

## 12B. CHEMICAL EQUILIBRIUM

### (Spectrometer Version)

#### Initial Question

In 1901, Henry Louis Le Châtelier combined explosive hydrogen gas with nitrogen gas in an attempt to form ammonia. His efforts met with disastrous results—he almost killed his assistant. Although he abandoned the synthesis of ammonia, he had a fine career that led him to discover the principle of chemical equilibrium, now known as Le Châtelier's Principle. This principle is used by chemical engineers to create processes that make the maximum amount of products.

How can a chemical reaction be manipulated to maximize yield (without blowing up your assistant)?

#### Materials and Equipment

##### Model 1

- Spectrometry Application
- Spectrometer
- Cuvettes (3)
- Beakers (3), 50-mL
- Mohr pipet, 10-mL
- Pipet bulb
- 0.0080 M Iron(III) nitrate ( $\text{Fe}(\text{NO}_3)_3$ ), 3.0 mL
- 0.0010 M Potassium thiocyanate (KSCN), 3.0 mL
- Kimwipes®

##### Model 2

- Test tube rack
- Distilled water, 2 mL
- Plastic pipets (3)
- Test tubes (3), 19 × 150 mm (medium)
- Gloves
- Marking pen
- Cobalt(II) chloride ( $\text{CoCl}_2$ ), 1.5 g
- 0.10 M Silver nitrate ( $\text{AgNO}_3$ ), 2 mL
- 6.0 M Hydrochloric acid (HCl), 2 mL
- Scoop
- Glass stirring rod

##### <sup>1</sup>Provide students with cobalt(II) chloride hexahydrate ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ). Model 3

- Beakers(2), 250-mL
- Hot plate
- Cobalt solution from Model 2
- Water for water baths
- Ice

##### Applying Your Knowledge

- Spectrometry Application
- Spectrometer
- Cuvettes
- Mohr pipet, 10-mL
- Pipet bulb
- Equipment and amounts depend on the procedure:
- Test tube, 19 × 150 mm (medium)
- Beakers, 50-mL
- Graduated cylinder, 10-mL
- 0.0010 M Potassium thiocyanate (KSCN)
- 0.0080 M Iron(III) nitrate ( $\text{Fe}(\text{NO}_3)_3$ )<sup>1</sup>
- Kimwipes®

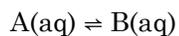
## Safety

Add these important safety precautions to your normal laboratory procedures:

- Hydrochloric acid is corrosive. If you come in contact with it, flush the area with plenty of water. It can cause severe tissue burns.
- Cobalt solutions are moderately toxic and are body tissue irritants. If you come in contact with it, flush the area with plenty of water.
- Silver nitrate will stain skin and clothing. Wear gloves when you work with it. If you do come in contact with it, flush the area with plenty of water.

## Getting Your Brain in Gear

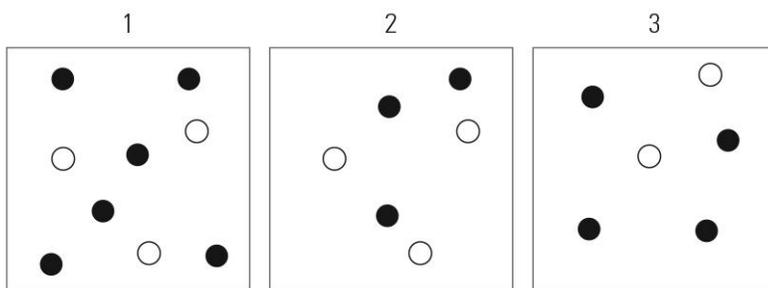
1. Consider the following equilibrium system:



- a. Write the equilibrium expression for this system.

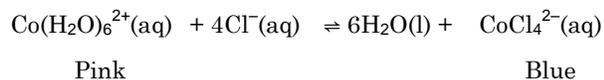
- b. If the value of  $K_c$  is 2, what is the ratio of the [A] to the [B]?

- c. Which picture(s) represent the system at equilibrium?



- d. Is there a single set of data for [A] and [B] that satisfies the equilibrium state?

2. Consider the following system:



a. Write the equilibrium expression for this system.

b. The reaction quotient  $Q$  expresses the relative ratio of products to reactants at a given instant. Write the reaction quotient expression for this system.

3. How is an equilibrium constant different from a reaction quotient?

---

---

---

4. When does the value of  $Q = K_c$ ?

---

---

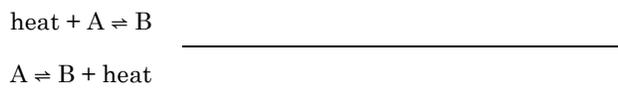
5. Explain the following statement: At constant temperature, there is only one equilibrium constant for a system but many different equilibrium states or positions. Provide three examples of product and reactant concentrations that will give  $K_c = 20$ .

---

---

---

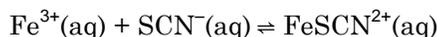
6. Label the following reactions as either endothermic or exothermic:



## MODEL 1

### Building Model 1 – $K_c$ as a Constant

When iron(III) nitrate ( $\text{Fe}(\text{NO}_3)_3$ ) and potassium thiocyanate ( $\text{KSCN}$ ) solutions react, the following equilibrium is created:



1. Connect the spectrometer to the data collection system using a USB cable connection, or wirelessly connect to the system through Bluetooth pairing and open the Spectrometry application.
2. Place 2.0 mL of 0.0080 M iron(III) nitrate and 2 mL of 0.00100 M potassium thiocyanate into separate 50-mL beakers. Record the molarity, volume, and color of the solutions in the Model 1 Data Table—Before reacting.
3. Pour the solutions into a third 50-mL beaker and swirl gently to mix thoroughly. Then pour the mixture into a cuvette. After the reaction occurs, record the color of the equilibrium mixture in the Model 1 Data Table.
4. Select Analyze Solution from the menu at the top of the screen.
5. Select Calibrate Dark from the Menu at the bottom of the screen. The Spectrometer will turn off all of its lights and perform the calibration. A check mark will appear when the calibration is finished.
6. Add distilled water to a cuvette. This should be the same distilled water that was used as a solvent for the solutions being analyzed. Place the cuvette into the spectrometer. Follow the cuvette handling guidelines listed below for the remainder of the investigation.
  - Always handle the cuvette by the ridged sides.
  - Wipe off any fingerprints using a lint free wipe (such as Kimwipes).
  - Place the cuvette into the spectrometer so that the ridged sides are facing the violet and green light icons and the clear sides face the white light and absorbance spectrum icons. The white light is what will pass through the samples.
7. Select Calibrate Reference to calibrate the spectrometer with the distilled water (the water sample is called a “blank”). A check mark will appear when the calibration is complete.
8. Start recording data. Use the Add Coordinate feature to find the maximum absorbance for the sample. Use Scale to Fit to see greater detail. Select the check mark when you have found the greatest absorbance. Record the Selected Wavelength and absorbance in Model 1 Data Table.
9. Stop Data Collection and clean up all solutions and equipment according to your instructor's instructions.



CALIBRATE DARK



CALIBRATE REFERENCE



START RECORDING



STOP RECORDING



EXPERIMENT OPTIONS



ANALYZE SOLUTION



ANALYZE CONCENTRATION



ANALYZE REACTION



SCALE TO FIT



ADD COORDINATE



SHOW LINEAR FIT



SHOW COMPARISON



SHOW SELECTION



SHOW DUAL Y-AXES

**Model 1 –  $K_c$  as a Constant**

Table 1: Model 1 Data Table—Before reacting

Parameter	Iron(III) nitrate	Potassium thiocyanate
Concentration		
Volume		
Color		

Table 2: Model 1 Data Table—After reacting

Parameter	Equilibrium Mixture
Color	
Wavelength	
Absorbance	

**Analyzing Model 1 –  $K_c$  as a Constant**

11. Consider the equilibrium system in Model 1. When the two solutions were mixed in the beaker, which of the following calculations represent the initial concentration of  $\text{Fe}^{3+}$  ions in the mixture? Circle your answer.

$$3.00 \text{ mL} \times 0.0080 \text{ M} = 2.40 \times 10^{-5} \text{ M Fe}^{3+} \quad \text{OR} \quad \frac{3.00 \text{ mL} \times 0.0080 \text{ M}}{6.0 \text{ mL (total volume of solution)}} = 0.0040 \text{ M Fe}^{3+}$$

12. What is the initial concentration of  $\text{SCN}^-$  ions in the mixture?

13. Complete the following ICE table and equilibrium expression for this equilibrium system using the volumes and concentrations of the reactants in Model 1.

Table 3: ICE table for calculating equilibrium concentrations

Condition	$\text{Fe}^{3+}$	$+ \text{SCN}^-$	$\rightleftharpoons$	$\text{FeSCN}^{2+}$
I (Initial concentration)				
C (Change)				
E (Equilibrium concentration)				

14. If  $K_c$  is not known, describe how you could use a spectrophotometer to find  $x$  or  $[\text{FeSCN}^{2+}]_{\text{eq}}$  in the lab.

*NOTE: This procedure is in the Light, Color, and Concentration lab.*

15. Determine the equilibrium constant. Assume (path length  $\times$  molar absorptivity) for this system is  $5900 \text{ M}^{-1}$  at  $401\text{nm}$ . Use wavelength this for your analysis.

16. How does the value of your equilibrium constant compare to the values of the other groups in your class?

Table 4: Compare class results

Group	Equilibrium Constant
1	
2	
3	
4	
5	
6	
7	
8	
9	
10	

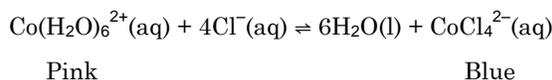
17. Is your data similar to that of your classmates? What should you do if your sample deviates by a significant amount?

*NOTE: Often the equilibrium constant is considered constant when it varies within a power of ten.*

## MODEL 2

### Building Model 2 – Adding Stress to an Equilibrium System

1. Obtain a test tube, test tube rack and marking pen.
2. Label the test tube “K” and place it in the test tube rack.
3. Add approximately 0.5 g of cobalt(II) chloride hexahydrate into the test tube. Then add 10 drops of distilled water using a pipet and mix the solution with a glass stirring rod. This solution will remain untouched during the lab and represents the original condition of the cobalt system:



4. Repeat the previous step for two more test tubes and label them “A” and “B”. Record your initial observations for all of the solutions in the Model 2 Data Table.

*NOTE: Hold the test tubes over a white background to make your observations easier.*

- ❓ 5. HCl will be added to both test tubes A and B. Will this addition increase or decrease the concentration of chloride ions in the equilibrium system? Explain.

---

---

---

6. While wearing gloves, carefully add 6.0 M HCl, drop-wise, to test tube A until a noticeable change has occurred. Then add the 6.0 M HCl, drop-wise, to test tube B. Record your observations in the Model 2 Data Table.

- ❓ 7. AgNO<sub>3</sub> is going to be added to test tube B and a precipitate will form. What reaction will occur to produce this precipitate? Write the net ionic reaction.

---

---

---

9. While wearing gloves, add 0.1 M AgNO<sub>3</sub> drop-wise to test tube B until a color change is produced. You should notice a precipitate on the bottom of the test tube. Record your observations in the Model 2 Data Table.

*NOTE: Don't discard the solutions. You will use the solution in test tube A in Model 3.*

## Model 2 – Adding Stress to an Equilibrium System

Table 5: Model 2 Data Table—Results of adding stress

Test Tube	Color of the Solution		
	Initial Observations	After Addition of HCl	After Addition of AgNO <sub>3</sub>
K			
A			
B			

### Analyzing Model 2 – Adding Stress to an Equilibrium System

10. In all test tubes, what color is the solution prior to the addition of the HCl or AgNO<sub>3</sub>?

---

11. Considering the appearance of the solution prior to the addition of HCl or AgNO<sub>3</sub>, are there more products or reactants present at equilibrium? Explain your reasoning.

---



---

12. After adding HCl, what observation indicated that the reaction shifted to re-establish equilibrium?

---



---

13. From the appearance of the solution in test tubes A and B after the addition of HCl, are there more products or reactants present at this re-established equilibrium position? Explain your reasoning.

---



---

14. Upon the addition of HCl, is the value of the reaction quotient  $Q$  greater than, less than or equal to value of  $K_c$ ? Write the reaction quotient and use it to explain your answer.

---

15. Based on the observations in Model 2, does the reaction shift to the left, increasing the concentration of the reactants or to the right, increasing the concentration of products upon the addition of HCl?

---

---

16. Have the concentrations of  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  and  $\text{CoCl}_4^{2-}$  increased or decreased after hydrochloric acid is added?

---

---

17. The addition of silver nitrate to the equilibrium system created a change to the system by removing  $\text{Cl}^-$  ions through a precipitation reaction. How does the new concentration of  $\text{Cl}^-$  in test tube B compare to the  $\text{Cl}^-$  concentration in test tube A?

The concentration of  $\text{Cl}^-$  in test tube B, after  $\text{Ag}^+$  is added, is \_\_\_\_\_ the concentration of  $\text{Cl}^-$  in test tube A. <, >, or =

18. Upon the addition of  $\text{AgNO}_3$ , is the value of the reaction quotient greater than, less than or equal to value of  $K_c$ ? Write the reaction quotient and use it to explain your answer.

---

---

19. Based on the observations in Model 2, does the reaction shift to the left (more reactants) or right (more products) upon the addition of  $\text{AgNO}_3$ ?

---

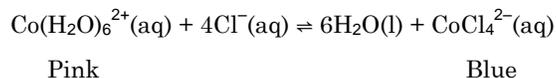
---

20. Did the concentrations of  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  and  $\text{CoCl}_4^{2-}$  increase or decrease after silver nitrate was added?

---

---

21. Model 2 dealt with the following equilibrium system:



- a. Complete the table to indicate how experimental stresses due to changing the amounts of substances in the solution shifted the equilibrium.

Table 6: Stress results due to changing reactant amounts

Stress	Resulting Color	Direction of Shift	Q vs $K_c$ (<, >, =)
Removal of $\text{Cl}^-$			$Q \text{ ___ } K_c$
Addition of $\text{Cl}^-$			$Q \text{ ___ } K_c$

- b. Predict how the following stresses in the amounts of substances would shift the equilibrium in the solution.

Table 7: Stress result predictions

Stresses That Could Cause This Shift	Resulting Color	Direction of Shift	Q vs $K_c$ (<, >, =)
Removal of $\text{Co(H}_2\text{O)}_6^{2+}$			$Q \text{ ___ } K_c$
Addition of $\text{Co(H}_2\text{O)}_6^{2+}$			$Q \text{ ___ } K_c$
Removal of $\text{CoCl}_4^{2-}$			$Q \text{ ___ } K_c$
Addition of $\text{CoCl}_4^{2-}$			$Q \text{ ___ } K_c$

22. The solutions in test tube K, test tube A (after the addition of HCl) and test tube B (after the addition of  $\text{AgNO}_3$ ) are all at equilibrium. Which of the following must be true about the solutions in the three test tubes? Circle the correct answer.

- They have the same amounts of reactants and products, same value of  $K_c$ , same color of equilibrium mixture.
- They have different amounts of reactants and products, different values of  $K_c$ , different color of equilibrium mixture.
- They have the same amounts of reactants and products, same value of  $K_c$ , different color of equilibrium mixture.
- They have different amounts of reactants and products, same value of  $K_c$ , different color of equilibrium mixture.

**MODEL 3****Building Model 3 – Endothermic or Exothermic**

3. Set up a warm water bath using a hot plate and a 250-mL beaker, and a cold water bath using ice water and a 250-mL beaker.

2. What lab observation will confirm that the reaction studied in Model 2 is endothermic? Why?

---



---



---

3. What lab observation will confirm that the reaction is exothermic? Why?

---



---



---

4. Place test tube A into the hot water bath for three minutes and then into the cold water bath for three minutes. Record your observation for each situation in the Model 3 Data Table.

5. Clean up all solutions and equipment according to your instructor's instructions.

**Model 3 – Endothermic or Exothermic**

Table 8: Model 3 Data Table—Results of hot and cold stress

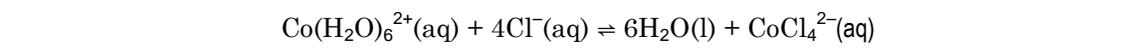
Condition	Resulting Color
After 3 minutes in hot water	
After 3 minutes in ice water	

**Analyzing Model 3 – Endothermic or Exothermic**

6. Is the cobalt equilibrium system endothermic or exothermic? Why? Provide evidence from your lab that supports your claim.

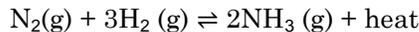
The reaction is endothermic because the solution turned blue in a hot water bath. The heat caused the reaction to shift towards the products.

7. Add energy to the appropriate side of the equation below.



## Connecting to Theory

Within five years of Henry Louis Le Châtelier abandoning his search for the synthesis of ammonia, Fritz Haber was able to create ammonia from hydrogen and nitrogen gas. The Haber process is used in industry to manufacture ammonia, a key component in fertilizer. Ammonia-based fertilizer is responsible for sustaining one-third of the earth's population, so this is a very important process. Ammonia is produced through the following catalyzed reaction:



Under normal conditions, the yield of ammonia is only 10–20%. This is not enough to keep up with global demand of ammonia.

Le Châtelier's principle is often used to manipulate the outcomes of reversible reactions to maximize yield. If a system in dynamic equilibrium is subjected to a stress such as changes in concentration, temperature, volume, and partial pressures, the concentration of products and reactants change to reestablish the equilibrium constant,  $K_c$ . Quantitatively, the direction the reaction shifts to re-establish equilibrium can be determined by comparing the value of  $Q$  to the value of  $K_c$ .

## Applying Your Knowledge – Determining a Constant Equilibrium Constant

1. With your group, design an experiment using the iron(III) thiocyanate equilibrium system to show that  $K_c$  remains constant when temperature is constant, within experimental error, despite different stresses added to the system. Record your procedure below.

While designing your lab, keep the following items in mind:

- Change only one variable when creating a stress to the system.
- Calibrate the spectrometer prior to use.
- Excess  $\text{SCN}^-$  produces colored side products; keep  $\text{SCN}^-$  as the limiting reactant at 0.0010 M.
- Keep all iron solutions at low concentrations (0.0080 M or lower) Solutions with higher concentration are too dark to be used in the spectrometer.
- You may dilute solutions more using distilled water.
- Minimize fingerprints.
- If using a spectrometer, use the maximum wavelength, to measure absorbance.
- If using a spectrometer, assume (path length  $\times$  molar absorptivity) for this system is  $5900 \text{ M}^{-1}$ .
- Create any data tables needed to organize data.
- Obtain your instructor's initials before you perform the lab.

Procedure:

Instructor Initials: \_\_\_\_\_

Data Table(s):

Calculations:

2. Does  $K_c$  remain constant after stresses are added to the equilibrium? Why? Provide evidence from your lab that supports your claim.

---

---

---