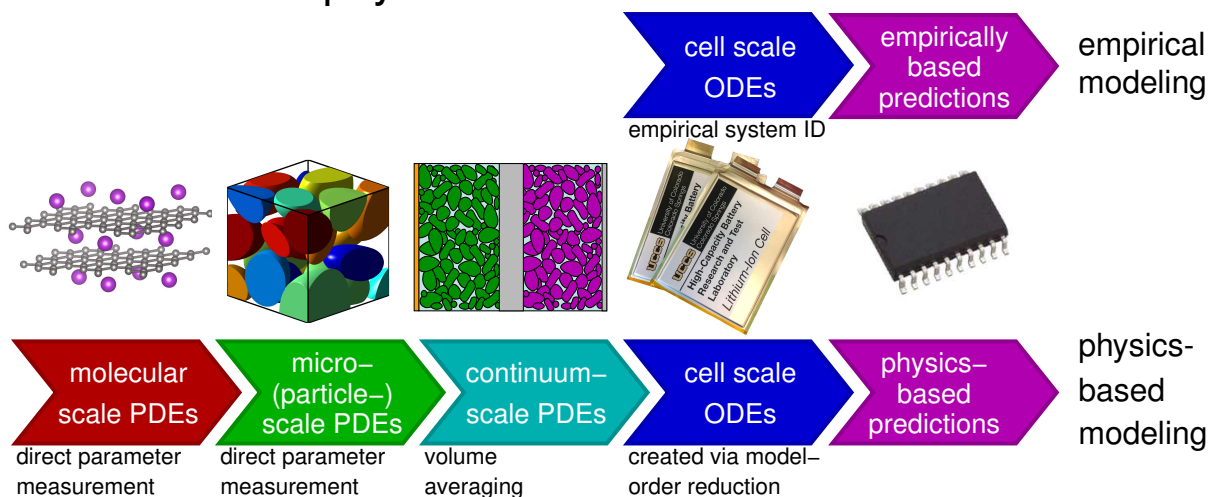


Microscale Cell Models

3.1: Chapter goals

- Our focus in this course is on creating generic mathematical models of lithium-ion cells, on finding the parameters for these models, and on simulating these models to predict cell performance.
- We have already seen a phenomenological approach to modeling, but we now turn to physics-based models.



- Empirical models (e.g., equivalent circuits) can match cell input-output and aging behavior well, but give limited predictions.
- Physics-based models are more difficult to formulate, but allow enhanced monitoring and prediction of individual mechanisms.
- The physics based-models start at the molecular scale (which we do not consider in this course).
 - Parameters of the models can be directly measured at this level.

- The next scale is the micro-scale, where we look at homogeneous materials: what happens in the solid electrode particles, and what happens in the electrolyte, *as considered separately*.
 - We can think of this scale as a volume average of the molecular scale, where impurities and imperfections are blended in, to create a homogenous material.
 - Model parameters also directly measured via lab tests at this level.
- The next scale is the continuum scale, where each volume considered in the volume average contains parts of the solid electrode material and parts of the electrolyte.
 - Modeling an object as a continuum assumes that the substance of the object completely fills the space it occupies, ignoring (averaging out) the details of the porous microstructure.
 - These “phases” are still considered separately, but their interactions within the volume must be factored in.
 - We will look at volume average approaches, with some assumptions. Detailed micro-scale simulations and surrogate modeling (curve fitting) are needed for better models.
- The next scale up converts the PDEs to a coupled set of ODEs, suitable for rapid simulation and controls purposes.
 - The final complexity of these cell-scale ODEs is similar to those created via empirical modeling, but the predictive power is much greater (can extrapolate beyond the data used to create the model, as the physics allows us to do so).
- Ultimately, the physics-based path is MUCH harder, but MUCH better.

Goals: Prove microscale model equations

- This chapter focuses on developing micro-scale models introducing some concepts in vector calculus and physical chemistry to do so.
 - Subsequent chapters focus on converting these to continuum models and cell-scale ODEs.
- In particular, our goal in this chapter is to develop the following model:

1. Charge conservation in the homogeneous solid:

$$\nabla \cdot \mathbf{i}_s = \nabla \cdot (-\sigma \nabla \phi_s) = 0.$$

2. Mass conservation in the homogeneous solid:

$$\frac{\partial c_s}{\partial t} = \nabla \cdot (D_s \nabla c_s).$$

3. Mass conservation in the homogeneous electrolyte:

$$\frac{\partial c_e}{\partial t} = \nabla \cdot (D_e \nabla c_e) - \frac{\mathbf{i}_e \cdot \nabla t_+^0}{F} - \nabla \cdot (c_e \mathbf{v}_0).$$

4. Charge conservation in the homogeneous electrolyte:

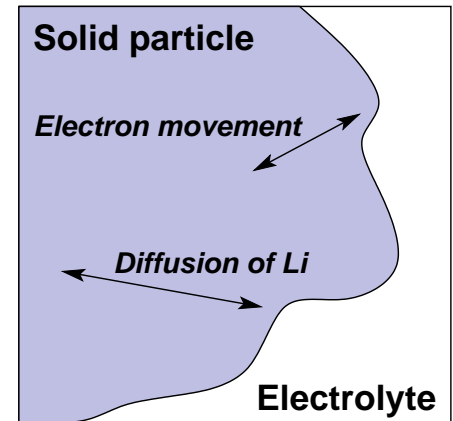
$$\nabla \cdot \mathbf{i}_e = \nabla \cdot \left(-\kappa \nabla \phi_e - \frac{2\kappa RT}{F} \left(1 + \frac{\partial \ln f_{\pm}}{\partial \ln c_e} \right) (t_+^0 - 1) \nabla \ln c_e \right) = 0.$$

5. Lithium movement between the solid and electrolyte phases:

$$j = k_0 c_e^{1-\alpha} (c_{s,\max} - c_{s,e})^{1-\alpha} c_{s,e}^{\alpha} \left\{ \exp \left(\frac{(1-\alpha)F}{RT} \eta \right) - \exp \left(-\frac{\alpha F}{RT} \eta \right) \right\}.$$

3.2: Charge conservation in solid

- We begin deriving the microscale equations for a lithium-ion cell with those that describe charge and mass conservation in the solid.
- These do not require knowledge of physical chemistry, so are the easier to understand and develop.
- We'll then need to look at some concepts from physical chemistry before proceeding to prove the remaining three equations.



Point form of Ohm's law

- We wish to solve for the electron current through the homogeneous solid matrix of the electrodes.

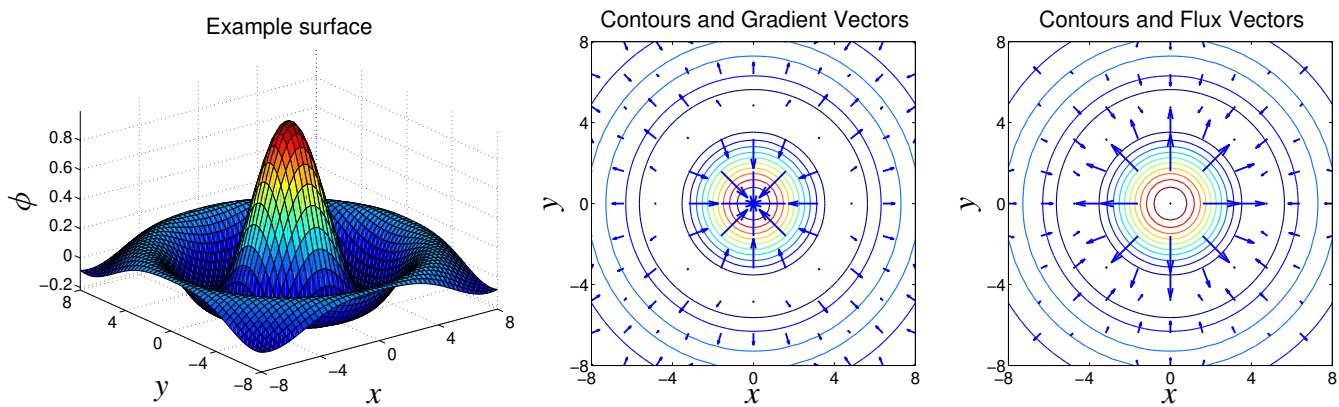
ASSUME: A linear media where Ohm's law applies.

- That is, current density is proportional to the applied electric field: $\mathbf{i} = \sigma \mathbf{E}$, where
 - $\mathbf{i}(x, y, z, t)$ [A m^{-2}] is the (vector) current density flowing through a representative cross-sectional area centered at a given location;
 - $\sigma(x, y, z, t)$ [S m^{-1}] is a material-dependent *conductivity* value;
 - $\mathbf{E}(x, y, z, t)$ [V m^{-1}] is the (vector) electric field at that location.

ASSUME: If we assume that magnetic effects are negligible, Maxwell tells us that

$$\mathbf{E} = -\nabla\phi,$$

and so $\mathbf{i} = -\sigma \nabla\phi$.



The continuity equation (Kirchhoff's current law)

- We apply Ohm's law to a representative homogeneous volume V with boundary surface S and with current density \mathbf{i} directed into the region.
- The net current i [A] *into* the region is the current flux

$$i = - \oiint_S \mathbf{i} \cdot \hat{\mathbf{n}} \, dS = dQ/dt,$$

the minus sign arising because our usual convention that the normal $\hat{\mathbf{n}}$ points *out* of the region.

- A net charge dQ [C] is supplied to V by the current within a time dt .
- Thus, the net charge in the region changes in time dt by an amount

$$\frac{dQ}{dt} = \frac{d}{dt} \iiint_V \rho_V \, dV \text{ and hence}$$

$$\oiint_S \mathbf{i} \cdot \hat{\mathbf{n}} \, dS = - \frac{d}{dt} \iiint_V \rho_V \, dV,$$

where ρ_V [C m^{-3}] is the *charge density* (of positive charges) within region V .

- This is the integral form of the so-called *equation of continuity*.
 - It is equivalent to a statement of conservation of charge.

- We've implicitly assumed that charge within V can be changed *only* by allowing it to enter or exit through the boundary.
 - Charge already contained in V is neither created nor destroyed.
- To arrive at a point form of the equation, define the *divergence* of a vector field \mathbf{F} as $\text{div } \mathbf{F} \equiv \nabla \cdot \mathbf{F} = \lim_{\Delta V \rightarrow 0} \frac{1}{\Delta V} \oiint_S \mathbf{F} \cdot \hat{\mathbf{n}} dS$.
- $\hat{\mathbf{n}}$ is a unit vector, perpendicular to the surface S , pointing *outward*.
 - In rectangular (x, y, z) coordinates,

$$\nabla \cdot \mathbf{F} = \frac{\partial F_x}{\partial x} + \frac{\partial F_y}{\partial y} + \frac{\partial F_z}{\partial z}.$$

- In cylindrical (ρ, ϕ, z) coordinates,

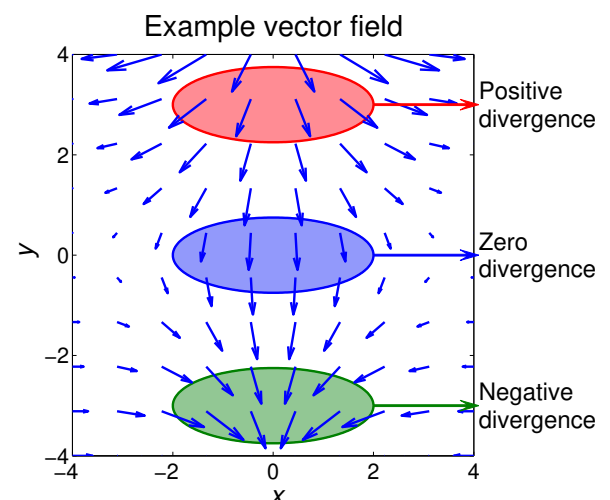
$$\nabla \cdot \mathbf{F} = \frac{1}{\rho} \frac{\partial(\rho F_\rho)}{\partial \rho} + \frac{1}{\rho} \frac{\partial F_\phi}{\partial \phi} + \frac{\partial F_z}{\partial z}.$$

- In spherical (r, θ, ϕ) coordinates,

$$\nabla \cdot \mathbf{F} = \frac{1}{r^2} \frac{\partial(r^2 F_r)}{\partial r} + \frac{1}{r \sin \theta} \frac{\partial(\sin \theta F_\theta)}{\partial \theta} + \frac{1}{r \sin \theta} \frac{\partial F_\phi}{\partial \phi}.$$

- The divergence of a vector field is the net flux per unit volume *out* of the surface enclosing that volume.

- Positive divergence means that we have a point source;
- Negative divergence means that we have a point sink.



- Convert the integral form of the equation of continuity to a point form:
- Divide both sides of the equation by the region's volume,
 - Take the limit as the volume shrinks to zero.

- That is,

$$\oiint_S \mathbf{i} \cdot \hat{\mathbf{n}} \, dS = -\frac{d}{dt} \iiint_V \rho_V \, dV$$

$$\oiint_S \mathbf{i} \cdot \hat{\mathbf{n}} \, dS = -\iiint_V \left(\frac{\partial \rho_V}{\partial t} \right) \, dV$$

$$\lim_{V \rightarrow 0} \frac{1}{V} \oiint_S \mathbf{i} \cdot \hat{\mathbf{n}} \, dS = \lim_{V \rightarrow 0} -\frac{1}{V} \iiint_V \left(\frac{\partial \rho_V}{\partial t} \right) \, dV$$

$$\nabla \cdot \mathbf{i} = -\frac{\partial \rho_V}{\partial t},$$

assuming that charge density is continuous, and that V is not time-varying (in second line, Liebnitz integral rule is used).

- Applying this identity to Ohm's law, we get

$$\nabla \cdot (-\sigma \nabla \phi) = -\frac{\partial \rho_V}{\partial t}.$$

ASSUME: That the rate of electron movement in the solid lattice is much faster than the rate of other processes in the electrochemical cell.

- Therefore, ρ_V is essentially constant and $\partial \rho_V / \partial t \approx 0$.
- Then, substituting subscript "s" for solid phase,

$$\nabla \cdot \mathbf{i}_s = \nabla \cdot (-\sigma \nabla \phi_s) = 0.$$

- We have now proven the first relation of this chapter: charge conservation in the homogeneous solid.

3.3: Mass conservation in solid

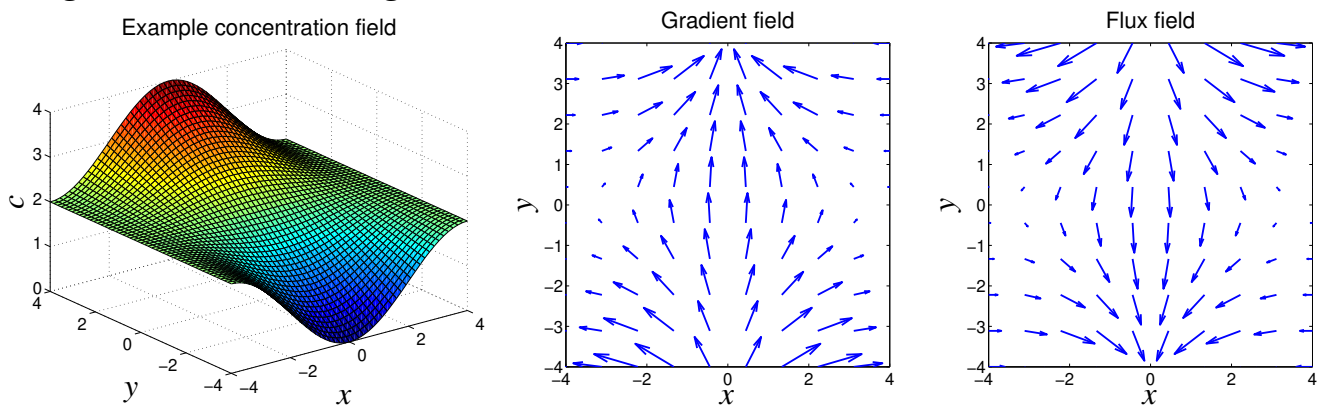
Point form of Fick's law

- We wish to solve for the movement of lithium atoms in either the negative- or positive-electrode solid matrix structures.
- First, the mole is a unit of measurement used to express amounts of a substance, equal to $N_A = 6.02214 \times 10^{23}$ molecules of that substance.
 - It is a base SI unit, and has the symbol mol.
 - The number of molecules in a mole (Avogadro's number, N_A) is defined so that the mass of one mole of a substance, expressed in grams, is exactly equal to the substance's mean molecular weight.
 - For example, the mean molecular weight of natural water is about 18.015, so one mole of water is about 18.015 grams.
- The mole is a convenient way to express the amounts of reactants and products of chemical reactions.
- For example, the reaction $2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O}$ implies that 2 mol of dihydrogen and 1 mol of dioxygen react to form 2 mol of water.
- The mole may also be used to express the number of atoms, ions, or other elementary entities in some sample.

ASSUME: Movement by diffusion only, in a linear media.

- That is, *molar flux* is proportional to the concentration gradient via Fick's first law: $\mathbf{N} = -D\nabla c$, where
 - $\mathbf{N}(x, y, z, t)$ [$\text{mol m}^{-2} \text{s}^{-1}$] is the (vector) *molar flux* of lithium flowing through a representative cross-sectional area of the solid that is centered at a given location and perpendicular to the flux;

- $D(x, y, z, t)$ [$\text{m}^2 \text{s}^{-1}$] is a material-dependent parameter called the *diffusivity*;
- $c(x, y, z, t)$ [mol m^{-3}] is the concentration of lithium in the neighborhood of a given location.



The continuity equation

- We apply Fick's law to a representative homogeneous volume V with boundary surface S and with lithium molar flux \mathbf{N} directed into it.
- The net molar current j [mol s^{-1}] *into* the region is the current flux

$$j = - \oiint_S \mathbf{N} \cdot \hat{\mathbf{n}} dS = dn/dt,$$

the minus sign arising because our usual convention that the normal $\hat{\mathbf{n}}$ points *out* of the region.

- A net quantity of lithium dn [mol] is supplied to V by the molar current within a time dt .
- Thus, the net quantity of lithium in the region changes in time dt by an amount $\frac{dn}{dt} = \frac{d}{dt} \iiint_V c dV$ and hence

$$\oiint_S \mathbf{N} \cdot \hat{\mathbf{n}} dS = - \frac{d}{dt} \iiint_V c dV,$$

where c [mol m^{-3}] is the *concentration* (of lithium) within region V .

- We can approximate the second spatial derivative using the forward or backward rule (repeated), or the central difference (C.D.) rule

$$\frac{\partial c_s(x, t)}{\partial x} \approx \frac{c_s(x + \Delta x, t) - c_s(x, t)}{\Delta x} \quad (\text{Fwd.})$$

$$\frac{\partial c_s(x, t)}{\partial x} \approx \frac{c_s(x, t) - c_s(x - \Delta x, t)}{\Delta x} \quad (\text{Bkwd.})$$

$$\frac{\partial^2 c_s(x, t)}{\partial x^2} \approx \frac{c_s(x + \Delta x, t) - 2c_s(x, t) + c_s(x - \Delta x, t)}{(\Delta x)^2}. \quad (\text{C.D.})$$

- Putting the equations together, we get

$$c_s(x, t + \Delta t) = c_s(x, t) + D_s \Delta t \frac{c_s(x + \Delta x, t) - 2c_s(x, t) + c_s(x - \Delta x, t)}{(\Delta x)^2}.$$

- Implementing this finite difference method requires care—it is stable only for certain combinations of Δt and Δx .
 - However, it is the simplest way to approximate a PDE in discrete time and space.
 - Other methods include finite volume (later this chapter) and finite element (next chapter). Either of these is generally preferred over finite difference for stability and accuracy.
- This MATLAB code implements the C.D. method, mirroring at edges.

```
c = 1:32; % initial concentration gradient (mol/(m^2*s))
D = 2; % diffusivity (m^2/s)
dt = 0.1; % time step (s)
dx = 1; % x step (m)

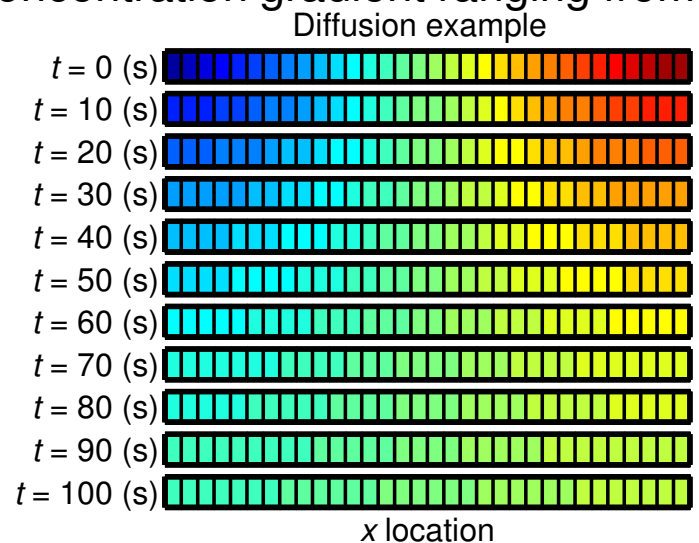
figure(1); clf; colormap(jet(31));
for k = 0:1000,
    % implement finite-difference diffusion equation using
    % explicit method and central differences
    c = c + D*dt/(dx^2)*([c(2:end) c(end)] - 2*c + [c(1) c(1:end-1)]);
```

```

if mod(k,100) == 0, % plot a snapshot
    subplot(11,1,k/100+1); image(c); grid on
    set(gca,'ytick',[],'xticklabel',[],'ticklength',[0 0]);
    set(gca,'xtick',1.5:1:100,'gridlinestyle','-','linewidth',4);
    h = ylabel(sprintf('t = %g (s)',k*dt));
    set(h,'rotation',0,'horizontal','right','vertical','middle')
end
end
xlabel('x location');
text(16,-14.25,'Diffusion example','horizontal','center');

```

- At time $t = 0$, the figure shows a concentration gradient ranging from 1 to 32 across the x dimension.
- As time progresses, material from higher-concentration areas flows into lower-concentration areas.
- By $t = 100$, the concentration is nearly uniform across the width of the simulation.
- We see that diffusion is actually pretty simple, even though the equation may look daunting.
- Soon, you'll be able to glance at an equation that looks like



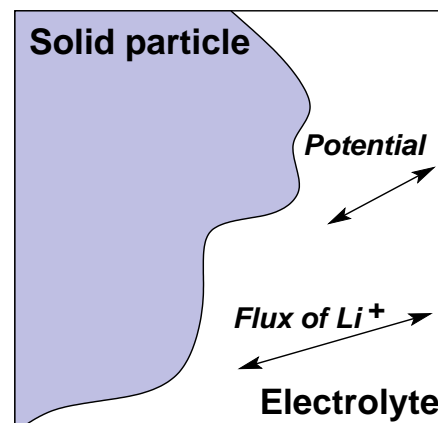
$$\frac{\partial c(x, t)}{\partial t} = \nabla \cdot (D \nabla c(x, t)) + r(x, t)$$

and say “that’s just a diffusion equation” and

- Know what you’re talking about;
 - Really think of it as pretty simple.
- Good news: Battery physics equations are predominantly diffusion equations (with migration and convection thrown in for fun).

3.4: Thermodynamics: Energy and thermodynamic potentials

- Now that we have proven the first two lithium-ion microscopic model equations, we begin to prove the other three.
- However, these require knowledge of a number of topics from physical chemistry, which we must look at first.
- We begin our brief study of physical chemistry by looking at thermodynamics, which looks at *energy* relationships in systems (including, but not limited to, heat/temperature aspects).
- We will also eventually look at kinetics: the *rate* of chemical reactions.



Thermodynamic potentials (Energy measures)

- We need to be able to think about a system's energy in different ways. To do so, the following four thermodynamic potentials are useful.

	Internal energy U (energy needed to create a system)	Helmholz free energy $A = U - TS$ (energy needed to create a system minus energy you can get from the environment)
<div style="display: flex; align-items: center;"> <div style="writing-mode: vertical-rl; transform: rotate(180deg); margin-right: 5px;">Add pV</div> <div style="margin-left: 10px;"> \Rightarrow Subtract TS </div> </div>	Enthalpy $H = U + pV$ (energy needed to create system plus work needed to make room for it)	Gibbs free energy $G = U + pV - TS$ (energy needed to create a system and make room for it minus the energy you can get from the environment)

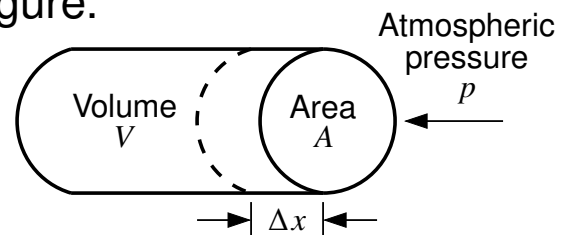
- Internal energy U is defined as the energy associated with the random, disordered motion of molecules in a system.

- It is separated in scale from the macroscopic ordered energy associated with moving objects; it refers to the invisible microscopic energy on the atomic and molecular scale.
 - This includes translational, rotational, and vibrational kinetic energy of atoms and molecules, and potential energy associated with the static rest mass energy of the constituents of matter, static electric energy of atoms within molecules or crystals, and the static energy of chemical bonds.
 - *How to think about it:* Internal energy is the energy needed to create the system, *excluding* energy required to displace the system's surroundings, energy associated with a move as a whole, or due to external force fields.
- To bring a system to internal energy level U , we can get some help from the environment.
- If the environment has (absolute) temperature T (in Kelvin, [K]), then some of the energy can be obtained by spontaneous heat transfer from the environment to the system.
 - The amount of this spontaneous energy transfer is TS where S is the final entropy of the system (defined later).
 - The bottom line is that if you accept energy from the environment, you don't have to put in as much energy as if you didn't.
 - Note that if a more disordered (higher entropy) final state is created, less work is required to create the system.
 - The Helmholtz free energy, computed as $A = U - TS$, is a measure of the amount of energy you have to put in to create a

system if the spontaneous energy transfer from the environment is accounted for (A is from the German *arbeit*, or “work”).

- Free energy is how much energy a system contains that can be harnessed to do work—we cannot always bring energy down to zero.
 - ◆ Consider a rock on the top of a cliff. It has the potential to provide useful work (*e.g.*, via a pulley), only until it rests at the bottom of the cliff (not yet at zero energy).
 - ◆ The environment places a constraint on how much energy is free/available.
- Note also that if the system is subjected to an external force field (*e.g.*, an electric field), any energy received from that field is considered to be a part of A (equation would need to be modified).
- *How to think about it:* Helmholtz free energy is the maximum amount of work a system can perform at constant temperature (and zero pressure).
- To understand enthalpy, consider the figure.
- Atmospheric air pressure p acts on surface area A with force $F = pA$, compressing system's volume V .
- The work that the atmosphere has done to the cylinder system is:

$$\Delta w = F \Delta x = (pA) \Delta x = p(A \Delta x) = p(-\Delta V) = -p \Delta V,$$
 noting that $\Delta V < 0$ and so $\Delta w > 0$.
- Enthalpy is defined as $H = U + pV$.
 - Internal energy U is the energy required to create a system without changes in temperature or volume.



- But if the process changes the volume (*e.g.*, chemical reaction produces gaseous product), work must be done to change volume.
 - For a constant-pressure process, the work you must do to produce a volume change ΔV is $p\Delta V$.
 - Then pV can be interpreted as the extra work you must do to “create room” for the system if you start with zero volume.
 - *How to think about it:* As heat and work change internal energy in equivalent ways (see “First Law,” later), enthalpy is the total amount of energy stored by the system that could be released as heat.
- The Gibbs free energy is defined as $G = U + pV - TS$.
- This is the energy required to create a system, starting from zero initial volume, in an environment having temperature T .
 - Note also that if the system is subjected to an external force field (*e.g.*, an electric field), any energy received from that field is considered to be a part of G (equation would need to be modified).
 - We will see that the change in Gibbs free energy in a reaction, ΔG , is a very useful parameter: it predicts the direction that a chemical reaction will spontaneously proceed.
 - *How to think about it:* Gibbs free energy is the maximum amount of work a system can perform at constant temperature and pressure.
- We use U and G a lot in this chapter; we’ll use H a lot in Chapter 7.

3.5: Two laws of thermodynamics and direction of reaction

State functions and inexact/exact differentials

- The first law of thermodynamics deals with a system's internal energy.
- Internal energy is a state function: a precisely measurable physical property whose value does not depend on the path taken to reach that specific value.
 - Other state functions include: pressure, volume, temperature, enthalpy, Helmholtz free energy, entropy, and Gibbs free energy.
 - For example, you might increase the temperature of an object and arrive at the same final temperature either by performing work (*e.g.*, via friction), or by adding heat (*e.g.*, by subjecting to a warm environment), or both. All that matters is the final temperature, which is a function of the system state.
- We can define what we mean by a state function mathematically.
- Let the state of the system be defined by the vector \mathbf{x} of parameters, and let $f(\mathbf{x})$ be some state function.
- Then, if the change in parameters is from an initial state \mathbf{x}_i to a final state \mathbf{x}_f , then the change in f is

$$\Delta f = \int_{\mathbf{x}_i}^{\mathbf{x}_f} df = f(\mathbf{x}_f) - f(\mathbf{x}_i).$$

- This relationship depends only on the initial and final points \mathbf{x}_i and \mathbf{x}_f .
 - It does not depend on the path taken between these two endpoints.
 - We say that df is an exact differential.

- In contrast, a quantity that is represented by an inexact differential is not a function of state.
- A simple example of an exact differential is the function $f = xy$.
 - Then, $df = d(xy) = y dx + x dy$.
 - Integrating df from any initial (x_i, y_i) to any final (x_f, y_f) will give the same answer of $(x_f \times y_f) - (x_i \times y_i)$ regardless of the path taken.
- A simple example of an inexact differential is the function $\delta g = y dx$.
 - A strikeout through the “d” is used to denote an inexact differential.
 - Then, integrating from $(0, 0)$ to $(1, 1)$ along the line $y = x$ gives

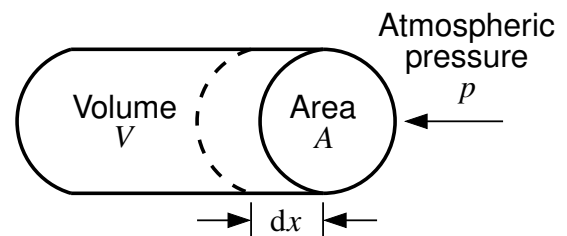
$$\Delta g_1 = \int_{(0,0)}^{(1,1)} y dx = \int_0^1 x dx = \left. \frac{x^2}{2} \right|_0^1 = \frac{1}{2}.$$
 - However, integrating from $(0, 0)$ to $(1, 0)$ along $y = 0$, and then to $(1, 1)$ along $x = 1$ gives

$$\Delta g_2 = \int_{(0,0)}^{(1,0)} y dx + \int_{(1,0)}^{(1,1)} y dx = 0.$$
 - The calculations for Δg_1 and Δg_2 had the same initial and final points, but yielded different results.

The first law of thermodynamics

- Returning to the problem at hand, the first law of thermodynamics is an energy conservation law.
- It states that $dU = \delta q + \delta w$, where δq is the amount of heat added to a system and δw is the amount of work done on the system during an infinitesimal procedure.

- We use δq and δw rather than dq and dw because they are not exact differentials—they merely denote some infinitesimal amount.
 - Heat added to a system and mechanical work done on the system are two equivalent ways to increase its internal energy.
 - This also implies that heat and work are forms of energy, and total energy is conserved.
- As shown in the figure, the work that the atmosphere has done to the cylinder system is:



$$\begin{aligned}\delta w &= F dx = (pA) dx = p(A dx) \\ &= p(-dV) = -p dV.\end{aligned}$$

The second law of thermodynamics

- The second law of thermodynamics points out the direction of chemical reactions, using a concept called entropy.
- The easiest way to understand entropy S is to define it as follows: S is a state function such that during an isothermal reversible (infinitesimally slow) process, we have:

$$\delta q \stackrel{\Delta}{=} T dS,$$

where T is the temperature that is kept constant.

- Therefore $dS = \delta q/T$ during isothermal reversible processes.
- The second law simply states that for any system:

$$dS \geq \frac{\delta q}{T},$$

where equality is possible only in reversible processes.

- When we consider the system (denoted by 1), we also need to consider the environment (denoted by 2).
- Assume they are both at temperature T . The heat transfer process (from 1 to 2, or vice versa) must follow $\delta q_1 = -\delta q_2$.
- According to the second law,

$$dS_1 \geq \frac{\delta q_1}{T} \quad \text{and} \quad dS_2 \geq \frac{\delta q_2}{T}.$$

- Therefore, $dS_1 + dS_2 \geq \frac{\delta q_1 + \delta q_2}{T} = 0$ and $dS = dS_1 + dS_2 \geq 0$.
- This equation is another form of the second law, which states that a closed system's entropy never decreases.

Gibbs free energy and spontaneous direction of reaction

- In a spontaneous chemical reaction, we must have $\Delta G \leq 0$.
- The tendency G to decrease derives from the tendency of increasing the total entropy of the system plus the environment.
- To show this, we need to write $G = U_1 + pV_1 - TS_1$ to emphasize that this entropy S_1 is only for the system.
- We denote the entropy of the environment as S_2 . Note for system 1

$$\begin{aligned} dG &= dU_1 + pdV_1 - TdS_1 \\ &= \delta q_1 + \delta w_1 + pdV_1 - TdS_1 \\ &= \delta q_1 - pdV_1 + pdV_1 - TdS_1 = \delta q_1 - TdS_1. \end{aligned}$$

- We assume the environment has reversible process $\delta q_2 = T dS_2$ and recall $\delta q_1 = -\delta q_2$,

$$dG = -\delta q_2 - T dS_1 = -T dS_2 - T dS_1 = -T dS \leq 0.$$

3.6: Electrochemical potential and Gibbs–Duhem equation

Partial molar quantities

- There are two sorts of physical parameters in thermodynamics:
 1. Extensive (absolute) property: If everything doubles, it doubles.
 - Examples: internal energy, Gibbs free energy, volume, mass.
 2. Intensive (normalized) property: Unchanged if everything doubles.
 - Examples: pressure, temperature, concentration, density.
- There are different ways to normalize intensive properties.
- When talking about solutions (a substance dissolved in a solvent, forming a mixture or solution), we use the terms molarity and molality:
 - The concentration of a solution is commonly expressed by its molarity: the number of moles of the dissolved solute per volume of solution (not per volume of the solvent).

$$c_i = \frac{n_{\text{solute } i}}{V_{\text{solution}}}$$

We will use units of mol m^{-3} when describing concentrations.

- This is not to be confused with the molality: the number of moles of the dissolved solute per kilogram of solvent (not per kg of solution).

$$m_i = \frac{n_{\text{solute } i}}{m_{\text{solvent}}}$$

in units of mol kg^{-1} .

- Extensive properties of a substance are proportional to the molar amount. But, if there are multiple species in the solution, it is then hard to find such a connection.

- For example, there are n_1 mol of species 1 and n_2 mol of species 2 in the solution.
 - If we double the molar amount of species 1 to $2n_1$, would the Gibbs free energy of the system double?
 - The answer is obviously no. Consequently, in multi-species systems, one has to define partial molar quantities.
- Partial molar quantities describe how much an extensive property changes if we add one mole of one species to the system or solution.

Electrochemical potential

- Electrochemical potential $\bar{\mu}$ is defined to be the partial molar Gibbs free energy in a multi-species system. For species i , we define:

$$\bar{\mu}_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_j(j \neq i)},$$

where n_i is the molar amount of species i , and where we keep temperature, pressure, and amounts of all other species constant.

- Note that electrochemical potential differs from chemical potential:
 - Chemical potential μ is related to the *internal* energy of a system (based on density, temperature, etc.);
 - Electrochemical potential $\bar{\mu}$ is related to the *total* energy of a system (including gravitational potential, magnetic potential, electric potential. . .).
 - Assuming that gravitational and magnetic potentials are negligible, chemical and electrochemical potentials are related via $\bar{\mu}_i = \mu_i + z_i F \phi$, where z_i is the charge number of the species.

Relation between Gibbs free energy and electrochemical potential

- We have seen that a species' electrochemical potential can be derived from the Gibbs free energy of the system.
- We can also find the Gibbs free energy from the electrochemical potentials if temperature and pressure are kept constant.
- After a short derivation (omitted here), we have

$$G = \sum_i n_i \bar{\mu}_i.$$

Gibbs–Duhem equation

- The intensive quantities of a solution are not all independent. One can be derived from the others.
- We start with the prior definition of the Gibbs function,

$$G = U + pV - TS$$

$$dG = dU + d(pV) - d(TS)$$

$$= \delta q + \delta w + pdV + Vdp - TdS - SdT.$$

- We know that $\delta w = -pdV$ and if we choose a reversible process, then $\delta q = TdS$, giving

$$dG = Vdp - SdT$$

$$\sum_{i=1}^r n_i d\bar{\mu}_i = Vdp - SdT.$$

- This can be re-arranged to be the Gibbs–Duhem equation:

$$S dT - V dp + \sum_{i=1}^r n_i d\bar{\mu}_i = 0.$$

- To understand the Gibbs–Duhem equation, it is best to study the simplest case. Assume temperature and pressure are all kept constant, and there are only two species.

$$n_1 d\bar{\mu}_1 + n_2 d\bar{\mu}_2 = 0.$$

- The Gibbs–Duhem equation states that in an isothermal and constant pressure two-species solution, if the electrochemical potential of one species increases, then it must decrease for the other species.
- We will use the Gibbs–Duhem equation for a multi-species solution at constant temperature and pressure:

$$\sum_{i=1}^r n_i d\bar{\mu}_i = 0 \quad \text{or} \quad \sum_{i=1}^r c_i d\bar{\mu}_i = 0.$$

- Key point: If we know $d\bar{\mu}_i$ for $i = 1 \dots r - 1$ then we can compute $d\bar{\mu}_r$.
- This eliminates one equation from the set of equations that we need.

3.7: Relative and absolute activity

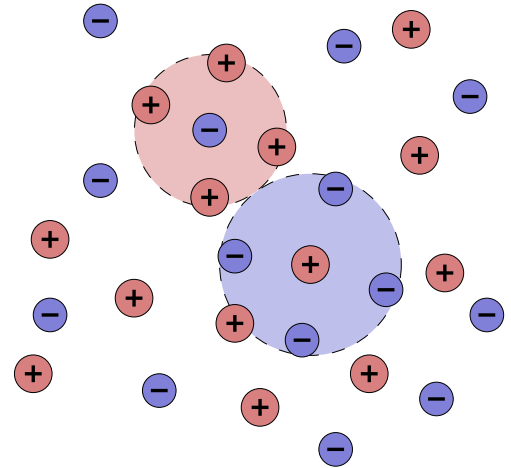
Debye–Hückel–Onsager theory

- In a solution, cations and anions are not located randomly.
- Coulomb forces cause a cation to have anions surrounding it and vice versa.
- As a consequence, the movement of ions in a solution is not simple.
- The alignment of cations and anions makes movement more difficult.
- Conductivity is lower than expected, as if the concentration of the solute had been diminished.
- This phenomenon was studied by Debye, Hückel, and Onsager.
- In order to neglect this phenomenon, one may introduce an “effective concentration” or “activity” $a_i < c_i$ for each species i .
- The activity of a species in a certain location reflects its “restlessness” there. The greater the activity, the more eager the species is to leave.
- One can define a molar activity coefficient f_i such that for species i , the activity

$$a_i = c_i f_i,$$

where f_i characterizes how activity differs from concentration.

- We call it the “molar” activity coefficient because the concentration used here is the molar concentration c_i .



Absolute activity based on molarity (concentration)

- It turns out that activity of species i is also related to the chemical potential μ_i for that species.
- Guggenheim defined an “absolute activity” λ_i for species i as follows

$$\lambda_i = \exp\left(\frac{\mu_i}{RT}\right),$$

or inversely

$$\mu_i = RT \ln \lambda_i.$$

- This is related to the prior definition of activity via,

$$\lambda_i = a_i a_i^\ominus,$$

such that λ_i can be broken down into three terms:

$$\lambda_i = c_i f_i a_i^\ominus.$$

- Here, a_i^\ominus is a constant of proportionality, independent of the concentration or the electric potential.
- But, a_i^\ominus does depend on the material types of solute and solvent, temperature as well as pressure (if there are gases).
- Combining relationships, we can write

$$\mu_i = RT \ln (a_i a_i^\ominus) = RT \ln (c_i f_i a_i^\ominus).$$

Absolute activity based on molality

- Absolute activity can also be written in terms of molality (instead of molarity, as we have just done).
- To do so, we must use the “molal” activity coefficient, which is denoted by γ_i . The new relation is

$$\lambda_i = m_i \gamma_i \lambda_i^\ominus.$$

- Again, λ_i^\ominus is a proportionality constant.
- Since we have used a different concentration scale, both the unit and the magnitude of λ_i^\ominus are different from a_i^\ominus .
- However, no matter whether one uses molarity or molality, they should give exactly the same value of λ_i (dimensionless).

3.8: Basic characteristics of binary electrolytes

Stoichiometric coefficient

- For a salt such as Na_2SO_4 , we define unsigned (positive) stoichiometric coefficients ν for both species (Na^+ and SO_4^{2-}).
 - Note: ν is the Greek letter “Nu” (think “number”).
- Since $\text{Na}_2\text{SO}_4 \rightarrow 2\text{Na}^+ + \text{SO}_4^{2-}$, we have $\nu_{\text{Na}^+} = 2$ and $\nu_{\text{SO}_4^{2-}} = 1$.

Charge number

- The charge number carried by an ion is represented by z .
- In Na_2SO_4 , we have $z_{\text{Na}^+} = 1$ and $z_{\text{SO}_4^{2-}} = -2$.
- Note that z is signed. A cation has $z > 0$ while an anion has $z < 0$.

Electroneutrality in binary electrolytes

- A macroscopic solution must satisfy the electroneutrality condition that $q = 0$, where q is the total charge.
- If the solution is an electrolyte, one must then have

$$\sum_i z_i \nu_i = 0.$$

- If the electrolyte is a binary electrolyte, then we use subscripts “+” for the cation, “-” for the anion, and “0” for the solvent.
- There are only two charged species in a binary electrolyte. Therefore, this expression reduces to:

$$z_+ \nu_+ + z_- \nu_- = 0.$$

- There is another way of stating the same concept. In a binary electrolyte, the concentration of an ion is proportional to its stoichiometric coefficient: $c_i \propto \nu_i$.
- Further, if we use “+” for the cation and “-” for the anion, then

$$\frac{c_+}{\nu_+} = \frac{c_-}{\nu_-}.$$

- The ratio is the concentration of the solute. We particularly use symbol c (no subscript) for this ratio and obtain the following:

$$\boxed{c = \frac{c_+}{\nu_+} = \frac{c_-}{\nu_-}} \quad (\text{Newman 11.17})$$

- By extension, we can write,

$$\sum_i z_i c_i = 0. \quad (\text{Newman 11.4})$$

- In particular, for a binary electrolyte,

$$\boxed{z_+ c_+ + z_- c_- = 0.}$$

- The boxed equations in this section are the characteristic equations for a binary electrolyte and will be used a lot.

An expression for current density

- The flux density \mathbf{N} of anything, at a particular point, through an infinitesimal cross sectional area, is defined as its velocity \mathbf{v} multiplied by its concentration c :

$$\mathbf{N} = c\mathbf{v} \quad [\text{mol m}^{-2} \text{s}^{-1}].$$

- We are particularly interested in the flux density of charged particles, which support the movement of electrical current.
- Electrolyte contains both positively-charged and negatively-charged ions. The total current density includes the contribution from both,

$$\mathbf{i} = \mathbf{i}_+ + \mathbf{i}_- \quad [\text{A m}^{-2}],$$

where \mathbf{i}_+ and \mathbf{i}_- represent contributions from the cations and anions, respectively.

- We can immediately write the expression for the current densities:

$$\mathbf{i}_+ = z_+ F \mathbf{N}_+ = z_+ F c_+ \mathbf{v}_+$$

$$\mathbf{i}_- = z_- F \mathbf{N}_- = z_- F c_- \mathbf{v}_-,$$

and

$$\mathbf{i} = z_+ F c_+ \mathbf{v}_+ + z_- F c_- \mathbf{v}_-$$

$$= F \sum_i z_i \mathbf{N}_i. \quad (\text{Newman 11.2})$$

Continuity equations

- The mass continuity equation states that at any point in the solution,

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot \mathbf{N}_i + R_i, \quad (\text{Newman 11.3})$$

where R_i is the generation rate of species i at that particular point.

- Note that $\nabla \cdot \mathbf{N}_i$ is the net flux out of the point, thus it is with a minus sign that it represents the contribution to the net increase of the concentration at that particular point.
- If there is no source of “generation” in the solution, this reduces to

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot \mathbf{N}_i.$$

- This equation is written for only one species. One can first multiply both sides by $z_i F$:

$$F \frac{\partial z_i c_i}{\partial t} = -F \nabla \cdot z_i \mathbf{N}_i + F z_i R_i,$$

and then sum over all the species to obtain:

$$\frac{\partial}{\partial t} F \sum_i z_i c_i = -\nabla \cdot \left(F \sum_i z_i \mathbf{N}_i \right) + F \sum_i z_i R_i. \quad (\text{Newman 11.13})$$

- We here allow “generation” because chemical reactions may generate new species. However, the species generated are charge balanced.
 - If a cation is generated, there would be certain number of anion(s) generated to balance the positive charge.
 - Therefore, even if we have $R_i \neq 0$, we always have $\sum_i z_i R_i = 0$.

- Hence, this equation simplifies to:

$$\frac{\partial}{\partial t} F \sum_i z_i c_i = -\nabla \cdot \left(F \sum_i z_i \mathbf{N}_i \right).$$

- In fact, both sides of this equation are zero.
 - The LHS is zero because (as we have already shown) $\sum_i z_i c_i = 0$.
 - We recognize the RHS to be $-\nabla \cdot \mathbf{i}$. Hence,

$$\boxed{\nabla \cdot \mathbf{i} = 0.} \quad (\text{Newman 11.14})$$

- This equation implies that charge can neither be stored nor created nor destroyed in a (charge-neutral) electrolyte solution.
- It can be regarded as a charge-continuity equation.

3.9: Electrolyte mass balance equation (Step 1a)

- We next look at mass balance in the electrolyte.
- “Dilute solution theory” uses Fick’s (relatively straightforward) approach, but does not approximate a lithium-ion cell very well.
- “Concentrated solution theory” uses Maxwell–Stefan theory and is more involved, but is a better approximation to a real cell.
- Thus, the goal of the next major section of notes is to derive the concentrated-solution mass-balance equation for the electrolyte,

$$\frac{\partial c}{\partial t} = \nabla \cdot \left[D \left(1 - \frac{d \ln c_0}{d \ln c} \right) \nabla c \right] - \frac{\mathbf{i} \cdot \nabla t_+^0}{z_+ \nu_+ F} - \nabla \cdot (c \mathbf{v}_0).$$

- This equation describes concentration changes due to three causes:
 - Diffusion: Ions moving because of a concentration gradient;
 - Migration: Ions moving because of the effects of an electric field;
 - Convection: Ions “sucked” along by the movement of the solvent.
- Steps in the (fairly long) derivation:
 1. Examine net force of collisions on a species (Maxwell–Stefan);
 2. Connect this force to the electrochemical potential of the species;
 3. Then, show how this produces a flux of ions;
 4. Finally, solve for mass balance via divergence of flux.

Step 1a. Maxwell–Stefan reln. (momentum loss due to collision)

- Maxwell–Stefan theory tells us about changes in momentum (and thus velocity) of multi-species systems due to collisions.

- The same basic result can be derived (differently) for ideal gases, dense gases, liquids, and polymers.¹
- Since the proof is clearer and more straightforward for ideal gases, we'll proceed in that way, starting with a two-species system and later extending to multi-species systems.
- Consider a unit volume containing two species of gas.
- Further, consider a single species-1 molecule with mass m_1 and original velocity \mathbf{v}_{m_1} , colliding with a single species-2 molecule with mass m_2 and original velocity \mathbf{v}_{m_2} . What happens?²
- After collision, the velocity of the species-1 molecule becomes \mathbf{v}'_{m_1} while the velocity of the species-2 molecule becomes \mathbf{v}'_{m_2} .
- The total momentum has to be conserved during any collision procedure. Hence, $m_1\mathbf{v}_{m_1} + m_2\mathbf{v}_{m_2} = m_1\mathbf{v}'_{m_1} + m_2\mathbf{v}'_{m_2}$.
- The momentum loss of species-1 molecule is:

$$\Delta(m_1\mathbf{v}_{m_1}) = m_1(\mathbf{v}_{m_1} - \mathbf{v}'_{m_1}).$$
- Because of randomness, we cannot know exactly particle velocity \mathbf{v}'_{m_1} .
- But, we can make progress if we concern ourselves with the average velocity of each species (instead of individual particle velocities).

¹ For dense gases, liquids, and polymers, the (concentration-dependent) diffusivities are not the same binary diffusivities as for an ideal-gas definition, however. See:

- Curtiss, C.F. and R.B. Bird, "Multicomponent diffusion," *Industrial Engineering Chemical Research*, 38, 2515–2522 (1999); (Correction in 40, 1791 (2001)).
- Curtiss, C.F. and R.B. Bird, "Diffusion-stress relations in polymer mixtures," *Journal of Chemical Physics*, 111, 10362-10370 (1999).

² Maxwell wrote and was known to sing: "Gin a body meet a body// flyin' through the air// Gin a body hit a body// will it fly, and where?" (Wikipedia).

- If the collisions are elastic (*i.e.*, the kinetic energy is conserved too), as is reasonably accurate for gas molecules,
 - Then, the average species velocity can be expressed as (note removal of subscript “ m ” when talking about species velocity):³

$$\mathbf{v}'_1 = \frac{m_1 \mathbf{v}_1 + m_2 \mathbf{v}_2}{m_1 + m_2}.$$

- The average momentum loss of species-1 molecules is then:

$$\begin{aligned} \Delta(m_1 \mathbf{v}_1) &= m_1 \left(\mathbf{v}_1 - \frac{m_1 \mathbf{v}_1 + m_2 \mathbf{v}_2}{m_1 + m_2} \right) \\ &= m_1 \frac{m_2 \mathbf{v}_1 - m_2 \mathbf{v}_2}{m_1 + m_2} = \frac{m_1 m_2}{m_1 + m_2} (\mathbf{v}_1 - \mathbf{v}_2). \end{aligned}$$

- This result tells us that the average amount of momentum transfer during a collision procedure is proportional to the original velocity difference between the two species.
- If we consider the subsystem of species-1 molecules only or species-2 molecules only, we find that collisions within either subsystem does not cause a change to the total momentum of that subsystem—because of momentum conservation.
- Therefore, considering subsystem-1, the only possibility to change its total momentum is when one (or more) of its molecules undergoes a collision with one (or more) of the species-2 molecules.
- That is, only the inter-subsystem collisions transfer momentum from species-1 to species-2, or vice versa.

³ Richard David Present, *Kinetic theory of gases*, McGraw-Hill (1958), §8.2.

3.10: Electrolyte mass balance equation (Steps 1b–2)

Step 1b. Maxwell–Stefan relationship (momentum change rate)

- The rate of change of momentum in a unit volume depends on:
 - The amount of momentum change per collision, as just found;
 - The frequency of collisions, which we now consider.
- This must be proportional to the concentration of species-1, as well as the concentration of species-2.
- Hence, we can write the momentum change rate of subsystem-1 as:

$$\left(\frac{d\mathbf{p}}{dt}\right)_V^{\text{subsystem 1}} \propto c_1 c_2 (\mathbf{v}_1 - \mathbf{v}_2),$$

where c_1 and c_2 are concentrations; \mathbf{p} denotes momentum (Caution: p is, however, pressure, and p_i are partial pressures); the subscript V on the left hand side denotes “per-unit-volume.”

- The concentrations are $c_i = n_i/V$, where n_i , is the number of moles of species- i ; V is the volume of the system.
- Next, we define the $x_i = n_i/n_{\text{tot}}$ to be the mole fraction. Then, $x_1 = n_1/n_{\text{tot}}$ and $x_2 = n_2/n_{\text{tot}}$. It immediately follows that $x_1 + x_2 = 1$.
- We denote the total concentration as

$$c_T = \sum_i c_i, \quad (\text{Newman 12.2})$$

where for a two-species system $c_T = c_1 + c_2$. Then, we know that $x_1 = c_1/c_T$ and $x_2 = c_2/c_T$.

- Combining, we modify our relation to be:

$$\left(\frac{d\mathbf{p}}{dt}\right)_V^{\text{subsystem 1}} \propto x_1 x_2 (\mathbf{v}_1 - \mathbf{v}_2).$$

- According to Newton's second law, $\mathbf{F} = d\mathbf{p}/dt$, and thus

$$\mathbf{F}_{1,V} \propto x_1 x_2 (\mathbf{v}_1 - \mathbf{v}_2),$$

where the subscript V , again, denotes unit volume.

- The problem is, what is the coefficient of proportionality? From our latest result, one can argue that the force is a sort of friction force.
- Define drag coefficient K_{12} so that $\mathbf{F}_{1,V} = K_{12} (\mathbf{v}_1 - \mathbf{v}_2)$.

- Written this way, however, our proportionality “constant” is not constant, but depends on values of x_1 and x_2 . That is,

$$K_{12} = \text{constant} \times x_1 x_2.$$

- Nevertheless, we can eliminate x_1 and x_2 by defining the “Maxwell–Stefan diffusion coefficient” or “Maxwell–Stefan diffusivity,”

$$\mathcal{D}_{ij} = \frac{x_i x_j}{K_{ij}} p,$$

which is \mathcal{D}_{ij} is inversely proportional to the drag coefficient K_{ij} .

- Since K_{ij} characterizes how difficult it is for the species to diffuse, \mathcal{D}_{ij} must characterize how easy it is for the species to diffuse.
- Inversely, we then have:

$$K_{12} = \frac{x_1 x_2}{\mathcal{D}_{12}} p = \frac{n}{V} \frac{RT x_1 x_2}{\mathcal{D}_{12}},$$

where we have used the ideal gas law, $pV = nRT$.

- Since $c_T = n/V$, $x_1 = c_1/c_T$, and $x_2 = c_2/c_T$, we can write

$$K_{12} = c_T \frac{RT \frac{c_1}{c_T} \frac{c_2}{c_T}}{\mathcal{D}_{12}} = \frac{RT c_1 c_2}{c_T \mathcal{D}_{12}}.$$

- If there are more than two species, we need to use subscripts i, j, \dots to denote species. In that case we can rewrite this as:

$$K_{ij} = \frac{RT c_i c_j}{c_T \mathcal{D}_{ij}}. \quad (\text{Newman 12.3})$$

- Note that this relationship utilizes the ideal gas law, but the same result can be developed for liquids using electrochemical potentials instead.
- Note that, according to Newton's third law, the drag forces are mutual. $K_{ij} = K_{ji}$. Therefore, we must also have

$$\mathcal{D}_{ij} = \mathcal{D}_{ji}. \quad (\text{Newman 12.4})$$

- Finally, we substitute (Newman 12.3) for K_{12} into the force equation to get the force per unit volume:

$$\mathbf{F}_{1,V} = \frac{RT c_1 c_2}{c_T \mathcal{D}_{12}} (\mathbf{v}_1 - \mathbf{v}_2),$$

which is also the momentum change rate of subsystem-1.

Step 2. Multicomponent diffusion equation

- In deriving the Maxwell–Stefan relation, we assumed the force is due to collisions.
- Now we consider that the force is not by collision, but by the gradient of electrochemical potential for charged species.
- We start with

$$\mathbf{F}_{1,V} = \frac{RT c_1 c_2}{c_T \mathcal{D}_{12}} (\mathbf{v}_1 - \mathbf{v}_2),$$

and relate the force to the electrochemical potential:

$$\mathbf{F}_1 = -\nabla G_1 = -\frac{\partial G_1}{\partial \bar{\mu}_1} \nabla \bar{\mu}_1 = -n_1 \nabla \bar{\mu}_1,$$

where we have used the prior result $n_i = \frac{\partial G}{\partial \bar{\mu}_i}$, and

$$\begin{aligned} \nabla G_1 &= \frac{\partial G_1}{\partial x} \hat{i} + \frac{\partial G_1}{\partial y} \hat{j} + \frac{\partial G_1}{\partial z} \hat{k} \\ &= \frac{\partial G_1}{\partial \mu_1} \left[\frac{\partial \mu_1}{\partial x} \hat{i} + \frac{\partial \mu_1}{\partial y} \hat{j} + \frac{\partial \mu_1}{\partial z} \hat{k} \right] \\ &= \frac{\partial G_1}{\partial \mu_1} \nabla \mu_1. \end{aligned}$$

- The force per unit volume is then:

$$\mathbf{F}_{1,V} = \frac{\mathbf{F}_1}{V} = -\frac{n_1}{V} \nabla \bar{\mu}_1 = -c_1 \nabla \bar{\mu}_1.$$

- Combining, we now have

$$c_1 \nabla \bar{\mu}_1 = RT \frac{c_1 c_2}{c_T \mathcal{D}_{12}} (\mathbf{v}_2 - \mathbf{v}_1).$$

- We can generalize to the multicomponent case, giving:

$$c_i \nabla \bar{\mu}_i = RT \sum_j \frac{c_i c_j}{c_T \mathcal{D}_{ij}} (\mathbf{v}_j - \mathbf{v}_i) = \sum_j K_{ij} (\mathbf{v}_j - \mathbf{v}_i). \quad (\text{Newman 12.1})$$

- A sum over all the species gives:

$$\sum_i c_i \nabla \bar{\mu}_i = \sum_i \sum_j K_{ij} (\mathbf{v}_j - \mathbf{v}_i). \quad (\text{Newman 12.5})$$

3.11: Electrolyte mass balance (Step 3)

Step 3. Concentrated binary electrolyte theory: Ion fluxes

- Our next goal is to prove the following relationship regarding flux of cations (and the corresponding relationship for anions)

$$\mathbf{N}_+ = c_+ \mathbf{v}_+ = -\frac{\nu_+ \mathcal{D}}{\nu RT} \frac{c_T}{c_0} \nabla \mu_e + \frac{\mathbf{i} t_+^0}{z_+ F} + c_+ \mathbf{v}_0. \quad (\text{Newman 12.8})$$

- Note that there are three new symbols in this equation:
 - The electrolyte chemical potential μ_e ;
 - The electrolyte average diffusivity \mathcal{D} ;
 - The transference number t_+^0 .
- We now define these quantities, and then prove (Newman 12.8).

Chemical potential of electrolyte

- The chemical potential of the binary electrolyte represents how much G changes when 1 mol of salt is added (the salt as a whole is neutral, so μ_e is merely a “chemical potential”):

$$\mu_e = \nu_+ \bar{\mu}_+ + \nu_- \bar{\mu}_-.$$

- To illustrate, suppose we have electrolyte comprising a solvent plus the salt Na_2SO_4 which has $\nu_+ = 2$ and $\nu_- = 1$.
 - If one mol of Na^+ is added, the system’s Gibbs free energy G increases by $\bar{\mu}_+$.
 - If one mol of SO_4^{2-} is added, G increases by $\bar{\mu}_-$.
 - If one mol Na_2SO_4 is added (the whole salt), then G increases by $2\bar{\mu}_+ + \bar{\mu}_-$, or, $\nu_+ \bar{\mu}_+ + \nu_- \bar{\mu}_- = \mu_e$.

- According to this definition, the gradient of μ_e is:

$$\nabla \mu_e = \nu_+ \nabla \bar{\mu}_+ + \nu_- \nabla \bar{\mu}_-.$$

- We can compute the $c \nabla \mu_e$ term in (Newman 12.8) if we can first compute $c \nu_+ \nabla \bar{\mu}_+ = c_+ \nabla \bar{\mu}_+$ and $c \nu_- \nabla \bar{\mu}_- = c_- \nabla \bar{\mu}_-$ terms.
- We get these by evaluating terms from (Newman 12.1)

$$c_+ \nabla \bar{\mu}_+ = K_{+0} (\mathbf{v}_0 - \mathbf{v}_+) + K_{+-} (\mathbf{v}_- - \mathbf{v}_+)$$

$$c_- \nabla \bar{\mu}_- = K_{-0} (\mathbf{v}_0 - \mathbf{v}_-) + K_{-+} (\mathbf{v}_+ - \mathbf{v}_-).$$

- Adding these equations gives (this result will be used later):

$$\begin{aligned} c \nabla \mu_e &= [K_{0+} (\mathbf{v}_0 - \mathbf{v}_+) + K_{+-} (\mathbf{v}_- - \mathbf{v}_+)] \\ &\quad + [K_{0-} (\mathbf{v}_0 - \mathbf{v}_-) + K_{-+} (\mathbf{v}_+ - \mathbf{v}_-)] \\ &= K_{0+} (\mathbf{v}_0 - \mathbf{v}_+) + K_{0-} (\mathbf{v}_0 - \mathbf{v}_-). \end{aligned}$$

Electrolyte average diffusivity

- The electrolyte average diffusivity \mathcal{D} is a weighted average of the diffusivities of the anion and cation with respect to the solvent.
- It will be convenient to express this average diffusivity in terms of the Maxwell–Stefan friction coefficients.
- When defining a weighted average diffusivity, we must recognize that diffusivities add like conductivities; *i.e.*, they add in reciprocal form.
- Accordingly, we define the weighted average diffusion coefficient \mathcal{D} in terms of the stoichiometric coefficients via the relationship

$$\frac{\nu}{\mathcal{D}} = \frac{\nu_+}{\mathcal{D}_{0+}} + \frac{\nu_-}{\mathcal{D}_{0-}},$$

where we recall that $\nu = \nu_+ + \nu_-$.

- Multiplying expression by c/c and recalling (Newman 11.17) gives \mathcal{D} in terms of concentrations, which allows us to write it also in terms of the Maxwell–Stefan friction coefficients using (Newman 12.3)

$$\begin{aligned}\mathcal{D} &= \frac{\nu c}{\frac{c_+}{\mathcal{D}_{0+}} + \frac{c_-}{\mathcal{D}_{0-}}} = \frac{RT c_0}{c_T} \left(\frac{\nu c}{\frac{RT c_0 c_+}{c_T \mathcal{D}_{0+}} + \frac{RT c_0 c_-}{c_T \mathcal{D}_{0-}}} \right) \\ &= \frac{RT c_0}{c_T} \left(\frac{\nu c}{K_{0+} + K_{0-}} \right) \\ &= \frac{\nu RT c_0 c}{c_T (K_{0+} + K_{0-})}.\end{aligned}$$

Transference numbers

- A transference number states the fraction of ionic current i carried by a certain ion *when there is no gradient in chemical potential*.
- In an electrolyte, the transference number of an ion is inversely proportional to the drag it experiences. We can write

$$t_+^0 \propto \frac{1}{K_{0+}} \quad \text{and} \quad t_-^0 \propto \frac{1}{K_{0-}}.$$

- The sum of transference numbers must sum to one, so we have

$$\begin{aligned}t_+^0 &= \frac{1/K_{0+}}{1/K_{0+} + 1/K_{0-}} = \frac{K_{0-}}{K_{0-} + K_{0+}} \\ t_-^0 &= \frac{1/K_{0-}}{1/K_{0+} + 1/K_{0-}} = \frac{K_{0+}}{K_{0-} + K_{0+}}.\end{aligned}$$

- So, we also see that—in a binary electrolyte—the transference number of the cation is proportional to the drag experienced by the anion, and vice versa.

Flux of ions

- Now we are ready to prove the following relation:

$$\mathbf{N}_+ = c_+ \mathbf{v}_+ = \underbrace{-\frac{\nu_+ \mathcal{D} c_T}{\nu RT c_0}}_A \underbrace{c \nabla \mu_e}_B + \underbrace{\frac{\mathbf{it}_+^0}{z_+ F}}_C + \underbrace{c_+ \mathbf{v}_0}_D. \quad (\text{Newman 12.8})$$

- We first look at term “A”:

$$\begin{aligned} -\frac{\nu_+ \mathcal{D} c_T}{\nu RT c_0} &= -\frac{\nu_+ c_T}{\nu RT c_0 c_T (K_{0+} + K_{0-})} \\ &= -\frac{c \nu_+}{K_{0+} + K_{0-}} = -\frac{c_+}{K_{0+} + K_{0-}}. \end{aligned}$$

- We now recall term “B” from before:

$$c \nabla \mu_e = K_{0+} (\mathbf{v}_0 - \mathbf{v}_+) + K_{0-} (\mathbf{v}_0 - \mathbf{v}_-).$$

- Multiplying terms “A” and “B” together gives

$$\begin{aligned} -\frac{\nu_+ \mathcal{D} c_T}{\nu RT c_0} c \nabla \mu_e &= -\frac{c_+}{K_{0+} + K_{0-}} [K_{0+} (\mathbf{v}_0 - \mathbf{v}_+) + K_{0-} (\mathbf{v}_0 - \mathbf{v}_-)] \\ &= -c_+ \mathbf{v}_0 + \frac{c_+}{K_{0+} + K_{0-}} [K_{0+} \mathbf{v}_+ + K_{0-} \mathbf{v}_-]. \end{aligned}$$

- Adding term “D” gives

$$-\frac{\nu_+ \mathcal{D} c_T}{\nu RT c_0} c \nabla \mu_e + c_+ \mathbf{v}_0 = \frac{c_+}{K_{0+} + K_{0-}} [K_{0+} \mathbf{v}_+ + K_{0-} \mathbf{v}_-].$$

- Term “C” is

$$\begin{aligned} \frac{\mathbf{it}_+^0}{z_+ F} &= \frac{z_+ F c_+ \mathbf{v}_+ + z_- F c_- \mathbf{v}_-}{z_+ F} \frac{K_{0-}}{K_{0-} + K_{0+}} \\ &= \frac{z_+ c_+ \mathbf{v}_+ - z_+ c_+ \mathbf{v}_-}{z_+} \frac{K_{0-}}{K_{0-} + K_{0+}} = \left(\frac{c_+}{K_{0-} + K_{0+}} \right) (K_{0-} \mathbf{v}_+ - K_{0-} \mathbf{v}_-). \end{aligned}$$

- Adding this term to the prior result gives

$$\begin{aligned} \text{RHS} &= \frac{c_+}{K_{0+} + K_{0-}} (K_{0+} \mathbf{v}_+ + K_{0-} \mathbf{v}_-) + \left(\frac{c_+}{K_{0-} + K_{0+}} \right) (K_{0-} \mathbf{v}_+ - K_{0-} \mathbf{v}_-) \\ &= c_+ \mathbf{v}_+. \end{aligned}$$

- So, we have now shown

$$\mathbf{N}_+ = c_+ \mathbf{v}_+ = -\frac{\nu_+ \mathcal{D} c_T}{\nu RT c_0} c \nabla \mu_e + \frac{\mathbf{it}_+^0}{z_+ F} + c_+ \mathbf{v}_0. \quad (\text{Newman 12.8})$$

- Using the same approach, we can obtain the flux of the anion as well:

$$\mathbf{N}_- = c_- \mathbf{v}_- = -\frac{\nu_- \mathcal{D} c_T}{\nu RT c_0} c \nabla \mu_e + \frac{\mathbf{it}_-^0}{z_- F} + c_- \mathbf{v}_0. \quad (\text{Newman 12.9})$$

3.12: Electrolyte mass balance (Step 4)

Step 4. An expression for the gradient of the chemical potential

- We have nearly reached our desired result. Before we finish, though, we need to express $\nabla \mu_e$ in a different form.
- Note that $\nabla \mu_e = \frac{\partial \mu_e}{\partial c} \nabla c$. We further break this up into

$$\frac{\partial \mu_e}{\partial c} = \frac{\partial \mu_e}{\partial \ln m} \frac{\partial \ln m}{\partial c},$$

where m is the molality of the solution.

- It is helpful to note that $m = \frac{m_+}{\nu_+} = \frac{m_-}{\nu_-}$ and that the molality is related to molarity via $m_i = \frac{c_i}{c_0 M_0}$, where M_0 is the molar mass of the solvent.
- Recall from our discussion of absolute activity that we can write $\mu_i = RT \ln(\lambda_i)$, where $\lambda_i = m_i \gamma_i \lambda_i^\ominus$, and that the electrochemical potential can be written as $\bar{\mu}_i = \mu_i + z_i F \phi$.
- For the electrolyte, $\mu_e = \nu_+ \bar{\mu}_+ + \nu_- \bar{\mu}_-$, so we can write

$$\begin{aligned} \mu_e &= \nu_+ RT \ln(m_+ \gamma_+ \lambda_+^\ominus) + \nu_- RT \ln(m_- \gamma_- \lambda_-^\ominus) + \underbrace{(\nu_+ z_+ + \nu_- z_-)}_0 F \phi \\ &= \nu_+ RT \ln(m_+ \gamma_+ \lambda_+^\ominus) + \nu_- RT \ln(m_- \gamma_- \lambda_-^\ominus) \\ &= \nu_+ RT \ln(m \nu_+ \gamma_+ \lambda_+^\ominus) + \nu_- RT \ln(m \nu_- \gamma_- \lambda_-^\ominus) \\ &= \nu_+ RT (\ln m + \ln \gamma_+ + \ln(\nu_+ \lambda_+^\ominus)) \\ &\quad + \nu_- RT (\ln m + \ln \gamma_- + \ln(\nu_- \lambda_-^\ominus)) \\ &= (\nu_+ + \nu_-) RT \ln m + RT (\ln \gamma_+^{\nu_+} + \ln \gamma_-^{\nu_-}) \\ &\quad + \nu_+ RT \ln(\nu_+ \lambda_+^\ominus) + \nu_- RT \ln(\nu_- \lambda_-^\ominus) \end{aligned}$$

$$= \nu RT (\ln m + \ln \gamma_{\pm}) + \nu_+ RT \ln(\nu_+ \lambda_+^{\ominus}) + \nu_- RT \ln(\nu_- \lambda_-^{\ominus}),$$

where we define $\gamma_{\pm}^{\nu} = \gamma_+^{\nu_+} \gamma_-^{\nu_-}$.

- Therefore, we compute the first term to be

$$\frac{\partial \mu_e}{\partial \ln m} = \nu RT \left(1 + \frac{\partial \ln \gamma_{\pm}}{\partial \ln m} \right).$$

- We now focus on the second term. We start by writing

$$m = \frac{m_+}{\nu_+} = \frac{c_+}{\nu_+ c_0 M_0} = \frac{c}{c_0 M_0}$$

$$\ln m = \ln c - \ln c_0 - \ln M_0$$

$$\frac{\partial \ln m}{\partial \ln c} = 1 - \frac{\partial \ln c_0}{\partial \ln c}$$

$$\frac{\partial \ln m}{\partial c} = \frac{1}{c} \left(1 - \frac{\partial \ln c_0}{\partial \ln c} \right).$$

- Putting the two results together, we get:

$$\nabla \mu_e = \frac{\nu RT}{c} \left(1 + \frac{d \ln \gamma_{\pm}}{d \ln m} \right) \left(1 - \frac{d \ln c_0}{d \ln c} \right) \nabla c.$$

Mass balance equation

- Here, we repeat (Newman 12.8),

$$\mathbf{N}_+ = -\frac{\nu_+ \mathcal{D} c_T}{\nu RT c_0} c \nabla \mu_e + \frac{\mathbf{it}_+^0}{z_+ F} + c_+ \mathbf{v}_0. \quad (\text{Newman 12.8})$$

- We now substitute in the value for $\nabla \mu_e$,

$$\begin{aligned} \mathbf{N}_+ &= -\frac{\nu_+ \mathcal{D} c_T c \nu RT}{\nu RT c_0 c} \left(1 + \frac{d \ln \gamma_{\pm}}{d \ln m} \right) \left(1 - \frac{d \ln c_0}{d \ln c} \right) \nabla c + \frac{\mathbf{it}_+^0}{z_+ F} + c_+ \mathbf{v}_0 \\ &= -\nu_+ \frac{\mathcal{D} c_T}{c_0} \left(1 + \frac{d \ln \gamma_{\pm}}{d \ln m} \right) \left(1 - \frac{d \ln c_0}{d \ln c} \right) \nabla c + \frac{\mathbf{it}_+^0}{z_+ F} + c_+ \mathbf{v}_0 \end{aligned}$$

- Newman comments that the Maxwell–Stephan diffusivity is not usually what is measured, but rather the value D in

$$D = \mathcal{D} \frac{c_T}{c_0} \left(1 + \frac{d \ln \gamma_{\pm}}{d \ln m} \right). \quad (\text{Newman 12.12})$$

- Therefore, we can write,

$$\mathbf{N}_+ = -\nu_+ D \left(1 - \frac{d \ln c_0}{d \ln c} \right) \nabla c + \frac{\mathbf{it}_+^0}{z_+ F} + c_+ \mathbf{v}_0.$$

- This can be put into the continuity equation

$$\frac{\partial c_+}{\partial t} = -\nabla \cdot \mathbf{N}_+$$

to obtain

$$\frac{\partial c_+}{\partial t} = \nabla \cdot \left[\nu_+ D \left(1 - \frac{d \ln c_0}{d \ln c} \right) \nabla c \right] - \nabla \cdot \left(\frac{\mathbf{it}_+^0}{z_+ F} \right) - \nabla \cdot (c_+ \mathbf{v}_0).$$

- Apply the identity that $c_+ = c\nu_+$,

$$\nu_+ \frac{\partial c}{\partial t} = \nu_+ \nabla \cdot \left[D \left(1 - \frac{d \ln c_0}{d \ln c} \right) \nabla c \right] - \nu_+ \frac{\nabla \cdot (\mathbf{it}_+^0)}{z_+ \nu_+ F} - \nu_+ \nabla \cdot (c \mathbf{v}_0),$$

which can be rearranged to be:

$$\frac{\partial c}{\partial t} = \nabla \cdot \left[D \left(1 - \frac{d \ln c_0}{d \ln c} \right) \nabla c \right] - \frac{\nabla \cdot (\mathbf{it}_+^0)}{z_+ \nu_+ F} - \nabla \cdot (c \mathbf{v}_0).$$

- Note that

$$\nabla \cdot (\mathbf{it}_+^0) = \mathbf{i} \cdot \nabla (t_+^0) + t_+^0 \nabla \cdot \mathbf{i},$$

and according to the charge continuity equation $\nabla \cdot \mathbf{i} = 0$, we can obtain:

$$\nabla \cdot (\mathbf{it}_+^0) = \mathbf{i} \cdot \nabla t_+^0.$$

- Finally we get:

$$\frac{\partial c}{\partial t} = \nabla \cdot \left[D \left(1 - \frac{d \ln c_0}{d \ln c} \right) \nabla c \right] - \frac{\mathbf{i} \cdot \nabla t_+^0}{z_+ \nu_+ F} - \nabla \cdot (c \mathbf{v}_0), \quad (\text{Newman 12.14})$$

which is the material balance equation.

- In practice, it is usually assumed that

$$\frac{d \ln c_0}{d \ln c} \approx 0,$$

as Doyle assumed. The simplified version is then:

$$\frac{\partial c}{\partial t} = \nabla \cdot (D \nabla c) - \frac{\mathbf{i} \cdot \nabla t_+^0}{z_+ \nu_+ F} - \nabla \cdot (c \mathbf{v}_0).$$

- Specializing to a lithium-ion cell: The salt in the electrolyte is typically LiPF_6 . This disassociates into Li^+ and PF_6^- .
- Therefore, $\nu_+ = z_+ = 1$ (usually true even if not LiPF_6).
- Further, we use subscripts “e” to distinguish between solid and liquid phases, which gives mass conservation equation:

$$\frac{\partial c_e}{\partial t} = \nabla \cdot (D \nabla c_e) - \frac{\mathbf{i}_e \cdot \nabla t_+^0}{F} - \nabla \cdot (c_e \mathbf{v}_0).$$

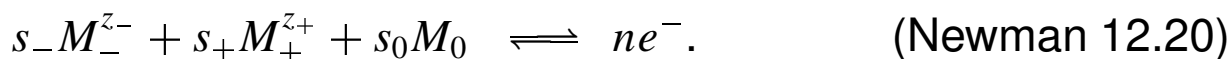
- This proves the third chapter relation: mass conservation in the homogeneous electrolyte.

3.13: Electrolyte charge balance equation: Electrolyte current

- We now want to introduce an electric potential in the solution as a driving force for the current and show that

$$\mathbf{i} = -\kappa \nabla \phi - \frac{\kappa}{F} \left(\frac{s_+}{n\nu_+} + \frac{t_+^0}{z_+\nu_+} - \frac{s_0c}{nc_0} \right) \nabla \mu_e. \quad (\text{Newman 12.27})$$

- The parameters s_i represent the signed stoichiometric coefficient of species i in the electrode reaction



Here, for generality, we assume that the solvent may participate in the electrode reaction.

- The potential is introduced by recognizing that the Gibbs free energy of the n moles of electrons is equal to $-nF\phi$, where ϕ is the electrical potential of the electrons.
- The energy of the product electrons must equal the energy of the reactants, so we have the energy balance

$$\sum_i s_i \bar{\mu}_i = -nF\phi,$$

(where the summation includes the solvent) and we therefore must also have

$$\sum_i s_i \nabla \bar{\mu}_i = -nF \nabla \phi. \quad (\text{Newman 12.21})$$

- We have seen expressions involving $\bar{\mu}_-$ and $\bar{\mu}_+$ before, but never any relating to $\bar{\mu}_0$. We create an expression for $\bar{\mu}_0$ by recalling the Gibbs–Duhem relationship

$$c_+ \nabla \bar{\mu}_+ + c_- \nabla \bar{\mu}_- + c_0 \nabla \bar{\mu}_0 = 0$$

$$\begin{aligned}
\nabla \bar{\mu}_0 &= -\frac{1}{c_0} (c_+ \nabla \bar{\mu}_+ + c_- \nabla \bar{\mu}_-) \\
&= -\frac{c}{c_0} (v_+ \nabla \bar{\mu}_+ + v_- \nabla \bar{\mu}_-) \\
&= -\frac{c}{c_0} \nabla \mu_e.
\end{aligned}$$

- So, we now have

$$s_+ \nabla \bar{\mu}_+ + s_- \nabla \bar{\mu}_- - s_0 \frac{c}{c_0} \nabla \mu_e = -nF \nabla \phi.$$

- For charge balance in the original reaction, we must have

$$s_+ z_+ + s_- z_- = -n \quad (\text{Newman 12.25})$$

$$s_- = - \left(\frac{z_+}{z_-} s_+ + \frac{n}{z_-} \right),$$

so the first terms in the prior equation can be found to be:

$$\begin{aligned}
s_+ \nabla \bar{\mu}_+ + s_- \nabla \bar{\mu}_- &= s_+ \nabla \bar{\mu}_+ - \frac{z_+}{z_-} s_+ \nabla \bar{\mu}_- - \frac{n}{z_-} \nabla \bar{\mu}_- \quad (\text{Newman 12.24}) \\
&= \frac{s_+}{v_+} \left(v_+ \nabla \bar{\mu}_+ - \frac{z_+ v_+}{z_-} \nabla \bar{\mu}_- \right) - \frac{n}{z_-} \nabla \bar{\mu}_- \\
&= \frac{s_+}{v_+} (v_+ \nabla \bar{\mu}_+ + v_- \nabla \bar{\mu}_-) - \frac{n}{z_-} \nabla \bar{\mu}_- \\
&= \frac{s_+}{v_+} \nabla \mu_e - \frac{n}{z_-} \nabla \bar{\mu}_-.
\end{aligned}$$

- Putting these results together, we now have

$$\begin{aligned}
\frac{s_+}{v_+} \nabla \mu_e - \frac{n}{z_-} \nabla \bar{\mu}_- - s_0 \frac{c}{c_0} \nabla \mu_e &= -nF \nabla \phi \\
\left(\frac{s_+}{nv_+} - \frac{s_0 c}{nc_0} \right) \nabla \mu_e - \frac{1}{z_-} \nabla \bar{\mu}_- &= -F \nabla \phi. \quad (\text{Newman 12.26})
\end{aligned}$$

- The next step is to find a relationship for $\nabla \bar{\mu}_-$, in terms of $\nabla \mu_e$ and \mathbf{i} .

- We start with a familiar result, via (Newman 12.1),

$$c_- \nabla \bar{\mu}_- = K_{0-} (\mathbf{v}_0 - \mathbf{v}_-) + K_{+-} (\mathbf{v}_+ - \mathbf{v}_-).$$

- To find the terms $(\mathbf{v}_0 - \mathbf{v}_-)$ and $(\mathbf{v}_+ - \mathbf{v}_-)$, we look at the (slightly rearranged) flux equations that we derived in the prior section

$$c_+ (\mathbf{v}_+ - \mathbf{v}_0) = -\frac{v_+ \mathcal{D} c_T}{v R T c_0} c \nabla \mu_e + \frac{\mathbf{i} t_+^0}{z_+ F} \quad (\text{Newman 12.8}^*)$$

$$c_- (\mathbf{v}_- - \mathbf{v}_0) = -\frac{v_- \mathcal{D} c_T}{v R T c_0} c \nabla \mu_e + \frac{\mathbf{i} t_-^0}{z_- F}. \quad (\text{Newman 12.9}^*)$$

- We're going to simplify these slightly before substitution by rewriting the \mathcal{D} term

$$\mathcal{D} = \frac{v R T c_0 c}{c_T (K_{0+} + K_{0-})},$$

giving revised but equivalent equations

$$\mathbf{v}_+ - \mathbf{v}_0 = -\frac{c}{K_{0+} + K_{0-}} \nabla \mu_e + \frac{\mathbf{i} t_+^0}{c_+ z_+ F} \quad (\text{Newman 12.8}^*)$$

$$\mathbf{v}_- - \mathbf{v}_0 = -\frac{c}{K_{0+} + K_{0-}} \nabla \mu_e + \frac{\mathbf{i} t_-^0}{c_- z_- F}. \quad (\text{Newman 12.9}^*)$$

- Subtracting the second equation from the first gives

$$\begin{aligned} \mathbf{v}_+ - \mathbf{v}_- &= \frac{\mathbf{i}}{F} \left(\frac{t_+^0}{c_+ z_+} - \frac{t_-^0}{c_- z_-} \right) \\ &= \frac{\mathbf{i}}{c_+ z_+ F} (t_+^0 + (1 - t_+^0)) = \frac{\mathbf{i}}{c_+ z_+ F}. \end{aligned}$$

- We can now find our expression for $\nabla \bar{\mu}_- / z_-$

$$\begin{aligned} \frac{1}{z_-} \nabla \bar{\mu}_- &= \frac{1}{c_- z_-} [K_{0-} (\mathbf{v}_0 - \mathbf{v}_-) + K_{+-} (\mathbf{v}_+ - \mathbf{v}_-)] \\ &= \frac{1}{c_- z_-} \left[K_{0-} \left(\frac{c}{K_{0+} + K_{0-}} \nabla \mu_e + \frac{\mathbf{i} t_-^0}{c_+ z_+ F} \right) + K_{+-} \left(\frac{\mathbf{i}}{c_+ z_+ F} \right) \right] \end{aligned}$$

$$\begin{aligned}
&= \frac{c}{c-z_-} \frac{K_{0-}}{K_{0+} + K_{0-}} \nabla \mu_e + \mathbf{i} \left(\frac{K_{0-} t_-^0}{c-z_- c+z_+ F} + \frac{K_{+-}}{c-z_- c+z_+ F} \right) \\
&= -\frac{c_+}{v_+ c+z_+} t_+^0 \nabla \mu_e - F \mathbf{i} \left(\frac{-K_{0-} t_-^0 - K_{+-}}{c-z_- c+z_+ F^2} \right) \\
&= -\frac{t_+^0}{v_+ z_+} \nabla \mu_e - \frac{F \mathbf{i}}{\kappa},
\end{aligned}$$

where we have recognized that the term multiplying \mathbf{i} has units of a molar conductivity, and we define (equivalent to Newman, but written in a different form that is more helpful here)

$$\frac{1}{\kappa} = \frac{-K_{0-} t_-^0 - K_{+-}}{c-z_- c+z_+ F^2}. \quad (\text{Newman 12.23}^*)$$

- We are nearly done: We simply substitute this result for $\nabla \bar{\mu}_- / z_-$ into our prior equation

$$\begin{aligned}
-F \nabla \phi &= \left(\frac{s_+}{n v_+} - \frac{s_0 c}{n c_0} \right) \nabla \mu_e - \frac{1}{z_-} \nabla \bar{\mu}_- \\
-F \nabla \phi &= \left(\frac{s_+}{n v_+} - \frac{s_0 c}{n c_0} + \frac{t_+^0}{v_+ z_+} \right) \nabla \mu_e + \frac{F \mathbf{i}}{\kappa} \\
\mathbf{i} &= -\kappa \nabla \phi - \frac{\kappa}{F} \left(\frac{s_+}{n v_+} - \frac{s_0 c}{n c_0} + \frac{t_+^0}{v_+ z_+} \right) \nabla \mu_e. \quad (\text{Newman 12.27})
\end{aligned}$$

3.14: Electrolyte charge balance equation final form

- We have now proven our desired result. However, in the literature, this equation is usually expressed in terms of $\nabla \ln c$ instead of $\nabla \mu_e$.
- We proceed by recognizing that $\mu_e = \nu_+ \bar{\mu}_+ + \nu_- \bar{\mu}_-$ and

$$\nabla \mu_e = \frac{\partial \mu_e}{\partial \ln c} \nabla \ln c.$$

- According to one definition of absolute activity,

$$\begin{aligned} \mu_+ &= RT \ln (c_+ f_+ a_+^\ominus) = RT \ln (\nu_+ c f_+ a_+^\ominus) \\ &= RT \ln (\nu_+) + RT \ln (c) + RT \ln (f_+) + RT \ln (a_+^\ominus). \end{aligned}$$

- Also, $\bar{\mu}_+ = \mu_+ + z_+ F \phi$. So,

$$\frac{\partial \bar{\mu}_+}{\partial \ln c} = RT + RT \frac{\partial \ln f_+}{\partial \ln c} + z_+ F \frac{\partial \phi}{\partial \ln c}.$$

- Similarly,

$$\frac{\partial \bar{\mu}_-}{\partial \ln c} = RT + RT \frac{\partial \ln f_-}{\partial \ln c} + z_- F \frac{\partial \phi}{\partial \ln c}.$$

- Therefore,

$$\begin{aligned} \frac{\partial \mu_e}{\partial \ln c} &= \nu_+ \frac{\partial \bar{\mu}_+}{\partial \ln c} + \nu_- \frac{\partial \bar{\mu}_-}{\partial \ln c} \\ &= (\nu_+ + \nu_-) RT + RT \frac{\partial \ln (f_+^{\nu_+} f_-^{\nu_-})}{\partial \ln c} + \underbrace{(\nu_+ z_+ + \nu_- z_-)}_0 F \frac{\partial \phi}{\partial \ln c}. \end{aligned}$$

- If we define $f_+^{\nu_+} f_-^{\nu_-} = f_\pm^\nu$, and recall that $\nu = \nu_+ + \nu_-$, then,

$$\frac{\partial \mu_e}{\partial \ln c} = \nu RT + RT \frac{\partial \ln f_\pm^\nu}{\partial \ln c} = \nu RT \left(1 + \frac{\partial \ln f_\pm}{\partial \ln c} \right).$$

- Therefore, our expression for ionic current becomes

$$\mathbf{i} = -\kappa \nabla \phi - \frac{\nu \kappa RT}{F} \left(\frac{s_+}{n \nu_+} - \frac{s_0 c}{n c_0} + \frac{t_+^0}{\nu_+ z_+} \right) \left(1 + \frac{\partial \ln f_\pm}{\partial \ln c} \right) \nabla \ln c.$$

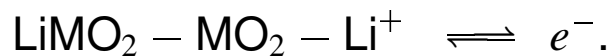
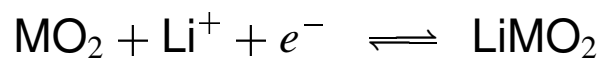
- The conservation of charge equation says $\nabla \cdot \mathbf{i} = 0$, which gives us

$$\nabla \cdot \left(-\kappa \nabla \phi - \frac{\nu \kappa RT}{F} \left(\frac{s_+}{n\nu_+} - \frac{s_0 c}{nc_0} + \frac{t_+^0}{\nu_+ z_+} \right) \left(1 + \frac{\partial \ln f_{\pm}}{\partial \ln c} \right) \nabla \ln c \right) = 0.$$

- Specializing to a lithium-ion cell: The negative-electrode reaction is



- From this, we conclude that $s_- = 0$, $s_+ = -1$, $s_0 = 0$, and $n = 1$.
- The positive-electrode reaction (where MO_2 is some metal oxide) is



- Again, $s_- = 0$, $s_+ = -1$, $s_0 = 0$, and $n = 1$.
- Also, $\nu_+ = \nu_- = z_+ = 1$, so the charge conservation equation for a lithium-ion cell is

$$\nabla \cdot \mathbf{i}_e = \nabla \cdot \left(-\kappa \nabla \phi_e - \frac{2\kappa RT}{F} \left(1 + \frac{\partial \ln f_{\pm}}{\partial \ln c_e} \right) (t_+^0 - 1) \nabla \ln c_e \right) = 0.$$

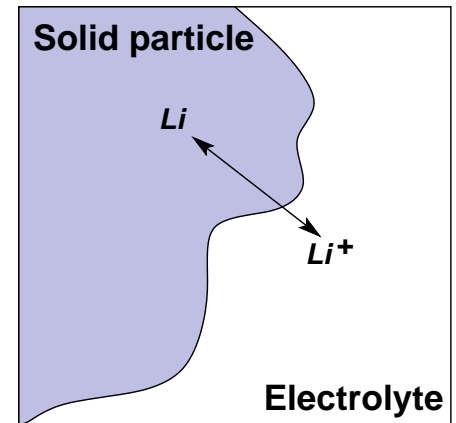
- Note that it is common to assume that $\partial \ln f_{\pm} / \partial \ln c_e = 0$ and to lump $\kappa_D = 2\kappa RT(t_+^0 - 1)/F$, giving

$$\nabla \cdot (-\kappa \nabla \phi_e - \kappa_D \nabla \ln c_e) = 0.$$

- We have now proven the fourth chapter relation: charge conservation in the electrolyte.

3.15: Butler–Volmer Equation: Preliminaries

- The final model equation couples the prior four PDEs together.
- It computes the rate of lithium moving between solid and electrolyte.
- As it deals with reaction rate, it is often called the “kinetics” equation.



Reaction rate

- For a chemical reaction, reactants \rightleftharpoons products, the reaction rate can be defined using the rate of overall product concentration change,

$$r = \frac{d}{dt} \left(\prod c_{\text{products}} \right).$$

- For “first-order” processes, we can model this as $r = k \prod c_{\text{reactants}}$, where k is the reaction rate constant for this chemical reaction.
- For now, we think about a single reactant species and a single product species, and later generalize to the multi-species case, so

$$r = \frac{dc_{\text{product}}}{dt} = kc_{\text{reactant}}.$$

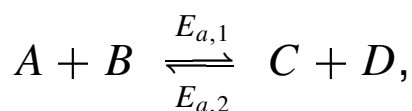
- The reaction rate “constant” generally depends on temperature and is usually modeled via the Arrhenius equation,

$$k = k_f^0 \exp\left(-\frac{E_a}{RT}\right), \quad \text{or} \quad r = k_f^0 c_{\text{reactant}} \exp\left(-\frac{E_a}{RT}\right),$$

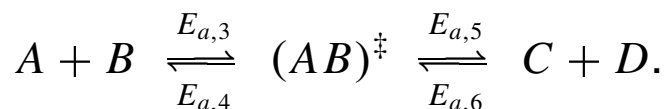
where E_a is the activation energy of the forward reaction, and where both E_a and k_f^0 are constants that are determined by experiments.

Activated complex theory

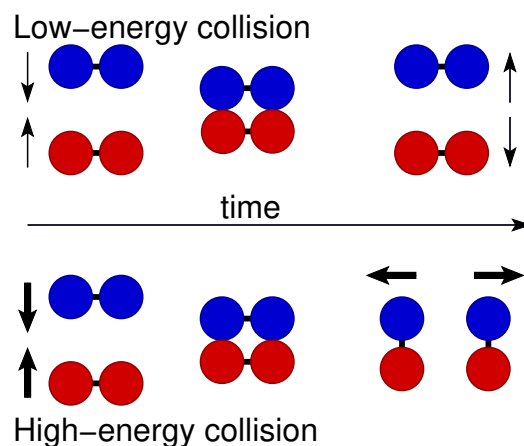
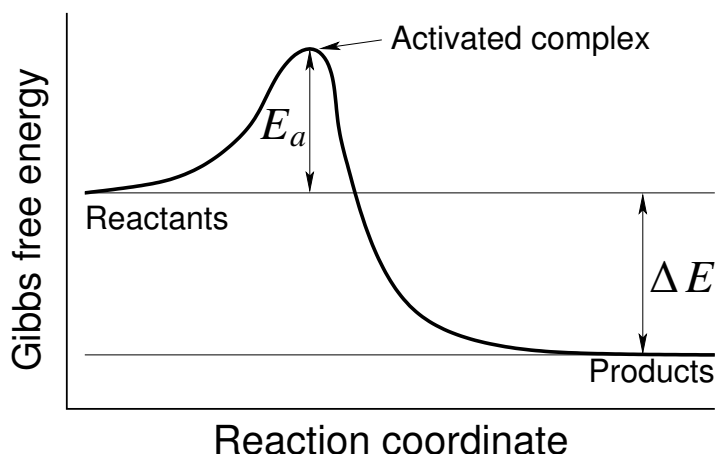
- Activated complex theory states that there is a transition state (sometimes called the “activated complex”) in chemical reactions.
- If $E_{a,x}$ are activation energies.



has transition state $(AB)^\ddagger$ where

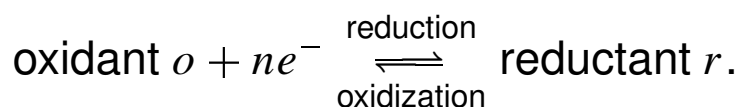


- Idea: Not every collision has enough energy to break the original chemical bonds and allow a reaction to occur.
- Most collisions result in elastic scattering.
- Only when there is sufficient energy will transition state form and reaction continue.



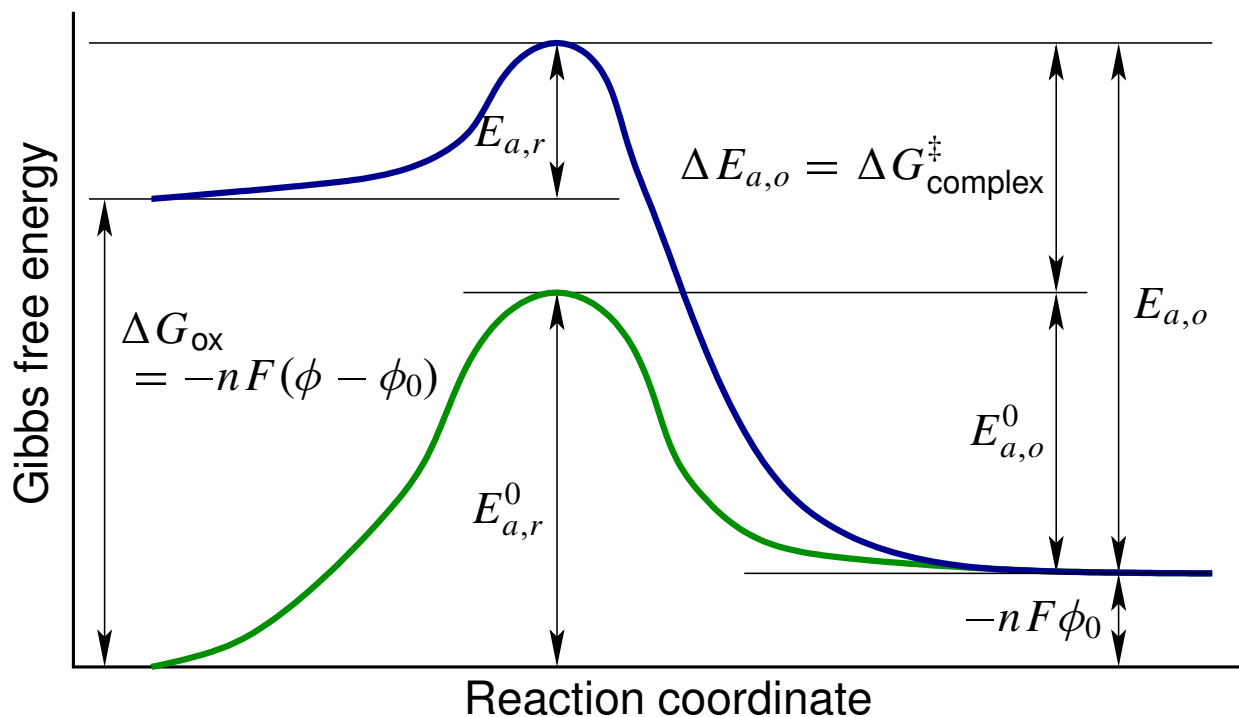
Electrodes

- In an electrode reaction, electrons are produced or consumed:



- The activation energies for reduction and oxidization reactions are denoted by $E_{a,r}$ and $E_{a,o}$, respectively.
- An electrode reaction differs from other types of reactions in that its activation energies are functions of the potential of the electrode.

- Consider reduction and an arbitrary initial electrode potential of ϕ_0 where the activation energy for reduction is $E_{a,r}^0$.



- If the potential is changed to ϕ , the total Gibbs free energy of the LHS (ox) changes because there are electrons on LHS; the total Gibbs free energy of RHS (red) remains unchanged.

$$\Delta G_{\text{ox}} = -nF(\phi - \phi_0),$$

where $-nF$ is the total charge of the electrons.

- The Gibbs free energy of the activated complex changes as well, but not as much as ΔG_{ox} :

$$0 < \left| \Delta G_{\text{complex}}^\ddagger \right| < \left| \Delta G_{\text{ox}} \right|.$$

- The Gibbs free energy variations during the reaction are shown in the figure, where two curves for electrode potentials ϕ_0 and ϕ are drawn.

3.16: Butler–Volmer Equation: Derivation

- We see from the figure that $E_{a,r} - nF(\phi - \phi_0) = \Delta E_{a,o} + E_{a,r}^0$, or

$$\begin{aligned}\Delta E_{a,o} &= E_{a,r} - E_{a,r}^0 - nF(\phi - \phi_0) \\ &= \Delta E_{a,r} - nF(\phi - \phi_0),\end{aligned}$$

where we have used

$$\Delta E_{a,r} \equiv E_{a,r} - E_{a,r}^0.$$

- We deduce that decreasing electrode potential as shown causes:
 - Activation energy for reduction reaction to decrease ($\Delta E_{a,r} < 0$).
 - Activation energy for oxidization reaction to increase ($\Delta E_{a,o} > 0$).
- However, by re-arranging we further derive that

$$\Delta E_{a,o} - \Delta E_{a,r} = -nF(\phi - \phi_0) = \Delta G_{\text{ox}},$$

implying that neither quantity is found uniquely from only $(\phi - \phi_0)$.

- So, we are curious that how much of the energy change is spent on decreasing $E_{a,r}$ while how much (the rest) is spent on increasing $E_{a,o}$.
- Define the charge-transfer coefficient $0 < \alpha < 1$ such that

$$\alpha = \left| \frac{\Delta E_{a,r}}{\Delta G_{\text{ox}}} \right|, \quad \text{and} \quad 1 - \alpha = \left| \frac{\Delta E_{a,o}}{\Delta G_{\text{ox}}} \right|.$$

- Then, we have $\Delta E_{a,r} = \alpha nF(\phi - \phi_0)$ and $\Delta E_{a,o} = -(1 - \alpha)nF(\phi - \phi_0)$.
- Putting all our results to date together,

1. Reduction

$$r_{\text{red}} = k_{\text{ox}}^0 c_{\text{ox}} \exp\left(-\frac{E_{a,r}}{RT}\right) = k_{\text{ox}}^0 c_{\text{ox}} \exp\left(-\frac{E_{a,r}^0 + \alpha nF(\phi - \phi_0)}{RT}\right)$$

2. Oxidization

$$r_{\text{ox}} = k_{\text{red}}^0 c_{\text{red}} \exp\left(-\frac{E_{a,o}}{RT}\right) = k_{\text{red}}^0 c_{\text{red}} \exp\left(-\frac{E_{a,o}^0 - (1-\alpha)nF(\phi - \phi_0)}{RT}\right).$$

- The production rate of e^- is the same as the production rate of positive charge, and hence: $i_{\text{red}} = -nFr_{\text{red}}$ and $i_{\text{ox}} = nFr_{\text{ox}}$.
- This gives

$$i_{\text{red}} = -nFk_{\text{ox}}^0 c_{\text{ox}} \exp\left(-\frac{E_{a,r}^0 + \alpha nF(\phi - \phi_0)}{RT}\right)$$

$$i_{\text{ox}} = nFk_{\text{red}}^0 c_{\text{red}} \exp\left(-\frac{E_{a,o}^0 - (1-\alpha)nF(\phi - \phi_0)}{RT}\right).$$

- Until now, we have assumed that the initial potential ϕ_0 was arbitrary. We now clean up our notation by setting $\phi_0 = 0$.
- Then, $E_{a,r}^0$ and $E_{a,o}^0$ correspond specifically to $\phi_0 = 0$, and

$$i_{\text{red}} = -nFk_{\text{ox}}^0 c_{\text{ox}} \exp\left(-\frac{E_{a,r}^0 + \alpha nF\phi}{RT}\right)$$

$$i_{\text{ox}} = nFk_{\text{red}}^0 c_{\text{red}} \exp\left(-\frac{E_{a,o}^0 - (1-\alpha)nF\phi}{RT}\right).$$

- Note that at equilibrium, $\phi = \phi_{\text{rest}}$. We define a new quantity, the overpotential $\eta = \phi - \phi_{\text{rest}}$, so that

$$i_{\text{red}} = -nFk_{\text{ox}}^0 c_{\text{ox}} \exp\left(-\frac{E_{a,r}^0 + \alpha nF(\phi_{\text{rest}} + \eta)}{RT}\right)$$

$$i_{\text{ox}} = nFk_{\text{red}}^0 c_{\text{red}} \exp\left(-\frac{E_{a,o}^0 - (1-\alpha)nF(\phi_{\text{rest}} + \eta)}{RT}\right).$$

- Now, at equilibrium, $\eta = 0$ and we have

$$i_{\text{red}} = -nFk_{\text{ox}}^0 c_{\text{ox}} \exp\left(-\frac{E_{a,r}^0}{RT}\right) \exp\left(-\frac{\alpha nF\phi_{\text{rest}}}{RT}\right)$$

$$i_{\text{ox}} = nFk_{\text{red}}^0 c_{\text{red}} \exp\left(-\frac{E_{a,o}^0}{RT}\right) \exp\left(\frac{(1-\alpha)nF\phi_{\text{rest}}}{RT}\right).$$

- Further, $i = i_{\text{ox}} + i_{\text{red}} = 0$. We may define a quantity i_0 such that

$$\begin{aligned} i_0 &= nFk_{\text{ox}}^0 c_{\text{ox}} \exp\left(-\frac{E_{a,r}^0}{RT}\right) \exp\left(-\frac{\alpha nF\phi_{\text{rest}}}{RT}\right) \\ &= nFk_{\text{red}}^0 c_{\text{red}} \exp\left(-\frac{E_{a,o}^0}{RT}\right) \exp\left(\frac{(1-\alpha)nF\phi_{\text{rest}}}{RT}\right). \end{aligned}$$

- Then, even when not at rest,

$$\begin{aligned} i_{\text{red}} &= -i_0 \exp\left(-\frac{\alpha nF\eta}{RT}\right) \\ i_{\text{ox}} &= i_0 \exp\left(\frac{(1-\alpha)nF\eta}{RT}\right). \end{aligned}$$

- The total electrode current density is then

$$i = i_{\text{ox}} + i_{\text{red}} = i_0 \left\{ \exp\left(\frac{(1-\alpha)nF\eta}{RT}\right) - \exp\left(-\frac{\alpha nF\eta}{RT}\right) \right\},$$

which is the Butler–Volmer equation.

3.17: Butler–Volmer Equation: Exchange current density

- The quantity i_0 is called the exchange current density. It is the value of oxidation and reduction currents when the cell is at rest.
- That is, it is the quantity of electrons exchanged back and forth, in a dynamic equilibrium.
- Note that its value depends on the concentration of various species involved in the chemical reaction.
- Recall that we can write i_0 as

$$\begin{aligned} i_0 &= nFk_{\text{ox}}^0 c_{\text{ox}} \exp\left(-\frac{E_{a,r}^0}{RT}\right) \exp\left(-\frac{\alpha nF\phi_{\text{rest}}}{RT}\right) \\ &= nFk_{\text{red}}^0 c_{\text{red}} \exp\left(-\frac{E_{a,o}^0}{RT}\right) \exp\left(\frac{(1-\alpha)nF\phi_{\text{rest}}}{RT}\right). \end{aligned}$$

- Setting $\mathcal{E}_{a,r}^0 = \exp\left(-\frac{E_{a,r}^0}{RT}\right)$ and $\mathcal{E}_{a,o}^0 = \exp\left(-\frac{E_{a,o}^0}{RT}\right)$ and equating these two equivalent versions of i_0 gives

$$k_{\text{red}}^0 c_{\text{red}} \mathcal{E}_{a,o}^0 \exp\left(\frac{(1-\alpha)nF\phi_{\text{rest}}}{RT}\right) = k_{\text{ox}}^0 c_{\text{ox}} \mathcal{E}_{a,r}^0 \exp\left(-\frac{\alpha nF\phi_{\text{rest}}}{RT}\right)$$

$$\frac{\exp\left(\frac{(1-\alpha)nF\phi_{\text{rest}}}{RT}\right)}{\exp\left(-\frac{\alpha nF\phi_{\text{rest}}}{RT}\right)} = \frac{k_{\text{ox}}^0 c_{\text{ox}} \mathcal{E}_{a,r}^0}{k_{\text{red}}^0 c_{\text{red}} \mathcal{E}_{a,o}^0}$$

$$\frac{(1-\alpha)nF\phi_{\text{rest}}}{RT} + \frac{\alpha nF\phi_{\text{rest}}}{RT} = \ln\left(\frac{k_{\text{ox}}^0 \mathcal{E}_{a,r}^0}{k_{\text{red}}^0 \mathcal{E}_{a,o}^0}\right) + \ln\frac{c_{\text{ox}}}{c_{\text{red}}}$$

$$\phi_{\text{rest}} = \underbrace{\frac{RT}{nF} \ln\left(\frac{k_{\text{ox}}^0 \mathcal{E}_{a,r}^0}{k_{\text{red}}^0 \mathcal{E}_{a,o}^0}\right)}_{\phi^\ominus} + \frac{RT}{nF} \ln\frac{c_{\text{ox}}}{c_{\text{red}}}$$

$$\phi_{\text{rest}} = \phi^{\ominus} + \frac{RT}{nF} \ln \frac{c_{\text{ox}}}{c_{\text{red}}}.$$

- This is the Nernst equation, and describes the concentration dependence of the rest potential.
- Substituting ϕ_{rest} back into i_0 gives

$$\begin{aligned} i_0 &= nFk_{\text{ox}}^0 c_{\text{ox}} \mathcal{E}_{a,r}^0 \exp\left(-\frac{\alpha nF}{RT} \left(\phi^{\ominus} + \frac{RT}{nF} \ln \frac{c_{\text{ox}}}{c_{\text{red}}}\right)\right) \\ &= nFk_{\text{ox}}^0 c_{\text{ox}} \mathcal{E}_{a,r}^0 \exp\left(-\frac{\alpha nF\phi^{\ominus}}{RT}\right) c_{\text{red}}^{\alpha} c_{\text{ox}}^{-\alpha} \\ &= nFk_{\text{ox}}^0 c_{\text{ox}}^{1-\alpha} c_{\text{red}}^{\alpha} \mathcal{E}_{a,r}^0 \exp\left(-\frac{\alpha nF\phi^{\ominus}}{RT}\right), \end{aligned}$$

and

$$\begin{aligned} i_0 &= nFk_{\text{red}}^0 c_{\text{red}} \mathcal{E}_{a,o}^0 \exp\left(\frac{(1-\alpha)nF}{RT} \left(\phi^{\ominus} + \frac{RT}{nF} \ln \frac{c_{\text{ox}}}{c_{\text{red}}}\right)\right) \\ &= nFk_{\text{red}}^0 c_{\text{red}} \mathcal{E}_{a,o}^0 \exp\left(\frac{(1-\alpha)nF\phi^{\ominus}}{RT}\right) c_{\text{ox}}^{1-\alpha} c_{\text{red}}^{\alpha-1} \\ &= nFk_{\text{red}}^0 c_{\text{ox}}^{1-\alpha} c_{\text{red}}^{\alpha} \mathcal{E}_{a,o}^0 \exp\left(\frac{(1-\alpha)nF\phi^{\ominus}}{RT}\right). \end{aligned}$$

- Since these two equations are equal, we can define an effective reaction rate constant

$$k_0 = k_{\text{ox}}^0 \mathcal{E}_{a,r}^0 \exp\left(-\frac{\alpha nF\phi^{\ominus}}{RT}\right) = k_{\text{red}}^0 \mathcal{E}_{a,o}^0 \exp\left(\frac{(1-\alpha)nF\phi^{\ominus}}{RT}\right),$$

so we end up with the final result

$$i_0 = nFk_0 c_{\text{ox}}^{1-\alpha} c_{\text{red}}^{\alpha}.$$

- It is interesting to evaluate k_0 more, starting with either side of the equation. For example,

$$\begin{aligned}
k_0 &= k_{\text{ox}}^0 \mathcal{E}_{a,r}^0 \exp\left(-\frac{\alpha n F \phi^\ominus}{RT}\right) \\
&= k_{\text{ox}}^0 \exp\left(\frac{-E_{a,r}^0}{RT} - \frac{\alpha n F \phi^\ominus}{RT}\right) \\
&= k_{\text{ox}}^0 \exp\left(\frac{-E_{a,r}^0}{RT} - \frac{\alpha n F}{RT} \left(\frac{RT}{nF} \left(\ln\left(\frac{k_{\text{ox}}^0}{k_{\text{red}}^0}\right) + \ln \mathcal{E}_{a,r}^0 - \ln \mathcal{E}_{a,o}^0\right)\right)\right) \\
&= k_{\text{ox}}^0 \exp\left(\frac{-E_{a,r}^0}{RT} - \alpha \left(\ln\left(\frac{k_{\text{ox}}^0}{k_{\text{red}}^0}\right) - \frac{E_{a,r}^0}{RT} + \frac{E_{a,o}^0}{RT}\right)\right) \\
&= k_{\text{ox}}^0 \left(\frac{k_{\text{ox}}^0}{k_{\text{red}}^0}\right)^{-\alpha} \exp\left(-\frac{1}{RT} \left((1-\alpha)E_{a,r}^0 + \alpha E_{a,o}^0\right)\right) \\
&= (k_{\text{ox}}^0)^{1-\alpha} (k_{\text{red}}^0)^\alpha \exp\left(-\frac{1}{RT} \left((1-\alpha)E_{a,r}^0 + \alpha E_{a,o}^0\right)\right).
\end{aligned}$$

- So, we see that the reaction-rate “constant” is a function of the charge-transfer coefficient α and furthermore a function of temperature.
- Generalizing to the case where there are multiple reactants and products, we have

$$i_0 = n F k_0 \left(\prod c_{\text{ox}}\right)^{1-\alpha} \left(\prod c_{\text{red}}\right)^\alpha.$$

- For a lithium-ion cell, $n = 1$. Lithium ions in the electrolyte are reduced to give lithium atoms in the solid.
- We then have $\prod c_{\text{ox}} = c_e (c_{s,\text{max}} - c_{s,e})$ where:
 - The term c_e is the concentration of lithium in the electrolyte,
 - The term $c_{s,\text{max}}$ is the maximum concentration of lithium in the solid,
 - The term $c_{s,e}$ is the surface concentration of lithium in the solid.

- So, $(c_{s,\max} - c_{s,e})$ is the concentration of available spaces for lithium atoms to enter.
- We also have $c_{\text{red}} = c_{s,e}$.
- Also, ϕ_{rest} is typically denoted as U_{ocp} , where “ocp” stands for “open circuit potential”.
- The direction of lithium flux depends on whether the potential difference between solid and electrolyte is above or below U_{ocp} , so,

$$\eta = (\phi_s - \phi_e) - U_{\text{ocp}}.$$

- The final Butler–Volmer relationship for a lithium-ion cell in [A m^{-2}] is then

$$i = Fk_0c_e^{1-\alpha}(c_{s,\max} - c_{s,e})^{1-\alpha}c_{s,e}^\alpha \left\{ \exp\left(\frac{(1-\alpha)F}{RT}\eta\right) - \exp\left(-\frac{\alpha F}{RT}\eta\right) \right\}.$$

- It is more often expressed in terms of [$\text{mol m}^{-2} \text{s}^{-1}$] as:

$$j = k_0c_e^{1-\alpha}(c_{s,\max} - c_{s,e})^{1-\alpha}c_{s,e}^\alpha \left\{ \exp\left(\frac{(1-\alpha)F}{RT}\eta\right) - \exp\left(-\frac{\alpha F}{RT}\eta\right) \right\},$$

where $j > 0$ indicates flux of lithium leaving the particle and $j < 0$ indicates flux of lithium entering the particle.

- We have now proven the fifth chapter relation: Butler–Volmer kinetics.

3.18: Boundary conditions

- To implement these five equations, you need a PDE solver.
- We're going to skip the simulation step in this chapter, but look at it in the next chapter. But, generally, the process is to:
 - Set up geometries of solid, electrolyte, and overall system;
 - Specify PDEs, algebraic equations that operate in each geometry;
 - Enter all parameters and functions;
 - Specify initial conditions, forcing functions, boundary conditions.
- We look at boundary conditions at the solid-electrolyte interface here.

Charge conservation in the solid

- Current entering/exiting the particle must be taken into account:

$$-\sigma \nabla \phi_s = \mathbf{i}_s$$

$$\hat{\mathbf{n}}_s \cdot \nabla \phi_s = -\frac{\mathbf{i}_s \cdot \hat{\mathbf{n}}_s}{\sigma}$$

$$\hat{\mathbf{n}}_s \cdot \nabla \phi_s = -\frac{Fj}{\sigma},$$

at the interface between the particle and the electrolyte.

Mass conservation in the solid

- Lithium entering/exiting the particle must be taken into account:

$$-D_s \nabla c_s = \mathbf{N}_s$$

$$\hat{\mathbf{n}}_s \cdot \nabla c_s = -\frac{\mathbf{N}_s \cdot \hat{\mathbf{n}}_s}{D_s}$$

$$\hat{\mathbf{n}}_s \cdot \nabla c_s = -\frac{j}{D_s},$$

at the interface between the particle and the electrolyte.

Mass conservation in the electrolyte

- These are a little more complex, but still very manageable.
- Current entering/exiting the particle must be equal on both sides of the boundary. Flux of cations, anions, and solvent at the interface between the particle and the electrolyte are:

$$\mathbf{N}_+ \cdot \hat{\mathbf{n}}_e = c \mathbf{v}_+ \cdot \hat{\mathbf{n}}_e = -j, \quad \mathbf{N}_0 \cdot \hat{\mathbf{n}}_e = c \mathbf{v}_0 \cdot \hat{\mathbf{n}}_e = 0,$$

$$\mathbf{N}_- \cdot \hat{\mathbf{n}}_e = c \mathbf{v}_- \cdot \hat{\mathbf{n}}_e = 0$$

where $\mathbf{N}_+ \cdot \hat{\mathbf{n}}_e = -j$ as j is flux from solid to electrolyte.

- Evaluating these equations

$$-j = -v_+ D \left(1 - \frac{d \ln c_0}{d \ln c_e} \right) \nabla c_e \cdot \hat{\mathbf{n}}_e + \frac{\mathbf{i}_e \cdot \hat{\mathbf{n}}_e t_+^0}{z_+ F} + v_+ c_e \mathbf{v}_0 \cdot \hat{\mathbf{n}}_e$$

$$0 = -v_- D \left(1 - \frac{d \ln c_0}{d \ln c_e} \right) \nabla c_e \cdot \hat{\mathbf{n}}_e + \frac{\mathbf{i}_e \cdot \hat{\mathbf{n}}_e t_-^0}{z_- F} + v_- c_e \mathbf{v}_0 \cdot \hat{\mathbf{n}}_e.$$

- Specializing to the lithium-ion case, $v_+ = v_- = 1$, $z_+ = -z_- = 1$, and assuming $\mathbf{v}_0 = 0$:

$$-j = -D \left(1 - \frac{d \ln c_0}{d \ln c_e} \right) \nabla c_e \cdot \hat{\mathbf{n}}_e + \frac{\mathbf{i}_e \cdot \hat{\mathbf{n}}_e t_+^0}{F}$$

$$0 = -D \left(1 - \frac{d \ln c_0}{d \ln c_e} \right) \nabla c_e \cdot \hat{\mathbf{n}}_e - \frac{\mathbf{i}_e \cdot \hat{\mathbf{n}}_e t_-^0}{F}.$$

- To eliminate \mathbf{i}_e , add t_+^0/t_-^0 times the second equation to the first

$$-j = -D \left(1 - \frac{d \ln c_0}{d \ln c_e} \right) \left(1 + \frac{t_+^0}{t_-^0} \right) \nabla c_e \cdot \hat{\mathbf{n}}_e$$

$$-t_-^0 j = -D \left(1 - \frac{d \ln c_0}{d \ln c_e} \right) \nabla c_e \cdot \hat{\mathbf{n}}_e.$$

- This gives us the boundary condition for ∇c_e

$$\hat{\mathbf{n}}_e \cdot \nabla c_e = \frac{1 - t_+^0}{D \left(1 - \frac{d \ln c_0}{d \ln c_e} \right)} j = \frac{t_-^0}{D \left(1 - \frac{d \ln c_0}{d \ln c_e} \right)} j.$$

Charge conservation in the electrolyte

- We can substitute this value for $\hat{\mathbf{n}}_e \cdot \nabla c_e$ into the flux equation to solve for \mathbf{i}_e at the boundary

$$-j = -D \left(1 - \frac{d \ln c_0}{d \ln c_e} \right) \frac{(1 - t_+^0) j}{D \left(1 - \frac{d \ln c_0}{d \ln c_e} \right)} + \frac{\mathbf{i}_e \cdot \hat{\mathbf{n}}_e t_+^0}{F}$$

$$0 = -D \left(1 - \frac{d \ln c_0}{d \ln c_e} \right) \frac{t_-^0 j}{D \left(1 - \frac{d \ln c_0}{d \ln c_e} \right)} - \frac{\mathbf{i}_e \cdot \hat{\mathbf{n}}_e t_-^0}{F}.$$

- Both expressions give identical results: $\mathbf{i}_e \cdot \hat{\mathbf{n}}_e = -jF$.
- Substituting this and the prior boundary condition into the \mathbf{i}_e equation:

$$-\kappa \nabla \phi_e - \kappa_D \nabla \ln c_e = \mathbf{i}_e$$

$$\hat{\mathbf{n}}_e \cdot \left(-\kappa \nabla \phi_e - \frac{\kappa_D}{c_e} \nabla c_e \right) = \hat{\mathbf{n}}_e \cdot \mathbf{i}_e$$

$$\nabla \phi_e \cdot \hat{\mathbf{n}}_e = \left(\frac{F}{\kappa} - \frac{\kappa_D}{\kappa c_e} \frac{t_-^0}{D \left(1 - \frac{d \ln c_0}{d \ln c_e} \right)} \right) j.$$

at the interface between the particle and the electrolyte.

- Additionally, ion flux is zero at external boundaries.

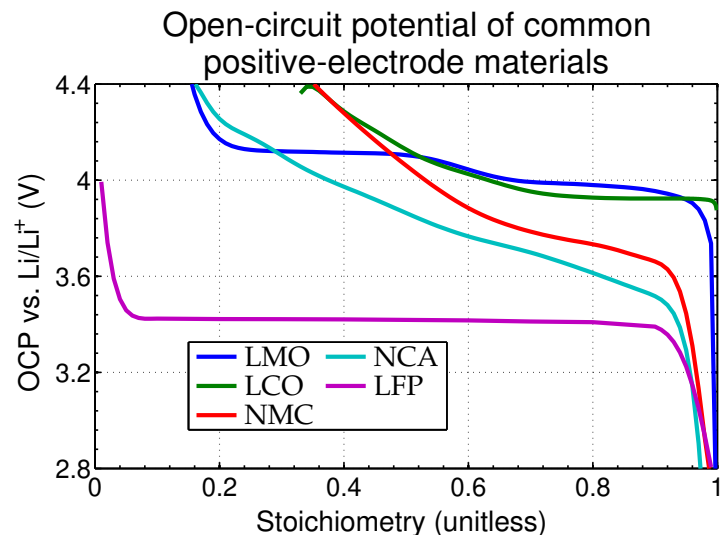
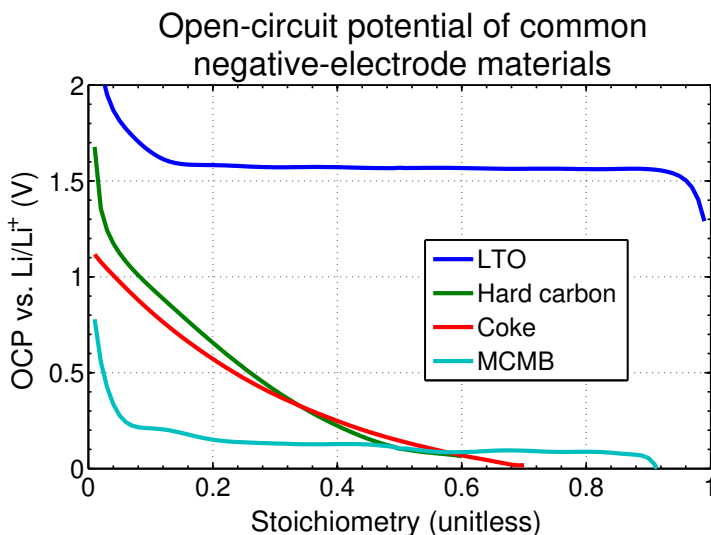
3.19: Cell-level quantities

Cell open-circuit voltage

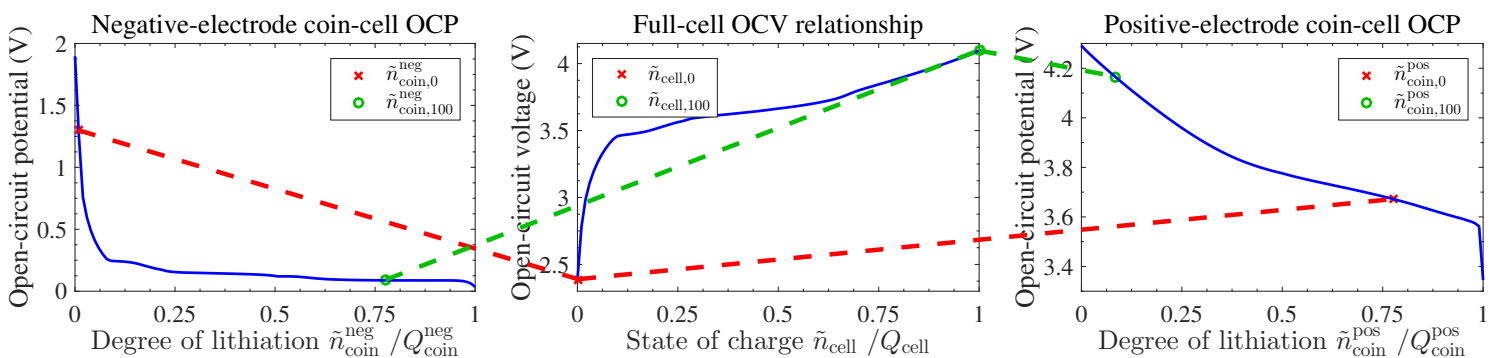
- Simulating an entire cell using the equations developed in this chapter is unreasonable given present-day computing power.
- But, some cell-level variables can be understood quite easily from these lower-level equations.
- As we saw in Chap. 2, the *open-circuit voltage* of a cell is the steady-state terminal voltage when the cell is allowed to rest.
- In terms of the model equations we have seen to date, this steady-state condition means that concentration of lithium is uniform in all solid particles in both electrodes and the concentration of lithium is uniform in the electrolyte.
- The cell open-circuit voltage, then, can be related to the *open-circuit potentials* of the two electrodes.

$$U_{\text{ocv}}^{\text{cell}} = U_{\text{ocp}}^{\text{pos}} - U_{\text{ocp}}^{\text{neg}}.$$

- High cell voltages (for high energy density), require high positive-electrode potential and low negative-electrode potential (vs. Li/Li^+).



- The figures show the OCP curves for common electrode materials.
- The negative is plotted versus $x = c_s^{\text{neg}} / c_{s,\text{max}}^{\text{neg}}$, where $c_{s,\text{max}}^{\text{neg}}$ is the total storage capability of the electrode solid material when the crystal lattice structure is completely full of lithium.
- The positive is plotted versus $y = c_s^{\text{pos}} / c_{s,\text{max}}^{\text{pos}}$.
- These relationships are measured in the laboratory, and are computed either by analytic function approximations or via table lookup. The course text has more details.
- An example lab result is shown, illustrating the determination of electrode operating windows compared to overall cell OCV versus SOC



Cell capacity

- Another cell-level quantity that can be quickly explained is the ampere-hour capacity of the cell.
- We develop a relationship to compute this quantity in a sequence of steps, starting with expressions for capacity of each electrode.
- To compute the Ah capacity of an electrode, we must first determine the capacity of the electrode in moles of lithium per unit volume.
- In an extreme case, this might be equal to $c_{s,\text{max}}$.

- But, practical cells don't use this entire capacity (to avoid boundaries, which lead either to rapid cell degradation or power depletion)
 - We use only from $x_{0\%}$ to $x_{100\%}$ in the negative electrode and from $y_{0\%}$ to $y_{100\%}$ in the positive electrode.

- The total used capacities of the negative and positive electrodes are

$$Q_V^{\text{neg}} = c_{s,\text{max}}^{\text{neg}} |x_{100\%} - x_{0\%}| \text{ mol m}^{-3}$$

$$Q_V^{\text{pos}} = c_{s,\text{max}}^{\text{pos}} |y_{100\%} - y_{0\%}| \text{ mol m}^{-3}.$$

- Next, we need to determine the total volume of the solid material in each electrode.
- We start with the total volume of the electrode, which equals electrode plate area A multiplied by electrode thickness L .
- However, not all of this volume is filled with solid—some is filled with electrolyte, filler, binder or other non-active materials.
- The value ε_s is the fraction of the total electrode volume that is occupied by the solid electrode material. Knowing this, we can now compute the total used capacities of each electrode in moles.

$$Q^{\text{neg}} = AL^{\text{neg}} \varepsilon_s^{\text{neg}} c_{s,\text{max}}^{\text{neg}} |x_{100\%} - x_{0\%}| \text{ mol}$$

$$Q^{\text{pos}} = AL^{\text{pos}} \varepsilon_s^{\text{pos}} c_{s,\text{max}}^{\text{pos}} |y_{100\%} - y_{0\%}| \text{ mol}.$$

- Finally, making use of Faraday's constant and knowing that there are 3600 s in 1 h, we can find ampere-hour capacity.

$$Q^{\text{neg}} = AFL^{\text{neg}} \varepsilon_s^{\text{neg}} c_{s,\text{max}}^{\text{neg}} |x_{100\%} - x_{0\%}| / 3600 \text{ Ah}$$

$$Q^{\text{pos}} = AFL^{\text{pos}} \varepsilon_s^{\text{pos}} c_{s,\text{max}}^{\text{pos}} |y_{100\%} - y_{0\%}| / 3600 \text{ Ah}.$$

- Often, one electrode has somewhat more capacity than the other, usually in order to minimize the occurrence of mechanisms that lead to cell degradation.
- The overall cell capacity is the minimum of the two electrode capacities:

$$Q = \min(Q^{\text{neg}}, Q^{\text{pos}}) \text{ Ah.}$$

Cell state of charge

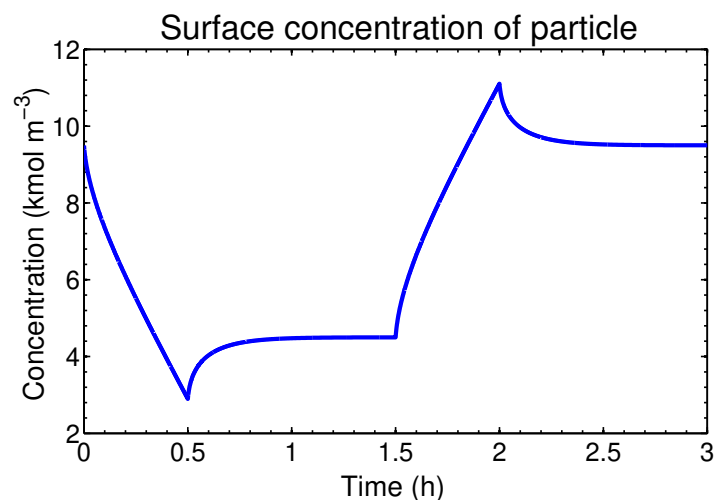
- Cell state of charge can be related either to the total amount of lithium in the negative or positive electrodes.
- Similarly, by dividing the total amount of lithium in either electrode by the total volume of the solid active material in which it resides, we can also relate state of charge to the *average* concentration of lithium in the negative or positive electrodes, where the average is computed over the entire electrode.
- When the cell is fully charged, the amount of lithium in the negative electrode is at its maximum allowable level, and the amount of lithium in the positive electrode is at its minimum allowable level.
- In terms of stoichiometry, $c_{s,\text{avg}}^{\text{neg}}/c_{s,\text{max}}^{\text{neg}} = x_{100\%}$ and $c_{s,\text{avg}}^{\text{pos}}/c_{s,\text{max}}^{\text{pos}} = y_{100\%}$.
- Similarly, when the cell is fully discharged, the amount of lithium in the negative electrode is at its minimum allowable level, and the amount of lithium in the positive electrode is at its maximum allowable level.
- In terms of stoichiometry, $c_{s,\text{avg}}^{\text{neg}}/c_{s,\text{max}}^{\text{neg}} = x_{0\%}$ (where $x_{0\%} < x_{100\%}$) and $c_{s,\text{avg}}^{\text{pos}}/c_{s,\text{max}}^{\text{pos}} = y_{0\%}$ (where $y_{0\%} > y_{100\%}$).

- State-of-charge varies linearly as the stoichiometry of the negative electrode varies between $x_{0\%}$ and $x_{100\%}$ (or, equivalently, as the stoichiometry of the positive electrode varies between $y_{0\%}$ and $y_{100\%}$).
- Therefore, we can compute cell-level state of charge as either

$$z = \frac{C_{s,\text{avg}}^{\text{neg}}/C_{s,\text{max}}^{\text{neg}} - x_{0\%}}{x_{100\%} - x_{0\%}} = \frac{C_{s,\text{avg}}^{\text{pos}}/C_{s,\text{max}}^{\text{pos}} - y_{0\%}}{y_{100\%} - y_{0\%}}.$$

3.20: Single-particle model

- It turns out that the diffusion of lithium inside the solid particles is the slowest process in a cell, so its dynamic contribution dominates.
- So, we can consider a single-particle model (SPM) of a cell, which simplifies each electrode by modeling it as a single spherical particle representative of a typical particle within the electrode.
 - Electrolyte concentration and potential dynamics are ignored.
- While crude, the SPM is a good learning tool for understanding how lithium-ion cells should respond to different input stimuli, and they can be used within control designs to give good state of charge estimates.
- To simulate diffusion of lithium within a single solid particle, we introduce a finite-volume method for discretizing the diffusion equation.
 - A single solid particle is divided into spherical shells having equal thickness (like an idealized onion).
 - Each time step, lithium flux from one shell to another is calculated, and the concentration of lithium within each shell is updated.
 - Imposed cell current forces lithium in/out of the outermost shell.
- Consider the following code for simulating a single particle, as the particle is discharged, rested, charged, and rested.
- The output of this code is plotted in the figure.




```

% Replace constants below with relevant values for your problem
R = 10e-6;      % particle radius [m]
Cmax = 12000;  % [mol/m^3]
c0 = 9500;     % initial concentration [mol/m^3]
j0 = 5000*R/3/1800; % lithium flux [mol/m^2/sec]
D = 1e-14;     % solid diffusivity, [m^2/s]

jk = [j0*ones(1,1800), zeros(1,3600)]; % discharge and rest
jk = [jk -jk]; % discharge and rest, then charge and rest

% Simulation control
Nr = 20;      % number of "shells" radially
dR = R/Nr;    % width of each "shell"
Sa = 4*pi*(R*(1:Nr)/Nr).^2; % outer surface area of each shell
dV = (4/3)*pi*((R*(1:Nr)/Nr).^3-(R*(0:Nr-1)/Nr).^3); % vol. of ea. shell
dt = 1; % time steps of 1 second

c = c0*ones(1,Nr); % concentration profile versus "r" dimension
cse = zeros(size(jk)); % concentration at surface
cse(1) = c0;

for timestep = 1:length(jk),
    N = -D*diff(c)/dR; % flux at surfaces between "bins"
    M = N.*Sa(1:end-1); % total moles crossing surface between bins
    c = c + ([0 M] - [M 0])*dt./dV; % conc. change via diffusion
    c(end) = c(end) - jk(timestep)*Sa(end)*dt/dV(end); % at boundary
    cse(timestep+1) = c(end);
end

figure(1); clf; plot((0:length(jk))/3600,cse/1000);
title('Surface concentration of particle')
xlabel('Time (h)'); ylabel('Concentration (kmol m^{-3})')

```

- In the code, the spherical particle is assumed to have N_r equal-thickness onion-like “shells”.
 - So, the thickness of any given shell is $dR = R_s/N_r$.
- We will also need to know the outer surface area of each shell and the volume of each shell.

- The innermost shell has volume $dV_1 = \frac{4}{3}\pi (dR)^3$ and outer surface area $Sa_1 = 4\pi (dR)^2$.
- The next shell has volume $dV_2 = \frac{4}{3}\pi (2dR)^3 - dV_1$ and outer surface area $Sa_2 = 4\pi (2dR)^2$.
- By extension, the n th shell has volume

$$dV_n = \frac{4}{3}\pi (ndR)^3 - \frac{4}{3}\pi ((n-1)dR)^3$$

and surface area $Sa_n = 4\pi (ndR)^2$.

- The variables dV and Sa in the code are vectors containing the volumes and outer surface areas of all shells, respectively.
- Now, consider converting the molar flux from a continuous function of distance r to a discrete function at the shell boundaries.

$$N = -D_s \nabla c_s = -D_s \frac{\partial c_s}{\partial r} \approx -D_s \frac{\Delta c_s}{\Delta r}.$$

- The flux at the boundary between shells n and $n+1$ can be written as

$$N_n \approx -D_s \frac{c_{n+1} - c_n}{dR}.$$

- When N_n is negative, flux is entering the n th shell from the $(n+1)$ st shell; when it is positive, flux is leaving the n th shell to the $(n+1)$ st shell.
- The vector N in the code computes this flux at all shell boundaries, except at the outer surface of the particle, which is computed separately. This flux has units $\text{mol m}^{-2} \text{s}^{-1}$.
- In the code, we then multiply N by the surface area of the shell through which the flux is passing to get a rate of material transfer. This is the M variable in the code, in units mol s^{-1} .

- Considering any shell, there are two boundaries through which this flux can come: the inner surface and the outer surface.
- The total increase in the number of moles in the n th shell is equal to $Sa_n N_n - Sa_{n-1} N_{n-1}$ in units mol s^{-1} .
- To get a change in concentration, we must multiply by Δt in seconds and divide by the volume of the n th shell.
- The concentration update equation uses this logic.
- How about boundary conditions?
 - We have an applied flux j in $\text{mol m}^{-2} \text{s}^{-1}$.
 - Multiplying j by $Sa_n \Delta t / V_n$ gives the change in concentration of the outer shell because of the applied flux every Δt seconds.
- To find the average interphase lithium flux in $\text{mol m}^{-2} \text{s}^{-1}$ for a given cell current in A, we must first convert the cell current from amperes to mol s^{-1} . Faraday's constant will help with this.
- Next, we need to know how many square meters of interphase area can be found in each electrode.
- To arrive at this answer, we must first calculate the specific interfacial area in $\text{m}^2 \text{m}^{-3}$.
- If we assume that all electrode particles are spherical with radius R_s , and that we have solid phase volume fraction ε_s , then

$$a_s = \frac{\text{total surface area of spheres in a given volume}}{\text{total volume of a sphere}}$$

$$= \varepsilon_s \frac{4\pi R_s^2}{\frac{4}{3}\pi R_s^3} = \frac{3\varepsilon_s}{R_s}.$$

- This results says how many square meters of particle surface area there are per cubic meter of total electrode volume. So, $a_s AL$ gives the total square meters of particle surface area in an electrode. So,

$$j = \frac{i_{\text{app}}}{a_s F A L} \text{ mol m}^{-2} \text{ s}^{-1}.$$

- Finally, while SOC depends on the average concentration of lithium in the electrode, voltage depends on the *surface* concentration of lithium (*i.e.*, at the interface between the solid and electrolyte).
- The code calls this $c_{s,e}$, which is what we have termed $c_{s,e}$ elsewhere.
- When simulating an entire cell using the single-particle method, one particle models the negative electrode and a second particle (using a copy of the above code) models the positive electrode.
- Cell voltage is then computed as $U_{\text{ocp}}^{\text{pos}}(y) - U_{\text{ocp}}^{\text{neg}}(x)$, where $y = c_{s,e}/c_{s,\text{max}}$ and $x = c_{s,e}/c_{s,\text{max}}$.

Where from here

- We have now completed the most difficult derivations in the course!
- From now on (until Chap. 7), we depart from topics in physical chemistry and electrochemistry and work with the models we have now developed, successively bringing them up in scale until we arrive at ordinary difference equations.
- But, these are the most accurate model equations we will have in the course. From now on, our goal is to approximate these equations with versions that are simpler to implement.
- At the same time, we will attempt to minimize the error that we introduce into the models.

Partial, but not-too-bad, glossary

- $c(x, y, z, t)$ [mol m^{-3}] is the concentration of lithium in the neighborhood of a given location.
- c_+ and c_- [mol m^{-3}] are the concentrations of the cation and anion in the electrolyte, respectively (cf. p. 3–28ff).
- $D(x, y, z, t)$ [$\text{m}^2 \text{s}^{-1}$] is a material-dependent *diffusivity*.
- $\mathcal{D}(x, y, z, t)$ [$\text{m}^2 \text{s}^{-1}$] is the Maxwell–Stefan *diffusivity* of a concentrated solution.
- $\mathbf{E}(x, y, z, t)$ [V m^{-1}] is the (vector) electric field at a point.
- $F = 96,485$ [C mol^{-1}] is Faraday’s constant.
- f_{\pm} [u/l] mean molar activity coefficient.
- G [J] Gibbs free energy of a sub/system.
- γ_{\pm} [u/l] mean molal activity coefficient.
- H [J] is the enthalpy of a system; dH is the heat added to or removed from a system by a chemical reaction.
- η [V] is the reaction overpotential.
- $\mathbf{i}(x, y, z, t)$ [A m^{-2}] is the (vector) current density flowing through a representative cross-sectional area centered at a given location.
- $j(x, y, z, t)$ [$\text{mol m}^{-2} \text{s}^{-1}$] is the rate of positive charge flowing *out of* a particle across a boundary between the solid and the electrolyte.
- K_{ab} [J s m^{-4}] is the Maxwell–Stefan friction coefficient between species a and b .
- κ [S m^{-1}] is the ionic conductivity.

- μ [J mol^{-1}] is the chemical potential of a system.
- $\bar{\mu}$ [J mol^{-1}] is the electrochemical potential of a system.
- $\mathbf{N}(x, y, z, t)$ [$\text{mol m}^{-2} \text{s}^{-1}$] is the (vector) *molar flux* of lithium flowing through a representative cross-sectional area of the solid centered at a given location.
- $N_A = 6.022 \times 10^{23}$ [mol^{-1}] is Avagadro's number.
- ν_+ and ν_- [u/l] are the stoichiometric coefficients of the cation and anion, respectively (cf. p. 3-28).
- $\mathbf{p}(t)$ [kg m s^{-1}] is the (vector) momentum of an object.
- p [Pa] is the pressure experienced by a system;
- p_i [Pa] is the partial pressure experienced by a subsystem within a system.
- $\phi(x, y, z, t)$ [V] is the scalar field representing the electric potential at a given point.
- $Q(x, y, z, t)$ [C] is the charge in the vicinity of a given point.
- $q(x, y, z, t)$ [J] is the heat, usually considered as a delta δq of added/removed heat to a system.
- $R = 8.314$ [$\text{J mol}^{-1} \text{K}^{-1}$] is the universal gas constant.
- $\rho_V(x, y, z, t)$ [C m^{-3}] is the *charge density* (of positive charges) in the vicinity of a given point.
- S [J K^{-1}] is entropy of a system.
- s_+, s_-, s_0 [u/l] is the signed stoichiometric coefficient (cf. p. 3-48).

- $\sigma(x, y, z, t)$ [S m^{-1}] is a material-dependent parameter called the *bulk conductivity* of homogenous materials without inclusions in the vicinity of a given point.
- $T(x, y, z, t)$ [K] is the temperature at a point.
- t_+^0 and t_-^0 [u/l] transference number of the cation and anion with respect to the solvent.
- U [J] internal energy of a system.
- \mathbf{v} [m s^{-1}] is the velocity of a species.
- w [J] is the work, usually considered as a delta δw of work done on or by a system.
- z_+ and z_- [u/l] are the signed charge numbers of the cation and anion, respectively (cf. p. 3-28).