Lecture 14B • 10/28/11

{lab exam review – extraction, tlc, spectroscopy}

extraction – polarity; immiscible solvents; technique; role of density; acid-base extraction; neutralization; selective use of pKa in extraction; series of acids of varying strengths and their conjugates; drying agent; recrystallization; melting point
tlc – polarity; stationary and mobile phases; preparing and developing a tlc plate; Rf values; identifying components of a mixture; visualization – chemical stain, UV
spectroscopy – mechanism of rxn; washes – sodium chloride, bicarbonate, water; general principles of spectroscopy; connection of infrared to bond vibration; identifying –OH peak; importance of presence or absence of –OH peak; identifying carbon-halogen bond; background

We're going to have a brief introduction to equilibrium. There's going to be two key things that we talk about today: this thing called a reaction progress diagram, and how it's different from a reaction diagram; we also need to address the idea of reversibility of reactions, so we're going to look a reaction coordinate diagram, but examine it from both the forward and reverse directions. Let's start there, in fact, because it'll lead us to equilibrium. In order even to start there, we need to talk about the principle of microscopic reversibility.

Imagine a situation like this: that you're here at De Anza, but the weather being nice, you might prefer to be in Santa Cruz instead. If I ask you, what's the easiest way to get from De Anza to Santa Cruz, you might give me some suggested pathway. Then I could ask you: what would be the shortest pathway, the easiest pathway in the reverse direction? If you ignore traffic and ignore other factors like that, if you just talk about the distance or the pathway itself, it would have to be exactly the same pathway in the reverse, because if you found an easier way in the forward direction, that would be the easier way in the reverse direction. The same thing is true for chemical reactions. Remember the way that I describe a reaction coordinate diagram as being this polydimensional space. You can imagine that if you're trying to look at that diagram certain ways, you might imagine this different valleys and peaks of higher and lower energy. Well, if you were to try to traverse that to find the energetically most-favorable pathway, the one that we call the reaction coordinate, automatically when you're travelling in the forward direction, those exact same valleys, those lower-energy points, are going to be the same one you encounter in the reverse direction. What that means is that if you have a reaction which is reversible, that the mechanism of the reaction in the forward direction is exactly the same as the mechanism – just reversed – when the reaction goes in the reverse direction. That also means that, energetically, at every point on the diagram, the forward reaction is just going to be a mirror reflection of the reverse reaction. That is this principle of microscopic reversibility. For a reversible reaction, the energetically most-favorable pathway of the forward reaction will be the same as the reverse reaction.

That means that on a reaction coordinate diagram, if we had the possibility of things going forwards and backwards, we now have to look at two sets of activations energies. Let's say we had an example like this. Forward direction there's two steps; because the reverse reaction has to be exactly the same, two steps in the reverse reaction. Two transitions states forward, two transition states backwards. In the forward direction, which I'll use green to show, let's figure out what the two different activation energies are. How would I correctly show the activation energies of the forward reaction? From the reactants up to the peak, that's the first activation energy. What about for the second one? Where should I start to draw that second activation energy? From the middle up to the next peak. I'll call this Eaf1 and Eaf2 – activation energy, forward, number 1 and number 2. In the forward direction, since the activation energy of that first step is greater than the activation energy of the second step, the first step is the rate-limiting step. This reaction, if there's enough energy to get to those transition states, would want to go forward, if we're not worrying about entropy at the moment, we're just looking at heat of reaction. Ignoring entropy, if all you're looking at is enthalpy, if you have an exothermic reaction, that's a favorable reaction; things roll downhill. So this reaction would want to occur. The reverse reaction, therefore, would not want to really occur, because you'd be pushing it, overall, higher in energy. But let's examine it from the reverse direction, because now, if we're starting from the bottom – formally, if we were writing activation energy, you'd start from the left of the intermediate, but that's because we were just doing the forward reaction. Now that we're doing the reverse reaction, we still measure the energy from wherever we start, so in this case it's going to be on the right, and we still go up to the transition state. So this is the first reverse activation energy, and then we have the second reverse activation energy, which in this case, the same kind of sentence is still true, that that first activation energy is larger than the second when going from the right in the reverse direction, so the first step that you encounter in reverse is the rate-limiting step. In other words, it's two different steps, depending on whether it's the forward or reverse process, which means you could have two entirely different rate laws.

Now let's see one more reaction coordinate diagram so we could talk about a little different scenario, to get us into this idea of equilibrium. Let's say we had a one-step reaction. We could look at the forward activation energy, and we could look at the reverse activation energy. This is going to be a very carefully, overly constructed case. Let's say that the first reaction, the forward reaction, involves one reagent A, and it's the only reagent, therefore, involved in the rate-limiting step. So, it's going to be first-order in A. Let's say that the product, B, is the only thing that's made, and so when it reacts in reverse, it's the only reagent that's also involved in its rate-limiting step.

In that case, we could write two rate laws: that the rate of the forward reaction is some rate constant for the forward reaction times the concentration of A, and then we could say that the rate of the reverse reaction is some rate constant, different one because we have a different activation energy, and then we have a concentration of B.

Let me give you the three definitions of equilibrium. There's three perspectives we can take equilibrium in. One is a thermodynamic perspective, so, energy. One of them is a kinetic perspective, so we could talke about rate. And one of them is the equilibrium perspective, what's the different concentrations of the reactants and products when you reach equilibrium? In that order, equilibrium is: the lowest-energy point in a reversible process – once you've reached that lowest point, you can't go any lower, so the change in energy at equilibrium is zero; in terms of kinetics – this is the way equilibrium is most frequently expressed – this is that the rates of the forward and reverse reactions or processes are exactly equal to each other – that should make sense because if you had an energy imbalance, that means that the reaction is going to want to shift one way or another; if that were true, one rate of reaction, either the forward or reverse, was out of balance with the other; if you are in balance in terms of rates, then you're not shifting the reaction one way or another, which means you're staying at the same energy point, that lowest energy point; because of that, that means that there's no observable net change in the concentrations of reactants or products, because if you had a change in either one, that means there's a reaction rate, which means you're out of balance; but if you're at the lowest-energy point, which means you're in-balance, that means that the concentrations aren't going to change.

How does this relate to the reaction coordinate diagram I just had? Let's look at this second definition again of equilibrium. In terms of rate, at equilibrium, the rates of the forward and reverse reactions would be the same. So at equilibrium, Rf = Rr, which means kf[A]=kr[B]. Here's an important point: rates have to be equal and equilibrium; rate constants do not. From this graph, that should be evident: in the forward reaction, you have a smaller reaction barrier; quicker reaction, which means if you formed reactants, they'd want to react. In terms of products, that's a large activation barrier, and realize that this is a reversible reaction, this means that's it's a system thats got the same energy. If I'm making this a perfect example – let's say we don't have to worry about the steric factors, we have one molecule and one molecule – in that case, the rate's going to be heavily influenced by just the activation energy. It's hard to get up that hill, so if the products form, they don't really want to go backwards; it's a slow reaction. If all other factors are equal – if we're at the same temperature, and if you ignore the steric factor – 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 less than the rate constant of the forward reaction.

What does that mean? Let's rewrite the equation up above. Let's divide through by k and divide through by concentration, let's do a quasi-separation of variables. If we wanted to see what our concentration of product versus concentration of reactant is, then in this highly stylized case, that's going to be dependent on the forward rate constant and on the reverse rate constant. This is what is behind the idea of K, the equilibrium constant, which is the balance of products and reactants at equilibrium. But, this is just an example, because it turns out it's not just those things that might happen to be in the rate law that end up affecting equilibrium. There is this more advanced idea of chemical potential, which is something link potential energy. This focuses back on the first definition [of equilibrium], there being no net energy change at equilibrium. Since all of the different reactants and products in solution might contribute to that potential energy, then all reactants and products in solution end up being in the true equilibrium constant.

If you have some reaction like this: a reversible reaction in which all of the reactants and products are in the same phase. Then, we write an equilibrium constant that looks like this: it's the concentration of products raised to the appropriate powers (their stoichiometric coefficients), and then divided by the concentrations of the reactants, [raised to the power of] their stoichiometric coefficients. The reason that all of these things show in here is because it's a measure of potential energy. That's our equilibrium constant.

Reaction progress diagrams

If you recall, when we did a reaction coordinate diagram, that was for looking at the progress of one set of reactants or products as they transition from one to the other. If you look at one molecule set and see how does that energy change as it makes products. But not all reactants are going to instantaneously turn into products; it's not like you snap your fingers and the whole solution's done reacting. That means that different sets of reactants and products will be at different energy points somewhere along the reaction. That's the idea behind the reaction progress diagram, which is a measure of the cumulative energy of all instances of a reaction as the solution moves from 100% reactants to 100% products. It is at this point where we now have to move from enthalpy to free energy, because enthalpy is really measuring that one set of reactants going to products. But if you have a solution full of reactants and products, then how is that energy being distributed through the solution? How is that matter being distributed through solution? That's entropy itself: homogenization of energy and matter. We're talking about he potential energy of an entire solution, then we have to take that entropy into account. So now we're going to be using free energy in the diagram that I'm about to show you.

Typical diagram might look like this: we still put reactants on the left, products on the right. There is an energy difference between these two points: that is delta G.

Since we had the terms exothermic and endothermic, you need to know the equivalent terms for delta G. If delta G is less than zero, that is known as exergonic If delta G is greater than zero, that is known as endergonic. This is an exergonic reaction I've showed you, because once you account of entropy in this case, reactants are going to lower energy to become products. This is a really off-the-wall example: imagine this piece of paper. If I hold the two ends of the paper at exactly the same level, notice there's a dip that occurs between them. If I were to raise one hand or the other, you can see that that dip moves more closely to whichever is lower. In a similar fashion, if you have a chemical reaction where there's a decrease in energy like this, then the lowest point of equilibrium is going to lie closer to that set of products, so the curve would look something like this. Equilibrium, then, would be at this point, towards the right of the curve. Your axis in this case is kinda abstract; you're going from just 100% reactants to 100% products. But you're never going to get all the way to the products, because that lowest-energy point occurs before then. You might say: if products are lower than reactants, wouldn't you want to make products? This is a reversible reaction. There has to always be some reactants and some products, if it's truly a reversible reaction. Because if you did convert 100% to products, there's no longer a forward rate of reaction, which means you're not at equilibrium because the rates aren't equal. There'll be only the reverse reaction happening, which means you'll make more reactants, which will then again be in balance with the reverse reaction. If you only had reactants and nothing had happened yet. But let's say it's an endergonic reaction where you have to add a whole bunch of energy. Still, if there's no products yet, there's no reverse reaction, there's only the forward reaction. Therefore, a little bit of reactants will react, even if it's not an overall favorable reaction. So the lowest point in equilibrium is always between reactants and products. That's the point of showing you a reaction progress diagram.

Let's see just what an endergonic process would look like on one of these diagrams. You can see in this case since the products are higher in energy, equilibrium is going to lie closer to the left. There is an equation that quantifies this relationship. That is the tie between thermodynamics and equilibrium: that, depending on the magnitude of this free energy change, that's going to determine the equilibrium constant. The more energy that the process ends up causing to be lost, the more that it wants to follow that process and so the more products that want to form. The greater [the] energy input that must be put in, the more that things would rather just stay as reactants. The direct tie between free energy and the equilibrium constant.

If we knew the free energy change and we knew the form of the equilibrium constant, we could then calculate how much of the products versus the reactants would form. The different rotomers of ethane: there are only two forms of ethane, two extreme forms, the staggered and the eclipsed. There's an energy difference between the two of those that you could calculate not just in terms of enthalpy, but in terms of free energy. If you take that free energy difference between the two forms, at whatever temperature that you happen to be talking about, then you could figure out what i the fraction that would be in staggered versus the fraction that would be eclipsed at any one time.

We need to talk about what if you mess with equilibrium. What if you put in more reactants? What if you pull products out? 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: Eaf1 > Eaf2, 1st step is RLS
reverse: Ear1 > Ear2, 1st step (in reverse) RLS
Rf = kf[A]; Rr = kr[B]

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

@equilibrium: Rf=Rr=kf[A]=kr[B]
If all other factors are equal (same T, ignore A0, since Ear>Eaf, kr<kf.
[B]/[A] = kf/kr = K – equilibrium constant; balance of products and reactants
aA + bB -> 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 the solution moves from 100% reactants to 100% products.
delta G<0 – exergonic; delta G>0 endergonic
delta G = –RT ln K

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Structures

Identical to those from lecture 14A (10/28/11)