Lecture 14A • 10/28/11

{lab exam review; extraction, tlc, t-pentyl halide}

extraction – technique; polarity; immiscible solvents; effect of density; identifying aqueous layer; acid-base extraction; selective neutralization based on pKa; melting point; purity; review of calculations
tlc – role of polarity; tug-of-war between solvent and plate; stationary and mobile phases; preparing, developing, and visualizing tlc plates; Rf values
spectroscopy – mechanism of conversion of alcohol to alkyl halide via mineral acid; purpose of washes – salt, bicarbonate, water; general principles of spectroscopy; excitation of bonds by infrared light; identifying –OH peak and alkyl halide peaks; significance of presence or absence of –OH; use of IR to verify success of reaction

Equilibrium – reversible reactions; reaction coordinate diagrams and reaction progress diagrams

The principle of microscopic reversibility. Let's say that we're here at De Anza right now, and, given the type of weather it looks like that we're going to have today, probably we'd all rather be some place like Santa Cruz at the moment. Let's say that I asked you what would be the easiest pathway from here to Santa Cruz, and's lets say we don't worry about traffic or road conditions, just distance-wise, what would be the easiest way to get from here to Santa Cruz? Highway 17. What would be the easiest way back? The same way, right? Because what ever the easiest way forward [was], if you found an easier way backwards, that would be easiest way forwards (ignoring traffic and all that, just distances). The same thing is true for a chemical reaction. If you think about reaction coordinate diagrams, what they are representations of, they're simplifications of this polydimensional space that's got all of these different mountains and valleys in it, the valleys being the lower-energy points as that reaction proceeds. If you follow that reaction coordinate, which is the energetically most-favorable pathway, whichever way you go in the forwards direction automatically has to be energetically most favorable process in the reverse direction. If you look at alkyl halides going back and forth from being alcohols, those mechanisms were just mirror images of each other – where a bond forms in the forward direction, when it goes backwards, that same bond breaks. Each of the sequences in the forward direction is mirrored and happens in the reverse when you go through the reverse reaction. That is the principle of microscopic reversibility – that for a reversible reaction, the energetically most-favorable pathway for the forward reaction will be the same as the reverse reaction. That means we can use one reaction coordinate diagram to show both a forward and a reverse reaction, because every point in energy that you go in one direction, you're going to encounter just in the opposite order when we go in the reverse direction.

Let's play around with a reaction coordinate diagram a little bit to get used to these reversible reactions. I'm going to draw up some arbitrary two-step reaction. How are you going to know it's got two steps? Because it's going to have two transition states. Remember that two transition states, each transition state corresponds to a step. Because I had two steps in the reaction, that means, automatically, I'm going to have two steps in the reverse reaction. Since they're the same pathways, it's the same transition state in each direction. The forward reaction is going to be the one that's more favorable – if we ignore entropy, if we are only looking at enthalpy, then if you release energy, that's a favorable process – things roll downhill. So this forward reaction is going to be more favorable that the reverse reaction because you're having to push up higher in energy, not going to be as favorable.

Let's write the activation energies on this diagram. Remind me what's the proper way to write an activation energy. There are two of them; how do we write the first one? Start at the reactant and go up to the transition state. I'll label that as Eaf1. What about the second activation energy? From the intermediate, not from down here, the intermediate up to the second hill. We'll label that Eaf2. For the forward reaction, if everything else is equal, since that first activation energy is greater than that second activation energy, that first step is the rate-limiting step. But now let's examine this from the reverse reaction. If we're going in a reverse reaction, we start from wherever it's going to be coming from, so now it's going to be coming from the right, and now we go up to that same transition state. In the reverse direction, the first step we get to, this is now the activation energy. I'll label this Ear1. What about for the second step? You start at the intermediate and go up to the next hill [to the left]; here is the second activation energy. For the reverse reaction, the same kind of statement is true, where the first step you encounter in the reverse reaction has a larger activation energy than the second, so again, in the reverse direction, that first step is now the rate-limiting step.

This is going to be a highly constructed example. There's going to be a lot of conditions I put on this to try to make a certain important point. Imagine that we have reactant A that converts into product B. Let's say this is a one-step reaction, where only one molecule is involved in either the forward or reverse directions. You could show the forward activation energy for this reaction, and it's rather apparent that it's greater than the reverse activation energy. If there is only one reagent or one product, only one molecule involved either in the forward or reverse reaction, then that makes it easy to write rate laws for this process. They would both be unimolecular. The rate of the forward reaction would be the forward rate constant times the concentration of A, and the rate of the reverse reaction would be the reverse rate constant times the concentration of B.

The last restriction that I'll put on this constructed example is, let's say that because only one molecule's involved in each case, let's say we're not even worried about steric factors (A).

Let me introduce to you what the three definitions of what equilibrium. Equilibrium literally means equal weight – librium (lb) weight. One definition definition of equilibrium is a thermodynamic one – that if you're going back and forth between reactants and products, there's going to be some lowest-energy point along that transition – not for a single molecule, but the whole solution that's reacting. Once you reach that lowest-energy point, you're not going to go any lower, so the energy is no longer going to change. So equilibrium is the lowest-energy point in a reversible process. Because it's at that lowest-energy point, that means there's no net change of energy in that system. So that's the thermodynamic definition. What about the kinetic? The only way that you could have it so that it's at this lowest-energy state, where nothing's really changing, is if the two processes, the forward and reverse processes, are exactly balanced in terms of rate. So in other words, the rate of the forward and reverse processes are equal to each other. If they weren't equal, then one's going faster than the other, you'd shift in your concentrations of either products or reactants, you'd change the energy of the system. From what I just said about products and reactants, that's really the third definition – the one that, you could say, is the equilibrium definition of equilibrium. It's this: there's no observable change in the concentration of reactants or products. This idea of dynamic equilibrium – that reactions are going on, reactants and products are exchanging back and forth, but if they're being reacted at the same rate, then overall the concentration isn't going to change. So here's our three definitions of equilibrium.

To tie this in to the reaction coordinate diagram up above, if these are the rate laws for this process, then what me might be able to do is say, well, at equilibrium, one of the definitions is that the rates should be equal, which means we could write this expression as the forward rate constant times the concentration of A would be equal to the reverse rate constant times the concentration of B. But now, if we're saying that this is only one molecule involved forming one molecule, so let's ignore A as a factor, and since this is a reversible reaction that's happening in the same reaction pot, we can say that temperature's the same for both of these, so if all other factors are equal – same temperature, ignore A – then since the activation energy of the reverse reaction is greater than the activation energy of the forward reaction, the rate constant of the reverse reaction is going to be less than the rate constant of the forward reaction. That's an important point: equilibrium means equal rates, not equal rate constants. We could rewrite the expression above as this: concentration of B divided by concentration of A is equal to kf divided by kr. That gives us a balance of how many products versus reactants we have, and that's what eventually leads us to this idea of big K, the equilibrium constant. I'll express that as the balance of products and [versus] reactants.

But this really is a contrived example, because you could have multiple reactions or multiple steps all occurring in a reaction mixture, and not all of the reagents are going to be in these rate laws. However, one of these definitions of equilibrium is that it does have something to do with energy, specifically in the form of potential energy. Since all the different reactants and products in solution could contribute to that overall potential energy, it turns out that all reactants and products that are in the same phase end up, in general, in the equilibrium constant. You'll eventually get to a concept called chemical potential – this idea of potential energy, which is used to come up with the law of mass action. This example I showed you is just to try to make a connection between kinetics and equilibrium, but really the tighter connection is between thermodynamics and equilibrium.

To get the general sense of how an equilibrium expression is written, I'll do what so many textbooks do and write up a generalized reaction. To write the equilibrium constant, it is the concentrations of the products raised to their stoichiometric coefficients, divided by the concentrations of the reactants, raised to their stoichiometric coefficients.

Let me tie this together. A reaction progress diagram is this: it's a measure of the cumulative energy off all instances of a chemical reaction as a solution moves from 100% reactants to 100% products. What in the world does that mean? A reaction coordinate diagram was looking at one set of molecules, a reactant turning into product, what's that energy difference. But if you have a solution, it's not going to be that you snap your fingers and the entire solution instantly turns from 100% reactants to 100% products. Some reactants will react right away, some may not. So, different sets of reactants and products will be in different steps along the way of that reaction. If you add up what all of the molecules are doing, and you look at their energy, it's actually something kinda like this. Imagine that I had this piece of paper, where I hold the two ends of that piece of paper at the same level, you'd get this bow in the paper that's right in between the two. If I drop one hand or the other, notice how the paper kinda shifts to whichever hand is in the lower position. Same type of thing ends up happening with energy in a chemical reaction. If you have reactants that are at a heck of a lot higher energy than products, the lowest-energy point in that solution is going to be somewhere close to the product side, in other words, something like this. The x-axis of this diagram is kinda abstract: it's just 100% reactants leading to 100% products. Since we are talking about equilibrium, which does have this close tie to thermodynamics, and since this is about a solution, we're now going to have to discuss energy in terms of free energy, not enthalpy. Remember that enthalpy is really just the difference in energy between reactants and products but, in some ways, ignoring what physically happens during that conversion. When you look at a solution, you've got to see: how is energy being distributed as that entire solution reacts? What is happening to matter? How is it being distributed as that entire solution reaction? So now, as we're doing this type of diagram, it's automatically going to be in terms of delta G. You can see that here is our overall change; this is one of those cases where delta G is less then zero. Since we have the terms exothermic and endothermic, you should know that a negative free energy change is called exergonic, and a positive free energy change is called endergonic.

One curious aspect of this diagram: notice that the lowest part of the diagram is not on the products itself; there's this litte upswing that occurs at the end. If you have a huge difference between the two, between reactants and products, then that dip really will almost be right on top of products. You might ask – if they're lower in energy, why don't they just convert completely into products? Because this is supposed to be describing a reversible process, a reversible process where the rates of the forward and reverse reaction are equal. If I don't have any reactants, I don't have any forward reaction, only the reverse reaction's going to occur. So at least a few reactants are going to reform, so that the rate of that reverse process again equals the rate of the forward process. If it was reversed, if you did have an endergonic process, then notice that that lowest point is not entirely on top of the reactants, because if you had no products, you'd only have the forward reaction, so at least a little bit in the way of products would form, to make those rates equal again. This lowest point is K. Since you can see that there is this tie-in between energy change and equilibrium, let me write the equation out that unites the two: delta G = - RT ln K. The more energy that you have to push into a reaction, the less products want to form and so the smaller the equilibrium constant's going to be. If the reaction releases a bunch of energy, equilibrium constant's going to be huge, which means you want to make products. I want to work through a thought puzzle related to how do we get to equilibrium, while will help explain a little bit why this lowest-energy point is not right on top of reactants or products but it's in between. Then we're going to talk about messing with equilibrium; that's Le Châtelier's principle.

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Lab #1 – Extraction
Technique of extraction; polarity, immiscible, density
Acid-base neutralization
Drying agent, recrystallization, MP

Lab #2 – TLC
Polarity as the basis of separation; stationary & mobile phases; preparing, developing, and visualizing a TLC plate; interpret Rf values

Lab #4 – Spectroscopy, mechanism, washes, outline of IR spectroscopy, verification of successful rxn

Principle of microscopic reversibility – For a reversible rxn, the energetically most favorable pathway for the forward rxn will be the same as the reverse rxn.
forward: $E_{af1} > E_{af2}$, 1st step is RLS
reverse: $E_{ar1} > E_{ar2}$, 1st step (in reverse) RLS
$R_f = k_f[A]$; $R_r = k_r[B]$

Equilibrium
1) thermo: the lowest-energy point in a reversible process – delta E = 0
2) kinetic: rate of forward & reverse processes are equal to each other.
3) equil: no observable change in the concentration of reactants or products

@equilibrium: $R_f = R_r = k_f[A] = k_r[B]$
If all other factors are equal (same T, ignore A_0, since $E_{ar} > E_{af}$, $k_r < k_f$.
$[B]/[A] = k_f/k_r = K$ – equilibrium constant; balance of products and reactants
$aA + bB \rightarrow cC + dD$; $K = [C]^c[D]^d/[A]^a[B]^b$

Reaction progress diagram
Measure of the cumulative energy of all instance of a chemical as a solution moves from 100% reactants to 100% products.
delta G<0 – exergonic; delta G>0 endergonic
delta G = –RT ln K

Structures

pKa   **5**   **7**   **10**   **16**

increasing acid strength

H_2CO_3 H_2O

HCO_3^- ^-OH

increasing base strength