Equilibrium: Le Chatelier's Principle and Chemical Stress

Minneapolis Community and Technical College
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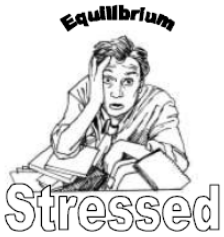
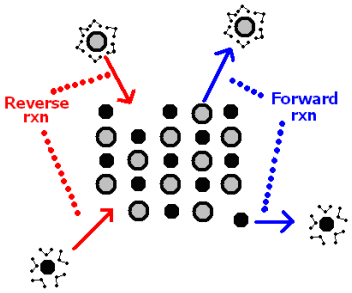


Introduction

At this point in your Principles of Chemistry course you have probably been introduced to the concept of equilibrium. In a chemical context, equilibrium occurs when a chemical process can occur in both the forward and reverse directions and the rates of the forward and reverse reactions are equal.

Consider the example (right) where solid NaCl is in contact with an already saturated NaCl solution.

$$NaCl_{(s)} \underset{\text{Reverse}}{\overset{H_2O \ \text{Forward}}{\rightleftharpoons}} Na^+_{(aq)} + Cl^-_{(aq)}$$



The forward reaction converts solid NaCl into aqueous (dissociated) species that have been surrounded by polar water molecules. The reverse reaction describes how simultaneously the aqueous species are converted back into the solid NaCl. When the solution is saturated both the forward and reverse reactions occur with the same rate. In other words, *the salt crystal is both dissolving and re-forming at the same time*. Thus, there is no measurable change in mass for the solid salt although it's appearance may change over a very long time (years).

Most chemical reactions are equilibrium situations. As product builds up (forward reaction), the reverse reaction becomes more significant and products are changed back into reactants. If maximum product is a priority, some means of minimizing the reverse reaction must be found. The problem solves itself if one of the products is a gas that leaves the reaction vessel and is therefore unavailable for the reverse reaction to occur. The formation of a solid product from an aqueous reaction can also minimize the reverse reaction thus promoting additional product formation.

The key to understanding how to maximize forward reaction product formation and minimize reverse reaction contributions is to examine the effects of "stress" on the equilibrium. We stress a chemical equilibrium when the concentration/pressure of a product/reactant or the temperature is increased or decreased. In today's experiments, you will examine many different equilibria and how they respond to stress.

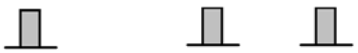
Chemical equilibria respond to changes in concentration, pressure, volume and temperature via **Le Chatelier's principle**: *When stressed, a system at equilibrium will "shift" in a direction to counteract or minimize the stress.*

Consider first preparing the NaCl chemical equilibrium as shown above. First, a saturated solution of NaCl and water is poured into a beaker followed by several grams of solid NaCl. The additional solid won't visibly dissolve in the already saturated solution and instead just falls to the bottom of the beaker. That's it. The solid is now in equilibrium with the dissolved species in solution. Even though you can't see it, Na^+ and Cl^- ions are in the process of dissolving and reforming the solid that appears to be unchanged at the bottom.

How would you stress the equilibrium? One way would be to add a highly concentrated solution containing Na^+ to the equilibrium mixture. By adding additional Na^+ ions, the overall concentration of Na^+ goes up and provides a stress that the equilibrium mixture must respond to.

Consider the original equilibrium amounts shown at right. The bar graphs below each species represent the concentrations of each species before the equilibrium has been stressed by additional Na^+.

$$NaCl_{(s)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$$

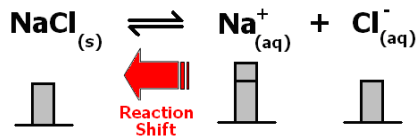


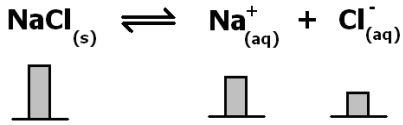
$$NaCl_{(s)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$$

Next, the equilibrium is stressed by adding the highly concentrated Na^+ solution indicated by a slight increase in the height of the Na^+ bar.

The concentrations represented by the new bar graphs at left are no longer equilibrium levels and changes are necessary.

The equilibrium is now stressed and will respond according to Le Chatelier's principle to counteract the stress. Because the Na^+ concentration is too high, the reaction shifts left to use up some of the excess Na^+ and along with it, some Cl^-.





After the shift occurs, the Na+ and Cl^- concentrations have been reduced while the amount of solid NaCl is increased as shown at right.

Notice that the system is now again in equilibrium even though the concentrations of Na^+ and Cl^- are different from what they were initially. We've also precipitated solid NaCl; this means more solid in the bottom of the container. However, this can't go on indefinitely since Cl^- levels drop and will eventually run out.

LeChatelier's Principle: Maximizing Product

So far, we've discussed how changes in the concentration of products and reactants can bring about reaction shifts. Consider the following reaction:

$$N_{2(g)} + 3\,H_{2(g)} \leftrightarrow 2NH_{3(g)}$$

If additional $N_{2(g)}$ is introduced to the reaction container, the reaction will shift right to produce more NH_3 so long as there is also $H_{2(g)}$ present. Increasing concentrations of both $N_{2(g)}$ and $H_{2(g)}$ guarantees neither reactant runs out and the formation of additional product.

Another way to improve product yield is to remove product as it is made. If $NH_{3(g)}$ is removed, the reaction will shift right to make *more* product just as long as there is still N_2 and H_2 left to react. Thus, removing product promotes product formation.

Pressure/Volume Effects on Product Formation.

The reaction above is also sensitive to changes in pressure and volume as there are gas phase species involved. Note that on the left, there is a total of 4 moles of reactants whilst on the right there are 2 moles of product.

$$\underset{\text{1 mole}}{1\,N_{2(g)}} + \underset{\text{3 mole}}{3\,H_{2(g)}} \leftrightarrow \underset{\text{2 mole}}{2NH_{3(g)}}$$

$$4\text{ mole}_{\text{total}} \qquad 2\text{ mole}_{\text{total}}$$

Because there is a difference in the number of moles of *gas phase* products and reactants, this equilibrium will shift when the pressure or volume is changed. Solids and liquids are considered incompressible and not part of the following rationale. From the balanced chemical equation we can calculate a value for Δn; the difference between product and reactant moles:

$$\Delta n = n_{\text{products}} - n_{\text{reactants}} = 2 - 4 = \mathbf{-2}$$

Because $\Delta n \neq 0$, this reaction *will* shift right or left when pressure and volume are changed. According to Boyle's law, an increase in pressure can be accomplished with a decrease in volume. Thus, an increase in pressure will produce the same effect as a decrease in volume.

In this case, there are more moles of reactants than products. If the reaction occurs in large volume, low pressure conditions, reactants are favored since their mole numbers are greater (4 vs 2) and the space can be more completely filled by shifting left and making more gas phase species. Thus, reactants are favored by increasing volumes or decreasing pressures when Δn is negative. Conversely, if the reaction occurs in small volume, high pressure conditions, the products are favored as their mole numbers are smaller and less "crowding" will result with fewer gas phase particles. Thus, products are favored by decreasing volumes or increasing pressures when when Δn is negative.

Summarizing, if Δn is negative and your goal is to improve product yield, you should use high pressures and small volumes. However, if Δn was positive, all of the above arguments are reversed and low pressures/large volumes favor increased product formation.

Temperature Effects on Product Formation

Changing a reaction's temperature can also bring about equilibrium shifts with changes in product formation. Whether a temperature change increases or decreases product yield depends on if the reaction is endothermic or exothermic. In this case ΔH = -91.8 kJ/mol

and the negative sign tells us the reaction is exothermic. Since an exothermic reaction produces heat energy, we can write the reaction to include "heat" as a product:

$$N_{2(g)} + 3\ H_{2(g)} \leftrightarrow 2NH_{3(g)} + \text{heat}$$

If we increase the temperature of the reaction container, we are adding heat to the reaction. Because heat is a product in the above reaction, it shifts left to reduce the amount of heat thus favoring the reactant side. If instead we cool the reaction container, we are removing heat from the product side and the reaction shifts right to replace it thus increasing the amount of NH_3 at the same time. Since temperature changes affect the relative amounts of products and reactants, their ratio (a.k.a. the equilibrium constant) also changes. In the example above, removing heat (cooler temperature) increases product and lessens reactant levels. Thus the equilibrium constant increases.

Whether a reaction is exothermic (product heat) or endothermic (reactant heat) can be determined by performing an experiment at different temperatures, identifying the reaction shift based on your observations, and then determining the location of the word "heat" that is consistent with your observations. Reactions are either exothermic or endothermic; not both.

II. PRELAB EXERCISE

Clearly answer these questions in INK in your lab notebook before coming to lab.

1. Which of the following two solutions contains more free floating ions and WHY? $H_2C_2O_{4(aq)}$ or $K_2C_2O_{4(aq)}$
2. Given the following exothermic combustion reaction, calculate Δn and list ways that would improve product yield.

$$C_6H_{12}O_{6(s)} + 6O_{2(g)} \leftrightarrow 6\ CO_{2(g)} + 6\ H_2O_{(g)}$$

3. An equilibrium reaction is determined to shift left when cooled. Is the reaction exothermic or endothermic?

III. Word Processed Report

Page 1: *Upper right hand corner Name, Lab section number and date*

Answer the following questions. Answers must be word processed, organized and understandable! ***(0.5 pt/question)***

Equilibrium #1 Questions:

1. Why was it necessary to prepare the original solution in anhydrous methanol?
   (Hint: What does anhydrous mean?)

2. How would adding too much water in step 2 affect the behavior of the equilibrium during Stress 3?

3. What was Stress 1? How did the equilibrium respond? (DETAILS!)

4. What was Stress 2? How did the equilibrium respond? (DETAILS!)

5. What was Stress 3? How did the equilibrium respond?
   Is the reaction exothermic or endothermic? Why?

Equilibrium #2 Questions:

1. Stress #1: How does the final Na^+ concentration compare to the initial Na^+ concentration?

2. Stress #2: Explain how the addition of ethanol precipitates solid NaCl.
   Hint: Determine how the polarities of ethanol and water compare. How would these differences affect the solubility of NaCl?

3. Stress #3: You added sodium ions ($NaNO_{3(aq)}$) and yet no solid NaCl precipitate formed. Why?

Equilibrium #3 Questions:

1. Which test tube (1 or 2) initially had the most solid precipitate? Why was there more ppt. in this test tube? (Hint: Which solution initially contains more free floating $C_2O_4^{2-}$ ions? ...$K_2C_2O_4$ or $H_2C_2O_4$?)

2. Stress #1: Explain how the addition of HCl shifts equilibria A, B and C.
   Explain how these changes/shifts affect the solubility of $CaC_2O_{4(s)}$.

3. Stress #2: Explain how the addition of NaOH affects equilibria A, B and C.
   Then explain how these changes/shifts affect the solubility of $CaC_2O_{4(s)}$.

IV. Procedure

In this experiment you will construct and stress three different equilibria as described below. Be sure to record all of your observations at each step in your lab notebook.

Equilibrium #1: Complex Ion Equilibrium

$$CoCl_4^{2-} + 6\,H_2O \leftrightarrow 4\,Cl^- + Co(H_2O)_6^{2+}$$

blue — pink

1. Add approximately 3 mL of the 0.15 M $CoCl_4^{2-}$ solution (in methanol) to a clean, DRY small test tube #1. Use the approximation that 15 drops = 1 mL.

2. Using an eyedropper, carefully add dropwise just enough water to change the color of the solution to pink. (Don't add too much water or the following steps may not work properly)

3. Remove half of the resulting solution and place it in another small test tube (test tube #2).

4. **Stress 1:** To test tube #1 carefully add concentrated (12 M) HCl (**DANGER**) dropwise until a color change is observed.

5. **Stress 2:** To test tube #1 add several drops of $AgNO_3$ solution.

6. **Stress 3:** Working in the fume hood, immerse test tube #2 in a hot water bath. Then cool test tube #2 in an ice bath. Repeat.

Equilibrium #2 : Saturated $NaCl_{(aq)}$

$$NaCl_{(s)} \leftrightarrow Na^+_{(aq)} + Cl^-_{(aq)}$$

1. Dispense approximately 3 mL of saturated NaCl solution into each of 3 small labeled test tubes.

2. **Stress 1:** Add 4 to 5 drops of conc. (12 M) HCl to test tube #1.

3. **Stress 2:** Add 15 drops of ethanol to test tube #2.

4. **Stress 3:** Add approximately 1mL of saturated $NaNO_3$ solution to test tube #3.

Equilibrium #3
Solubility Equilibrium & Multiple, Linked Equilibria

A. $H_2C_2O_{4\,(aq)} \rightleftharpoons HC_2O_4^-{}_{(aq)} + H^+_{(aq)}$

B. $HC_2O_4^-{}_{(aq)} \rightleftharpoons C_2O_4^{2-}{}_{(aq)} + H^+_{(aq)}$

C. $Ca^{2+}_{(aq)} + C_2O_4^{2-}{}_{(aq)} \rightleftharpoons CaC_2O_{4\,(s)}$

Obtain 2 small test tubes.

1. Test tube #1: Add 3 mL of 0.05 M $CaCl_2$ solution and 5 drops of 0.50 M $H_2C_2O_4$

2. Test tube #2: Add 3 mL of 0.05 M $CaCl_2$ solution and 5 drops of 0.50 M $K_2C_2O_4$.

Carefully compare test tubes #1 and #2. Identify the test tube with the greatest amount of precipitate.

3. Test tube #2 Stress Tests:

a. Stress 1: Dropwise, add 15 drops of 6 M HCl to test tube #2. Mix well with each additional drop and record your observations.

b. Stress 2: Dropwise, add an additional 20 drops of 6 M NaOH solution to test tube #2. Mix well with each additional drop and record your observations.