MIT OpenCourseWare
http://ocw.mit.edu

3.091SC Introduction to Solid State Chemistry, Fall 2010
Transcript – Exam 3 Problem 4

The following content is provided under a creative commons license. Your support will help MIT OpenCourseWare continue to offer high quality educational resources for free. To make a donation or view additional materials from hundreds of MIT courses, visit MIT OpenCourseWare at ocw.mit.edu.

JOCELYN: Hi. Jocelyn here and today we're going to go over fall 2009 exam three problem number four.

Starting with part A-- let's read the problem. In the 1920s, Jack Breitbart of Revlon laboratories found that acne could be treated by the use of benzoyl peroxide. The oxygen-oxygen bond in peroxide is weak and under the influence of modest heating, benzoyl peroxide readily decompose to form free radicals according to the reaction given. The rate of decomposition is measured at 92 degrees C at various concentrations and found to be-- and you're given two different concentrations and two different rates.

So part A asks, determine the order of reaction for the decomposition of benzoyl peroxide. The first thing to do is, when asked for the order of the decomposition reaction, we want to think about the general rate loss, right? We're given concentrations. We're given rates. We're asked for the order. Something you might want to have written down on your equation sheet or look up is the general rate law equation. Remember that students taking these exams did have an equation sheet so they could have this ready. The important part is that you know when to use this equation, what each of the terms mean.

So r is the rate. k is a rate constant. It is a function of temperature, but if you're at the same temperature, that rate constant will not change. It's constant. c is your concentration. And n is your reaction order.

So this would be the place to start for this question. And now we know that we're solving for n. So what is n in this case? Looking at what we're given, we can write two different equations. The first line gives us a specific rate for a specific concentration. The second line gives us another rate for a second concentration. So now we have two equations and two unknowns. That means we can solve for one of the unknowns and then could solve for the other one if we wanted to, but here we only care about n.

So how I'm going to choose to solve this and you may choose to do it differently-- I'm going to divide the first line by the second line and I get rate one over rate two equals c1 divided by c2 all to the n power.

So that made the k drop out, which is one of the unknowns that I don't care about because the problem isn't asking for that.

Now all we need to do is solve for n. So if we remember algebra, we're going to take the log of both sides. Because of the properties of the log, we can bring the n out front. So n equals-- and plugging in the numbers given in the problem-- they're given in the same units so everything will cancel out and that's good-- we get that the n equals one. So this is a first order reaction. Now you could've probably done that by inspection if you're familiar with the rate law and how to determine that by just seeing that as the concentration went down by a fourth, the rate also went down by a fourth.

However, the question asks for you to determine the order of reaction and so we were looking for more of a derivation of the problem instead of just an inspection because that shows that you have a familiarity with the general rate law equation.

So now moving to part B-- we are asked, on the plot below, sketch the variation in energy with extent of reaction for the decomposition of benzoyl peroxide. Assume that the ratio of activation energy to-- delta e, which is the energy of the reaction-- equals -2.5. Label the energy states and label the delta e of reaction, the activation energy for the forward reaction and the activation energy for the backward reaction.

So that's asking us to do a lot. So first we're going to write down, what are we actually asked to do? So the main thing is that we're asked for the variation in energy with the extent of reaction. So as the reaction progresses, what's the energy of the molecule? The energy state that it's going through? In that plot, we're asked to label the energy states of the reactant and product and we're asked to label the delta e of reaction. So what's the net change in energy as well as the activation, both forward and backward?

I would always write this to the side or scrap piece of paper or something because this is a lot of things to put on one plot and this will be a nice reference to help us to make sure we answered all the things the question is asking.

So on the plot given, which I'll reproduce here, it has axes of extent of reaction and energy.

The first thing to do would be to label the beginning and start energy states. So because we know at 92 degrees C, this-- the benzoyl peroxide-- decomposes readily, we can assume that there's a decrease in energy. So we'll have our products start at a higher energy than our-- sorry-- our reactant start at a higher energy than our products. And because the question asks us to label that, we're going to put in the actual labels.

And so that's your reactant and then we have the radical product.

Now that we have our beginning and end energy states, we need to think about what's happening in the middle. A clue is that he talks about the activation energy, right? And we know that most processes that we talk about have a certain activation energy. You can't just go straight from the molecule to the radical. You have to have a little bit of energy cuffed. And so we know we're going to have some type of hill that we have to go over. Furthermore, in the problem he states that the activation energy divided by the delta e is -2.5. So we know that because this is a negative delta e-- so this is our delta e here and it's negative-- our activation energy is two and a half times as large as that net change in energy. So we want to kind of just eyeball that in here. You didn't have to be exact, but relatively-- it's going to be larger than twice the distance between here. And remember that activation energy is the hill, the energy costs that you have to go through to get to your lower energy state in the product size.

So now that we have all of our energy states, we want to draw a smooth curve to show the variation of energy with the reaction. So connecting all these points, we get two valleys and a hill, right? We have two stable energy states and we have an activated complex corresponding to the activation energy there.

So we have our energy diagram, but we need to go back to what the question is asking and see that we've labeled the energy states, we've labeled the delta e of reaction, but we need to label both the forward and backwards activation energy. And this is one of the things people had issues with-- the backward activation.

So forward activation is pretty self explanatory, right? It's the energy we need to overcome the activation of this process and so this is the Ea of the forward.

Now the activation energy of the backward reaction is just the same concept, but going backwards. So if we started down here, what is the energy we need to get over this activation barrier? And so that's this full energy, this full amount of energy here. And so we can see that it's bigger than the activation energy for the forward reaction by the delta e of the reaction.

So going back to our checklist here, we've answered all over the questions and so we can move to part C.

So part C asks us, on the same plot above-- which we have over here to the right-- sketch the variation in energy with extent of reaction for the decomposition of benzoyl peroxide under the influence of a catalyst.

So with a catalyst-- first to answer this question, we need to know what a catalyst does. And in class, we learned that a catalyst will lower the activation barrier, thus allowing for the reaction to proceed faster. You don't necessarily get more product because that's governed by a different set of laws, but you do get the product faster. And so the way we can change this is that instead of having our activation barrier up there, we can say it's going to be somewhere here. It's going to be lowered by the presence of the catalyst. So we want to make a smooth curve again and connect this lower activation barrier. And you'd want to label this-- I'll label it in white-- this is the catalyzed curve there.

As long as you've showed that the activation barrier was lowered by the presence of a catalyst, that's fine. That was what the question was asking for.

So we've labeled everything, answered all the questions and we're done with this problem.

MIT OpenCourseWare
http://ocw.mit.edu

3.091SC Introduction to Solid State Chemistry, Fall 2010

Please use the following citation format:

> Donald Sadoway, 3.091SC Introduction to Solid State Chemistry, Fall 2010. (Massachusetts Institute of Technology: MIT OpenCourseWare). http://ocw.mit.edu (accessed MM DD, YYYY). License: Creative Commons Attribution-Noncommercial-Share Alike.

Note: Please use the actual date you accessed this material in your citation.

For more information about citing these materials or our Terms of Use, visit: http://ocw.mit.edu/terms