CHEMICAL EQUILIBRIUM: A COLORFUL INVESTIGATION/ AP CHEMISTRY/collins/huron h.s.

Background:

Equilibrium systems

Until now, most of the chemical reactions we have studied have been assumed to go to completion. In these reactions, a color change was observed, a precipitate was formed, or a gas evolved with bubbling and fizzing. These reactions had been carried out under conditions that favor product formation.

In many chemical changes, the reaction does not go all the way to completion. Chemists refer to this as the equilibrium state. In this state, some amount of all reactants and products are present in varying amounts.

One equilibrium system that is constantly being stressed by changes in reaction conditions is happening inside you right now. Hemoglobin is responsible for the transport of oxygen and carbon dioxide in our bodies. The oxygen, O_2, is in equilibrium with the oxygenated (HbO_2) and deoxygenated (Hb) forms of hemoglobin, the iron containing molecule in the blood that carries oxygen to our cells and carbon dioxide back to the lungs.

The equilibrium can be represented as: $Hb + O_2 \rightleftharpoons HbO_2$

In the lungs, the pressure of oxygen is relatively high, so at the reaction conditions, the equilibrium is said to favor the formation of HbO_2. The oxygen-rich blood then leaves the lungs and is carried to the cells of the body where the pressure of the oxygen is much lower and the equilibrium then no longer favors the formation of HbO_2. The reverse reaction is favored and oxygen is released into the cells as the equilibrium is now said to favor the reactant side of the reaction.

At the same time, the pressure of carbon dioxide is elevated in the cell and so the CO_2 molecule combines with the Hb molecule in an equilibrium similar to that responsible for oxygen transport. When the blood reaches the lungs again, the carbon dioxide is released from the hemoglobin as the pressure of CO_2 is now much lower and the reactants Hb and CO_2 are now favored.

A third equilibrium system involves hemoglobin and carbon monoxide, CO (a highly toxic gas):

$$Hb + CO \rightleftharpoons HbCO$$

The reason carbon monoxide is so poisonous is that the affinity between hemoglobin and carbon monoxide is approximately 200 times stronger than the affinity between oxygen and hemoglobin. This means that a CO poisoning victim will be starved of oxygen because the CO is binding to hemoglobin in blood and oxygen is not being transported to cells.

Treatment for CO poisoning involves the administering of oxygen at higher pressures which will increase the amount of oxygenated hemoglobin in blood.

Chemical equilibrium means that there are forward and reverse reactions occurring simultaneously at the same rates. This means that the amounts of both the reactants and the products remain constant. That is, the reactants are consumed to generate products at the same rate that the products react to regenerate the reactants. No net change in concentration occurs. To the outside observer, it appears as if nothing is happening on the macroscopic level because no observable changes are evident. This is known as dynamic equilibrium. If you were able to see individual atoms and molecules, this environment would be incredibly busy and dynamic. There would be a crazy amount of activity.

Equilibrium systems are described mathematically using concentrations or gas pressures in what is known as a “mass action expression”. The equilibrium constant is the mathematical result of these calculations. Equilibrium constants are temperature dependent. In other words - one thing that will always affect K, the equilibrium constant, is temperature.

For the generalized reaction:

$$aA\ (aq) + bB\ (aq) \rightleftharpoons cC\ (aq) + dD\ (aq)$$

the mass action expression, which at equilibrium will be called an equilibrium expression is:

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

K_c is called the equilibrium constant and [ ] denotes concentration of each substance.

The only substances involved in an equilibrium expression are those that have a concentration, which means that pure solids and pure liquids are not included. Therefore, liquid water and solids are never included in equilibrium equations.

Consider the following equilibrium scenario:

$$2NO_2\ (g) \rightleftharpoons N_2O_4(g) + \text{heat}$$

brown colorless

TABLE 14.1 The NO_2–N_2O_4 System at 25°C

INITIAL CONCENTRATIONS (M)		EQUILIBRIUM CONCENTRATIONS (M)		RATIO OF CONCENTRATIONS AT EQUILIBRIUM	
$[NO_2]$	$[N_2O_4]$	$[NO_2]$	$[N_2O_4]$	$\frac{[NO_2]}{[N_2O_4]}$	$\frac{[NO_2]^2}{[N_2O_4]}$
0.000	0.670	0.0547	0.643	0.0851	4.65×10^{-3}
0.0500	0.446	0.0457	0.448	0.102	4.66×10^{-3}
0.0300	0.500	0.0475	0.491	0.0967	4.60×10^{-3}
0.0400	0.600	0.0523	0.594	0.0880	4.60×10^{-3}
0.200	0.000	0.0204	0.0898	0.227	4.63×10^{-3}

Notice that the initial data (the first column) starts with products only, moves into mixtures of reactants and products, and finishes with reactants only. The equilibrium concentrations look random until the law of mass action is used. In the appropriate format, all K values display similar values at 25C.

LeChatelier's Principle

Henri Le Chatelier studied and published extensively on the subject of equilibrium in solutions. His principle states:

"If a change in concentration, temperature, pressure, or volume is imposed on a chemical system at equilibrium, then the equilibrium shifts by changing concentration or pressure to counteract the imposed change and establish a new equilibrium."

These changes in conditions are often referred to as stresses. We say the equilibrium system has been stressed by the change and can predict the subsequent changes in concentrations or pressures by examining the stress. The principle is applied to predict changes in relative amounts of reactants and products called the equilibrium position, in the following manner.

For the generalized equilibrium system:

$$aA\ (aq) + bB\ (aq) \leftrightarrows cC\ (aq) + dD\ (aq)$$

At constant temperature and pressure, adding substance A to the system when it is at equilibrium will cause a stress on the system by increasing the concentration of a reactant. This will increase the rate of the forward reaction and the result will be an increase in the amounts of the products, C and D, and a reduction in the amount of B as it is consumed by the now faster forward reaction. The increase in concentration of C and D increases the rate of the reverse reaction until eventually a new equilibrium is established. We say that the equilibrium position shifts to the right when a stress is applied to the left.

A stress of removing either substance A or B would have the reverse effect. In this case, the reduction in the concentration of the reactants causes the rate of the forward reaction to decrease and this momentarily faster reverse reaction would cause an increase in the previously reduced concentration of A and B until eventually the forward and reverse reaction are again occurring at the same rates and equilibrium is re-established. Le Chatelier's Principle states that the equilibrium has adjusted to the stress by shifting to the left.

In reactions involving gases, the pressure of the gas is important. The partial pressure of a gas is analogous to concentration. So changes in pressure have the same effect as changes in concentration. More commonly, pressures are changed by changing the volume of a system. In this case, stoichiometry of the equilibrium reaction must be examined to determine the effect of the applied stress. A volume increase will favor the production of substances on the side of the reaction with the highest total number of gas molecules. A reduction in pressure will favor the production of substances on the side of the reaction with the most gas molecules.

Finally, the equilibrium constant is temperature dependent. Heat can be treated as a reactant in endothermic systems and as a product in exothermic systems. Just as with adding or removing a particular substance, heat can be added (temperature increase) or removed (temperature decrease). An equilibrium system responds in the same way as if a substance is added or removed by shifting the equilibrium position to remove the stress. Thus increasing the temperature of an exothermic system will result in a shift toward reactants. Cooling this same system, results in a shift toward products.

Pre-lab Questions:

Examine the following equilibrium systems using an online simulation.

Cobalt Chloride Equilibrium

https://www.youtube.com/watch?v=WxHtKHTTbhQ

1. How does adding chloride ions to the cobalt complex ion, $[Cu(H_2O)_6]^{2+}$, change the reaction conditions?
2. How does adding water to the blue complex ion, $[CoCl_4]^{2-}$, change the reaction conditions?
3. Why do these changes in reaction conditions cause reactions to occur? Use a reaction equation to illustrate how these changes in reaction conditions alter the position of the equilibrium.

NO_2/N_2O_4 Equilibrium

http://www.mhhe.com/physsci/chemistry/animations/chang_7e_esp/kim2s2_5.swf

1. Each time the animation stops, count the number of NO_2 and N_2O_4 molecules present. What do you observe?
2. After watching the animation segment that includes the white clouds around bond formation and bond breaking, describe what is happening simultaneously to keep the number of each molecule constant.
3. Explain how this animation illustrates the dynamic nature of equilibrium.

Bromine Gas/Liquid Equilibrium

https://www.youtube.com/watch?v=WxHtKHTTbhQ

1. When the animation stops, count the number of Br_2 (l) and Br_2 (g) molecules present. What do you observe?
2. Is this a chemical or physical equilibrium?

Procedure:

You will be shown a series of demonstrations. These demonstrations will reveal many different types of equilibrium phenomena. Possible equilibrium systems for your use are described later in this handout. You will need to observe all of them and prepare to discuss the stresses and shifts in equilibrium that accompany them. Be sure to discuss your proposed stresses with your partner before attempting to describe them as observations/data. Once you have observed all of the investigations you should feel pretty confident describing the process of reactions reaching equilibrium. Be sure to include a balanced equation and an equilibrium expression for each investigation. If you can add heat to your equations, that would be great.

Possible Equilibria:

An Acid-Base Indicator

Acid-base indicators are large organic molecules that can gain or lose hydrogen ions to form substances that have different colors. The reaction of the indicator bromothymol blue (BTB) is well known. Investigate its behavior in water with dilute acid and base. To create the equilibrium add 1 ml of BTB to 25 ml of water. Investigate the shifts that can be observed by applying a stress to small amounts of this solution using 0.1 M NaOH and 0.1 M HCl.

Complex Ion Equilibria

An equilibrium system can be formed in solution with iron (III) chloride and potassium thiocyanate. The ion that forms in their combination is the $FeSCN^{2+}$ ion. To create the equilibrium mixture, add about 20 ml of 0.10 M KSCN solution into a beaker and then add 20 ml of distilled water and 5 drops of 0.20 M $Fe(NO_3)_3$ solution. Investigate shifts in equilibrium by applying a stress to small amounts of this solution in a small test tube. You have 0.10 M KNO_3, solid $FeCl_3$, solid KSCN, and Na_3PO_3 solid.

An equilibrium system can be formed in a solution with copper (II) sulfate and ammonia. To create the equilibrium mixture, take 25 ml of 0.25 M $CuSO_4$ and add concentrated NH_3 solution drop-wise until a precipitate forms. Continue adding the ammonia solution until the precipitate disappears. Investigate shifts that can be observed by applying a stress to small amounts of this solution in the test tubes provided using 0.10 M HCl and the original reagents.

An equilibrium system can be formed in a solution with copper (II) chloride in water. The copper ion bonds to six water molecules to form the hydrated complex ion $[Cu(H_2O)_6]^{2+}$ (aq) while the Cl^- ion remains in solution. To create the equilibrium mixture, add about 2 grams of solid copper (II) chloride dihydrate to 25 ml of water. Investigate the shifts that can be observed by applying a stress to small amounts of the solution in the test tubes provided. You have concentrated HCl and water.

Hydrated Cobalt Complex Ions in Alcohol Solution Equilibrium

To create the mixture, add 2 grams of cobalt (II) chloride hexahydrate to 25 ml of 95% ethanol in a beaker. The equilibrium reaction is endothermic as written below:

$$Co(H_2O)_6^{2+}\text{ (alc)} + 4\ Cl^-\text{ (alc)} + \text{heat} \leftrightarrows [CoCl_4]^{2-}\text{ (alc)} + 6\ H_2O\text{ (alc)}$$

Investigate the shifts that can be observed by applying a stress to small amounts of this solution in a test-tube. You have solid NaCl, water, acetone, concentrated HCl and $AgNO_3$ (aq). You also have ice and hot water.

Chemical Equilibrium

You will observe glass ampules that contain the equilibrium mixture of NO2 and N2O4. Heat and cold will be applied to the system with hot and cold water baths. Attempt to describe the thermochemistry of this system and be sure to place heat in your equilibrium reaction.

Physical Equilibrium

You will take a saturated solution of KCl and you will add concentrated HCl to it drop wise and make an observation.

You may skip calculations, conclusion, error analysis and post-lab questions. Yippee!!!