

Notes T - Transport and Kinetics

Chapter 1 - The Postulates

Why physicochemical mechanics? At the end of Chapter 5 on Statistical Mechanics, we talked a bit about reactions, when old molecules disappear and new ones appear; and in Chapter 6, we talked more about how molecules move around randomly by diffusion, or drift due to an applied force, such as from an electric field in electrophoresis. Because of friction, transport in the presence of an external force quickly reaches the terminal drift velocity. After that, the friction force balances the applied force, and it is the drift velocity, and not the acceleration, which is proportional to the applied force. Aristotle already recognized this over 2300 years ago.

Thought experiment: In about 1590 Galileo Galilei dropped two balls of different mass and diameter from the leaning tower of Pisa, and concluded that they fell at the same rate. But if he had measured more carefully, given air friction, what would he have noticed?

In this final part of our tour of physical chemistry, we will use the equations we have derived in statistical mechanics to derive any of the basic transport and equilibrium equations in chemistry. We'll call this "Physicochemical Mechanics," which extends thermodynamics by two more postulates, so one can discuss how systems out of equilibrium settle into equilibrium.

The postulates of physicochemical mechanics We have already discussed all the major ideas we need in previous Chapters on thermodynamics and statistical mechanics. Thermodynamics has 3 Postulates or 'laws' that we derived from the two Postulates of statistical mechanics: (1) energy conservation, (2) entropy increases spontaneously, and (3) entropy is minimized at 0 K. Physicochemical mechanics is based on two additional postulates that go beyond classical thermodynamics, and that we also derived or motivated already from statistical mechanics:

Postulate 1. *The potential that describes all the driving forces on molecules is the position-dependent chemical potential, or 'physicochemical potential' for each type of molecule "i"*

$$\mu_{gi}(x) = \mu_i(T, P, n, \dots, x)$$

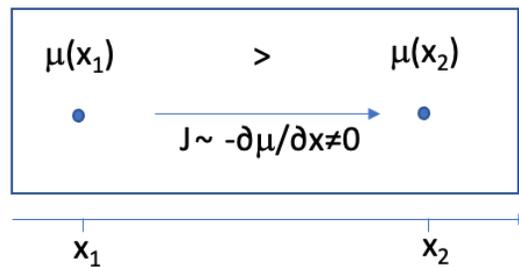
Postulate 2. *At every position x the rate of diffusive transport of chemical component i in the direction x , also known as the flux J_{xi} , (units of moles/area/time), is given by*

$$J_{xi} = -U_i c_i \frac{d\mu_{gi}}{dx}.$$

Postulate 1 replaces the familiar position-independent chemical potential (partial molar free energy) in the Gibbs ensemble by a position-dependent chemical potential, so the system can be out of equilibrium: μ can have different values in different places in the system. As we saw in Chapters 3, " μ is the quantity that is equalized when particle number stops changing." Postulate 2 says that the flux of particles is proportional to $-\partial\mu/\partial x$, so $\mu(x)$ acts as a 'driving force' for particles to move. We derived this in the previous chapter using stat mech for a protein in a gel.

The picture below illustrates what happens. Let's say we have a system with molecules at x_1 and x_2 , and the chemical potential is initially higher at x_1 than x_2 so the system is out of equilibrium. The molecules will move to equalize the chemical potentials at x_1 and x_2 (and hence minimize overall free energy G). Thus, there is a net flux J of molecules from x_1 to x_2 , from higher to lower chemical potential. The flux causes $\mu(x_1)$ to go down and $\mu(x_2)$ to go up because $\mu = \mu^{(0)} + RT \ln(c)$,

so increasing concentration c on the right will increase μ , and *vice versa* on the left. Eventually, $\mu(x_1) = \mu(x_2)$ and the flux of particles stops because $J \sim -\partial\mu/\partial x = 0$. Then equilibrium has been reached.



Note that our two postulates do not include the effect of random forces, except as they relate to drift velocity. Thus they do not describe a single molecule, but rather the motion of many molecules. So, in the above picture we can't make the sub-volumes around x_1 or x_2 too small. They must contain a fair number of molecules, such that concentration is a smooth function of position. By the Central limit theorem, the fluctuations scale as $1/\sqrt{N}$, where N is the number of particles in the sub-volume. So by the time you have 900 particles, $\sqrt{N}=30$ and you are making a 3% error. A syringe of vaccine typically contains mRNA molecules at 0.5 mM in 0.3 ml of solution, or 10^{17} mRNA molecules. So the error would be only $1/\sqrt{(10^{17})} \approx 3 \cdot 10^{-9}$. So our formulas for transport and equilibration should be pretty accurate in many practical situations.

The μ_i in Postulate 1 accounts for the presence of other position-dependent 'forces f ' that can push molecule "i" besides T and P , like an applied force $F(x)$ or an electric potential $V_e(x)$. Just like the energy is $E=TS-PV+\mu n + \dots$, where the " \dots " accounts for other pairs of conjugate thermodynamic variables such as $-FL$ or (force times length for a spring), these bilinear terms have to be added to the chemical potential μ_i if the system is more complicated.

Homework Problem T1.1: Looking at Chapter 3, what other terms besides $-FL$ (force \times distance = energy) could one add to the energy or chemical potential, to account for a charge Q in an electric potential V_e , or for surface area A with surface tension σ ?

In order to use Postulate 2, we need to calculate the derivative of the physicochemical potential. Using the chain rule for partials,

$$\frac{d\mu_{gi}}{dx} = \frac{\partial\mu_i}{\partial x} + \frac{\partial\mu_i}{\partial T} \frac{dT}{dx} + \frac{\partial\mu_i}{\partial P} \frac{dP}{dx} + \frac{\partial\mu_i}{\partial n_i} \frac{dn_i}{dx} + \dots$$

We can simplify this equation a bit. For example, in Chapter 5 we showed that for ideal solutions, $\mu_i = \mu_i^{(0)} + RT \ln(c_i)$, so the first of the derivatives above can be simplified to $\partial\mu_i^{(0)}/\partial x$, and the last to $\partial\mu_i/\partial n_i \cdot dn_i/dx = \partial\mu_i/\partial c_i \cdot dc_i/dx = RT/c_i \cdot dc_i/dx = RT d \ln(c_i)/dx$ since $n_i \sim c_i$ and $(1/y) \partial y/\partial x = \partial \ln(y)/\partial x$. and Also, the order of second derivatives does not matter, so

$$\frac{\partial^2 G}{\partial n_i \partial T} = \frac{\partial}{\partial n_i} \frac{\partial G}{\partial T} = -\frac{\partial S}{\partial n_i} = -s_i = \frac{\partial^2 G}{\partial T \partial n_i} = \frac{\partial}{\partial T} \frac{\partial G}{\partial n_i} = \frac{\partial \mu_i}{\partial T}$$

with a similar result equating $\partial\mu_i/\partial P$ to the partial molar volume v_i . Thus,

$$\frac{d\mu_{gi}}{dx} = \frac{\partial\mu_i^{(0)}}{\partial x} + RT \frac{d \ln c_i}{dx} - s_i \frac{dT}{dx} + v_i \frac{dP}{dx} + \dots$$

This tells us how the driving force for the flux J of molecules depends on standard chemical potential gradient, concentration gradient (in the ideal case), temperature gradient, pressure gradient, and other variables such as electric fields that are externally applied to our system.

We already derived Postulate 2 from statistical mechanics in the last chapter. The flux is proportional to a driving force given by the local gradient of the physicochemical potential multiplied by concentration. The proportionality coefficient, called the mobility $U_i \equiv 1/\gamma_i$, has units of velocity/force and tells us that the terminal drift velocity of a molecule “ i ” in a gas or solution is proportional to the applied force.

The combination of the two postulates easily leads to expressions for the rates of all major transport processes. We will work through some examples in the next couple of chapters.

Equilibrium and steady-state. In thermodynamics, the two equilibrium conditions for a system are $dG = 0$ and $d^2G > 0$. In that case, the flux is $J=0$. For example, if there are two phases, the first condition is satisfied if the chemical potential of component i is the same everywhere in the system: $\mu_{gi}(x) = \text{constant}$, so $d\mu_g/dx \sim J=0$. As another example, if a chemical reaction occurs, the first condition is satisfied if $\Delta G = \sum_i \mu_i \nu_i = 0$, where the ν_i are stoichiometric coefficient. These equations were discussed in Chapter 5 of Statistical Mechanics. The flux J vanishes when all chemical, mechanical, electric, etc. driving forces balance each other, leading to equations describing steady state, or equilibrium in the absence of external forces.

The system may be out of equilibrium, but in what we call ‘steady-state,’ if the concentration of molecules depends on position but not on time. As an example, let us consider the particularly simple case where

$$J = 0 \sim \frac{d\mu_{gi}}{dx} = \frac{\partial \mu_i^{(0)}}{\partial x} + RT \frac{\partial \ln c_i}{\partial x} \Rightarrow d\mu_i^{(0)} = -RT d \ln c_i$$

that is, the only position variation of the physicochemical potential comes from variations in the standard chemical potential and concentration variations. An example would be Mg^{2+} inside a cell, with some distribution of macromolecular polyelectrolytes as the ‘standard’ reference condition. In one region of the cell there may be a large negatively charged RNA, resulting in a lower standard chemical potential for Mg^{2+} ; at another position x , there may be a positively charged protein, resulting in a higher local standard chemical potential. Integrating the above equation after setting the flux equal to 0 (equilibrium) and solving for concentration, we have

$$c_i(x) = c_{i0} e^{-\mu_{0i}(x)/RT}.$$

where c_{i0} is the integration constant such that $\int dV c_i(x) = n_i$, i.e. the concentration integrated over the whole volume equals the mole number of component i in the system. Thus, physicochemical mechanics predicts that the magnesium ions will be distributed according to the [Boltzmann factor](#), which is the answer expected when a canonical ensemble reaches thermal equilibrium.

Homework problem T1.2: The concentration of Mg^{++} ions near a negatively charged RNA molecule is 5 time greater than in the surrounding solvent, so the RNA has a ‘Mg-cloud’ around it. Using the Boltzmann factor, how much lower, in kJ/mole, is the chemical potential for the ions near the RNA than in the bulk solution?

As another qualitative example, if there were positive charges distributed in the system, and a constant electric field is turned on that permeates the system, then the charges will migrate to the side of the system with the lower potential, until that lowering of the energy is offset by

charge-charge repulsion. Again, the physicochemical potential will then be constant throughout the system, even though the concentration of charges is not.

So, constant physicochemical potential everywhere: nothing happens. Different physicochemical potential at different positions: molecules diffuse around until μ is equalized everywhere.

Chapter 2 - Deriving all the ‘classic’ transport and equilibrium equations

We now get the pay-off of adding two postulates to the standard three thermodynamic postulates: our ability to derive easily all the equilibrium and kinetic laws in chemistry, from the Nernst equation to the transition state theory.

Fick’s law. Let’s start with Fick’s law of diffusion. For an ideal solution with one dissolved component and no external fields, temperature, or pressure gradients, $\mu_g(x) = \mu^{(0)} + RT \ln c(x)$

$$\frac{d\mu_{gi}}{dx} = RT \frac{\partial \ln c}{\partial x}$$

is the only term that survives in Postulate 1. (I’m using the partial on the right side because we will also consider the time dependence of c). Inserting into Postulate 2,

$$J_x = -RTUc \frac{\partial \ln c}{\partial x} = -RTU \frac{\partial c}{\partial x},$$

where we used the equality $d \ln y / dx = (1/y) dy / dx$. But $RTU = RT/\gamma = D$, the diffusion coefficient, as we saw in Statistical Mechanics. Thus

$$J_x = -D \frac{\partial c}{\partial x}$$

This is Fick’s first law of diffusion. It says that if there is a concentration gradient, there will be a flux of molecules from higher to lower concentration.

Inserting Fick’s first law into the continuity equation,

$$\frac{\partial c}{\partial t} = -\frac{\partial J_x}{\partial x} = +D \frac{\partial^2 c}{\partial x^2} \text{ or } \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}.$$

This is Fick’s second law of diffusion. It is a differential equation we can use to calculate how any initial concentration distribution will diffuse until equilibrium (constant concentration) is reached.

Homework problem T2.1: Let $c(x) = c_0 e^{-\frac{x^2}{2\Delta x^2}}$, i.e. the concentration initially looks like a Gaussian of width Δx and maximum concentration c_0 at $x=0$. For a protein, $D=50 \mu\text{m}^2/\text{s}$, $c_0=1 \text{ mM}$ and $\Delta x = 1 \text{ mm}$ initially, at what rate is the protein concentration changing at $x=0$? Is it increasing or decreasing according to the sign you get?

Faraday’s law of electrophoresis. Now consider an ideal solution of ions with molar charge $z=q\mathcal{F}$, where $\mathcal{F} \sim 94,600 \text{ Coulombs/mole}$ is Faraday’s constant and q is the charge in elementary charge units. All other gradients, including the concentration gradient, are 0. Therefore

$$\frac{d\mu_g}{dx} = z \frac{\partial V_e}{\partial x},$$

and it follows from Postulate 2 that

$$J = -Uc \frac{d\mu_g}{dx} = -Ucz \frac{\partial V_e}{\partial x}.$$

If we make use of the fact that $\partial V_e / \partial x = -\mathcal{E}$ is the electric field in the x direction, and $J=cv$ (Statistical Mechanics, Chapter 6) says flux equals drift velocity times concentration,

$$v = zU\mathcal{E} = zD\mathcal{E}/RT$$

This is Faraday’s law for electrophoresis, which states that the ion migration velocity is proportional to applied field, proportional to charge, and inversely proportional to the viscosity of the fluid (since $U=D/RT=1/\gamma \sim 1/\eta$). That is why proteins move on a gel.

For cations the flux is directed towards the decrease of electric potential, and for anions it is the opposite, because the force changes its sign. If we know diffusion coefficients, we can

calculate the mobility for an ion, and *vice versa*. For example, at room temperature, typical values for the diffusion coefficient D of low molecular weight impurities in water are near 10^{-9} m²/s, which corresponds to a mobility $U = D / RT \approx 4 \times 10^{-13}$ m²/Joules = m/Newton in the units.

Homework problem T2.2: For a DNA of charge $-10e$ per molecule (e is the elementary charge), field of 10 V/cm and diffusion coefficient of $10 \mu\text{m}^2/\text{s}$, at what velocity does the DNA move through the solution? Tip: remember, in Chapter 6 of Stat Mech, we talked about Langevin's equation, which relates $D = U k_B T$ and $\gamma = 1/U$ (in per molecule units; $D = URT$ in molar units).

Ohm's law. Now consider flow of charges in a conductor of cross sectional area A and length L in the direction of current flow. In that case, current $I = zJA = z(cv)A$ (Coulombs/s), $v = zU\varepsilon$ as before, and electric field is related to voltage by $\varepsilon = V_e/L$. Substituting $v = zU\varepsilon$ and the electric field ε into the equation $I = zcvA$, we obtain

$$I = V_e/R$$

where we define a constant called 'resistance' R such that $R = L/(z^2 U c A)$. This is Ohm's law, with a resistance proportional to the length of the conductor, and inversely proportional to carrier mobility U , carrier concentration c and cross section of the carrier.

Thought experiment: What happens if I make a resistor twice as long? Or if I put two same length resistors one after another? From that thought, can you write down the equation for total resistance R of two resistors R_1 and R_2 in series? Two resistors in parallel have twice the cross section A as a single resistor, but R is inversely proportional to A . So what do you think the formula for resistance in parallel would look like?

Nernst equation. So far we have only considered a single driving factor at a time. However, the multiple gradients in Postulate 1 can be non-zero at the same time, and will balance each other out when equilibrium is reached. Let us consider one such example and the resulting equilibrium law: when only concentration and electric field are driving factors, and the chemical potential of solute "i" is independent of position within the system (e.g. a screened ion or neutral molecule). In that case Postulate 1 simplifies to

$$\frac{d\mu_{gi}}{dx} = RT \frac{\partial \ln(c_i)}{\partial x} + z_i \frac{\partial V_e}{\partial x}$$

where the last term is the molar charge multiplied by the gradient of the electrical potential V_e . Inserting into Postulate 2, we obtain

$$J_i = -U_i c_i \left(RT \frac{\partial \ln(c_i)}{\partial x} + z_i \frac{\partial V_e}{\partial x} \right)$$

At equilibrium the fluxes due to the electric potential and concentration gradients should be equal but oppositely directed, and the net flux of solute i is zero. Thus setting equation J_i to zero and equating the two terms in parentheses,

$$\frac{\partial V_e}{\partial x} = - \frac{RT}{z_i} \frac{\partial \ln(c_i)}{\partial x}$$

Integrating this equation on both sides,

$$\int_0^x dx' \frac{\partial V_e}{\partial x'} = - \frac{RT}{z_i} \int_0^x dx' \frac{\partial \ln(c_i)}{\partial x'},$$

and evaluating the integrals we have

$$V_e(x) - V_e(0) = -\frac{RT}{q_i \mathcal{F}} \ln \frac{c_i(x)}{c_i(0)},$$

where we have replaced the molar charge z_i by its definition in terms of the integer charge q_i and Faraday's constant \mathcal{F} . This is the famous Nernst equation for an electric potential formed due to the concentration difference of solute i in a solution. If we had a reaction with two species "i" $2A^+ \rightarrow B^{2+}$ ($0 \rightarrow -2A^+ + B^{2+}$ in the notation of Chapter 5), and $x=0$ is at standard conditions ($[A_0]=[B_0]=c(0)=1$), adding the second species to the above equation yields

$$V_e(x) = V_e(0) - \frac{RT}{2\mathcal{F}} \ln c_B + \frac{RT}{\mathcal{F}} \ln c_A \quad \text{or} \quad V_e = V_e^{(0)} - \frac{RT}{2\mathcal{F}} \ln \frac{[B]}{[A]^2},$$

where we use the notation $c_A=[A]$, $c_B=[B]$, and $n=2$ is the stoichiometric coefficient for the number of electrons moving. This should look familiar from freshman chemistry!

Homework problem T2.3: Two KCl solutions are connected by a salt bridge, so a current can flow through electrodes connected to the outside of the cell via a Volt meter. If one cell (let's say the one located at $x=0$) has 0.1 M KCl, and the other has 10 M KCl in it, what is the voltage difference between the cells? So, it is possible to make a battery even with just one ionic solution, as long as the concentrations are different. How many of these would you have to stack to get 1.5 V? An actual measurement will often show a smaller voltage, unless things are very carefully set up. Give one possible reason for why you might not get the full voltage out.

Osmosis. Of course we can pick any pair of driving factors out of Postulate 1, set the flux equal to zero, and obtain the corresponding equilibrium law. We consider a few more examples here, without reiterating all the steps again in detail.

We begin with a case of interest in osmosis, when a large solute is unable to pass through a membrane, and instead the small solute diffuses to equalize solute concentration on both sides of the membrane, causing increased pressure on one side of the membrane. We have the following two driving factors in the flux, concentration, and pressure:

$$J_x = -Uc \left(RT \frac{\partial \ln c}{\partial x} + v \frac{\partial P}{\partial x} \right)$$

As a reminder, v is the molar volume of the substance in question. Setting the flux to zero as in the previous example, we obtain after integrating over x in steady-state

$$-\frac{v\Delta P}{RT} = \ln \frac{c(x)}{c(0)} = \ln \frac{\Delta c + c(0)}{c(0)} \quad \text{or} \quad \Delta P = -\frac{RT}{v} \frac{\Delta c}{c(0)} = -RT\Delta c$$

Here, Δc is the concentration difference between $c(0)$ on one side of the membrane, and $c(x)$ on the other side. For an ideal solute, partial molar volume (liters/mole) is just the inverse of concentration (moles/liter), so they cancel out. This is the famous law for osmotic pressure of a solute, which is really pressure applied to counteract the flow of water from the region of lower solute to higher solute concentration.

Homework problem T2.4: In a cell, total protein concentration is ~20 mM. If a cell is dunked in distilled water, what's the osmotic pressure on its membrane due to the proteins?

Gravitational equilibrium. OK, maybe you count this as Physics from PHYS 102, but let's see what our physicochemical postulates predict about atmospheric pressure vs. height in the mountains. Consider a gravitational potential V_g ($\text{kg m}^2/\text{s}^2$) = mgx , where on Earth $g=9.81\text{m/s}^2$:

For an ideal gas at constant temperature, the ratio of concentrations that we have dealt with so far can be replaced by the ratio of partial pressures. Proceeding as before by keeping the pressure and concentration terms in Postulate 1, inserting in Postulate 2, and integrating on both sides, we obtain the equation showing the balance of concentration and gravitational force in equilibrium:

$$\ln \frac{P_2}{P_1} = - \frac{mg(x_2 - x_1)}{RT}$$

Thus, we obtain the well-known equation describing the decrease of the partial pressure of a gas with the height above the surface of the Earth in isothermal conditions, showing that the pressure decreases exponentially with height. This is very important in global warming calculations, although the equation also has to have temperature terms added to it because temperature is not constant in the atmosphere. Another application is in centrifugation. As you'll see in problem T2.5, a significant concentration gradient due to gravity requires km height difference because gravity is such a weak force. But by spinning something at 10000 g, we can shorten the distance $x_2 - x_1$ to cm, and sort molecules by density in a small centrifuge tube.

Table - Major equilibrium and transport relations

		1	2	3	4	5	6	7
	Conjugate variables	RTlnC Number of moles	Electric potential	Pressure	Gravitational potential	Surface tension	Temperature	Magnetic Potential
1	Concentration	Fick's law	Boltzmann equation	Van't Hoff relation	Barometric formula	Adsorption isotherm, (Kelvin)	Thermo diffusion (Soret)	Magneto-phoresis
2	Charge	Nernst equation	Faraday's and Ohm's laws	Piezo effect	Sedimentation potential, Dorn effect	Electro capillary effect (Lippmann)	Seebeck effect	Hall effect
3	Volume	Van't Hoff	Electroconstriction and expansion effect	Baro-diffusion	Hydrostatic effect	Young-Laplace, Kelvin, Ostwald	Clausius-Clapeyron	Piezomagnetic effect
4	Mass	Gravitational anomaly	Gravitoelectric effect	Hydrostatic balance	Newton's law	Capillary rise	Thermogravity effect	Gravitomagnetic effect
5	Surface area	Gibbs adsorption isotherm, Kelvin equation	Electro capillary (Lippmann) equation	Young-Laplace, Kelvin, Ostwald	Capillary rise	Surface diffusion, Marangoni effect	Thomson effect	Magnetotension
6	Entropy	Dufour effect	Peltier effect	Clausius-Clapeyron equation	Thermogravity	Expansion cooling or heating	Thermal conductivity	Thermomagnetic effect (Righi-Leduc)
7	Current	Particle gradient fields	Galvano magnetic and Ettingshausen effect	Piezo magnetic effect	Gravitomagnetic effect	Villari effect	Thermomagnetism Spin-Seebeck effect	Lorentz equation

Homework problem T2.5: Derive the above equation connecting pressure and gravity in detail from Postulates 1 and 2, using the same steps as for the Nernst equation. For a molar mass of air

$m=0.029$ kg/mol and assuming a constant $T = 298$ K, what is the pressure 1 km above sea level? How do you think temperature changes and humidity could affect the equation?

Summary of driving forces and transport phenomena We could of course go on with many more such examples, but the utility of the postulates of physicochemical mechanics should now be obvious: Any diffusive transport phenomenon in chemistry can be derived in a few lines by writing down μ_g with the appropriate driving forces for the case of interest and computing the flux. The continuity equation may be used to eliminate flux from the transport relations thus derived and replace it by $\partial c/\partial t$ to compute how concentrations change in time. Furthermore, any equilibrium relation, based on diffusional processes, can now be derived simply by setting the flux equal to zero.

The above Table summarizes all major transport and mutual equilibrium laws for chemical and other types of transport, derived using the physicochemical potential approach. For example, when concentration is the only variable of interest and the only driving factor, Fick's law results as seen in the previous chapter. If concentration is the variable of interest, driven by electric potential, the Nernst equation is obtained, or *vice-versa*, the Boltzmann law.

Chapter 3 - The integrated form of flux and kinetics

We have seen how physicochemical mechanics can be used to describe the rates and equilibrium conditions of transport processes for a variety of driving forces. Now we will consider an integrated form of the flux J , which may be used to describe many kinetic phenomena covered by the physicochemical postulates. The purpose of this chapter is to give you a general description of the fundamental equation with a few simple applications, such as deriving the transition state theory of chemical reactions going over activation barriers.

The integral form can be derived from postulate 2 and does not contain additional information about the model. However, the integral form allows us to see what the leading driving factors of transport are, and what determines transport resistance. It also leads to an explanation of basic thermodynamic laws such as Le Châtelier's principle and the equilibrium condition. The approach may be further extended to the kinetics of processes where instead of a Cartesian spatial coordinate x , we can use a more abstract coordinate, such as chemical reaction coordinate, the size of a colloid particle, and even an order parameter for phase transitions. Here we will use activated chemical reaction kinetics to show how easily transition state theory can be derived from physicochemical mechanics.

Derivation of the integrated form of the flux So far, to describe flux of a chemical component in a solution, we wrote down the differential equation

$$J = -Uc \frac{d\mu_g}{dx}.$$

What about steady-state situations where the flux is constant, but not zero? '0' would be equilibrium, but there are many cases out-of-equilibrium that are characterized by not just any random flux, but by a constant flux. For example, a current flowing through a wire, or a chemical reaction in a reactor producing protein, or the slow melting of ice in the Antarctic because the average temperature has increased.

In Chapter 5 of Stat Mech, we split the chemical potential into two pieces, the value $\mu^{(0)}$ at a reference concentration $c=1$, and the contribution from entropy increasing with volume (or decreasing with concentration), $-RT\ln c$. The same split applies to the physicochemical potential, when μ depends on position: $\mu_g(x) = \mu^{(0)}(x) + RT\ln c(x)$. This equation allows us to write concentration as a function of μ : $c = \exp[(\mu_g - \mu^{(0)})/RT]$. If temperature is constant, after substitution we have

$$J = -RTU e^{\frac{\mu_g - \mu^{(0)}}{RT}} \frac{d(\mu_g/RT)}{dx}.$$

We can rewrite this in terms of differentials as

$$J \frac{e^{\frac{\mu^{(0)}}{RT}}}{RTU} dx' = -e^{\frac{\mu_g}{RT}} d(\mu_g/RT).$$

Note the usual trick of renaming x to x' because we want to integrate next from 0 to x on both sides and not confuse the integration limit x with the integration variable dx' . In steady state, the flux J is constant, and after integration from $x'=0$ to $x'=x$, we have the final integral form of equation for flux.

$$J = - \frac{e^{\frac{\mu_g(x)}{RT}} - e^{\frac{\mu_g(x=0)}{RT}}}{\int_0^x dx' \frac{e^{\mu^{(0)}(x')/RT}}{RTU(x')}}.$$

This is the ‘integrated form’ of the flux. Note the Boltzmann factors in it, which, if you recall, indicate the probability of a system being at a certain energy (or chemical potential) as a function of temperature.

Le Châtelier’s principle. Let us consider an important consequence of the integrated flux. In equilibrium, $J=0$. Thus, the left and right hand sides of the numerator in the above equation must be equal, leading to familiar relation $\mu_g(x) = \mu_g(x = 0)$ as we have seen earlier: particles stop flowing when the chemical potential is equalized.

What about the minus sign in the above equation, or generally in the equation $J=-Uc \, d\mu_g/dx$? It tells us that a chemical potential difference induces a flux from higher to lower chemical potential, to reduce the free energy of the system. However as that happens, the lower chemical potential begins to increase because $\mu = \mu^{(0)} + RT\ln(c)$ and $\ln(c)$ increases as c increases. Likewise, the higher chemical potential will decrease as molecules move away from that spot. Eventually, $\mu_g(x) = \mu_g(x = 0)$ and then the flux stops and equilibrium is reached. Thus “If a system is moved out of equilibrium such that there is a chemical potential difference, the flux will oppose the difference until equilibrium is restored.” This is **Le Châtelier’s principle**, which is derived here in a more general form than the common discussion in terms of the mass action law. A system not too far from equilibrium due to application of some combination of forces will respond by counteracting the effect of those forces to restore equilibrium.

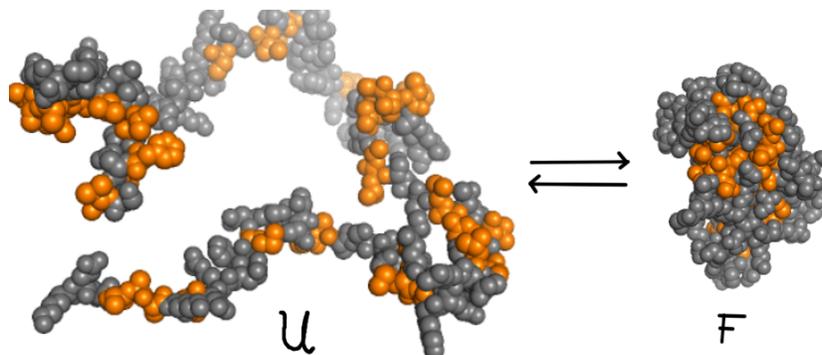


Figure: A protein contracting to fold

Thought experiment: When one pressurizes a protein, it actually unfolds. By Le Châtelier’s principle, that means the unfolded protein must have *smaller* molar volume than the folded protein! How do you rationalize this counter-intuitive result, given that we tend to think of unfolded proteins as *larger* than folded proteins, e.g. in the above picture?

Bayesian formulation of the flux If the mobility U is independent of x and we use the definition of the diffusion coefficient $D=RTU$, the integrated flux equation simplifies to

$$J = -\frac{D}{x} \frac{c(x)e^{\frac{\mu^{(0)}(x)}{RT}} - c(0)e^{\frac{\mu^{(0)}(0)}{RT}}}{\frac{1}{x} \int_0^x dx' e^{\frac{\mu^{(0)}(x')}{RT}}}$$

Note that in the numerator, we have pulled the $RT\ln(c)$ term out of $\mu_g(x)=\mu^{(0)}(x)+RT\ln(c)$, so only the standard potential $\mu^{(0)}$ now appears in the exponentials everywhere. If you look at the two terms in this equation, they are each a normalized inverse Boltzmann factor that can be interpreted as a probability:

$$J = -\frac{D}{x}[c(x)P(0|x) - c(0)P(x|0)]$$

$P(x|0)$ is the conditional probability that a molecule moves to x if it started at 0, and conversely for $P(0|x)$. We therefore can call $J_f = \frac{D}{x}c(0)P(x|0)$ the forward flux from 0 to x , and $J_b = \frac{D}{x}c(x)P(0|x)$ the backward flux from x to 0. When the two conditional probabilities, weighted by the concentrations, cancel one another, then equilibrium is reached. Thus the flux has a very general probabilistic interpretation, no matter what the details of the function $\mu^{(0)}(x)$ are: It's the probability of going from 0 to x weighted by the concentration at 0 (forward direction), minus the probability of going from x to 0 weighted by the concentration at x (backward direction), scaled by the diffusion coefficient and the distance from 0 to x .

Homework T3.1: In steady-state, flux is 0. Use the Bayesian formula to write the ratio of concentrations in terms of a ratio of conditional probabilities. In equilibrium, $c(0)=c(x)$, so what relationship is there between the conditional probabilities in equilibrium? This is an example of the **principle of microscopic reversibility**: the probability of getting from 'a' to 'b' must be the same as getting from 'b' to 'a', then the system is in equilibrium.

Deriving activated rate theory One of the biggest achievements of physical chemistry is understanding that reaction rates are limited by barriers, and providing a formula for what the rate is. Activated reaction rate theory, originally embodied by Arrhenius' empirical relation

$$k = a \exp[-\Delta E_a / RT]$$

is one of the key results in physical chemistry. The original derivation of transition state theory by Eyring makes a number of unnecessary assumptions, such as an equilibrium between the bottom of the reactant well and the top of the barrier. An improved derivation was provided by Kramers, who considered the effect of friction and diffusion on the reaction rate. The derivation based on statistical mechanical transport equations is accurate, but rather cumbersome. (If you think the flux J is cumbersome, read Kramers' 1940 derivation!)

The physico-mechanical model naturally allows for the calculation of steady-state flux at position x for a diffusive process on a free energy surface $\mu(x)$, where we drop the 'standard' or '(0)' for notational convenience. We will now consider x to be a reaction coordinate rather than a macroscopic Cartesian coordinate. For example, x could measure the extension of a bond from its equilibrium value until the bond 'breaks' and a new one is 'made.' What we mean by 'breaks'/'made' is that as we stretch the bond, the standard chemical potential goes up, but eventually, it reaches a maximum as the new bond begins to form and then decreases as the new bond reaches its equilibrium value.

The integrated flux contains both a backward flux from x to 0 (first term in the numerator) and a forward flux from 0 to x (second term in the numerator). If we are only interested in the forward reaction, we obtain for the forward flux and velocity (remember, 'flux=concentration times velocity' in Chapter 6 of Statistical Mechanics):

$$\frac{J_f}{c(0)} = v_f = D \frac{e^{\frac{\mu(0)}{RT}}}{\int_0^x dx' e^{\frac{\mu(x')}{RT}}}$$

Now consider the Figure below, where a molecule has to be energized by random bumps from the surrounding solvent to cross the barrier to form product at $x=x^\ddagger$. (1) The chemical potential is

referenced to $\mu=0$ at $x=0$, eliminating the exponential from the numerator in the above equation. (2) The function $\mu(x')$ has a maximum $\Delta\mu^\ddagger$ at position x^\ddagger . We don't know the exact value of the function $\mu(x')$ between $x=0$ and x^\ddagger , but we do know that it is less than $\Delta\mu^\ddagger$ between 0 and x^\ddagger . Therefore the integral is less than $x^\ddagger e^{\Delta\mu^\ddagger/RT}$, and we can say the integral equals $\chi^{-1}x^\ddagger e^{\Delta\mu^\ddagger/RT}$, where the number $\chi \geq 1$. (3) The rate coefficient of going from $x=0$ to x^\ddagger is related to the velocity by $k_f = v_f / x^\ddagger$. Inserting the results (1) through (3) into the equation above,

$$k_f = \frac{\chi D}{(x^\ddagger)^2} e^{-\Delta\mu^\ddagger/RT}.$$

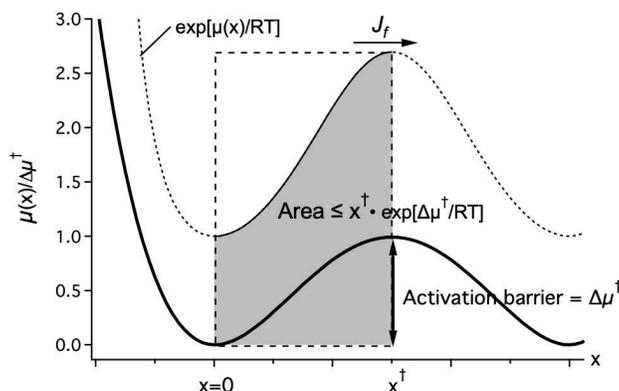


Figure: Chemical potential (solid curve) as a function of reaction coordinate x , and its exponential (dotted curve). The physicochemical potential is plotted in units of barrier height. The system reaches a forward flux J_f at x^\ddagger , and the area (integral) under the exponential is less than the value shown, leading to the Arrhenius equation with a transmission coefficient χ .

We now have obtained the Arrhenius equation, but with a more accurate description than the Eyring prefactor of $k_B T/h$. It can be seen that the prefactor depends on a transmission coefficient χ (dependent on the shape of the barrier), and on the ratio of diffusion coefficient D to reaction distance squared (typically $\sim 1 \text{ \AA}$ for bond-breaking reaction), which is the characteristic diffusion time scale for the reaction. The above result is not quite as general as the full Kramers solution, but if we knew how $U(x)$ depends on x and what the shape of the barrier is, we also could get the most general answer.

In-class exercise: A typical diffusion coefficient for an ion in water at room temperature is $10^{-9} \text{ m}^2/\text{s}$. If that value is characteristic of diffusion along the reaction coordinate in solution, and the reaction distance is 0.5 \AA what prefactor do we obtain when the transmission coefficient is equal to 1?

Homework problem T3.2: At higher temperatures (more typical of a reactions with a barrier), the viscosity decreases by a factor of *ca.* 5 for every $100 \text{ }^\circ\text{C}$, and χ is typically $1/2$, as seen in the Figure above. If the data for the in-class exercise was at $25 \text{ }^\circ\text{C}$, what would be the prefactor at $225 \text{ }^\circ\text{C}$, and what would be the rate constant k if the maximum in the free energy profile is at $\Delta\mu^\ddagger = 100 \text{ kJ/mole}$? [Hint: the relationship between diffusion coefficient, friction and viscosity is discussed in Chapter 6 of Stat Mech.]

Homework problem T3.3: On the other hand, for a protein folding reaction at room temperature, the characteristic reaction distance is $\sim 1 \text{ nm}$ (size of a helix or beta strand that need to diffuse together to fold the protein), and the diffusion coefficient is $\sim 10^{-10} \text{ m}^2/\text{s}$. What is the prefactor in

that case? We call this the “speed limit” of protein folding, and some small proteins come remarkably close to this value, so protein evolution has optimized the folding reaction of some proteins. In a sentence, why do you think not all protein folding reaction rates would be optimized by evolution to be as fast as possible?

With that homework problem, you have reached the end of our journey through the most important ideas in physical chemistry. Starting with the quantum world, we saw that position and momentum are *not* independent variables. As a rule, quantum mechanics predicts that molecules have discrete energy levels, which we can verify by seeing that light is absorbed at very specific frequencies that are like a ‘fingerprint’ for every molecule. This allows us to ‘diagnose’ molecules using light at a distance, with applications ranging from discovering the composition of exoplanets to determining your blood oxygen with an LED on your smartwatch. Then we moved to statistical mechanics and saw that the ‘three laws’ of thermodynamics can actually be derived from two basic postulates. Stat mech told us that at a temperature T , the probability of being in an energy level E_i is proportional to $\exp[-E_i/RT]$, the Boltzmann factor. We used the thermodynamic laws to see that the second law $\Delta S_{\text{tot}} > 0$ can be formulated for an open system as $\Delta G_{\text{sys}} < 0$, so we don’t need to worry about the whole world. Using that, we calculated a formula for the equilibrium constant of chemical reactions. Finally, by adding two more ‘laws’, also derived from statistical mechanics, to the three laws of thermodynamics, we came up with a three-line derivation method of any equilibrium or transport equation in chemistry, from the Nernst equation of electrochemistry to the transition state theory. Along the way, we checked out the formulas with various examples, from gel electrophoresis to global warming. For all of these phenomena, scientists use physical chemistry to estimate and predict what is going to happen. Of course, predictions are only as good as the input data and the accuracy of the formulas derived. Thus, it is always important to understand what the limitations of formulas are. The best way to understand that is what ‘postulates’ were used, and what additional assumptions were made to come up with a formula, and whether the assumptions are likely to hold or break down. This checking of quantitative models against experiments and observations from the real world is one of the most important features of science, allowing models to be improved with time.

For the final, make sure you have gone over every thought experiment, exercise, and problem. A selection from them will show up on the final in modified form. Good luck!