

Introduction to Equilibrium

Pre Lab Exercise

Name: _____

1. Write the equation for the reaction of hydrogen and fluorine to make hydrogen fluoride.



2. Write the concentration equilibrium constant expression for the above reaction.

$K_c =$

3. If the value of K_c for the above expression is large what does that imply about the relative value of [HF] compared to $[H_2]$ and $[F_2]$?
4. If K_c is small (less than 1) then the _____ are favored.
5. If K_c is large (greater than 1) then the _____ are favored.
6. If the concentration of a reactant is doubled what happens to the value of the equilibrium constant?
7. If the concentration of a product is doubled what happens to the value of the equilibrium constant?
8. Look up **Le Chatelier's Principle** for equilibria from a reliable source; restate the principle in your own words in the space below.

Introduction to Equilibrium

Purpose

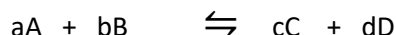
1. To observe the effects of concentration and temperature changes on chemical systems initially at equilibrium.
2. To correctly write equilibrium constant expressions and interpret the meaning of the equilibrium constant.

Introduction

Many reactions are reversible. That is to say that the products of a reaction can react to yield the starting materials.

A chemical reaction has reached equilibrium conditions when the forward and reverse reactions occur at the same rate, therefore relative amounts of "product" and "reactant" remain unchanged.

The ratio of the mathematical product of the concentration of products to reactants is called the equilibrium expression and it is a constant value for a reaction (at the specified temperature) known as the **equilibrium constant K**. The general form for the equilibrium constant expression for any reaction involving compounds A, B, C, and D :



is given by:
$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

where a, b, c, and d are the coefficients of the balanced equation.

When you are heating or cooling a system it is sometimes helpful to consider **heat** as part of the equation, e.g.

Endothermic reactions: Reactants + **heat** $\rightleftharpoons$ Products

Exothermic reactions: Reactants $\rightleftharpoons$ Products + **heat**

When you warm a solution that is the same as adding heat and when you cool it you are removing heat. So for an endothermic reaction for example, warming the container is analogous to adding more of a reactant whereas cooling the container is analogous to removing one of the reactants. Heat can be added or removed without changing the temperature, as the equilibrium reaction will shift in response to the change, replacing any heat removed or absorbing any heat added.

Experimental Chemistry

Part I Irreversible Reaction

Some chemical reactions “go to completion” and are not reversible (irreversible). A precipitation reaction will demonstrate this type of reaction.

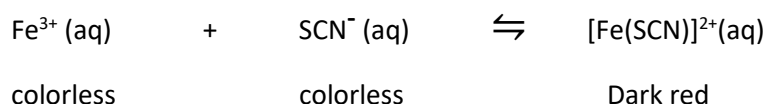
1. Add 10 drops 0.2 M BaCl_2 to a clean test tube. Add 15 drops 0.2 M Na_2SO_4 .
2. Record your observations:
3. Apply the solubility rules to determine the products and write the balanced equation for the reaction:
4. Centrifuge the mixture and transfer the supernatant to a clean test tube.
5. Add 3 drops of the Na_2SO_4 solution; record your observations:

Write a conclusion based on the observations of step 5. Specifically, how do your observations indicate that the reaction of BaCl_2 with Na_2SO_4 is irreversible?

Explain on a molecular level why you arrived at this conclusion.

Part II Ion - Complex and Reversible Equilibria: Iron(III) thiocyanate ion complex

In this part of the laboratory you will be investigating the reversible formation of the $[\text{Fe}(\text{SCN})]^{2+}$ ion. This ion-complex forms when iron III and the thiocyanate ion are present in the same solution. The dark red color of the ion-complex is the evidence of its formation. The net ionic equation is:



Equilibrium expression:

Write the concentration equilibrium expression for the reaction of the iron(III) cation with the thiocyanate anion:

$$K_c =$$

Prepare the solution:

1. Prepare a solution of the $[\text{Fe}(\text{SCN})]^{2+}$ ion by mixing equal volumes (approximately 2mL each) of the 0.05M iron(III) nitrate and 0.05M potassium thiocyanate solutions and dilute the mixture to about 10x the volume (~40 mL total volume).

Based on the color you observe, would you predict this reaction to have a K_c value less than one (larger concentration of starting reagents) or a K_c greater than one (larger concentration of the product; the ion complex)?

Prediction:

Concentration of reactants:

Competing reactions to the ion-complex reaction will change the concentration of the free iron and free thiocyanate ions that are present in solution. Changes to the free ion concentrations causes the concentration of the ion-complex to change. The following procedures explore the selective removal of one of the reactants.

2. Pour about 5 mL of your prepared $[\text{Fe}(\text{SCN})]^{2+}$ solution into a test tube. Add one drop at a time of 2M NaOH.

What do you observe?

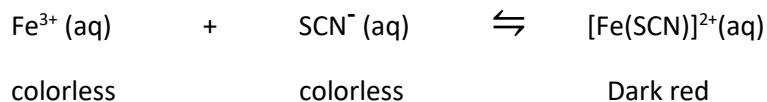
Add additional drops of 2M NaOH until no further changes are observed.

Centrifuge the mixture and transfer the supernatant (liquid) to two clean test tubes (split into two aliquots).

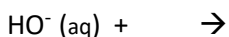
Add one drop KSCN solution to one clear supernatant; what do you observe?

Add one drop 0.05M iron(III) nitrate to the other, what do you observe?

Based upon your observations, which ion did the hydroxide OH⁻, react with when added to the equilibrium reaction?



Write the chemical equation that supports this observation:



 **Explain** how your observations are related to the equation for the $[\text{Fe}(\text{SCN})]^{2+}$ ions? Specifically, how does adding NaOH, which does not react with $[\text{Fe}(\text{SCN})]^{2+}$ ions result in the loss of the red $[\text{Fe}(\text{SCN})]^{2+}$ ions?

3. Add 10 – 20 drops of dH₂O to the solid from the centrifugation of the mixture from step 2. Acidify the mixture with 3-5 drops 2 M HNO₃, mixing and stirring until the solid dissolves. Write the chemical equation for this reaction.

Add three drops KSCN, record you observations:

Explain on the molecular level why acidification was required before ion-complex formation could take place.

4. Add 10 drops of 0.1 M AgNO₃. Record your observations. Silver thiocyanate (AgSCN) is insoluble in water. Write the equation for this precipitation reaction.

Explain how adding silver ions affected the concentration of $[\text{Fe}(\text{SCN})]^{2+}$ ions.

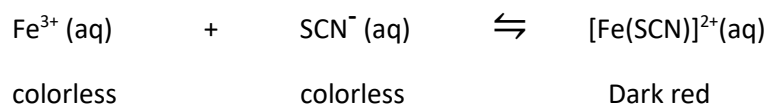
Part III: Temperature and Equilibrium:

Prepare a hot water bath and an ice bath. Pour about 5 ml of your prepared $[\text{Fe}(\text{SCN})]^{2+}$ solution into two separate test tubes. Place one test tube in each water bath and allow the reactions to reach new states of equilibrium (8 - 10 min).

Record your observations:

Explain the effect of the addition or removal of heat energy on the equilibrium of the reaction:

Should head be listed as a product or a reactant? Is this reaction, exothermic or endothermic?



Computer Simulations of Reversible Reactions

Open the Reversible Reactions simulation created by The Univ. of Colorado using the link provided below. Firefox or Chrome internet browsers are recommended.

<https://phet.colorado.edu/sims/cheerpi/ideal-gas/latest/ideal-gas.html?simulation=reversible-reactions>

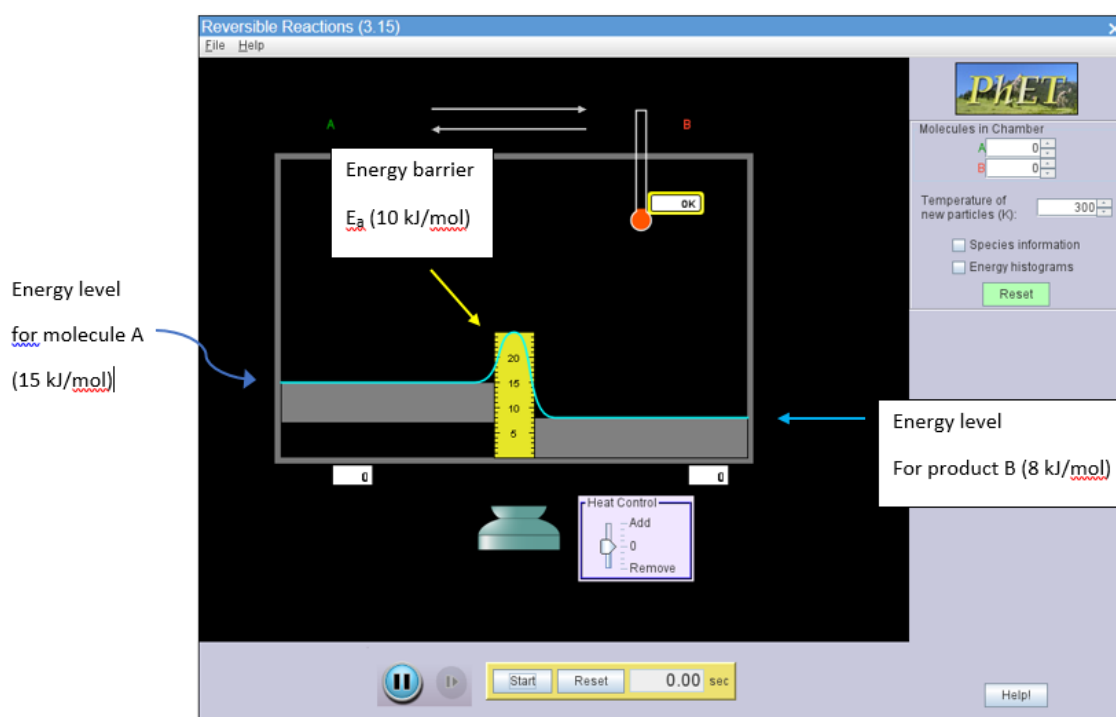


Figure 1. Reversible reactions simulator

Explore the simulation by 'clicking and dragging' on the various settings to see what variables can be adjusted. Note: if the energy barrier is too large, no reaction will occur; if the temperature is too low, no reaction will occur.

Add some molecules to the Reaction Chamber by typing numbers or using the increase/decrease arrow buttons. Note: once a simulation trial is started, energy levels are not changed or adjusted during the simulation. Consider how the **ratio** of green molecules to red molecules changes with time.

With reasonable energy and temperature settings, the simulation reaches a dynamic equilibrium state (DES) after enough time has elapsed. That is, a situation in which components of the system are moving and reacting in both directions, but no net change is observed.

Part IV: Exothermic Reversible Reaction

A. Follow the instructions below and answer the questions:

1. Refresh the page in your browser () for the simulation to adopt its initial settings.
(Potential energy of A = 15 kJ/mol and pot. energy of B = 8 kJ/mol. Activation energy barrier (forward) is 10 (25-10 kJ/mol, yellow scale) as depicted in Figure 1.
The reaction is Exothermic, $\Delta H_{\text{reaction}} = -7 \text{ kJ} / \text{mol}$
2. Set the temperature of new particles to 500 K.
3. Add 100 molecules of "A" (starting molecules) and leave "B" (products) set at zero.
4. Press 'Start' and allow the simulation to proceed.

Questions:

1. When A and B are essentially equal in number, has the reaction reached equilibrium? Circle: YES / NO
2. What is the ratio of B to A when the system reaches Equilibrium?
3. Write the equilibrium expression for the Reaction: $A \rightleftharpoons B$: $K_c =$
4. Calculate the value of K_c using the numbers from your simulation.

B. Follow the instructions below and answer the questions:

1. Reset the simulation using the Green button.
2. Set the temperature of new particles to 500 K.
3. Add 100 molecules of B to the product side.
4. Press Start and allow the simulation to proceed.

Question:

5. What is the ratio of B to A when the system reaches Equilibrium? How does this compare to the ratio in question 3 above?

C. Follow the instructions below and answer the questions:

1. Reset the simulation using the Green button.
2. Set the temperature of new particles to 500 K.
3. Add any number of particles greater than 200 to either side.
4. Press Start and allow the simulation to proceed.

Question:

6. Based on your results, does the equilibrium constant change as the initial numbers of reactant or product are changed, or is it independent of the initial numbers of reactant and product, and remain constant?

Part V: Endothermic Reversible Reaction

A. Follow the instructions below and answer the questions:

1. Reset the simulation using the green button.
2. Switch the energy levels of A and B. Lower A to 8 KJ/mol and raise B to 15 KJ/mol. The reaction is now ENDOTHERMIC, $\Delta H_{\text{reaction}} = +7\text{kJ} / \text{mol}$
3. Set the temperature of new particles to 500 K.
4. Add 100 A molecules.
5. Press Start and allow the simulation to proceed. **Keep it running for Part VI.**

Questions:

7. Which side of the reaction has more molecules when equilibrium is reached? Why?
8. What is the ratio of B to A when the system reaches Equilibrium? How does this compare to the ratio in Exothermic simulation?
9. Calculate the value of the equilibrium constant, Kc.

10. For the simple reversible reaction, $A \rightleftharpoons B$, there will be (more , less) of the **lower energy** molecules, and (more , less) of the **higher energy** molecules, and K_c will be (less than, greater than) 1 for exothermic reactions, and, for an endothermic reaction, K_c will be (less than, greater than) 1.
11. Does the reaction ever stop? Explain your answer to demonstrate your new understanding of equilibrium.

Part VI. LeChatelier's Principle

A. Addition of molecules

1. Go back to the simulation which should be at equilibrium, and without resetting it, or changing any of the parameters, add at least 25 more A molecules to the system.
2. Observe what happens as you add the molecules of A.

Questions.

12. What happens to the number of A molecules over time after initially adding more?
13. What happens to the number of B molecules over time after adding more A?
14. Which direction would you say the reaction shifts upon the addition of A molecules? Towards the reactants or products?
15. Once the system reaches Equilibrium, calculate the value of K_c . How does K_c compare to the value from question 9?

B. Removal of Molecules.

1. Go back to the simulation which should be at equilibrium, and without resetting it, or changing any of the parameters, **REMOVE** at least 25 of the A molecules in the system.
2. Observe what happens as you remove the molecules of A.

Questions.

16. What happens to the number of A molecules after removing some?
17. What happens to the number of B molecules after removing some of the A molecules?
18. Which direction would you say the reaction shifts upon the removal of A molecules? Towards the reactants or products?
19. Once the system reaches Equilibrium, calculate the value of K_c . How does K_c compare to previous values, from questions 9 and 15?

An Equilibrium reaction is one that (is constantly, has stopped) reacting.

By adding or removing molecules from a reaction at equilibrium, the equilibrium will be disturbed.

As a result, the equilibrium reaction will shift (towards, away from) the molecules that are added;

the equilibrium reaction will shift (towards, away from) the molecules that are removed.

The value of the equilibrium constant will (become smaller, become larger, remain the same) when the reaction is disturbed.