**Introduction**

Many chemical reactions reach a state of equilibrium if conditions are right. In an equilibrium system, forward and reverse reactions occur at equal rates so that no net change is produced. When equilibrium is reached by a reaction in a test tube, it appears that changes have stopped in the tube. Once equilbrium has been reached, is it possible to produce further observable changes in the tube? If so, can you control the kinds of changes? If not, why are further observable changes impossible? You will observe several chemical systems in this laboratory activity. A careful study of your observations will enable you to answer these questions.

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**Purpose**

To study factors which can disturb an equilibrium system.

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**Safety Considerations**

Wear protective glasses and an apron at all times. Avoid skin contact with solids and solutions. Exercise caution and use proper technique to handle hot materials safely. Dispose of all solutions in the containers provided by your teacher. Wash your hands before leaving the laboratory.

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**Procedure**

1. Obtain a test tube rack, six small (13 x 100 mm) test tubes that are clean but don't have to be dry, and a test tube clamp. The test tubes should be placed open end up in the test tube rack.
2. Prepare a hot water bath: Half-fill a 250 mL beaker with tap water. Start to heat the water (as your teacher directs) so that the water will be near boiling when you are ready to use it.
3. Prepare an ice water bath: Fill a 250 mL beaker with crushed ice. Add enough tap water to make "slush".
4. Set up a data table with column headings as indicated below (The last column will be completed after data have been collected.)

|  |  |  |  |
| --- | --- | --- | --- |
| 1. System | 1. Disturbance | 1. Observed Change | 1. Direction of Shift |
| 1. 1 |  |  |  |
| 1. 2 |  |  |  |
| 1. etc. |  |  |  |

1. As you set up equilibrium systems and add disturbances to them in the procedure, enter appropriate information in each of the first three columns of your data table.
2. Mix chemicals in test tubes by holding the top of the tube with one hand while you flick the bottom of the tube with your other hand until the tube contents.

**System 1: Iron(III) and thiocyanate**

*Setting Up the Equilibrium*

1. Half-fill the first tube in your rack with distilled water.
2. Add two drops of 0.1 M Fe(NO3)3 and two drops of 0.1 M KSCN to this tube. Mix the contents thoroughly.
3. If the contents of the tube are not red-orange, repeat Step 2 until the solution is red-orange.
4. Divide the red-orange solution in the first tube among six tubes so each tube contains the same volume.

*Chemical Equation for the Equilibrium System*

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Fe3+(aq) | + | SCN-(aq) |  | FeSCN2+(aq) | + | heat |
| Colorless |  | Colorless |  | Red-orange |  |  |
| from Fe(NO3)3 |  | from KSCN |  |  |  |  |

*Disturbing the Equilibrium*

1. Leave Tube 1 undisturbed; use it as a control.
2. Use a clean, dry spatula to add a small crystal or two of solid iron(III) nitrate, Fe(NO3)3, to Tube 2. Mix. Under Disturbance on your data table, record what you did or added to the system to cause the change you observed. In this and all other observations, pay particular attention to color and color change. Always compare with the control tube or you may miss slight color changes. Phrase your Observed Change so the kind of change you observe is indicated, e.g., "lighter red" or "from grey to pink."
3. Use a clean, dry spatula to add one or two small crystals of solid potassium thiocyanate, KSCN, to Tube 3. Mix. Record observations.
4. Add 5 drops of 0.1 M sodium hydroxide, NaOH, to Tube 4. Mix, observe, and record.
5. Use a test tube clamp to place Tube 5 in a hot water bath. When the contents of the tube are hot, observe and record.
6. Use a test tube clamp to place Tube 6 in an ice water bath. When the contents of the tube are cold, observe and record. (Data check: Obtain your teacher's initials.)
7. Discard all test tube contents in the waste container provided by your teacher. Do not pour anything in the sink. Rinse the tubes with tap water; remove as much water as possible by shaking before standing the tubes upright in the test tube rack. Follow these same disposal and rinsing procedures after you complete each system below.

**System 2: Bromothymol blue**

*Setting Up the Equilibrium*

1. Half-fill three test tubes with distilled water.
2. Add three drops of bromothymol blue indicator to each tube. Mix thoroughly.

*Chemical Equation for the Equilibrium*

Bromothymol blue is a weak organic acid with a complex formula. For our purpose, its formula can be abbreviated to HBb.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| HBb(aq) |  | H+(aq) | + | Bb-(aq) |
| Yellow |  | Colorless |  | Blue |

(Green can be observed if approximately equal amounts of yellow and blue forms are present.)

*Disturbing the Equilibrium*

1. To Tube 2 add two drops of 0.1 M hydrochloric acid, HCl, and mix. Observe and record.
2. To Tube 3 add two drops of 0.1 M sodium hydroxide, NaOH, and mix. Observe and record.
3. Explore what happens when you now add NaOH to Tube 2 or HCl to Tube 3. See whether your observations are in agreement with observations you have already recorded.

**System 3: Complex Ions of Copper(II) (Cu2+)**

*Setting Up the Equilibrium*

1. Half fill a test tube with 1.5 M copper(II) chloride, CuCl2, solution.
2. Divide so five tubes contain approximately equal volumes. Equilibrium has already been established in the solution.

*Chemical Equation for the Equilibrium*

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| CuCl42-(aq) | + | 4 H2O(l) |  | Cu(H2O)42+(aq) | + | 4 Cl-(aq) | + | heat |
| Green soln |  | Colorless |  | Light blue soln |  | Colorless |  |  |

*Disturbing the Equilibrium*

1. To Tube 2 add a small quantity (the size of a rice grain) of solid calcium chloride, CaCl2. Mix to dissolve the solid. Repeat the addition and dissolving of solid CaCl2 until no more solid will dissolve. Observe and record.
2. To Tube 3 add enough ethyl alcohol, C2H5OH, to triple the volume of the solution. Mix, observe, and record.
3. Place Tube 4 in a hot-water bath. When the solution is hot, observe and record.
4. Place Tube 5 in an ice-water bath. When the solution is cold, observe and record.

**System 4: Dinitrogen tetroxide (N2O4)**

*Setting Up the Equilibrium*

Dinitrogen tetroxide, N2O4, can decompose into nitrogen dioxide, NO2, a reddish brown poisonous gas. So that you may work with these substances safely, your teacher will provide two sealed tubes each containing a mixture of these subtances. Equilibrium between N2O4 and NO2 has already been established in the tubes.

*Chemical Equation for the Equilibrium*

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| N2O4(g) | + | heat |  | 2 NO2(g) |
| Colorless |  |  |  | Reddish brown |

*Disturbing the Equilibrium*

1. (Caution: N2O4 and NO2 in the sealed glass tubes are poisonous. Handle the tubes carefully to avoid breaking the tubes and releasing the gases.) Place one sealed tube containing the equilibrium system in a hot water bath. When hot, compare to the unheated tube and record.
2. After removing the tube from the hot water bath, cool it under running cold tap water. Then place the tube in an ice-water bath. When cold, compare to the unchilled tube and record.

**System 5: Complex Ions of Cobalt(II) (Co2+)**

*Setting Up the Equilibrium*

1. Half-fill a test tube with 1.5 M cobalt(II) chloride, CoCl2.
2. Divide the solution so five tubes contain approximately equal volumes. Equilibrium has already been established in the solution.

*Chemical Equation for the Equilibrium*

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| heat | + | Co(H2O)62+(aq) | + | 4 Cl-(aq) |  | CoCl42-(aq) | + | 6 H2O(l) |
|  |  | Red |  | Colorless |  | Blue |  | Colorless |

*Disturbing the Equilibrium*

1. To Tube 2 add a small quantity (the size of a rice grain) of solid calcium chloride, CaCl2. Mix to dissolve the solid. Repeat the addition and dissolving of solid CaCl2 until no more solid will dissolve. Observe and record.
2. To Tube 3 add enough acetone, CH3COCH3, to double the volume of the solution. Mix, observe, and record.
3. Place Tube 4 in a hot water bath. When the solution is hot, observe and record.
4. Place Tube 5 in an ice water bath. When the solution is cold, observe and record.
5. Wash hands thoroughly before leaving the laboratory.

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**Data Analysis, Concept**

1. To complete the fourth column on the right side of your data table (headed Direction of Shift), decide whether each disturbance caused the equilibrium system to shift left or right. Record the direction of shift in this column. How do you decide direction of shift? Consider the equilibrium system

|  |  |  |
| --- | --- | --- |
| 1. A |  | 1. B |
| 1. Yellow |  | 1. Green |
| 1. If a disturbance causes the system to become more yellow, chemists would say that the equilibrium position has shifted to the left because the system must have moved to produce more of the yellow molecules shown on the left side of the chemical equation. If the system shifted to the right you would observe more green in the system. The direction of shift is "right". Use these ideas to decide and record the direction of shift caused by each disturbance. | | |

1. Use your data table to find all cases where a disturbance was caused by heating. After you have found all of these cases, answer the following:
   1. How does the direction of shift relate to the side of the chemical equation on which the heat term is written?
   2. Write a rule which would allow you to predict how other equilibrium systems would shift when disturbed in this way.
2. Use your data table to find all cases where equilibrium systems were disturbed by cooling.
   1. How does the direction of shift relate to the side of the chemical equation on which the heat term is written?
   2. Write a rule which would allow you to predict how other equilibrium systems would shift when disturbed in this way.
3. Use your data table to examine all cases where a disturbance was caused by increasing the concentration of a substance already present in the equilibrium system. Hint: Adding solid Fe(NO3)3 to System 2 increases the concentration of Fe3+(aq) and NO3-(aq) when the solid dissolves. Adding HCl solution to System 3 increases the concentration of both H+(aq) and Cl-(aq) in the system. Write a rule which would explian how the direction of shift relates to the side of the chemical reaction on which the substance with increased concentration is written.
4. In some cases the equilibrium system was disturbed by decreasing the concentration of a substance in the system. Usually this is done by adding another substance not involved in the equilibrium which reacts with a substance in the system, changing it to a different substance. For example, in System 1 you added 0.1 M NaOH (containing aqueous Na+ and OH- ions). OH- reacts with Fe3+ to form the precipitate Fe(OH)3(s). This decreases the concentration of Fe3+(aq) remaining in the solution. Concentration can also be decreased by adding another solvent (acetone or alcohol) to dilute the water in the system. Identify substances whose concentration is decreased in as many cases as you can. For each, explain what causes the concentration of a particular substance to decrease. Write chemical equations where possible.  The equation for the example above is:

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| 1. Fe3+(aq) | 1. + | 1. 3 OH-(aq) |  | 1. Fe(OH)3(s) |

1. For each case involving a decrease in concentration, identify the substance that is decreased in concentration, on which side of the equation this substance is found, and which way the equilibrium is observed to shift.
2. Consider cases where equilibrium was disturbed by decreasing the concentration of a substance in the equilibrium system.
   1. How does the direction of shift relate to the side of the chemical equation on which the substance with altered concentration is written?
   2. Write a rule which would allow you to predict how other equilibrium systems would shift when disturbed in this way.
3. Write a general rule that would cover all of the types of disturbances you have observed. Write your rule so it can be used to predict the effect of any temperature or concentration disturbance on an equilibrium system.

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**Imply, Apply**

1. Explain why no visible changes can be observed when a system is at equilibrium. Express your answer in terms of the rates of the forward and reverse reactions.
2. What effect would each of the following have on the rate of a reaction?
   1. increasing the concentration of a reactant
   2. decreasing the concentration of a reactant
   3. increasing the temperature of the system
   4. decreasing the temperature of the system
3. Are the rates of both the forward and reverse reactions still equal immediately after an equilibrium system is disturbed? Support your answer with observations you have made.
4. Which direction of shift would you observe if only
   1. the rate of the forward reaction is increased?
   2. the rate of the reverse reaction is increased?
   3. the rate of the forward reaction is decreased?
   4. the rate of the reverse reaction is decreased?
5. Can shifts in equilibrium systems be explained by considering the effect of a disturbance on the separate rates of forward and reverse reactions? Support your answer with evidence.
6. Consider the equilibrium system

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| 1. PbSO4(s) | 1. + | 1. 2 I-(aq) | 1. + | 1. heat |  | 1. PbI2(s) | 1. + | 1. SO42-(aq) |
| 1. White |  | 1. Colorless |  |  |  | 1. Yellow |  | 1. Colorless |

1. Indicate the Direction of Shift and the Predicted Observable Change, given the following:
   1. add NaI solution
   2. add AgNO3 solution
   3. Ag+(aq) + I-(aq) AgI(s)
   4. add Ba(NO3)2 solution
   5. Ba2+(aq) + SO42-(aq)  BaSO4(s)
   6. add Na2SO4 solution
   7. heat the system
   8. cool the system
2. Ammonia, NH3, is produced industrially by the reaction:

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| 1. N2(g) | 1. + | 1. 3 H2(g) |  | 1. 2 NH3(g) | 1. + | 1. heat |

1. Discuss at least three ways a chemist could shift this equilibrium system so that a greater amount of ammonia is produced at equilibrium.
2. Assume that you add water to a certain ionic solid and stir, but observe that the solid will not completely dissolve. The solubility equilibrium of the ionic solid is represented by the equation:

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| 1. AB(s) | 1. + | 1. heat |  | 1. A+(aq) | 1. + | 1. B-(aq) |

Discuss two things you could possibly do to get the solid to dissolve more completely.