Every man has the right to risk his own life in order to save it.--Rousseau

Factors Affecting Equilibrium---LeChâtelier's Principle

From your studies of collision theory and the factors which the rate of a chemical reaction, you have the fundamental information needed to understand the changes which take place in a system at equilibrium when some condition changes. Equilibrium is defined as a state at which two opposing processes occur simultaneously at the *same rate*. Thus the factors which affect the rate of a reaction will likely affect the equilibrium also.

Recall the following factors which were effective in changing the *rate* of a reaction:

a. temperature
b. concentration
c. pressure
d. catalyst

Except for the last one, each of these factors also affects the state of equilibrium in a system. Catalysts have no effect on the final equilibrium state since they affect the rates of *both* the forward and reverse reactions by lowering the activation energy requirement for *both* processes. Each of the other factors preferentially influences the rate of reaction in only <u>one</u> direction. These effects can be understood with reference to collision theory and the reaction energy profile.

In this experiment you will be investigating the following systems:

$Cr_2O_7^{2-}(aq) + H_2O(\ell) \leftrightarrows 2\ CrO_4^{2-}(aq) + 2\ H^+(aq)$ (1)
orange yellow

$heat + Cu^{2+}(aq) + 4\ Br^-(aq) \leftrightarrows CuBr_4^{2-}(aq)$ (2)
blue green

$N_2O_4(g) \leftrightarrows 2\ NO_2(g)$ (3)
colorless brown

In each of the systems chosen, the reactants and products have different colors. Thus by following the color changes as you alter concentration, temperature and pressure, you can determine in which direction the rate of reaction has temporarily increased because of the change you made. That will allow you to generalize some rules for the behavior of equilibrium systems when subjected to change.

Preparing to experiment

You will be provided with the following materials:

1. 0.10 M $K_2Cr_2O_7/K_2CrO_4$ solution
2. 2 M H_2SO_4 solution
3. 2 M NaOH solution
4. 2 M KBr solution
5. 2 M $CuSO_4$ solution
6. solid $NaNO_2$
7. 30 mL syringe with sealed end
8. small vial
9. small test tubes
10. ice

Design an experiment to determine the effect of changing H^+ concentration in reaction (1) using NaOH and H_2SO_4. [see **Technique**]

Design an experiment to determine the effect of temperature on reaction (2). [see **Technique**]

Design an experiment to determine the effect of pressure on reaction (3). [see **Technique**]

Technique

1. General comparisons

For the first two reacting systems, the simplest way to make comparisons is to have three *small* samples (about 1 mL) in separate test tubes. One can be a "control" and you can make changes on the other two (e.g., add acid or add base, heat one and cool the other, etc.)

2. Proper disposal of Cr(VI) solutions

Chromium in its +6 state is a suspected carcinogen (when powders containing it are inhaled) and should not be carelessly discarded into the public sewer system. It can, however, be easily reduced to Cr(II) or Cr(III), relatively harmless species. **YOU** are responsible for emptying your used chromium solutions into a collection beaker. Your instructor will take care of the final disposal.

3. Collecting gases for pressurization

The technique used for this experiment is fairly simple: a gas is generated by adding a few mL of sulfuric acid (perhaps 5) to a small amount of solid $NaNO_2$ (*sample amount shown in fume hood*) in a vial. [note: this must be done in the hood and the vial should be left there after the gas has been collected]. The body of a sealed-end syringe is quickly placed over the mouth of the vial until the gas has filled it. Then it is quickly removed and stoppered with its plunger. At this point the filled syringe can be brought back to the work area. Pushing on the plunger will pressurize the gas.

What should you expect to see? If the gas is a non-mutable (doesn't change) colored material, when it is squeezed together it should look darker because more colored material is pushed into a smaller space. If there is an *equilibrium* condition with the colorless N_2O_4 then what should you expect? Will the color ever completely disappear? These are the kinds of questions you should ask yourself as you do this part of the activity. The changes in the syringe are subtle and require careful observation. Holding the syringe over white paper will help. Also, depressing the plunger quickly makes the subtle changes easier to observe. Try the process several times. [note: the changes as the gas is depressurized are generally too subtle to be observed]

The chemicals

Potassium dichromate is a bright orange-red solid, soluble in water (11.7 g per 100 g at 20°C). It is used in tanning, dyeing, painting and decorating porcelain, printing, staining wood, pyrotechnics and safety matches. The chemical is a common strong oxidizing agent for organic chemicals. It has been used medicinally as an astringent and topical antiseptic. However, it is a corrosive poison. 30 grams taken internally has been reported as fatal within 35 min. Inhalation of dust has been reported as causing cancer of the lungs.

Sodium nitrite is a white or slightly yellow crystalline solid, soluble in 1.5 parts cold water, slightly soluble in ethanol. It is decomposed by even weak acids with the evolution of brown fumes. It is used in the manufacture of dyes and in bleaching flax, silk and linen. It also had medical and veterinary applications, mainly as a relaxant for smooth muscle tissue.

Analysis

1. For reactions (1) and (3) explain your results in terms of collision theory, i.e., why do the changes in the system equilibrium position take place when you make the changes in concentration or pressure?

2. For reaction (2) explain your results with respect to a hypothetical reaction energy diagram for the reaction---sketch one and use it accompany your explanation.

3. Taken together, your observations and the generalizations that can be drawn from them constitute the main ideas behind LeChâtelier's Principle. Based on your results, generalize the effects on a system at equilibrium when the following changes are made:

a. increase concentration of a reactant in a system at equilibrium
b. increase concentration of a product in a system at equilibrium
c. same as (a), but *decrease*
d. same as (b), but *decrease*
e. heat a system at equilibrium
f. cool a system at equilibrium
g. pressurize a gas system at equilibrium
h. reduce the pressure on a gas system at equilibrium