{2+}}^{s} - \bar{\mu}_{AgCl}^{0AgCl} + \bar{\mu}_{Cl^-}^{0s} \\
&\quad + RT\ln a_{Cl^-}^{s} + \bar{\mu}_{Fe^{3+}}^{0s} + RT\ln a_{Fe^{3+}}^{s} + \bar{\mu}_{Ag}^{0Ag}
\end{aligned} \tag{8}$$

$$E = \frac{1}{F}\left(\bar{\mu}_{Fe^{2+}}^{0s} + \bar{\mu}_{AgCl}^{0AgCl} - \bar{\mu}_{Cl^-}^{0s} - \bar{\mu}_{Fe^{3+}}^{0s} - \bar{\mu}_{Ag}^{0Ag} + RT\ln\left(\frac{a_{Fe^{2+}}^{s}}{a_{Cl^-}^{s}a_{Fe^{3+}}^{s}}\right)\right)$$

Since the cell potential doesn't depend on anything related to M, the cell potential is totally independent from the choice of M.

Problem 2.11

Transference numbers are often measured by the Hittorf method as illustrated in this problem. Consider the three compartment cell:

$$\ominus Ag/AgNO_3(0.100M)//AgNO_3(0.100M)//AgNO_3(0.100M)/Ag\oplus$$

where the double slashes (//) signify sintered glass disks that divide the compartments and prevent mixing, but not ionic movement. The volume of $AgNO_3$ solution in each compartment is 25.00 mL. An external power supply is connected to the cell with the polarity shown, and current is applied until 96.5 C have passed, causing Ag to deposit on the left Ag electrode and Ag to dissolve from the right Ag electrode.

(a) How many grams of Ag have deposited on the left electrode? How many mmol of Ag have deposited?

(b) If the transference number for Ag^+ were 1.00 (i.e. $t_{Ag^+} = 1.00, t_{NO_3^-} = 0.00$), what would the concentrations of Ag^+ be in the three compartments after electrolysis?

(c) Suppose the transference number for Ag^+ were 0.00 (i.e. $t_{Ag^+} = 0.00, t_{NO_3^-} = 1.00$), what would the concentrations of Ag^+ be in the three compartments after electrolysis?

(d) In an actual experiment like this, it is found experimentally that the concentrations of Ag^+ in the anode compartment (right) has increased to $0.121M$. Calculate t_{Ag^+} and $t_{NO_3^-}$.

Answer:

(a) 96.5 C have passed meaning $\frac{96.5\text{ C}}{94687\text{ C/mol}} = 1$ mmol or 1 mmol $\times$ 107.86 g/mol $=$ 108 mg Ag have deposited.

(b) If the transference number for Ag^+ were 1.00, all of the current would be carried by the silver ions. Since equal amounts of silver are being deposited on the left electrode and dissolved from the right electrode, the concentration of Ag^+ would be the same in each of the three compartments.

(c) If the transference number for Ag^+ were 0.00, all of the current would be carried by the NO_3^- ions. Since silver is being deposited in the left electrode and dissolved from the right electrode, the amount of silver in the left electrode would have decreased by 1 mmol to 1.5 mmol (0.06 M), while the right compartment would increase by 1 mmol to 2.5 mmol (0.14 M). The concentration in the center compartment would stay the same.

(d) If experiments find that the concentration of Ag^+ ions has increased in the right side to 0.121 M, that means 0.525 mmol of silver (out of 1.00 mmol dissolved) has stayed in the R compartment (i.e. 47.5% of the current was carried by the Ag^+). This means $t_{NO_3^-} = 0.525$ and $t_{Ag^+} = 0.475$.

References

Allen J Bard, Roger Parsons, Joseph Jordan, and International Union of Pure and Applied Chemistry. *Standard potentials in aqueous solution*. New York : M. Dekker, 1985.