Chemistry: Challenges and Solutions
Unit 12: Kinetics and Nuclear Chemistry
Rates of Reaction
Hosted by Wilton Virgo

From an instantaneous explosion, to the slow rusting of iron, the rates at which different chemical reactions proceed can vary tremendously.

Chemists strive to control those rates. Sometimes, like with the rotting of food, they want to slow them down.

But often the goal is to speed them up. One way to do this is to use a catalyst.

AMIR HOVEYDA: The catalyst is a magician's wand. If a magician is standing by a black hat, nothing is in the hat until he touches the hat with the wand and the rabbit comes out. That's what catalysts can do.

But the rate of some chemical reactions is unchangeable. This is the case with nuclear or radioactive decay. Using PET scans, we can take advantage of this steady constant rate to detect disease.

GEORGES EL-FAKHRI: It is one of the most sensitive tools we have, and it saves lives.

The study of the rates of chemical reactions is called chemical kinetics. And it is about more than just speed. It is about understanding the intricate, elegant and sublime story that is a chemical reaction.

[Title: Unit 12 – Kinetics and Nuclear Chemistry]

[SEGMENT 1]

WILTON VIRGO: Hi, I'm Wilton Virgo, a chemistry professor at Wellesley College. If you think of this bumper car as a molecule, it cannot react with another molecule unless it collides with it.

One way to increase the chances of a collision happening is to increase the total number of molecules present. And this is one strategy chemists use to speed up a chemical reaction – we increase the concentrations of reactants.

But just because two molecules collide, they still may not react with one another. The reactant molecules must collide with enough energy to break their old bonds and reach a temporary state of higher energy.

Chemists often refer to this as a hill that you must get over, and for a given reaction, the energy needed to get over that hill is referred to as that reaction's activation energy.
WV: The activation energy can be high or low, or anywhere in between depending on the specific reaction.

One way to get over that hill and speed up that reaction is to raise the temperature.

Let's take a look at a demonstration of activation energy.

[SEGMENT 2: DEMO – Activation Energy]

DANIEL ROSENBERG: In this test tube I have a mixture of hydrogen and chlorine gases. Now hydrogen and chlorine would like to react to form hydrogen chloride, but in the dark, in this test tube, the hydrogen and the chlorine can coexist without reacting for a very long time.

The way to get them to react is by giving them enough energy to get started. And that energy is called activation energy.

I have a dark cloth over this test tube because for this reaction, light can provide the activation energy.

And we're going to use a spectrum of LEDs to test what that activation energy is. And we're going to start with red, and red light has the lowest frequency and the smallest amount of energy per photon of these LEDs. Then we're going to move to yellow, which has a slightly higher frequency and a little more energy. Green, which is about in the middle of the spectrum. Blue, which is at the high frequency end of the spectrum and has a lot of energy per photon. And finally ultraviolet light, which is beyond the end of the spectrum and has the most energy per photon.

So, without further ado. Red light, yellow. The green, even though it's bright, green light doesn't have enough energy to start this reaction going. Blue light. Ultraviolet.

BAM!

Sets it right off. So what we've demonstrated is that it takes the energy of ultraviolet light to set this reaction going.

Now that is some activation energy.

[SEGMENT 3: Catalysts]

WILTON VIRGO: Raising the temperature is not the only way to increase the speed of a reaction or the likelihood that it will occur. Instead of trying to get over the hill, another option is to create an alternative pathway that requires less energy – a smaller hill. And this can be done with a catalyst.

WILTON VIRGO: You can think of a catalyst as kind of like this train. If I were to walk from one side of this amusement park to the other, it would take me about twenty minutes. But using my catalyst, the train, I have an alternative pathway. And it only takes about ten minutes to achieve the same results.

WILTON VIRGO: And the train, after it drops me off, is available to transport more people around the park. A catalyst acts in the same manner – it changes during the reaction, but once the reaction is over the catalyst returns to its original state and can be used in subsequent reactions.

Let's take a look at an example of a catalyst in action.

[SEGMENT 4: DEMO – Elephant's Toothpaste]

DANIEL ROSENBERG: We are going to catalyze a reaction. And the chemical reaction that we are going to catalyze is the decomposition of hydrogen peroxide. So I've just added hydrogen peroxide to this flask.

Now hydrogen peroxide is H_2O_2 and when it decomposes, it decomposes into water and oxygen gas.

Now it's inherently unstable. So if I let this hydrogen peroxide sit for a year, I would come back, all of the oxygen would have decomposed, and all I'd have left is water. But that would take a year. And if I want that reaction to happen more quickly, I can use a catalyst.

A catalyst is some material that makes a reaction happen more quickly, takes part in the reaction, and then at the end of the reaction, it's reconstituted so that the catalyst is still in the same form at the end of the reaction as it is at the beginning of the reaction.

So, with hydrogen peroxide decomposition, the catalyst of choice is potassium iodide. Now, potassium iodide forms a clear solution, clear and colorless. But when I put it into the hydrogen peroxide, the iodide is activated. And the active form of the catalyst has a brown color to it, and you're going to see that as the reaction takes place. At the end of the reaction, the catalyst is reconstituted and so the brown color will fade away to a colorless solution.

So let's see what happens when we add this catalyst.

And it turns brown instantly. Oxygen starts to bubble from the hydrogen peroxide as the reaction is sped up by a factor of a million or so. The solution is getting hotter and hotter. It's starting to boil. A plume of steam and oxygen rises. And back in the flask, the last few bubbles of oxygen come off of what used to be hydrogen peroxide, and what is now just water, hot water, and potassium iodide.

Now, how do I actually know that the potassium iodide, the catalyst, is still in there? One way we can test is by adding some more hydrogen peroxide and seeing whether we get the active form, and whether we get oxygen production again. So let's give that a try - color change, there's oxygen production, steam, catalyst is still there.

But you know we can have a little fun with this reaction in a demonstration we call "elephant's toothpaste." Now elephant's toothpaste starts with the hydrogen peroxide, but we mix in a bunch of dish detergent so that we can capture the oxygen as it bubbles out of the reaction. The catalyst is potassium iodide dissolved in water. And we dissolve it in water to make a solution so that when we add these two solutions, they mix instantly and react as quickly as they mix.

So first I add the hydrogen peroxide and soap. And then I add the catalyst solution.

And that is elephant's toothpaste.

[SEGMENT 5: Molecular Architects]

WILTON VIRGO: At Boston College, Professor Amir Hoveyda and his team have developed a set of catalysts that may provide a new blueprint for how we approach catalyst development for years to come.

AMIR HOVEYDA**:** A catalyst is as close as you get to magic. It is a magician's wand. So, my research group is constantly looking to discover and develop new catalysts. And I think what we do is we are architects. We are sculptors. And we sculpt and we design molecules that have function, just like a building, just like anything else that you have, you use. And we try to find new ways to sculpt and new ways to design effective molecules.

WILTON VIRGO: What they've designed is a set of catalysts that can efficiently make alcohols and amines – molecules that are used as building blocks in a wide variety of practical applications, including making drugs to treat cancer, osteoporosis and countless other diseases. The breakthrough is not that they are able to create alcohols and amines - that was possible before. But with these catalysts, they can do it in a much cheaper and more sustainable way. It starts with a very common amino acid – Valine.

DANIEL SILVIERIO: So this is Valine. And it's found in the bodies of many many living things including ourselves. We're not really going to run out of it, because if we do, we sort of run out of life on this planet and that's an issue. Like, way bigger issue than running out of this catalyst.

WILTON VIRGO: Starting with a cheap renewable resource is helpful, but what makes this process even more extraordinary is how easy it is to build the catalyst from the Valine.

AMIR HOVEYDA: You know it is almost like playing a game of Lego . . . click. So we start with Valine, and any amino acid has two very important ends. Amine, acid – two basically outlets that you can plug in. We plug in one small organic molecule to the left, one small organic molecule to the right and that's our catalyst.

WILTON VIRGO: Cheap, efficient and easy to make are not the only requirements for a good catalyst. They also have to be selective in the products they help to create.

AMIR HOVEYDA: There are many forms of selectivity. One interesting, very unusual form of selectivity that nature uses commonly is called handedness. Handedness means that if you put your hand, your left hand in front of your right hand, it looks like you are looking at the mirror images of the two hands. And they are not superimposable. You cannot put the two hands superimposed exactly on top of each other. So molecules can be handed, which means, if you take a molecule and put it in front of a mirror, its mirror image is a different molecule. And they are not superimposable on top of each other.

And that allows nature to work in a very specific way and recognize with much more accuracy the targets that her molecules need to recognize. A good example is if you assume your body is like a glove. And a drug that goes, or a molecule that you take is like the hand. The wrong hand will not fit the glove.

WILTON VIRGO: In chemistry, they do not call these mirror image molecules hand; they call them enantiomers.

ERIKA VIEIRA: Most medicines that we ingest are only one enantiomer and the potential is if you ingest the wrong enantiomer of the molecule, it will either be ineffective and not cure what you have or potentially do the opposite and be detrimental to your health. So in our case, we are trying to select between two enantiomers from forming. And a catalyst can choose and really control how that reaction is occurring.

ERIKA VIEIRA: So, this is a typical product distribution of what we would see if we didn't use our catalyst. And what you will see is that we get equal mixtures of the two enantiomers that are possible from the two reactants that we're using.

However if we look where we did use our catalyst, we can exclusively get at least 97% of one and minimal amount of the other.

WILTON VIRGO: This precise selectivity is made possible by the Valine.

AMIR HOVEYDA: Valine is handed, so if you want this hand you use one hand of Valine. If you want this hand you use the other hand of Valine.

WILTON VIRGO: For Hoveyda and his team this catalyst possessed every characteristic they look for – it is cheap, efficient, effective and highly selective. But there was one problem remaining.

AMIR HOVEYDA: We had no idea how it works, no idea! We had some idea, but in retrospect it was idiotic. And the way it actually we think it works, and you never say in science this is the way it works, you don't know. The way we think it works is far more elegant, far more beautiful than we thought.

The whole thing is fueled by a proton. The proton is basically a small point of positive charge, which can bring negative charges and attract them. These negative charges would repel each other, but if you put a proton in the middle then you can bring all of these negative charges and the proton just says, just brings them together and allows them to come together.

So what the catalyst does is, first it absorbs the proton from the solution. So now, the catalyst is armed. Then what it does, the molecules that we are going to react, they come and attach themselves So now, they're all there, and it's all because of the proton. The proton basically is the MC of this party. And because now they are sitting right next to each other, they react.

And then you have your product, and it's attached to your catalyst. Now there is a very important step. The catalyst has to let go of the product. If the catalyst doesn't let go of the product, the catalyst cannot go and do more reactions because the catalyst needs to do a lot of these. Again the proton walks in. The proton that started the whole thing, it jumps to the product from the catalyst, and that causes the product to be released from the catalyst. And then this catalyst goes and picks up another proton and does it again. That in a nutshell is how this catalyst turns over and does its job.

That took us several years to understand. And once we understood it, it was really sublime. And now we are trying to use that understanding to take this catalyst to the next level. And this is going to fuel a lot more development, not only in my labs but in the labs of other people in the world who are going to read our paper, and that is extremely important. So this project raises a number of new questions, new possibilities in many areas and that is what makes it so important, and that, I think, is a signature of really good science.

[SEGMENT 6: Radioactivity]

WILTON VIRGO: Some reactions cannot be slowed down or sped up. No matter what you do to them, they just proceed at a steady constant rate, like this carousel. The common example of a reaction with a constant rate is called nuclear, or radioactive decay.

WILTON VIRGO: The term “radioactivity” was coined by scientist Marie Curie to describe the steady emission of rays she observed in uranium and thorium. Along with her husband Pierre, Curie accurately proposed what was a revolutionary idea for its time - that this behavior was the result of something happening inside the atom.

Atoms want to be stable, and their stability is determined by the ratio of neutrons to protons in their nuclei. This ratio of stability varies from element to element. If an element has an unstable nucleus, it will shed particles in order to become stable. The emission of these particles is what we call radioactivity or radioactive decay.

Reaching stability is often a multi-step process. Take Uranium-238, for instance. Eventually, it will decay to lead, which is stable, but it will take on many other unstable forms along the way.

The regular rate at which an element decays is often expressed in terms of its half life – which is the time it takes for half of a sample to decay into an isotope of another element. So in one half-life, half of the atoms will have decayed, and then after a second half-life, half of the remaining atoms will have decayed . . . and so on, and so on. Some elements, like Uranium-238, have very long half-lives, while others, like Carbon-11 decay in a matter of minutes.

[SEGMENT 7: PET Scans]

WILTON VIRGO: At Massachusetts General Hospital, half-lives play a crucial role in performing PET scans, which stands for Positron Emission Tomography.

GEORGES EL-FAKHRI: We inject very small amounts of radioactive material, and we can detect minute amount of disease. One of the main applications is in cancer. It’s one of the most sensitive tools we have, and it saves lives.

WILTON VIRGO: PET scans let doctors see where the body has the highest rates of metabolism - such as where cancer cells are rapidly consuming large amounts of radioactive glucose.

They rely on radioactive materials that decay by emitting particles called positrons. Inside the body, when an unstable isotope emits a positron, the positron will collide with an electron. The electron and positron annihilate, creating two photons, light particles that shoot off in opposite directions exactly 180 apart from one another.

GEORGES EL-FAKHRI: And those particles are sort of the GPS that tells us where we are inside the body.

WILTON VIRGO: The scanner detects the two photons and can map their point of origin to create an image.

GEORGES EL-FAKHRI: To give you an idea, we have several billions of lines of response and we have to look at those billions of lines of response every nanosecond to know where the events came from. That's what a PET scanner is. All you have to do is look at ten, twenty billion lines of response every nanosecond, and you'll have your signal.

WILTON VIRGO: But before they perform the scan, they have to make the radioactive material. This happens early every morning in the cyclotron, which sits in a vault in the basement of the hospital, secured with five-foot thick concrete walls and one very big door. They make many different compounds for PET scans, but one of the most common is Fluorine-18, or F-18. To make the F-18, the cyclotron accelerates particles, in this case, protons, that they shoot at a stable target material.

RON MOORE: The actual target material which goes in here is a couple milliliters of special water – it's not just natural water – it's water that's enriched with oxygen-18. And so in the cyclotron, we accelerate protons and then it comes through a valve and from there the proton knocks out a neutron in the O-18 and the proton stays, turning it into the radioactive F-18. So, what's really interesting about this process is we are taking stable matter and making it unstable through this bombardment process and transforming it. It's sort of a modern day alchemy.

WILTON VIRGO: Fluorine-18 has a half-life of just under two hours, which is useful because once in the body, it will not be radioactive for long. But it also means that once they make it, they are on the clock.

GEORGES EL-FAKHRI: The bad news is we are losing the activity, the good news is that we now how much activity we made and we know exactly how much time we have before losing half of it, and then half of it again, so that means that we can schedule all our work for the work day based on how much activity we made at what time to make sure that we can inject a patient shortly enough after that to have enough activity in the patient. And then we can schedule our scan shortly soon enough after that in order to make sure that we can then have an image that is of good quality.

WILTON VIRGO: Before it is injected the radioactivity needs to be attached to glucose so they can target specific areas in the body

NEIL VASDEV: If we took fluoride straight out of the cyclotron without attaching it to a glucose, fluoride itself would just end up in the bone. Specifically in cancer, tumors take up, utilize a lot of glucose, so by making glucose radioactive, we can actually visualize the tumors as hot spots on the scan.

So once the fluorine-18 is made, it's in water. And that's transported through tubing directly onto one of these robotic boxes. We dry it, and then we transfer it to a reaction vessel, which looks like this. And this is where we make fluorine-18 labeled, fluorodeoxyglucose, or more commonly referred to as FDG. The whole thing can be done within about thirty to forty minutes ready for injection.

WILTON VIRGO: When they inject the radioactive glucose into a patient, it will travel to the different areas of the body where the glucose is needed, and these areas will show up on the PET scan because of the radioactive material.

GEORGES EL-FAKHRI: So for example, there should be a lot of glucose in your brain. That's because you are using a lot of energy in your brain, so the uptake in the brain will be high, you will have a lot of signal. Your heart is beating, it's a muscle, it's using energy, so you'll have a lot of uptake in the heart. You can have a lot of uptake in the bladder, because we are eliminating the radioactive glucose through the bladder. So all of this is normal physiological uptake.

What we are interested in is this. This is the disease; these are areas of disease that mean there is tumors there, unfortunately for this patient. But it is very important because now we can tell what is the stage of the patient, what's the widespread of the tumors, and whether or not that patient can have surgery, or whether he's a better candidate or she's a better candidate for chemotherapy and then radiation therapy.

WILTON VIRGO: PET Scans are not only bearers of bad news; they are also used to indicate the effectiveness of treatment. This is a scan of a patient with cancer one day before treatment, and this is that same patient one day after treatment.

GEORGES EL-FAKHRI: And you can see that most of these tumors are gone. So all of these tumors that were here are gone. You should see the face of a patient when we have a negative scan after treatment and we say, "yep, you're clean, you can go home." That's like gaining their life again back and that is worth, you know, a lot of hours being here.

[WRAP-UP]

WILTON VIRGO: The positive or sometimes negative effects of a chemical reaction are often due to the rate at which that reaction proceeds. The ideal rate of a reaction can change a drug from harmful to helpful, or a fuel from dirty to clean.

To be sure, reaction rates are not the only determining factor in chemistry, but understanding them increases our ability to manipulate matter to our advantage and allows for a deeper understanding of the world around us.

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