Science-1A Lecture: Week-11, Friday, March 26, 2021
Chemical Equilibrium and Reaction Rate

There are two main characteristics of a chemical reaction – equilibrium and reaction rate – which are quite independent. Examples of these are listed in the handout entitled "Chemical Reactions – Extent and Speed" at
https://yosemitefoothills.com/Science-1A/Handouts/Week-11/ReactionExtentAndSpeed.pdf .
Read that handout and then the following discussion which explains more about the 'why' behind those examples.

Chemical Equilibrium

In an earlier lab, we saw an animation of evaporating gas atoms at
https://yosemitefoothills.com/Science-1A/Handouts/Week-04/EvaporationIntoVacuum-25K.gif .
It showed how atoms in a liquid get kicked by thermal agitation into a vacuum region above it. The rate at which atoms are kicked out of the liquid is very sensitive to the liquid temperature. At the start of the simulation, the region above the liquid is empty, but as the simulation proceeds the number of atoms in the gas increases.

This increase does not continue forever. After colliding with each other and with the walls of that region, many atoms find themselves plunging back into the liquid. The number returning increases as the number in the gas increases. Eventually, so many atoms are in the gas that the returning number per unit time matches the number thermally ejected out of the liquid per unit time. That balance point is called an **equilibrium** condition. Once attained, the density of atoms in the gas will remain very nearly constant.

If the liquid temperature is increased, the number of atoms in the gas will increase until a new equilibrium point is reached. This process of approaching and attaining equilibrium is typical of all chemical processes. It happens because they involve large numbers of atoms or molecules whose *average* behavior follows the laws of thermodynamics.

When an atom (think of a ball) bounces off a wall recoils, its momentum has reversed direction. It has momentarily exerted a force on the wall at the point where it hit. Now imagine a large number of atoms bouncing off a 1 m^2 area of wall each second, each exerting a small force on that area so that the wall feels a total force on that area proportional to the number of atoms and their average speeds. Since pressure is force per unit area, that means the wall feels a pressure from the atoms. This pressure is called the **vapor pressure** of the liquid.

The animation linked above simulated a liquid temperature of about 25 K. Here is another animation simulating 40 K:
https://yosemitefoothills.com/Science-1A/Handouts/Week-04/EvaporationIntoVacuum-40K.gif
At this higher temperature, there is greater thermal agitation in the liquid and the number of atoms that escape into the gas will be greater. But, also the average impact of each gas atom on the walls will be greater because the atoms have a greater kinetic energy at the higher temperature and therefore bounce harder. These effects make the vapor pressure greater and very sensitive to changes of temperature.

We saw this rapid change in vapor pressure with temperature in an earlier lab demonstration where we made a soft drink can implode by heating up a small amount of water in it to 100 °C until steam poured out of its opening leaving only water vapor without any air in the can. Suddenly plunging the can top down into cool water at 22 °C condensed that steam to a pressure about 100 times smaller. The cold water covered the opening and the surrounding air pressure then squeezed the can until it imploded. The atmospheric air pressure also pushed some water up into the inside of the can.

At any specific temperature, water will have a certain equilibrium vapor pressure. If the amount of moisture in the air increases beyond that point, it will condense becoming rain or fog.

Keep this example of equilibrium in mind since all chemical reactions balance competing processes in this manner.

For example, if NaCl crystals are placed in water, they will start to dissolve into Na^+ and Cl^- ions. As more ions collect in the liquid, a point will be reached when some will meet together and form new salt crystals as fast as others are dissolving. That is the point of equilibrium concentration for the salt solution. The solution is then said to be a **saturated solution**.

In terms of chemical equations, our vapor pressure example can be written as

$$H_2O(\text{liquid}) + \text{energy} \Leftrightarrow H_2O(\text{gas})$$

and our salt solution example can be written as

$$NaCl(\text{solid}) + \text{energy} \Leftrightarrow Na^+(\text{aqueous}) + Cl^-(\text{aqueous})$$

Usually, we do not write the words (liquid), (gas), (solid) or (**aqueous**), but instead use (l), (g), (s), or (aq).

Two other symbols are also used (↑) to indicate gas bubbling upward, and (↓) to indicate a solid (**precipitate**) falling down. A **precipitate** is a reaction product that is not significantly dissolved in the water and therefore collects at the bottom of the container when produced. Our electrolysis of water had an undesirable orange precipitate of FeOOH from some iron being extracted from the stainless steel electrode that was producing oxygen bubbles.

Reactions can absorb energy like those shown above, but others release energy. Our electrolysis experiment absorbed electric energy when the hydrogen and oxygen gases were slowly being made over several hours, but quickly released that energy when we caused the reaction go in reverse with a spark to make our explosion. Next week, we will talk about balancing combustion equations where energy is always released.

Chemical equilibrium is like an automatic mechanical balance scale. Adding more mass to one side will cause the automatic system to add weights to the other side until the balance is once again achieved. Adding excess vapor to our simulation of water evaporation will cause the excess vapor to join the liquid. The final vapor pressure will once again match that for the liquid temperature.

In the absence of thermal agitation, all reactions would proceed to the point of lowest energy. All gas atoms would fall into a liquid, and in fact, all liquid atoms would cease moving any more than is required by quantum mechanics. All liquids become solids at absolute zero temperature except helium which remains a liquid unless compressed to 25 times atmospheric pressure. Quantum motions keep helium liquid even at absolute zero.

It is a balance between thermal agitation and minimizing energy that determines chemical equilibrium balances. This was obvious in our simulation of the effect of gravity on a gas. See the animation at
https://yosemitefoothills.com/Science-1A/Handouts/Week-04/GasAt12K400HeGravity4.gif
where gravity attempts to pull the gas atoms down while thermal agitation is kicking them up. The simulation starts with a uniform distribution of gas atoms throughout the box, but eventually an equilibrium condition is achieved which has a greater density of atoms at lower altitudes.

Reaction Rate

Equilibrium tells us about the final state of a system, but nothing about how quickly that state will be reached. Equilibrium in a salt solution might take overnight at room temperature, but happen very quickly at 70 ºC. The rate at which salt dissolves depends on many factors – temperature, how tightly the salt ions are held by the crystal, and the strength of the pull of the dipole moments of the water molecules.

An extreme example of a slow reaction rate is diamond, a crystalline state of carbon atoms. Diamond is not the equilibrium state of a collection of carbon atoms. That would be graphite (think charcoal). There is a very large energy barrier for the conversion of diamond to its lower energy state of carbon. It may be useful to review the discussion about energy barriers in our March 17 lecture notes:
https://yosemitefoothills.com/Science-1A/OnlineLectureAndLabNotes/Week-10-Lab-Wednesday-March-17-2021.pdf
Diamond is created at high temperatures and under high pressure, and will last "forever" at room temperatures, but can be burned to carbon dioxide in air at about 1200 kelvin.

Reaction rates are critically dependent on the height of the reaction energy barrier. Doubling the energy barrier can be the difference between a reaction time of 1 s and 1 year depending on the ratio of barrier energy to thermal energy.

When we did our electrolysis of water demonstration, the hydrogen and oxygen gas were stored together in a soft plastic bag. They bumped into each other, but did not react at room temperature because there was an energy barrier to the reaction which was too great for room temperature agitation to overcome. Adding a spark started a chain reaction as the heat of the spark caused some nearby hydrogen and oxygen molecules to react. They released enough energy to cause progressively more distant molecules to react leading to an explosive chain reaction.

A favorite demonstration is to add vinegar (a dilute solution of acetic acid CH_3COOH) to baking soda $NaHCO_3$, washing soda Na_2CO_3 , and calcium carbonate (chalk) $CaCO_3$. In all three cases, CO_2 is released, but baking soda does it so dramatically that it is used in schools for volcano simulations. Washing soda also reacts, but much less vigorously. Calcium carbonate reacts very slowly, producing barely visible bubbles of CO_2.