MiraCosta College
Introductory Chemistry Laboratory
Experiment 9

Chemical Equilibrium and Le Chatlier’s Principle

EXPERIMENTAL TASK

Examine a number of chemical reaction systems at equilibrium, predict the shifts they will undergo when certain external stresses are applied, and test these predictions.

Objectives

After completing this experiment, the student will be able to:

1. Observe a chemical reaction system to determine the relative position of equilibrium.
2. Apply a stress to a chemical reaction system, and observe the changes that occur.
3. Predict the direction a chemical reaction system will shift when a particular external stress is applied to it.

Additional Reading

- General, Organic and Biological Chemistry, by Timberlake, sections 6.6 – 6.8

Background

As presented in Timberlake and in Experiment 8—“Chemical Reactions and Equations”, *chemical reactions* are processes in which one of more substances change into new substances. However, for many reactions these changes from reactants to products are not complete. That is, when the reactants are mixed and the reaction proceeds, the reaction will reach a point where it will not produce any more of the products, even though some amount of each reactant remains. When all of the reactants and products of a given chemical reaction system are present in some amount and in contact with each other at the same time, and the reaction is not producing or using up any of them, the reaction is said to be in *equilibrium*.

The equation for a reaction that reaches equilibrium instead of going to completion is written using two arrows instead of one, with one arrow representing the forward direction and the other the reverse direction:

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g)$$

A closer look at a chemical reaction system at equilibrium will show that the products and reactants are not just sitting there, doing nothing—instead, the reactants are reacting to produce products, but the products are also reacting with each other to make more of the reactants. At equilibrium these two reaction directions, *forward* and *reverse*, proceed at the same rate, giving the illusion that nothing is happening.

When the reactants are first mixed together, they begin producing products right away and with a particular *reaction rate*. The rate of the reaction, or amount of product produced per second, generally depends on a number of factors including the concentrations of the reactants (see Timberlake, section 6.7), so it is fastest when the reactants are first mixed together. As the reactants undergo the chemical change to become products, the amounts of the reactants left decrease and therefore the concentrations of the reactants go down, and the reaction becomes slower in producing products from reactants. At the same time, as products are created, they will begin to react with each other to go BACKWARD and make the reactants all over again. However, this reverse reaction is much slower at first than the forward reaction, because the concentrations of products are too low to get the reverse reaction going yet, and therefore the observer will see an overall increase in the amount of products. As the forward reaction uses up more reactants and produces more products, making the forward reaction slower and the reverse reaction faster, eventually they reach a point where the reverse reaction makes reactants at exactly the same rate that the forward reaction uses them up—this is equilibrium.

Once a reaction reaches equilibrium, the system will remain at equilibrium unless something from the outside influences it. For instance, if a reaction is at equilibrium and an some more of one of the products is added to the system, the rate of the reverse reaction will increase temporarily due to the increase in the concentration of the products. This addition of product is called a *stress*, because it exerts a kind of “force” on the equilibrium, “pushing” the “position” of equilibrium back toward the reactants. After a period of time, equilibrium will be reestablished, but it the concentrations of reactants and products will be a bit different than at the original equilibrium, so it is said that the position of equilibrium has shifted toward the reactants in response to the stress of adding products.

The shifting of the equilibrium position in response to an external stress is summarized as **Le Chatlier's Principle**: When a chemical system at equilibrium is subjected to an external stress, the position of equilibrium will shift in order to relieve the stress. Timberlake gives an alternate wording: "When we alter a reaction that is at equilibrium…the rates of the forward and reverse reactions will change to relieve that stress." (page 209). If some amount of a reactant is *added*, the forward reaction rate *increases*, changing some of the added reactant into products, which shifts the position of equilibrium *toward products*. If some amount of reactant is *removed* from the system, the forward reaction rate *decreases*, allowing the reverse reaction to make more reactant than is being used up by the forward reaction, so the equilibrium position shifts *toward reactants*.

Another factor that affects the position of equilibrium for a chemical reaction system is the energy (most commonly heat) produced or absorbed by a reaction. If a reaction is exothermic, it produces heat in the forward direction, so if the temperature of the equilibrium system goes up, the stress put on the equilibrium will push it back toward the reactants. If a reaction is endothermic, it absorbs heat in the forward direction, so raising the temperature of the system will push the position of equilibrium toward the products.

In this experiment you will prepare a number of chemical reaction systems, observe them at equilibrium, subject the system to a stress, and observe the shift of the system in response to that stress. <u>It is important to think ahead and try to PREDICT the shift before the stress is applied, and then see if your prediction is correct.</u>

The final result for each chemical reaction system will be A) observations of the each system before, during and after the stress is applied; and B) the direction the reaction equilibrium shifts in response to application of the stress.

Pre-lab Questions

1. .Dinitrogen tetraoxide (colorless gas) is converted to nitrogen dioxide (dark reddish brown gas) according to this balanced reaction, which is **endothermic** in the forward direction:

$$\mathbf{N_2O_4\ (g) \rightleftharpoons 2\ NO_2\ (g)}$$

A. If a closed container containing a mixture of these two gases at equilibrium is a light brown in color when it is at room temperature (20.0°C), what change would you expect to observe if the container is placed in boiling water (100.0 °C)?

B. If a closed container containing a mixture of these two gases at equilibrium is a light brown in color when it is at room temperature (20.0°C), what change would you expect to observe if the container is placed in ice water (0.0 °C)?

2. Hydrogen gas (colorless) reacts with iodine vapor (purple) to give hydrogen iodide gas (colorless) according to this balanced equation:

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g)$$

A. If the mixture of these three gases at equilibrium is light purple in color, what change would you expect to observe if more hydrogen gas were added to the system?
B. If the mixture of these three gases at equilibrium is light purple in color, what change would you expect to observe if some of the hydrogen iodide gas were removed from the system?

BEFORE STARTING THE EXPERIMENT

Safety

Always keep in mind the rules presented in both the "MCC Laboratory Safety Rules" and the Laboratory Handbook for General Chemistry. It is your responsibility to make sure that you follow all safety rules at all times, and to graciously help everybody else in the laboratory (including the instructor) to do the same.

Hazardous Materials

Concentrated hydrochloric acid is a strong irritant and toxic, and emits corrosive, toxic vapors—you must wear gloves while handling it, use it in the **fume hood only**, and immediately wash it of exposed skin if spilled.
Iron(III) chloride solution, potassium thiocyanate solution and **cobalt(II) chloride solution** are irritants and toxic—you must wear gloves while handling it, and immediately wash it off of exposed skin if spilled.
Aqueous silver nitrate is a strong irritant and toxic, and will stain your skin—you must wear gloves while handling it, and immediately wash it off of exposed skin if spilled.
Chromate and dichromate compounds are highly toxic, corrosive, and are suspected carcinogens/mutagens—you must wear gloves while handling them, and immediately wash them off of exposed skin if spilled.

ALL WASTES MUST BE DISCARDED IN THE APPROPRIATE WASTE CONTAINERS, AS DIRECTED BY THE INSTRUCTOR.

EXPERIMENT PROCEDURE

Part A: The Effect of Temperature on Equilibrium

Reaction Equation:

$$Co(H_2O)_6^{2+}\,(aq) + 4\,Cl^- \rightleftharpoons CoCl_4^{2-}\,(aq) + 6\,H_2O\,(l) \qquad \textbf{Endothermic}$$

Pink — **Blue**

Set up a hot plate with a 250 mL beaker on it, and add about 150 mL of water to the beaker. Turn on the hot plate to its highest heat setting, allow the water to boil, then turn the heat setting to about 3 or 4. Use a 400 mL beaker to obtain about 300 mL of ice. Add enough water to this ice just to bring the water level up to the top of the ice, but without making the ice float (some ice will melt, of course, but that is OK).

Obtain about 6 mL of cobalt(II) chloride solution. When dissolved in water, $CoCl_2$ reacts with water to give the $Co(H_2O)_6^{2+}$ ion and chloride (Cl^-) ions. Label three small test tubes as follows:

1. Aqueous cobalt(II) + chloride at room temperature
2. Aqueous cobalt(II) + chloride at 0.0 °C
3. Aqueous cobalt(II) + chloride at 100.0 °C

Put about 2 mL of cobalt(II) chloride solution to each test tube, place the test tubes in the test tube rack, and then take the test tube rack with the test tubes to the fume hood. Add 25 drops of 12 M HCl to each of the three test tubes. Take the test tube rack and test tubes back to the lab bench. Observe the color of the solutions and record these observations.

PREDICT the change that will be observed for test tubes 2 and 3 BEFORE placing them in their respective temperature baths, and record these predictions.

Keep test tube 1 in the test tube rack. Place test tube 2 in the ice water, and place test tube 3 in the boiling water. Observe and record any changes (allow a few minutes if changes are not evident immediately).

All solutions go in the “Liquid Inorganic Waste” container.

Part B. The Effect of Changes in Concentrations on Equilibrium

Reaction System 1—Iron(III) and Thiocyanate

Reaction Equation:

Fe^{3+} (aq) +	**SCN^{-} (aq)**	$\rightleftharpoons$	**$FeSCN^{2+}$ (aq)**
Light yellow	**Colorless**		**Dark Red**

In a 10-mL graduated cylinder, add 2 mL of aqueous 0.1 *M* $FeCl_3$ and to the same graduated cylinder add2 mL of aqueous 0.1 *M* KSCN. Prepare a solution of the **reaction system** by adding this 4-mL mixture to a 250-mL beaker containing 100 mL of DI water. Swirl to mix.

Label 4 *large* test tubes and place them in a test tube rack:

	Predicted Change or Color
1. $FeSCN^{2+}$ equilibrium control	____________________
2. $FeSCN^{2+}$ equilibrium + Fe^{3+}	____________________
3. $FeSCN^{2+}$ equilibrium + SCN^{-}	____________________
4. $FeSCN^{2+}$ equilibrium + Ag^{+}	____________________

Add about 5 mL of the **reaction system** solution you just made to each test tube. Observe the solution and record your observations. BEFORE proceeding, PREDICT what will happen to test tubes 2, 3 and 4 when you add the solutions as directed below, and record your predictions above. **Note:** Adding Ag^{+} ions to the mixture has the effect of removing SCN^{-} ions, because AgSCN precipitates, so you will see the solution in test tube 4 get cloudy in addition to whatever color change takes place.

Once you have recorded your predictions, add solutions to the test tubes as directed here:

Test tube 2: Add about 1 mL of 0.1 *M* $FeCl_3$ solution (increases Fe^{3+} ion concentration)

Test tube 3: Add about 1 mL of 0.1 *M* KSCN solution (increases SCN^{-} ion concentration)

Test tube 4: Add 0.1 *M* $AgNO_3$ solution drop by drop until a change becomes evident (decreases SCN^{-} ion concentration as Ag^{+} reacts with SCN^{-} to give solid AgSCN)

Record your observations of each test tube. Dispose of all solutions in the "Liquid Inorganic Waste" container.

Reaction System 2—Chromate and Dichromate

Reaction Equations:

$2\ CrO_4^{2-}$ (aq)	**+ $2\ H^+$**	$\rightleftharpoons$	**$Cr_2O_7^{2-}$ (aq) + H_2O (l)**
Yellow	**Colorless**		**Orange**
$Cr_2O_7^{2-}$ (aq) +	**$2\ OH^-$**	$\rightleftharpoons$	**$2\ CrO_4^{2-}$ (aq) + H_2O (l)**
Orange	**Colorless**		**Yellow**

Obtain about 2 mL of 0.1 *M* potassium chromate and of 0.1 *M* potassium dichromate (if using dropper bottles, you can add these solutions directly to your test tubes). Label four small test tubes as follows:

	Predicted Change or Color
1. 0.1 *M* potassium chromate + 12 *M* HCl	______________________
2. 0.1 *M* potassium chromate + 6 *M* NaOH	______________________
3. 0.1 *M* potassium dichromate + 12 *M* HCl	______________________
4. 0.1 *M* potassium dichromate + 6 *M* NaOH	______________________

Add 5 drops of potassium chromate solution to test tubes 1 and 2. Add 10 drops of potassium dichromate solution to test tubes 3 and 4. Place the test tubes in a test tube rack and record your observations. PREDICT the changes that will be observed for each solution when either HCl or NaOH is added BEFORE you add them. Record these observations. ***Note that the first reaction should be used in predicting results for test tubes where HCl is added (test tubes 1 and 3), and the second reaction should be used in predicting results for test tubes where NaOH is added (test tubes 2 and 4).***

Once you have recorded your predictions, take the test tube rack with the test tubes to the fume hood. Use a dropper to add 1 drop of 12 M HCl to test tube 1 and 1 drop to test tube 3. Then, take the test tube rack to the reagent cart, and add one drop of 6 M NaOH to test tubes 2 and 4. (Never pipette directly from a reagent bottle.) Record your observations.

Dispose of all solutions AS DIRECTED BY THE INSTRUCTOR.