

# TOPIC 4: CHEMICAL EQUILIBRIUM

## APPENDICES

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## Appendix 4.1: Preparation of Equilibrium Systems (Demonstration)

### Nitrogen Dioxide–Dinitrogen Tetraoxide (NO<sub>2</sub>–N<sub>2</sub>O<sub>4</sub>) System

Prepare nitrogen(IV) oxide by treating copper turnings with concentrated nitric acid in a fume hood. Collect the gas in three vials of approximately 15 mL capacity. When the vials are filled with gas, quickly seal the ends. The colour intensity in each vial should be about the same.

**Caution:**

- Wear rubber gloves and goggles for personal protection.
- Prepare the vials in a fume hood.
- See Material Safety Data Sheets (MSDS) for further information.

#### Procedure (Demonstration)

1. Place the three vials in beakers of water at 0°C, 100°C, and room temperature respectively. The depth of colour shown in the three vials is a direct indication of the extent of the thermal dissociation in the reaction:



2. Have students compare the colours of the gases in the three vials.
3. Illustrate reversibility by placing the vial at 100°C into the water at 0°C. The vials can also be removed from the 0°C and 100°C beakers and allowed to reach room temperature.

**Note:** These manipulations can also be useful in the discussion of Le Châtelier's principle.

### Tetrachlorocobalt(II)–Aquocobalt(II) (CoCl<sub>4</sub><sup>2-</sup>–Co(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>) System

#### Materials

two 600 mL beakers  
 two 500 mL Erlenmeyer (conical) flasks  
 hot plate  
 2-propanol (isopropyl alcohol)  
 absolute ethanol (95% ethanol can be substituted for the absolute ethanol)  
 water  
 concentrated hydrochloric acid

#### Procedure

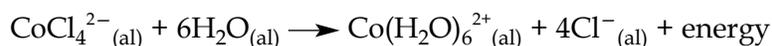
1. In one beaker, dissolve 10 g of cobalt(II) chloride (CoCl<sub>2</sub>) in 500 mL of ethanol. In the other beaker dissolve 10 g of cobalt(II) chloride in 500 mL of water. Note the colours of the solutions. (The blue colour is due to the tetrahedrally coordinated CoCl<sub>4</sub><sup>2-</sup>. The pink colour is due to the octahedrally coordinated Co(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>.)

Appendix 4.1: Preparation of Equilibrium Systems (Demonstration) (continued)

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2. Slowly add **just enough** water to the blue ethanol solution to change the colour to pink. Divide this pink solution into two equal volumes in the Erlenmeyer flasks. Add concentrated hydrochloric acid to one flask until the blue colour reappears. Heat the other portion of pink solution on the hot plate until it turns blue again. The hot solution may be cooled in an ice bath to restore the pink colour.

**Note:** A similar solution can be prepared directly by mixing 20 mL of 0.50 mol/L cobalt(II) chloride solution with 16 mL of saturated sodium chloride (NaCl) solution. When this mixture is chilled in cold water, it will turn pink, and when it is heated for a brief time in a Bunsen flame, it will turn blue. The process may be repeated at will.



## Appendix 4.2: Solving Equilibrium Problems Using the ICE Table Method

A convenient way to organize data for equilibrium problems is to use an ICE table:

- I** Initial—the initial concentrations of the reactants and products
- C** Change—the change in reactants and products from the initial conditions to equilibrium
- E** Equilibrium—the concentrations of the reactants and products at equilibrium

To set up the table, record the balanced chemical equation. Write the letters I, C, and E on the left side of the table. Insert the known values in the table, and use  $x$  to represent the value that needs to be calculated. See the example below.

### Sample Problem

In a lab experiment, 0.500 mol hydrogen ( $\text{H}_2$ ) and 0.500 mol iodine ( $\text{I}_2$ ) are placed in a 1.00 L flask at  $430^\circ\text{C}$ . The equilibrium constant,  $K_{\text{eq}}$  is 54.3 at this temperature. Calculate the concentrations of  $\text{H}_2$ ,  $\text{I}_2$ , and hydrogen iodide (HI) at equilibrium.

*Solution:*

- Set up the ICE table and fill in known values.

	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	$\rightleftharpoons$	$2\text{HI}(\text{g})$
<b>I</b>	0.500 mol/L		0.500 mol/L		0 mol/L
<b>C</b>	$-x$		$-x$		$2x$
<b>E</b>	$0.500 \text{ mol/L} - x$		$0.500 \text{ mol/L} - x$		$2x$

- Write the equilibrium expression for the reaction.

$$K_{\text{eq}} = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

- Substitute the values at equilibrium into the expression.

$$54.3 = \frac{(2x)^2}{(0.500 - x)(0.500 - x)}$$

- Take the square root of both sides.

$$7.37 = \frac{2x}{0.500 - x}$$

Appendix 4.2: Solving Equilibrium Problems Using the ICE Table Method (continued)

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5. Rearrange the equation and solve for  $x$ .

$$7.37(0.500 - x) = 2x$$

$$3.685 - 7.37x = 2x$$

$$3.685 = 2x + 7.37x$$

$$3.685 = 9.37x$$

$$x = \frac{3.685}{9.37} = 0.393 \text{ mol/L}$$

6. At equilibrium, the concentration of  $\text{H}_2$ ,  $\text{I}_2$ , and  $\text{HI}$  are as follows:

$$[\text{H}_2] = 0.500 \text{ mol/L} - x = 0.500 \text{ mol/L} - 0.393 \text{ mol/L} = 0.107 \text{ mol/L}$$

$$[\text{I}_2] = 0.500 \text{ mol/L} - x = 0.500 \text{ mol/L} - 0.393 \text{ mol/L} = 0.107 \text{ mol/L}$$

$$[\text{HI}] = 2x = (2)0.393 \text{ mol/L} = 0.786 \text{ mol/L}$$

## Appendix 4.3: Solving for $K_{\text{eq}}$ Using the BIR/PEC Accounting Method

The BIR/PEC accounting method is used in finding  $K_{\text{eq}}$ . It is optimally used when not all substances are given at equilibrium.

<b>B</b>	Balanced equation	
<b>I</b>	Initial (moles)	What you begin with before anything happens.
<b>R/P</b>	Reacted or Produced (moles)	Derived from the coefficients. Use ratio and proportion.
<b>E</b>	Equilibrium (moles)	The quantities of each substance at equilibrium. Reactants are subtracted from Initial. Products are added to Initial.
<b>C</b>	Concentration (mol/L)	The number of moles divided by the total volume.

### Question 1

Reactants A and B are mixed in a 1.00 L container, each with initial amounts of 0.80 mol. They react to produce C and D, so that



At equilibrium, the amounts of C and D are found to be 0.60 mol. Find  $K_{\text{eq}}$ .

*Answer:*

<b>B</b>	A	+	B	$\rightleftharpoons$	C	+	D
<b>I</b>	0.80 mol		0.80 mol		0 mol		0 mol
<b>R or P</b>	-0.60 mol		-0.60 mol		+0.60 mol		+0.60 mol
<b>E</b>	0.20 mol		0.20 mol		<b>0.60 mol</b>		<b>0.60 mol</b>
<b>C</b>	0.20 mol/1 L =[0.20]		0.20 mol/1 L =[0.20]		0.60 mol/1 L =[0.60]		0.60 mol/1 L =[0.60]

$$K_{\text{eq}} = \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]} = \frac{[0.60][0.60]}{[0.20][0.20]} = \frac{0.36}{0.04} = 9$$

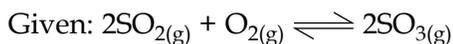
Appendix 4.3: Solving for  $K_{\text{eq}}$  Using the BIR/PEC Accounting Method (continued)**Question 2**

In a lab investigation, 2.00 mol of sulphur dioxide ( $\text{SO}_2$ ) and 3.0 mol of nitrogen dioxide ( $\text{NO}_2$ ) are mixed in a 2.00 L container and reacted. Once equilibrium is reached, the container is found to have 0.50 mol of sulphur trioxide ( $\text{SO}_3$ ). Calculate the value of  $K_{\text{eq}}$  for this reaction.

Answer:

<b>B</b>	$\text{SO}_{2(\text{g})}$	+	$\text{NO}_{2(\text{g})}$	$\rightleftharpoons$	$\text{SO}_{3(\text{g})}$	+	$\text{NO}_{(\text{g})}$
<b>I</b>	<b>2.00 mol</b>		<b>3.00 mol</b>		0 mol		0 mol
<b>R or P</b>	-0.50 mol		-0.50 mol		+0.50 mol		+0.50 mol
<b>E</b>	1.50 mol		2.50 mol		<b>0.50 mol</b>		0.50 mol
<b>C</b>	$1.50/2 = [0.75]$		$2.50/2 = [1.25]$		$0.50/2 = [0.25]$		$0.50/2 = [0.25]$

$$K_{\text{eq}} = \frac{[\text{SO}_3][\text{NO}]}{[\text{SO}_2][\text{NO}_2]} = \frac{[0.25][0.25]}{[0.75][1.25]} = \frac{0.0625}{0.9375} = 0.067$$

**Question 3**

Initially, 2.00 mol of  $\text{SO}_2$ , 1.00 mol of  $\text{O}_2$ , and 0.100 mol of  $\text{SO}_3$  are all mixed in a 15.0 L reaction container. After the reaction reaches equilibrium, 0.200 mol of  $\text{O}_2$  are found to remain. Calculate the value of the equilibrium constant.

Answer:

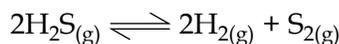
<b>B</b>	$2\text{SO}_{2(\text{g})}$	+	$\text{O}_{2(\text{g})}$	$\rightleftharpoons$	$2\text{SO}_{3(\text{g})}$
<b>I</b>	<b>2.00 mol</b>		<b>1.00 mol</b>		<b>0.100 mol</b>
<b>R or P</b>	-1.60 mol		-0.80 mol		+1.60 mol
<b>E</b>	0.40 mol		<b>0.200 mol</b>		1.70 mol
<b>C</b>	$0.40/15 = [0.0267]$		$0.20/15 = [0.0133]$		$1.70/15 = [0.113]$

$$K_{\text{eq}} = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} = \frac{[0.113]^2}{[0.0267]^2[0.0133]} = \frac{0.0128}{0.0000095} = 1350$$

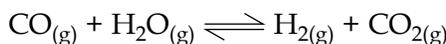
## Appendix 4.4: Equilibrium Problems

### Problems

- For the reaction  $\text{N}_{2(g)} + \text{O}_{2(g)} \rightleftharpoons 2\text{NO}_{(g)}$ , an analysis of the equilibrium mixture in a 1.00 L flask gives the following results: nitrogen 0.50 mol, oxygen 0.50 mol, and nitrogen monoxide 0.020 mol. Calculate  $K_{\text{eq}}$  for the reaction.
- Hydrogen sulphide is a pungent, poisonous gas. At 1400 K, an equilibrium mixture was found to contain 0.013 mol/L hydrogen, 0.18 mol/L hydrogen sulphide, and an undetermined amount of sulphur in the form of  $\text{S}_{2(g)}$ . If the value of  $K_{\text{eq}}$  is  $2.4 \times 10^{-4}$ , what concentration of  $\text{S}_{2(g)}$  is present at equilibrium at this temperature?



- The following reaction increases the proportion of hydrogen gas for use as a fuel.



This reaction has been studied at different temperatures to find the optimum conditions. At 700 K, the equilibrium constant is 8.3. Suppose that you start with 1.00 mol of  $\text{CO}_{(g)}$  and 1.00 mol of  $\text{H}_2\text{O}_{(g)}$  in a 5.00 L container. What amount of each substance will be present in the container when the gases are at equilibrium at 700 K?

### Solutions

- $K_{\text{eq}} = 0.0016$
- $[\text{S}_{2(g)}] = 0.046 \text{ mol/L}$
- $[\text{CO}_{(g)}] = 0.020 \text{ mol/L}$   
 $[\text{H}_2\text{O}_{(g)}] = 0.020 \text{ mol/L}$   
 $[\text{H}_{2(g)}] = 0.18 \text{ mol/L}$   
 $[\text{CO}_{2(g)}] = 0.18 \text{ mol/L}$

## Appendix 4.5: Chemical Equilibrium: Lab Activity

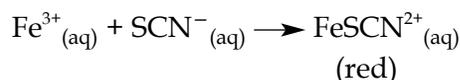
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### Introduction

Chemical reactions occur in order to approach a state of chemical equilibrium. The equilibrium state can be characterized by specifying its equilibrium constant (i.e., by indicating the numerical value of the mass action expression when the system is at equilibrium).

### Purpose

In this experiment, you will determine the value of the equilibrium constant for the following reaction:



### Procedure

1. Thoroughly clean six small test tubes, rinse with distilled water, and drain. Add 5 mL of 0.0020 mol/L sodium thiocyanate (NaSCN) solution to each of these test tubes.
2. To the first test tube, add 5 mL of 0.20 mol/L iron(III) nitrate ( $\text{Fe}(\text{NO}_3)_3$ ) solution. This tube will serve as the standard.
3. Proceed as follows with the remaining test tubes:
  - Add 10 mL of 0.20 mol/L iron(III) nitrate solution to a graduated cylinder, fill the cylinder to 25 mL with distilled water, and stir thoroughly to mix. Pour 5 mL of the resulting diluted solution (0.080 mol/L iron(III),  $\text{Fe}^{3+}$ ) into test tube 2.
  - Discard all but 10 mL of the diluted solution in the graduated cylinder. Refill the cylinder with distilled water to 25 mL, and stir thoroughly. Add 5 mL of the resulting solution (0.032 mol/L  $\text{Fe}^{3+}$ ) to test tube 3.
  - Discard all but 10 mL of the solution in the cylinder, and again dilute to 25 mL. Continue this procedure until you have added to each successive test tube 5 mL of progressively more dilute iron(III) ( $\text{Fe}^{3+}$ ) solution.
4. To determine the  $[\text{FeSCN}^{2+}]$  in each test tube, determine the percent transmission of each test tube using a colorimeter or spectrometer set to the wavelength  $\lambda = 460 \text{ nm}$ . Set the transmission of the blank to 100%. Then determine the percent transmission of test tubes 1 to 6.

## Appendix 4.5: Chemical Equilibrium: Lab Activity (continued)

**Data**Optical density (absorbance) =  $-\log$  (percent transmission)

	Percent Transmission	Optical Density (Absorbance)
Test tube 1	_____	_____
Test tube 2	_____	_____
Test tube 3	_____	_____
Test tube 4	_____	_____
Test tube 5	_____	_____
Test tube 6	_____	_____

**Results**

Test Tube	Initial Concentrations		Equilibrium Concentrations			K
	[Fe <sup>3+</sup> ]	[SCN <sup>-</sup> ]	[FeSCN <sup>2+</sup> ]	[Fe <sup>3+</sup> ]	[SCN <sup>-</sup> ]	
1						
2						
3						
4						
5						
6						

**Note:**

When calculating equilibrium concentrations, assume that all the initial thiocyanate ion (SCN<sup>-</sup>) in test tube 1 has been converted to the thiocyanatoiron(III) ion (FeSCN<sup>2+</sup>). This provides the [FeSCN<sup>2+</sup>] in test tube 1.

The [FeSCN<sup>2+</sup>] in the remaining test tubes can be determined using the idea that *the concentration of a coloured substance is directly proportional to the optical density (absorbance)*.

**Appendix 4.5: Chemical Equilibrium: Lab Activity** *(continued)*

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When calculating initial concentrations, assume that iron(III) nitrate ( $\text{Fe}(\text{NO}_3)_3$ ) and sodium thiocyanate ( $\text{NaSCN}$ ) are completely dissociated. Remember also that mixing two solutions dilutes both of them. Equilibrium concentrations of iron(III) ion ( $\text{Fe}^{3+}$ ) and thiocyanate ion ( $\text{SCN}^-$ ) are obtained by subtracting thiocyanatoiron(III) ion ( $\text{FeSCN}^{2+}$ ) formed from the initial iron(III) ion and thiocyanate ion concentrations. Calculate the value of the equilibrium constant  $K$  for test tubes 2 to 6.

**Questions**

1. What assumptions are made in this experiment?
2. Why can you **not** determine a value for an equilibrium constant  $K$  for test tube 1?
3. Using the average value of  $K$ , determine  $[\text{SCN}^-]$  in test tube 1 at equilibrium.
4. Approximately how complete is this reaction? Explain.
5. Compare and contrast ions in solution with gas molecules.
6. Why is this particular equilibrium suitable for study in our laboratory?

## Appendix 4.6A: An Analogy for an Equilibrium Reaction: Lab Activity

### Purpose

- To illustrate the experimental conditions necessary to have a system of experimental equilibrium.
- To illustrate the effect of applying stress to a system in equilibrium.
- To illustrate graphically the changes that lead to the establishment of equilibrium.

### Apparatus/Materials

two 25 mL graduated cylinders  
two drinking straws of different diameters  
graph paper

### Procedure

1. Copy the table below into your lab book and record your data as you perform the experiment.

#### Data Table

Number of Transfers	Volume of Water Cylinder A (mL)	Volume of Water Cylinder B (mL)
0	25	0
1		
2		
3		
etc.		

2. Label a 25 mL cylinder as **cylinder A** (reactants) and fill it to the 25 mL mark with water. Label a second 25 mL cylinder as **cylinder B** (products).
3. Working with your partner, transfer water simultaneously from one cylinder to the other, using straws of different diameters. Lower the straws into the respective cylinders, and when each straw touches the bottom of the cylinder, place your index finger over the open end of the straw. Transfer the water collected to the other cylinder and allow the straw to drain.
4. Remove each straw and record the volume of water in each cylinder, being careful to read the meniscus to the nearest 0.1 mL.
5. Return the straws to their original cylinders and repeat the process, recording the volumes after each transfer.
6. After three successive transfers result in no other change in volume, add 5 mL of water to cylinder A. Record the volume in each cylinder. Then resume the water transfer until three successive transfers again result in identical volumes.

**Appendix 4.6A: An Analogy for an Equilibrium Reaction: Lab Activity (continued)**

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**Calculations**

Plot the volume of water for both cylinder A and cylinder B on the  $y$ -axis of the same piece of graph paper against the number of transfers on the  $x$ -axis. Join each set of points with a smooth curve.

**Questions**

1. Describe, based on your graph, the changes in volume (analogous to concentration) and corresponding rates that occur in each curve up to the point where the extra 5 mL was added.
2. Describe the change that occurs in the curve for cylinder A at the point where the 5 mL of water is added.
3. What significance can be attributed to
  - a) the point where the two curves meet?
  - b) the first flat portions of the two curves?
  - c) the second flat portions of the curves?
4. What change in the final volume of water in cylinder B results from the addition of the 5 mL of water to cylinder A?
5. What is the evidence that equilibrium has been established if
  - a) the data for the water transfers are observed?
  - b) the plotted data are observed?
6. Why is this particular system called *closed*?
7. The additional 5 mL of water constitutes a “stress” on the system.
  - a) What analogous stress would be involved if the system really represented a chemical reaction in equilibrium?
  - b) Name two other stresses that could be imposed on a chemical system.
8. What factor controls the relative volumes of water in each cylinder at equilibrium in this exercise?
9. Consult with other members of your class to see whether their graphs are similar to, or different from, yours. Account for any differences you find.
10. In a real chemical system, what factor would control the relative concentrations of reactants and products present at equilibrium?

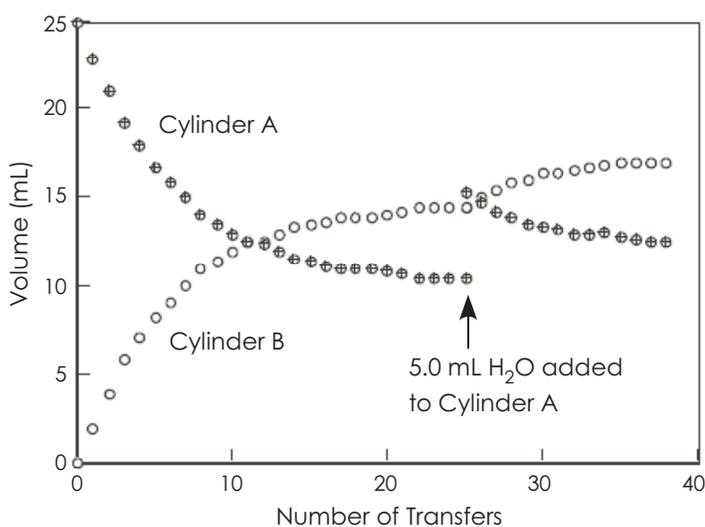
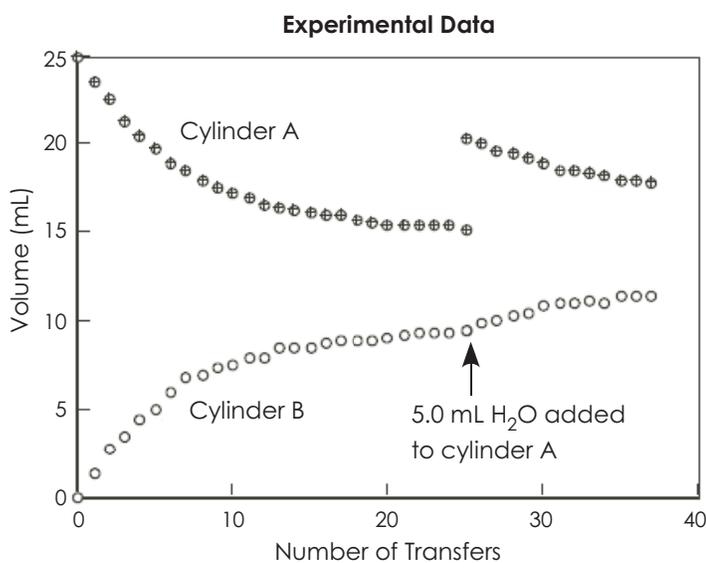
## Appendix 4.6B: An Analogy for an Equilibrium Reaction: Lab Activity (Teacher Notes)

### Background

For this experiment, it is **very important** to use two straws of different diameters so that the equilibrium position is not half of the initial volume. It is also helpful to use one coloured solution and one colourless solution.

Experimental results will depend upon the types of straws used and the starting cylinder of each straw. The graphs below illustrate actual experimental data using the procedure described in Appendix 4.6A.

**Note:** One coloured solution and one colourless solution could be used.



## Appendix 4.6C: An Analogy for an Equilibrium Reaction: Lab Report Checklist

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Does the lab report include the following components?

### Purpose

### Observations (from Procedures)

#### Qualitative Data

- Describe the properties of water and the straws.
- In general, what happened to the volume of water in the two graduated cylinders?
- When was equilibrium achieved?
- What happened to the system when the volume of cylinder A was changed?
- At what point was equilibrium re-established?

#### Quantitative Data Table

#### Calculations (Graph)

- axes labelled
- title
- points joined with a smooth curve
- descriptions of
  - the system's initial volumes (for cylinders A and B)
  - how we know from the graph that equilibrium is achieved
  - the change in volume of cylinder A due to the stress
  - the change in volume of cylinder B due to the stress

#### Conclusions

- What happened when a stress was added to the system?
- What happens to the slope of the graph when the system achieves equilibrium?

#### Answers to Questions

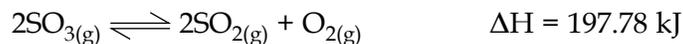
#### Sources of Error

**Appendix 4.7: Equilibrium and Le Châtelier's Principle (Pre-lab)**

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**Questions**

1. Define *equilibrium*.
2. State Le Châtelier's principle.
3. Consider the following reaction.



For this reaction, indicate how the amount of  $\text{SO}_{2(g)}$  present at equilibrium would be affected by

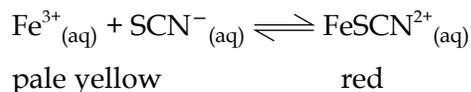
- a) adding  $\text{SO}_3$
- b) raising the temperature
- c) decreasing the volume
- d) removing some  $\text{O}_2$
- e) adding some  $\text{SO}_2$
- f) adding a catalyst
- g) removing some  $\text{SO}_3$

## Appendix 4.8A: Qualitative Equilibrium: Lab Activity

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### Introduction

A standard laboratory example for demonstrating the effect of changing concentrations on the equilibrium positions is shown below:



The position of equilibrium can be determined from the colour of the solution. When the iron(III) nitrate and potassium thiocyanate solutions are mixed, the colour of the mixture is orange at equilibrium. If the equilibrium lies to the right, the solution is a dark red colour. If the equilibrium lies to the left, the solution is a pale yellow colour.

### Apparatus/Materials

well plate  
0.020 mol/L iron(III) nitrate ( $\text{Fe}(\text{NO}_3)_3$ )  
0.002 mol/L potassium thiocyanate (KSCN)  
1.0 mol/L sodium hydroxide (NaOH)  
toothpicks

### Procedure

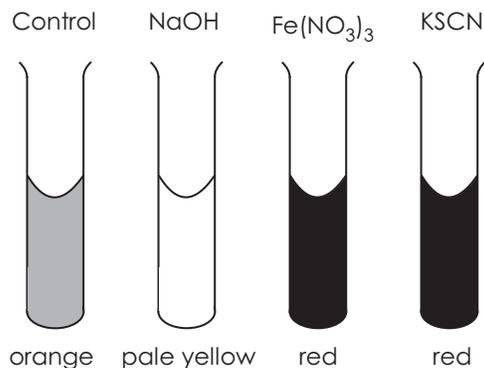
1. In each of four wells, add 5 drops of iron(III) nitrate and 5 drops of potassium thiocyanate. Mix each solution with a toothpick.
2. Do not alter the first well. It will act as your control.
3. To the second well, add 10 drops of sodium hydroxide. Record your observations.
4. To the third well, add 10 drops of iron(III) nitrate. Record your observations.
5. Add 10 drops of potassium thiocyanate to the fourth well. Record your observations.

### Observations and Analysis

Use Le Châtelier's principle to explain the results from steps 3 to 5 of the procedure.

**Appendix 4.8B: Qualitative Equilibrium: Lab Activity (Teacher Notes)**

Consider the demonstration below:



If salts contain  $\text{Fe}^{3+}$ ,  $\text{SCN}^-$ , or both, the colour of the solution becomes a deeper red. This suggests a shift in equilibrium to the right. To use up some of the added reactant, the rate of the forward reaction increases, thereby increasing the concentration of  $\text{FeSCN}^{2+}$  and establishing a new equilibrium position.

When NaOH is added to the system, the solution turns to a pale yellow. The hydroxide ions from the NaOH combine with iron(III) ions to produce an insoluble complex of iron(III) hydroxide. Precipitating out the iron ions reduces the iron ion concentration. The system responds to the change by favouring the reverse reaction and replacing some of the “lost” iron. A change to a pale yellow colour indicates a shift in the equilibrium to the left and a reduction in the  $\text{FeSCN}^{2+}$  ion concentration.

## Appendix 4.9: Disrupting Equilibrium Systems: Lab Activity

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### Introduction

Le Châtelier's principle describes the effect that applying various types of stresses will have on the position of equilibrium – whether or not it will shift to increase or decrease the concentration(s) of products in the equilibrium system. These stresses include changes in factors such as concentrations of reactants or products, temperature of the system, and, for reactions involving gases, pressure.

Some investigations are done with systems in a water solution. In these systems, where gases are not involved, the volume of the system is generally defined by the volume of the solution, and pressure is of little or no consequence.

### Purpose

The purpose of this experiment is to let you observe for yourself what Le Châtelier's principle means.

### Apparatus

- fume hood
- 50 mL beaker
- well plate (12 wells)
- scoopula
- 10 mL graduated cylinder
- eyedropper pipettes
- hot plate
- ice bath

### Materials

- distilled water
- solid cobalt(II) chloride ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}_{(s)}$ )
- solid calcium chloride ( $\text{CaCl}_{2(s)}$ )
- 0.1 mol/L silver nitrate ( $\text{AgNO}_3$ )
- 12 mol/L hydrochloric acid (HCl)
- ethanol

## Appendix 4.9: Disrupting Equilibrium Systems: Lab Activity (continued)

**Procedure**

1. Gather all equipment.
2. Measure out 10 mL of ethanol and place it in the 50 mL beaker.
3. Place several pieces of the solid cobalt(II) chloride in one of the wells in your well plate. Note both its colour and the formula for the compound, as shown on the label of the stock bottle.
4. Add 4 or 5 crystals of the cobalt(II) chloride to the ethanol in the beaker until a blue solution results. Add more crystals, if necessary.
5. Using an eyedropper pipette, transfer one-fifth of the blue solution to four of the wells in the well plate. Be sure to leave a small amount in the beaker.
6. To one of the wells from step 5, add 5 drops of distilled water, one drop at a time. Record your observations after each drop. Repeat this step in two more wells so that all three of them exhibit the same colour.
7. Take your well plate to the fume hood.  
Use the eyedropper pipette provided in the acid bottle of 12 mol/L hydrochloric acid and carefully add one drop at a time until you have added 5 drops to the first well from step 6.
8. To the second well from step 6, add 2 small lumps of solid calcium chloride.
9. To the third well from step 6, add 10 drops of 0.1 mol/L silver nitrate.
10. Retain the solution in the fourth well to use for comparison purposes.
11. To the remaining solution in the beaker, add just enough distilled water to get a purple colour that is about halfway between the blue and pink shades. Place the beaker on a hot plate and warm the beaker until a colour change occurs. Make sure you do not let the ethanol come to a boil.
12. Chill the beaker in an ice bath to see if the colour change in step 11 is reversible.

**Warning:**

Hydrochloric acid is caustic and corrosive. Avoid contact, and immediately rinse all spills with copious amounts of water.

**Caution:**

Silver nitrate will stain your skin and clothing.

## Appendix 4.9: Disrupting Equilibrium Systems: Lab Activity (continued)

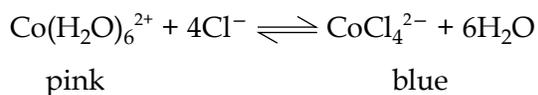
## Observations

Before Reactions	
	Colour
Distilled water	
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}_{(s)}$	
$\text{CaCl}_{2(s)}$	
0.1 mol/L $\text{AgNO}_3$	
12 mol/L HCl	
Ethanol	

After Reactions	
	Colour
Add distilled water ( $\text{H}_2\text{O}$ )	
Add hydrochloric acid (HCl)	
Add calcium chloride ( $\text{CaCl}_{2(s)}$ )	
Add silver nitrate ( $\text{AgNO}_3$ )	
Add heat	
Remove heat	

## Analysis

- The net ionic equation for the equilibrium reaction you have been investigating is



On the reagent bottle, the formula for the solid cobalt(II) chloride is  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ . What name do we give to compounds that have water molecules bound to their structure?

## Appendix 4.9: Disrupting Equilibrium Systems: Lab Activity (continued)

- Which cobalt complex was favoured by the addition of water in step 6 of the procedure? Use Le Châtelier's principle to explain the colour change.
- Which cobalt complex was favoured in both steps 7 and 8 of the procedure? What ion is common to both of the reagents that caused the colour changes? Use Le Châtelier's principle to explain why the colour change occurred in each case.
- What colour was the solid you formed in step 9 of the procedure? Why must it have been this colour? To what colour did the liquid in the well turn? Which complex of cobalt was favoured? Explain. Use Le Châtelier's principle to explain why the liquid in the well underwent the colour change that you observed.
- Which cobalt complex was favoured by the addition of heat in step 11 of the procedure? Rewrite the equation for the reaction, including the energy term directly in the equation. The value of  $\Delta H$  for the process is +50 kJ/mol. Use Le Châtelier's principle and the equation that you just wrote to explain the colour changes that resulted from the heating and cooling.

**Discussion**

Provide two sources of error. If any of your results do not match what the colour change should have been, talk about it in your discussion.

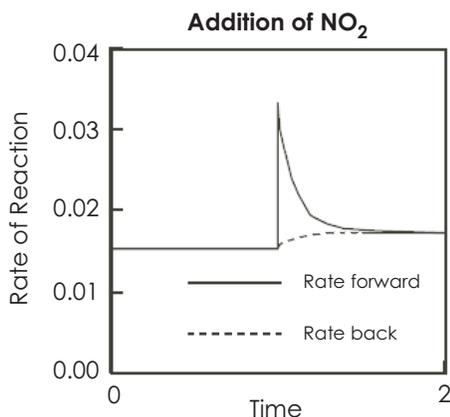
**Conclusion**

State what the colour change should be – not necessarily what you saw.

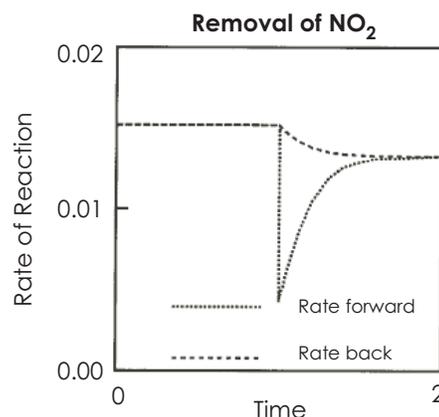
"Stress"	Colour Change	Shift
Addition of H <sub>2</sub> O		
Addition of HCl		
Addition of CaCl <sub>2</sub>		
Addition of AgNO <sub>3</sub>		
Addition of heat		
Removal of heat		

## Appendix 4.10: Interpreting Equilibrium Graphs

The graphs below illustrate rate changes for the  $\text{NO}_2\text{-N}_2\text{O}_4$  equilibrium system. In preparing the graphs, it was assumed that the system was at equilibrium initially, then a stress was applied, and, after an instantaneous change, the system was allowed to re-establish equilibrium.



Graph A



Graph B

### Graph A

Initially, the reaction is at equilibrium—both the forward and the reverse rates are equal. At the instant when more reactant  $\text{NO}_2$  is added, the forward rate increases. As the reactant is consumed in the reaction, the forward rate decreases to a constant value.

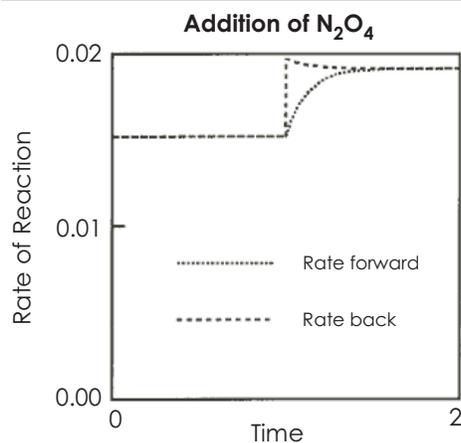
Initially, the reverse rate is unchanged. However, as more product is formed, the rate of the back reaction increases to the new constant value.

### Graph B

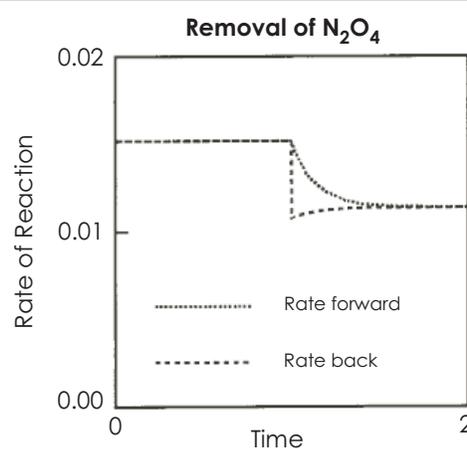
Initially, the reaction is a equilibrium—both the forward and reverse rates are equal. At the instant when reactant  $\text{NO}_2$  is removed, the forward rate decreases. As more  $\text{NO}_2$  is produced through the back reaction, the forward rate increases to a new constant value.

Initially, the reverse rate is unchanged. However, since product is no longer being formed at the same rate, the rate of the back reaction decreases as the amount of product decreases (and more reactant is formed).

## Appendix 4.10: Interpreting Equilibrium Graphs (continued)



Graph C



Graph D

**Graph C**

At the instant when product  $N_2O_4$  is added, the reverse rate goes up. Then, as some product concentration is decreased by reaction, the reverse rate decreases until it reaches a constant value.

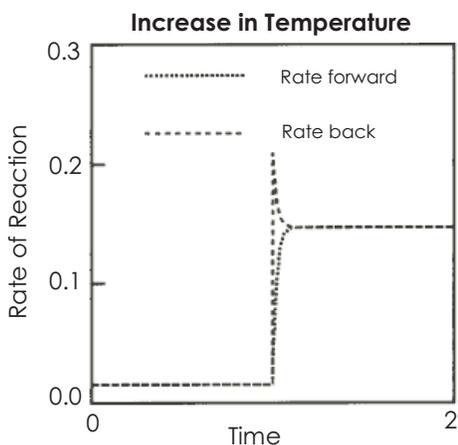
At the instant when product  $N_2O_4$  is added, the forward rate is unchanged. As the “reactant” concentration increases, through reaction, the forward rate increases to its new constant value.

**Graph D**

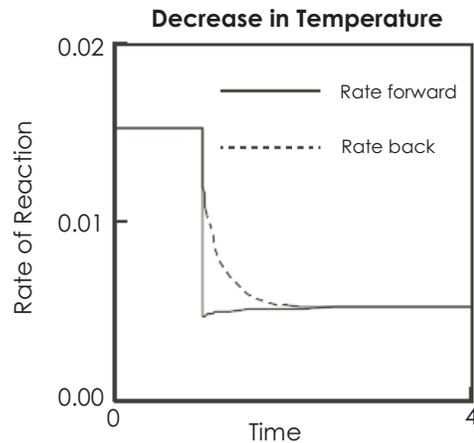
At the instant when product  $N_2O_4$  is removed, the reverse rate goes down. Then, as more product is formed by reaction, the reverse rate increases to a new constant value.

At the instant when product  $N_2O_4$  is removed, the forward rate is unchanged. Then, as more reactant is used up in producing more of the product, the forward rate decreases to a new constant value.

## Appendix 4.10: Interpreting Equilibrium Graphs (continued)



Graph E



Graph F

**Graph E**

Initially, the system is at equilibrium—the rates of the forward and reverse reactions are equal.

When the temperature is increased, both the forward and the reverse rates increase. Because the reaction is exothermic, the reverse rate goes up more than the forward reaction does.

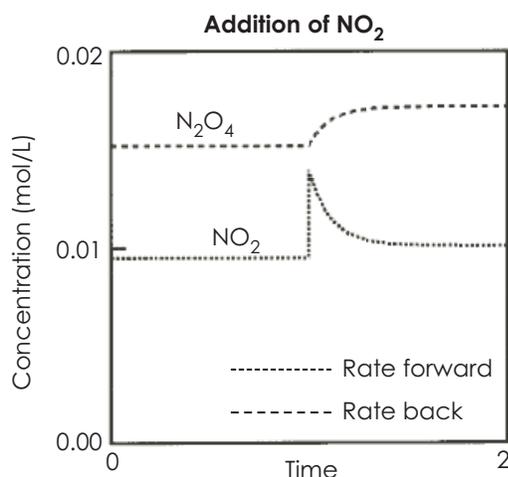
**Graph F**

Initially, the system is at equilibrium—the rates of the forward and reverse reactions are equal.

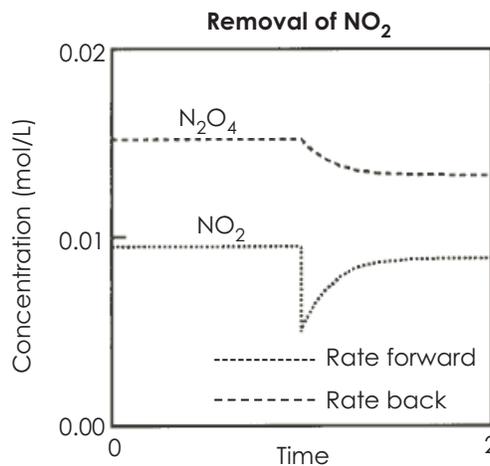
When the temperature is lowered, both the forward and reverse rates decrease. Because the reaction is exothermic, the reverse rate goes down less than the forward reaction does.

## Appendix 4.11: Interpreting Concentration versus Time Graphs

The graphs below illustrate concentration changes for the  $\text{NO}_2\text{-N}_2\text{O}_4$  equilibrium system. In preparing the graphs, it was assumed that the system was at equilibrium initially, then a stress was applied, and, after an instantaneous change, the system was allowed to re-establish equilibrium.



Graph A



Graph B

### Graph A

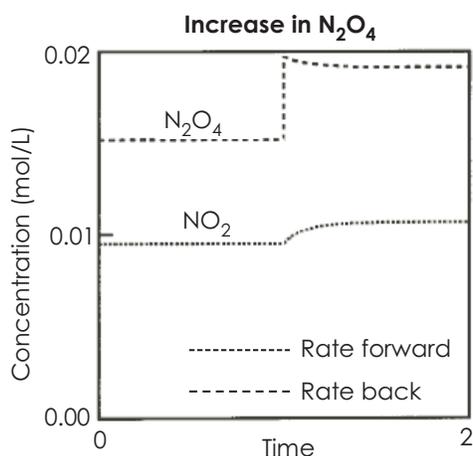
Initially, the reaction is at equilibrium – the concentrations of reactant  $\text{NO}_2$  and product  $\text{N}_2\text{O}_4$  are constant. At the instant when more reactant  $\text{NO}_2$  is added, the  $[\text{NO}_2]$  increases abruptly. As the reactant is consumed in the reaction, its concentration decreases to a constant value.

Initially,  $[\text{N}_2\text{O}_4]$  is unchanged. However, as reaction proceeds, more product is formed, and  $[\text{N}_2\text{O}_4]$  increases to a new constant value, a new equilibrium position.

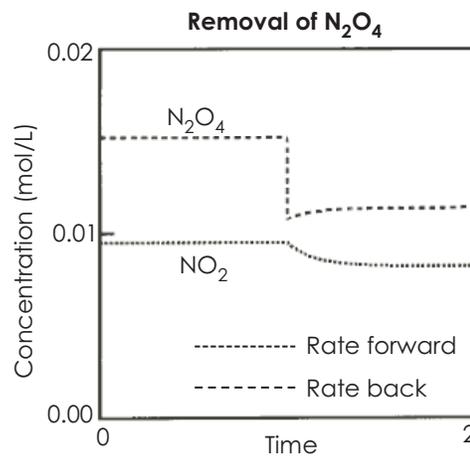
### Graph B

Initially, the reaction is at equilibrium – the concentrations of reactant  $\text{NO}_2$  and product  $\text{N}_2\text{O}_4$  are constant. At the instant when more reactant  $\text{NO}_2$  is removed, the  $[\text{NO}_2]$  decreases abruptly. As more  $\text{NO}_2$  is produced through the back reaction, its concentration increases to a new constant value.

Initially,  $[\text{N}_2\text{O}_4]$  is unchanged. However, since product is no longer being formed at the same rate, its concentration decreases to a new constant value, a new equilibrium position.

Appendix 4.11: Interpreting Concentration versus Time Graphs (*continued*)

Graph C



Graph D

**Graph C**

At the instant when product  $\text{N}_2\text{O}_4$  is added,  $[\text{N}_2\text{O}_4]$  goes up abruptly. Then, as the product concentration is decreased by reaction, the reverse rate decreases until it reaches a constant value.

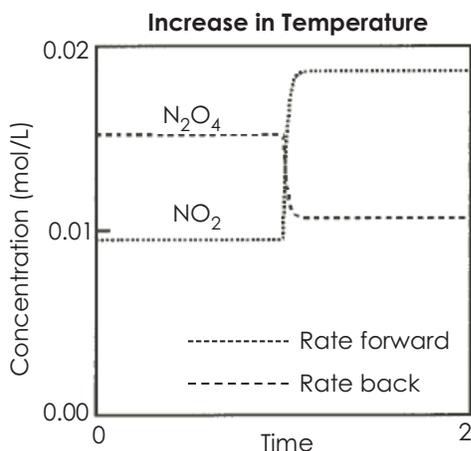
At the instant when product  $\text{N}_2\text{O}_4$  is added, the forward rate is unchanged. As the “reactant” concentration increases, through reaction, the forward rate increases to its new constant value.

**Graph D**

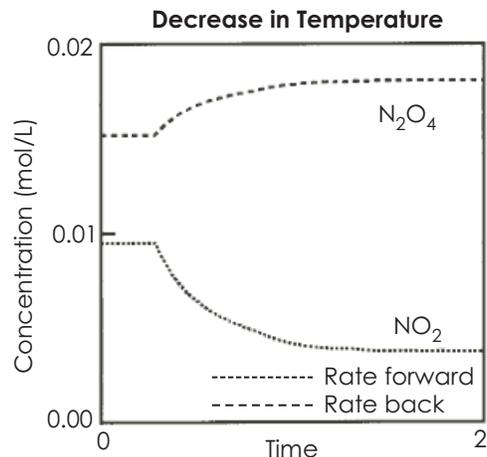
At the instant when product  $\text{N}_2\text{O}_4$  is removed, the reverse rate goes down. Then, as more product is formed by reaction, the reverse rate increases to a new constant value.

At the instant when product  $\text{N}_2\text{O}_4$  is removed, the forward rate is unchanged. Then, as more reactant is used up in producing more of the product, the forward rate decreases to a new constant value.

## Appendix 4.11: Interpreting Concentration versus Time Graphs (continued)



Graph E



Graph F

**Graph E**

Initially, the system is at equilibrium –  $[\text{NO}_2]$  and  $[\text{N}_2\text{O}_4]$  are constant.

The reaction is exothermic –  $K_{\text{eq}}$  decreases when the temperature increases. When the temperature is increased, the system is not at equilibrium under the new conditions.  $[\text{NO}_2]$  increases to establish a new equilibrium.

**Graph F**

Initially, the system is at equilibrium –  $[\text{NO}_2]$  and  $[\text{N}_2\text{O}_4]$  are constant.

The reaction is exothermic –  $K_{\text{eq}}$  increases when the temperature decreases. When the temperature is decreased, the system is not at equilibrium under the new conditions.  $[\text{N}_2\text{O}_4]$  increases to establish a new equilibrium.

