

Properties of Systems in Chemical Equilibrium—Le Châtelier's Principle

When working in the laboratory, one often makes observations that at first sight are surprising and hard to explain. One might add a reagent to a solution and obtain a precipitate. Addition of more of that reagent to the precipitate causes it to dissolve. A violet solution turns yellow on addition of a reagent. Subsequent addition of another reagent brings back first a green solution and then the original violet one. Clearly, chemical reactions are occurring, but how and why they behave as they do is not at once obvious.

In this experiment we will examine and attempt to explain several observations of the sort we have mentioned. Central to our explanation will be recognition of the fact that chemical systems tend to exist in a state of equilibrium. If one disturbs the equilibrium in one way or another, the reaction may shift to the left or right, producing the kinds of effects we have mentioned. If one can understand the principles governing the equilibrium system, it is often possible to see how one might disturb the system, such as by adding a particular reagent or heat, and so cause it to change in a desirable way.

Before proceeding to specific examples, let us examine the situation in a general way, noting the key principle that allows us to make a system in equilibrium behave as we wish. Consider the reaction



where A, B, and C are molecules or ions in solution. If we have a mixture of these species in equilibrium, it turns out that their concentrations are not completely unrelated. Rather, there is a condition that those concentrations must meet, namely that

$$\frac{[B] \times [C]}{[A]} = K_c \quad (2)$$

where K_c is a constant, called the equilibrium constant for the reaction. For a given reaction at any given temperature, K_c has a particular value.

When we say that K_c has a particular value, we mean just that. For example, we might find that, for a given solution in which Reaction 1 can occur, when we substitute the equilibrium values for the molarities of A, B, and C into Equation 2, we get a value of 10 for K_c . Now, suppose we add more of species A to that solution. What will happen? Remember, K_c can't change. If we substitute the new higher molarity of A into Equation 2 we get a value that is smaller than K_c . This means that the system is not in equilibrium, and *must* change in some way to get back to equilibrium. How can it do this? It can do this by shifting to the right, producing more B and C and using up some A. It *must* do this, and *will*, until the molarities of C, B, and A reach values that, on substitution into Equation 2, equal 10. At that point the system is once again in equilibrium. In the new equilibrium state, [B] and [C] are greater than they were initially, and [A] is larger than its initial value but smaller than if there had been no forced shift to the right.

The conclusion you should reach on reading the last paragraph is that *one can always cause a reaction to shift to the right by increasing the concentration of a reactant*. An *increase* in concentration of a *product* will force a *shift to the left*. By a similar argument we find that a *decrease* in *reactant* concentration causes a *shift to the left*; a *decrease* in *product* concentration produces a *shift to the right*. This is all true because K_c does not change (unless you change the temperature). The changes in concentration that one can produce by adding particular reagents may be simply enormous, so the shifts in the equilibrium system may also be enormous. Much of the mystery of chemical behavior disappears once you understand this idea.

Another way one might disturb an equilibrium system is by changing its temperature. When this happens, the value of K_c changes. It turns out that the change in K_c depends upon the enthalpy change, ΔH , for the reaction. If ΔH is positive, greater than zero (endothermic reaction), K_c increases with increasing T . If ΔH is negative (exothermic reaction), K_c decreases with an increase in T . Let us return to our original equilibrium between A, B, and C, where K_c equals 10. Let us assume that ΔH for Reaction 1 is -40 kJ. If we raise the temperature, K_c will go down ($\Delta H < 0$), say to a value of 1. This means that the system will no longer be in equilibrium. Substitution of the initial values of [A], [B], and [C] into Equation 2 produces a value that is too big, 10 instead of 1. How can the system change itself to regain equilibrium? It must of necessity shift to the left, lowering [B] and [C] and raising [A]. This will make the expression in Equation 2 smaller. The shift will continue until the concentrations of A, B, and C, on substitution into Equation 2, give the expression a value of 1.

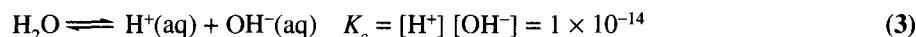
From the discussion in the previous paragraph, you should be able to conclude that an equilibrium system will shift to the left on being heated if the reaction is exothermic ($\Delta H < 0$, K_c goes down). It will shift to the right if the reaction is endothermic ($\Delta H > 0$, K_c goes up). Again, since we can change temperatures very markedly, we can shift equilibria a long, long way. An endothermic reaction that at 25°C has an equilibrium state that consists mainly of reactants might at 1000°C exist almost completely as products.

The effects of concentration and temperature on systems in chemical equilibrium are often summarized by Le Châtelier's principle. The principle states that:

If you attempt to change a system in chemical equilibrium, it will react in such a way as to counteract the change you attempted.

If you think about the principle for a while, you will see that it predicts the same kind of behavior as we did by using the properties of K_c . Increasing the concentration of a reactant will, by the principle, cause a change that decreases that concentration; that change must be a shift to the right. Increasing the temperature of a reaction mixture will cause a change that tends to absorb heat; that change must be a shift in the endothermic direction. The principle is an interesting one, but does require more careful reasoning in some cases than the more direct approach we employed. For the most part we will find it more useful to base our arguments on the properties of K_c .

In working with aqueous systems, the most important equilibrium is often that which involves the dissociation of water into H^+ and OH^- ions:



In this reaction the concentration of water is very high and is essentially constant at about 55 M; it is incorporated into K_c . The value of K_c is very small, which means that in **any** water system the product of $[\text{H}^+]$ and $[\text{OH}^-]$ must be very small. In pure water, $[\text{H}^+]$ equals $[\text{OH}^-]$ equals 1×10^{-7} M.

Although the product, $[\text{H}^+] \times [\text{OH}^-]$ is small, that does not mean that both concentrations are necessarily small. If, for example, we dissolve HCl in water, the HCl in the solution will dissociate completely to H^+ and Cl^- ions; in 1 M HCl, $[\text{H}^+]$ will become 1 M, and there is nothing that Reaction 3 can do about changing that concentration appreciably. Rather, Reaction 3 must occur in such a direction as to maintain equilibrium. It does this by lowering $[\text{OH}^-]$ by reaction to the left; this uses up a little bit of H^+ ion and drives $[\text{OH}^-]$ to the value it must have when $[\text{H}^+]$ is 1 M, namely, 1×10^{-14} M. In 1 M HCl, $[\text{OH}^-]$ is a factor of ten million *smaller* than it is in water. This makes the properties of 1 M HCl quite different from those of water, particularly where H^+ and OH^- ions are involved.

If we take 1 M HCl and add a solution of NaOH to it, an interesting situation develops. Like HCl, NaOH is completely dissociated in solution, so in 1 M NaOH, $[\text{OH}^-]$ is equal to 1 M. If we add 1 M NaOH to 1 M HCl, we will initially raise $[\text{OH}^-]$ ions way above 1×10^{-14} M. However, Reaction 3 cannot be in equilibrium when both $[\text{H}^+]$ and $[\text{OH}^-]$ are high; reaction must occur to re-establish equilibrium. The added OH^- ions react with H^+ ions to form H_2O , decreasing both concentrations until equilibrium is established. If only a small amount of OH^- ion is added, it will essentially all be used up; $[\text{H}^+]$ will remain high, and $[\text{OH}^-]$ will still be very small, but somewhat larger than 10^{-14} M. If we add OH^- ion until the amount added equals in moles the amount of H^+ originally present, then Reaction 3 will go to the left until $[\text{H}^+]$ equals $[\text{OH}^-]$ equals 1×10^{-7} M, and both concentrations will be very small. Further addition of OH^- ion will raise $[\text{OH}^-]$ to much higher

values, easily as high as 1 M. In such a solution, $[H^+]$ would be very low, 1×10^{-14} M. So, in aqueous solution, depending on the solutes present, we can have $[H^+]$ and $[OH^-]$ range from about 1 M to 10^{-14} M, or 14 orders of magnitude. This will have a tremendous effect on **any** other equilibrium system in which $[H^+]$ or $[OH^-]$ ions are reactants. Similar situations arise in other equilibrium systems in which the concentration of a reactant or product can be changed significantly by adding a particular reagent.

In many equilibrium systems, several equilibria are present simultaneously. For example, in aqueous solution, Reaction 3 must **always** be in equilibrium. There may, in addition, be equilibria between the solutes in the aqueous solution. Some examples are those in Reactions 4, 5, 7, 8, 9, and 10 in the Experimental Procedure section. In some of those reactions, H^+ and OH^- ions appear; in others, they do not. In Reaction 4, for example, H^+ ion is a product. The molarity of H^+ in Reaction 4 is *not* determined by the indicator HMV, since it is only present in a tiny amount. Reaction 4 will have an equilibrium state that is fixed by the state of Reaction 3, which as we have seen depends markedly on the presence of solutes such as HCl or NaOH. Reactions 8 and 9 can similarly be controlled by Reaction 3. Reactions 5 and 7, which do not involve H^+ or OH^- ions, are not dependent on Reaction 3 for their equilibrium state. Reaction 10 is sensitive to NH_3 concentration and can be driven far to the right by addition of a reagent such as 6 M NH_3 .

WEAR YOUR SAFETY GLASSES WHILE
PERFORMING THIS EXPERIMENT

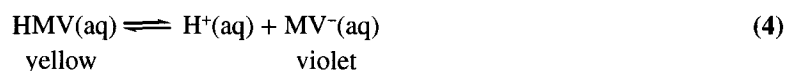


Experimental Procedure

In this experiment we will work with several equilibrium systems, each of which is similar to the A-B-C system we discussed. We will alter these systems in various ways, forcing shifts to the right and left by changing concentrations and temperature. You will be asked to interpret your observations in terms of the principles we have presented.

A. Acid-Base Indicators

There is a large group of chemical substances, called acid-base indicators, which change color in solution when $[H^+]$ changes. A typical substance of this sort is called methyl violet, which we will give the formula HMV. In solution HMV dissociates as follows:

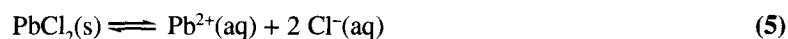


HMV has an intense yellow color, while the anion MV^- is violet. The color of the indicator in solution depends very strongly on $[H^+]$.

- Step 1** Add about 5 mL of distilled water to a regular (18 × 150 mm) test tube. Add a few drops of methyl violet indicator. Report the color of the solution on the Data page.
- Step 2** How could you force the equilibrium system to go to the other form (color)? Select a reagent that should do this and add it to the solution, drop by drop, until the color change is complete. If your reagent works, write its formula on the Data page. If it doesn't, try another until you find one that does. Work with 6 M reagents if they are available.
- Step 3** Equilibrium systems are reversible. That is, the reaction can be driven to the left and right many times by changing the conditions in the system. How can you force the system in Step 2 to revert to its original color? Select a reagent that should do this and add it drop by drop until the color has become the original one. Again, if your first choice was incorrect, try another reagent. On the Data page write the formula of the reagent that was effective. Answer all the questions for Part A before going on to Part B.

B. Solubility Equilibrium; Finding a Value for K_{sp}

Many ionic substances have limited water solubility. A typical example is PbCl_2 , which dissolves to some extent in water according to the reaction



The equilibrium constant for this reaction takes the form

$$K_c = [\text{Pb}^{2+}] \times [\text{Cl}^{-}]^2 = K_{sp} \quad (6)$$

The PbCl_2 does not enter into the expression because it is a solid, and so has a constant effect on the system, independent of its amount. The equilibrium constant for a solubility equilibrium is called the solubility product, and is given the symbol K_{sp} .

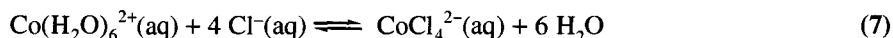
For the equilibrium in Reaction 5 to exist, there *must* be some solid PbCl_2 present in the system. If there is no solid, there is no equilibrium; Equation 6 is not obeyed, and $[\text{Pb}^{2+}] \times [\text{Cl}^{-}]^2$ must be *less* than the value of K_{sp} . If the solid is present, even in a tiny amount, then the values of $[\text{Pb}^{2+}]$ and $[\text{Cl}^{-}]$ are subject to Equation 6.

- Step 1** Set up a hot-water bath, using a 400-mL beaker half full of water. Start heating the water with a burner while proceeding with Step 2.
- Step 2** To a regular test tube add 5.0 mL 0.30 M $\text{Pb}(\text{NO}_3)_2$. In this solution $[\text{Pb}^{2+}]$ equals 0.30 M. Add 5.0 mL 0.30 M HCl to a 10-mL graduated cylinder. In this solution $[\text{Cl}^{-}]$ equals 0.30 M. Add 1 mL of the HCl solution to the $\text{Pb}(\text{NO}_3)_2$ solution. Stir, and wait about 15 seconds. What happens? Enter your result.
- Step 3** To the $\text{Pb}(\text{NO}_3)_2$ solution add the HCl in 1-mL increments until a noticeable amount of white solid PbCl_2 is present after stirring. Record the total volume of HCl added at that point.
- Step 4** Put the test tube with the precipitate of PbCl_2 into the hot-water bath. Stir for a few moments. What happens? Enter your observations. Cool the test tube under the cold-water tap. What happens?
- Step 5** Rinse out your graduated cylinder and then add about 5.0 mL of distilled water to the cylinder. Add water in 1-mL increments to the mixture in the test tube, stirring well after each addition. Record the volume of water added when the precipitate just dissolves. Answer the questions and do the calculations in Part B before proceeding.

C. Complex Ion Equilibria

Many metallic ions in solution exist not as simple ions but, rather, as complex ions in combination with other ions or molecules, called ligands. For example, the Co^{2+} ion in solution exists as the pink $\text{Co}(\text{H}_2\text{O})_6^{2+}$ complex ion, and Cu^{2+} as the blue $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ complex ion. In both of these ions the ligands are H_2O molecules. Complex ions are reasonably stable but may be converted to other complex ions on addition of ligands that form more stable complexes than the original ones. Among the common ligands that may form complex species, OH^{-} , NH_3 , and Cl^{-} are important.

An interesting Co(II) complex is the CoCl_4^{2-} ion, which is blue. This ion is stable in concentrated Cl^{-} solutions. Depending upon conditions, Co(II) in solution may exist as either $\text{Co}(\text{H}_2\text{O})_6^{2+}$ or as CoCl_4^{2-} . The principles of chemical equilibrium can be used to predict which ion will be present:



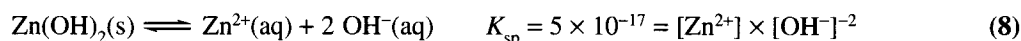
- Step 1** Put a few small crystals (~0.1 g) of $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ in a regular test tube. Add 2 mL of 12 M HCl **CAUTION:** and stir to dissolve the crystals. Record the color of the solution.
- Step 2** Add 2-mL portions of distilled water, stirring after each dilution, until no further color change occurs. Record the new color.

- Step 3** Place the test tube into the hot-water bath and note any change in color. Cool the tube under the water tap and report your observations. Complete the questions in Part C before continuing.

D. Dissolving Insoluble Solids

We saw in Part B that we can dissolve more PbCl_2 by either heating its saturated solution or by simply adding water. In most cases these procedures won't work very well on other solids because they are typically much less soluble than PbCl_2 .

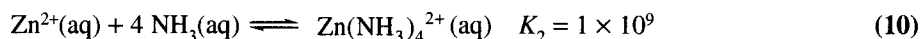
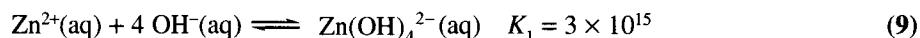
There are, however, some very powerful methods for dissolving solids that depend on their effectiveness upon the principles of equilibrium. As an example of an insoluble substance, we might consider Zn(OH)_2 :



The equilibrium constant for Reaction 8 is very small, which tells us that the reaction does not go very far to the right or, equivalently, that Zn(OH)_2 is almost completely insoluble in water. Adding a few drops of a solution containing OH^{-} ion to one containing Zn^{2+} ion will cause precipitation of Zn(OH)_2 .

At first sight you might well wonder how one could possibly dissolve, say, 1 mole of Zn(OH)_2 in an aqueous solution. If, however, you examine Equation 8, you can see, from the equation for K_{sp} , that in the saturated solution $[\text{Zn}^{2+}] \times [\text{OH}^{-}]^2$ must equal 5×10^{-17} . If, by some means, we can lower that product to a value *below* 5×10^{-17} , then Zn(OH)_2 will dissolve, until the product becomes equal to K_{sp} , where equilibrium will again exist. To lower the product, we need to lower the concentration of either Zn^{2+} or OH^{-} very drastically. This turns out to be very easy to do. To lower $[\text{OH}^{-}]$ we can add H^{+} ions from an acid. If we do that, we drive Reaction 3 to the left, making $[\text{OH}^{-}]$ very, very small—small enough to dissolve substantial amounts of Zn(OH)_2 .

To lower $[\text{Zn}^{2+}]$ we can take advantage of the fact that zinc(II) forms stable complex ions with both OH^{-} and NH_3 :



In high concentrations of OH^{-} ion, Reaction 9 is driven strongly to the right, making $[\text{Zn}^{2+}]$ very low. The same thing would happen in solutions containing high concentrations of NH_3 . In both media we would therefore expect that Zn(OH)_2 might dissolve, since if $[\text{Zn}^{2+}]$ is very low, Reaction 8 must go to the right.

- Step 1** To each of three small test tubes add about 2 mL 0.1 M $\text{Zn(NO}_3)_2$. In this solution $[\text{Zn}^{2+}]$ equals 0.1 M. To each test tube add one drop 6 M NaOH and stir. Report your observations.
- Step 2** To the first tube add 6 M HCl drop by drop, with stirring. To the second add 6 M NaOH, again drop by drop. To the third add 6 M NH_3 . Note what happens in each case.
- Step 3** Repeat Steps 1 and 2, this time using a solution of 0.1 M $\text{Mg(NO}_3)_2$. Record your observations. Answer the questions in Part D.

DISPOSAL OF REACTION PRODUCTS. The residues from Parts B and C should be poured in the waste crock. Those from Parts A and D may be poured down the sink.

Name _____ Section _____

Experiment 22**Data and Observations: Properties of Systems in Chemical Equilibrium****A. Acid-Base Indicators**

1. Color of methyl violet in water _____
2. Reagent causing color change _____
3. Reagent causing shift back _____. Explain, by considering how changes in $[H^+]$ will cause Reaction 4 to shift to right and left, why the reagents in Steps 2 and 3 caused the solution to change color. Note that Reactions 3 and 4 must both go to equilibrium after a reagent is added.

B. Solubility Equilibrium; Finding a Value for K_{sp}

2. Vol. 0.30 M $Pb(NO_3)_2 = 5.0$ mL No. moles $Pb^{2+}(M \times V(\text{lit})) = 1.5 \times 10^{-3}$ moles

Observations:

3. Vol. 0.30 M HCl used _____ mL No. moles Cl^- added _____ moles
4. Observations: in hot water _____ in cold water _____
5. Volume H_2O added to dissolve $PbCl_2$ _____ mL

Total volume of solution _____ mL

- a. Explain why $PbCl_2$ did not precipitate immediately on addition of HCl. (What condition must be met by $[Pb^{2+}]$ and $[Cl^-]$ if $PbCl_2$ is to form?)
- b. Explain your observations in Step 4. (In which direction did Reaction 5 shift when heated? What must have happened to the value of K_{sp} in the hot solution? What does this tell you about the sign of ΔH in Reaction 5?)
- c. Explain why the $PbCl_2$ dissolved when water was added in Step 5. (What was the effect of the added water on $[Pb^{2+}]$ and $[Cl^-]$? In what direction would such a change drive Reaction 5?)

(continued on following page)

- d. Given the numbers of moles of Pb^{2+} and Cl^- in the final solution in Step 5, and the volume of that solution, calculate $[\text{Pb}^{2+}]$ and $[\text{Cl}^-]$ in that solution.

$[\text{Pb}^{2+}]$ _____ M; $[\text{Cl}^-]$ _____ M

Noting that the molarities just calculated are essentially those in equilibrium with solid PbCl_2 , calculate $[\text{Pb}^{2+}] \times [\text{Cl}^-]^2$. This is equal to K_{sp} for PbCl_2 .

$K_{\text{sp}} =$ _____

C. Complex Ion Equilibria

1. Color of $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$

Color in solution in 12 M HCl

2. Color in diluted solution

3. Color of hot solution

Color of cooled solution

Formula of Co(II) complex ion present in solution in

- a. 12 M HCl

- b. diluted solution

- c. hot solution

- d. cooled solution

Explain the color change that occurred when

- a. water was added in Step 2. (Consider how a change in $[\text{Cl}^-]$ and $[\text{H}_2\text{O}]$ will shift Reaction 7.)
- b. the diluted solution was heated. (How would Reaction 7 shift if K_c went up? How did increasing the temperature affect the value of K_c ? What is the sign of ΔH in Reaction 7?)

(continued on following page)

D. Dissolving Insoluble Solids

1. Observations on addition of a drop of 6 M NaOH to $\text{Zn}(\text{NO}_3)_2$ solution:
2. Effect on solubility of $\text{Zn}(\text{OH})_2$:
 - a. of added HCl solution
 - b. of added NaOH solution
 - c. of added NH_3 solution
3. Observations on addition of one drop of 6 M NaOH to $\text{Mg}(\text{NO}_3)_2$ solution:

Effect on solubility of $\text{Mg}(\text{OH})_2$:

- a. of added HCl solution
- b. of added NaOH solution
- c. of added NH_3 solution

Explain your observations in Step 1. (Consider Reaction 8; how is it affected by addition of OH^- ion?)

In Step 2a, how does an increase in $[\text{H}^+]$ affect Reaction 3? (What does that do to Reaction 8?) Explain your observations in Step 2a.

In Step 2b, how does an increase in $[\text{OH}^-]$ affect Reaction 9? What does that do to Reaction 8? Explain your observations in Step 2b.

In Step 2c, how does an increase in $[\text{NH}_3]$ affect Reaction 10? What does that do to Reaction 8? Explain your observations in Step 2c.

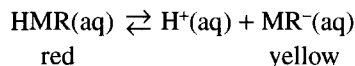
In Step 3, you probably found that $\text{Mg}(\text{OH})_2$ was similar in some ways in its behavior to that of $\text{Zn}(\text{OH})_2$, but different in others.

- a. How was it similar? Explain that similarity. (In particular, why would any insoluble hydroxide tend to dissolve in acidic solution?)
- b. How was it different? Explain that difference. (In particular, does Mg^{2+} appear to form complex ions with OH^- and NH_3 ? What would we observe if it did? If it did not?)

Name _____ Section _____

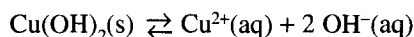
Experiment 22**Advance Study Assignment: Systems in Chemical Equilibrium**

1. Methyl red, HMR is a common acid-base indicator. In solution it ionizes according to the equation:



If methyl red is added to distilled water, the solution turns yellow. If a drop or two of 6 M HCl is added to the yellow solution, it turns red. If to that solution one adds a few drops of 6 M NaOH the color reverts to yellow.

- Why does adding 6 M HCl to the yellow solution of methyl red tend to cause the color to change to red? (Note that in solution HCl exists as H^+ and Cl^- ions.)
 - Why does adding 6 M NaOH to the red solution tend to make it turn back to yellow? (Note that in solution NaOH exists as Na^+ and OH^- ions. How does increasing $[\text{OH}^-]$ shift Reaction 3 in the discussion section? How would the resulting change in $[\text{H}^+]$ affect the dissociation reaction of HMR?)
2. Copper hydroxide is only very slightly soluble in water. The reaction by which it goes into solution is:



- Formulate the expression for the equilibrium constant, K_{sp} , for the above reaction.
- It is possible to dissolve significant amounts of Cu(OH)_2 in solutions in which the concentration of either Cu^{2+} or OH^- is very, very small. Explain, using K_{sp} , why this is the case.
- Explain why Cu(OH)_2 might have very appreciable solubility in 1 M HCl. (Consider the effect of Reaction 3 on the Cu(OH)_2 solution reaction.)