Unit 9: Kinetics and Equilibrium

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Building a Cheaper Catalyst

By DOUGLAS QUENQUA

The chemical reactions that help produce margarine, medications, cleaner car exhaust and countless other useful things rely on valuable metals like platinum, rhodium and ruthenium as catalysts. But such metals are rare, expensive and occasionally toxic. For years, scientists have tried to develop methods of catalysis using cheap, common, nonpolluting metals like iron and cobalt.

Now, three separate teams of researchers say they have developed catalysts based on cheap metals that can either match or outperform those based on precious metals. The three studies were published in the journal Science.

In one study, University of Toronto researchers showed that attaching certain organic molecules to iron, then dissolving it in a solution, created an efficient catalyst for producing alcohols and amines used in perfumes and medications. The chemical industry has traditionally relied on ruthenium, an extremely rare metal, to catalyze such reactions.

"It shows that with the right organic molecule attached to it, we can make iron do things that weren't thought possible before," said Robert H. Morris, an author of the study. There are likely more iron catalysts to be found, he said, but cautioned that there is "still a ways to go between discovery and application."

Still, all three studies presented different approaches to cheap-metal catalyzing, illustrating that "there is no exclusive single 'recipe' for success," wrote R. Morris Bullock, a chemist with the Pacific Northwest National Laboratory, in an accompanying article.

What's So EQUAL About EQUILIBRIUM?

By Michael Tinnesand

It is a word you hear all the time. Get off a wild carnival ride and it takes a while to restore your sense of *equilibrium*. The directions for setting up a new fish tank advise you to wait until the water reaches *equilibrium* before you add fish. When growing communities finally see population increases level off, the news might report the area population is nearing *equilibrium*.

Have you heard the word in science class? Physical science classes sometimes talk about levers and pivots at equilibrium. Astronomers debate whether the universe is expanding, contracting, or reaching an equilibrium. And one of the most important and reported discussions in science is about the atmosphere and climate change: What is happening to the Earth's atmosphere that might upset its equilibrium?

PHOTODISC

It's easy to get confused about a word used in so many ways. One of the most common misconceptions about equilibrium is that it means things have stopped changing. But let's think about the community example—the one in which the population has reached an equilibrium. When a population is growing, the number of people new to the community is greater than people leaving the community. Babies are born; new people move in; numbers grow. But that's not the whole story. At the same time, people move away and people die.

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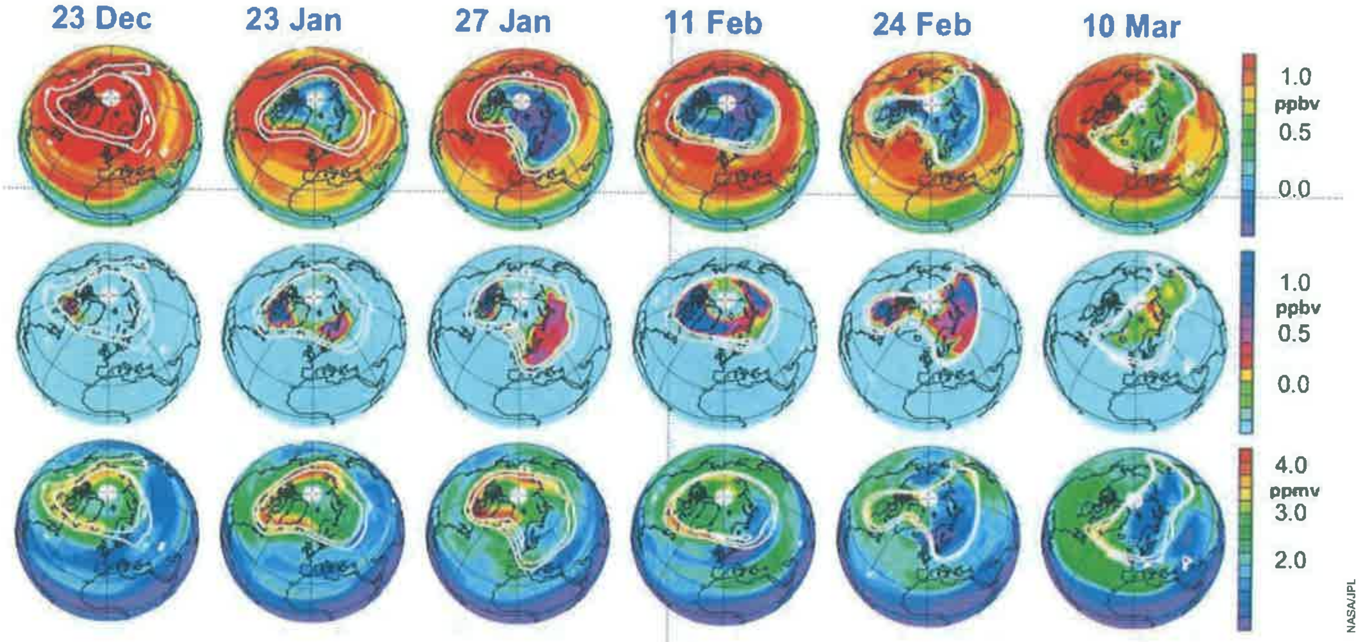
But, let's do the math. When the population is growing, the rate of adding new people is greater than the loss of people who leave or die. At some point the population may reach a stable number. Has change stopped? No. People still move into the community and they still leave; it's just that they are doing it at equal and opposite rates. Equal opposing actions. That's equilibrium.

Take the example of the fish tank. Perhaps you fill the tank with water from your tap and find it is fairly cold and contains a lot of dissolved chlorine. As you let it sit for a few days, the temperature gradually begins to rise and the smell of chlorine begins to decrease. Finally, the tank reaches a steady state where the temperature is constant. You test for chlorine and find that the amount is staying constant as well. So, the tank has stopped changing, right? Wrong! Scientists call this situation a *dynamic* equilibrium. And understanding how this kind of balancing act works is important to understanding a great deal about how the world works.

Here's what's going on with the chlorine concentrations in the fish tank. Two things are happening at once. Chlorine is leaving the tank to mix with and dissolve in the surrounding room air. Initially, this rate is pretty large, because there's a lot more chlorine in the water than in the air. But it's possible for some atoms of chlorine in the air near the tank to find their way back into the aquarium. Possible. But, with a whole room full of air in which to escape, chlorine is very, very unlikely to do that. Eventually, the amount of chlorine in the tank stabilizes. Most of the chlorine has left the tank, so the rate of chlorine still leaving has become very small. Here's the important point: Although the concentration of chlorine in the tank is constant, there is still a very small amount leaving and a very small amount entering the water. The leaving and entering rates are the same—that's *dynamic* equilibrium.

Now think about the chemical reactions you've observed and described in class. It's



Maps of chemical concentrations from Aura's Microwave Limb Sounder instrument help us better understand the complex equilibria of the atmosphere. Shown above are the concentrations of hydrogen chloride (top), chlorine monoxide (center), and ozone (bottom) for selected days during the 2004-2005 Arctic winter.

easy to get the impression that reactions only go in one direction. In fact, the way most textbooks show and represent reactions in written equations just reinforces this one-way-street idea. Take the reaction of hydrogen with oxygen. When hydrogen burns, it reacts rapidly with oxygen, giving off a great deal of energy. The reaction is usually represented as

$$2H_2 + O_2 \rightarrow 2H_2O + \text{Heat}$$

The way it's written, it looks like the hydrogen reacts with the oxygen and makes water until the reactants run out. End of the story. But, again, the system is not that simple. It turns out that the reverse reaction can also happen. Given enough energy input, water can break down into component hydrogen and oxygen atoms. But since water is so stable, it doesn't happen often. In this reaction, equilibrium is reached when virtually all the reactants have been used up, lowering the formation of more water to almost nothing. This action is opposed by an equal vanishingly small number of water molecules breaking down into separate atoms. It's an equilibrium—a *dynamic* equilibrium.

So why doesn't this discussion come up when the textbook describes the reaction of hydrogen with oxygen? It is because this reaction, like many others you are learning about, is so favorable to the formation of products that it is barely worth mentioning that the reverse reaction is also taking place.

Some chemical reactions, however, are a different story! The reaction of hydrogen with nitrogen to make ammonia is a good example. The formula for this reaction is always written as

$$3H_2 + N_2 \rightleftarrows 2NH_3$$

Why the different reaction arrow? Under typical standard conditions, equilibrium for this reaction is reached well before all the reactants are consumed. With the double arrow, the chemist shows that when a reaction "stops happening", it has really just come to an equilibrium of the forward and reverse reactions. The reaction for making ammonia (NH_3)—a component in fertilizers and other products—is very important. Chemists worked for many years to learn how to shift this equilibrium to favor the products. As a result, industry can produce vital ammonia in a cost-effective manner.

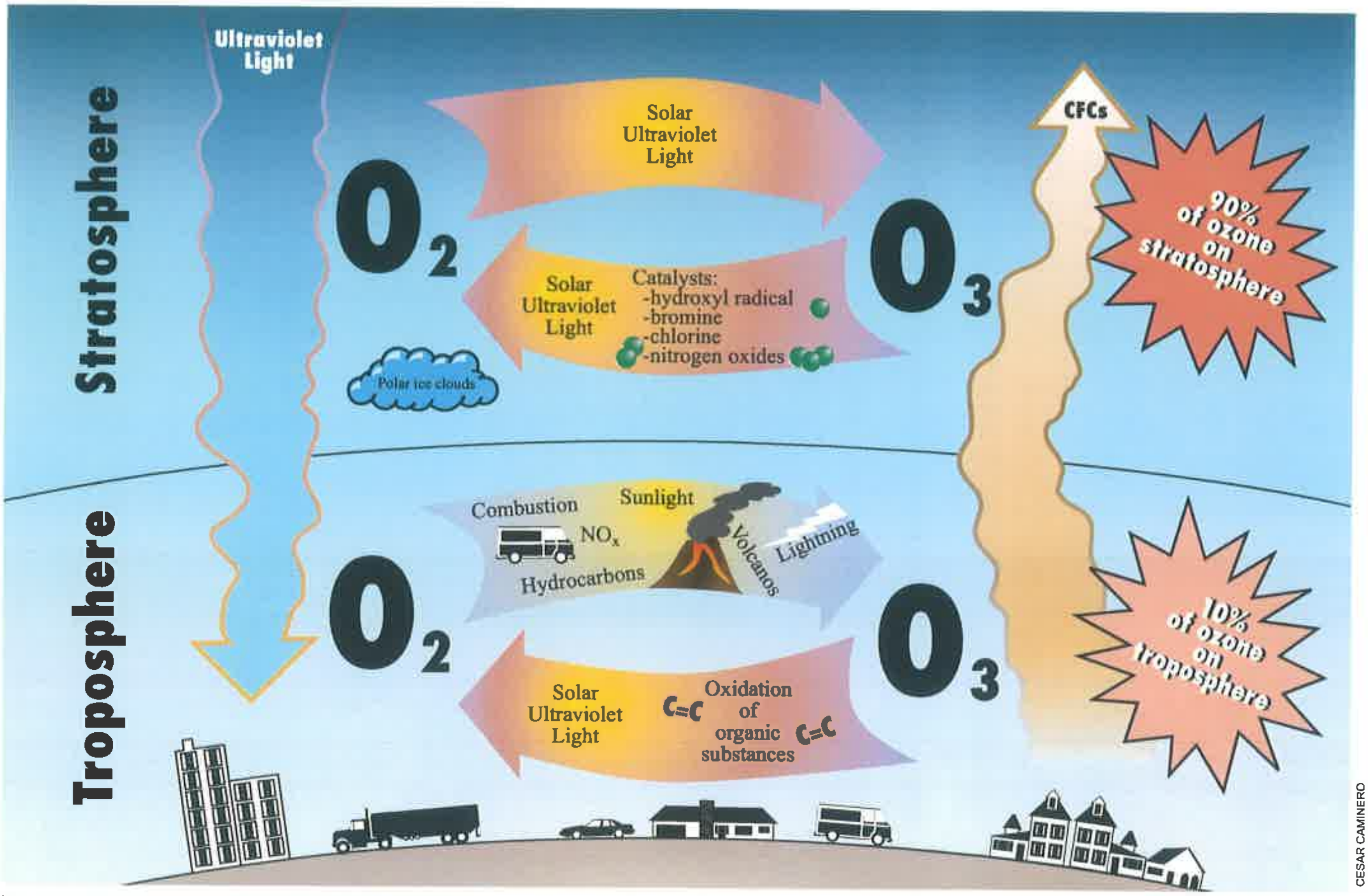
The idea of a shifting equilibrium is another important concept. Think back to our example of the population in a community. The population number may be in equilibrium for a long time. But suppose something happens to shift one of the rates—like maybe a new industry moving into the area. This might cause the rate of people moving into the area to increase, raising the population. Eventually, this higher population will result in crowding, housing shortages, and even higher death rates. As a result, the rate of people leaving will finally balance the rate of people entering the area, establishing a new dynamic equilibrium.

In a similar way, a chemical equilibrium can shift. It may be influenced by factors like increasing the concentration of reactants, removing products, and changing the pressure or temperature. This principle was summarized in the late 19th century by French chemist and engineer Henri-Louis Le Chatelier.

The chemistry of the Earth's atmosphere contains many examples of various equilibrium systems, each complex on its own. But they become even more complex when the relationships among all of these chemical systems are taken into account. We would have fewer worries if the atmosphere retained its long-term equilibrium. But such is not the case. Natural and human-generated changes are constantly influencing our atmosphere, making it essential for us to study and understand the complex web of chemical reactions that define our atmosphere.

Examples of various systems and factors that influence their equilibrium abound.

Consider the ozone (O_3) layer in the stratosphere. The ozone layer is important because it absorbs and screens out a portion of the ultraviolet light coming from the sun. Without the ozone layer, the amount of UV reaching the earth's surface would reach dangerous levels. This thin layer of O_3 reaches peak concentration in the upper atmosphere between altitudes of 19 and 23 km.



The concentration of various substances in the atmosphere depends on complex and interrelated reactions. In the stratosphere, ultraviolet light creates ozone. Catalysts such as bromine and chlorine break ozone down to form oxygen. If the rate of ozone formation is the same as the rate of ozone destruction, the amount of ozone in the stratosphere will remain constant. In the troposphere we have a slightly different story. Most of the ozone is caused by combustion, either from human activities or natural sources. The reaction products react in the sunlight to form ozone. Ground level ozone is destroyed when it reacts with substances such as organic material, or when it is exposed to UV light.

Ozone forms when ultraviolet light from the sun breaks oxygen molecules apart. This atomic oxygen can join existing O_2 molecules to form O_3. By a reverse reaction, chemicals in the upper atmosphere cause the ozone to break apart. During times of increased sunspot activity the amount of ultraviolet light from the sun increases. This increase in UV light increases the rate at which ozone is formed.

By these naturally opposing reactions, the net effect is this: More ozone eventually leads to more ozone breaking down. The equilibrium is reestablished at a high concentration of ozone. But the opposite shift can also happen. An increase in the concentration of substances that react with ozone to break it down can increase the rate of ozone destruction. If the rate of ozone formation stays constant, then the total amount of ozone will fall until the rate of destruction falls and a new equilibrium is established at a lower ozone concentration.

This is exactly what was observed in the 1970s. Chemists noticed that the concentrations of ozone were decreasing—well beyond what could be explained by natural processes. It was soon discovered that the concentration of ozone-depleting substances was increasing, mostly due to human use of gases for refrigeration and spray can products. Fortunately, worldwide efforts to reduce production and use of these damaging substances seem to be helping, and recent measurements indicate that the ozone concentrations may be stabilizing.

At the same time, scientists have observed a cooling in the stratosphere. This may be, in part, due to an increase in the insulating layer of greenhouse gases (H_2O, CO_2, CH_4, O_3, N_2O, and others). Their increase in concentration means less solar energy is radiated back into the upper atmosphere as heat. When temperatures drop below −88 °C, thin clouds form. The presence of stratospheric clouds in the polar regions appears to increase the rate of ozone destruction. The surface of ice crystals in the stratospheric polar clouds can accelerate reactions between O_3 and substances that destroy ozone. The overall effect is a shift in the equilibrium and a decrease in the ozone levels at the Earth's poles.

On a global scale, equilibrium gets very complicated. System after system, changes occur in intricate and sometimes unexpected ways, both in response to natural conditions and also because of human action. Aura and the other scientific satellites in orbit are gathering data that will play a crucial role in developing an understanding of our atmosphere. As hard as it is, understanding these equilibria and how one thing leads to another is a vital step in deciding strategies for preserving the lives and well-being of all who call this planet home.

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