



Chemical Equilibrium: Le Chatelier's Principle

Examples of Chemical Equilibria

Objective

- Observe several interesting and colorful chemical reactions that are examples of chemical systems at equilibrium.
- See how these chemical systems respond to changes in the concentrations of reactants or products or to changes in temperature.
- Learn how the shift in equilibrium tends to at least partially offset the change in conditions, a principle first clearly stated by Le Châtelier.

Discussion

A state of equilibrium is the point of balance where the rate of the forward reaction equals the rate of the reverse reaction. For these reactions, the same point of equilibrium can be reached from either end of the reaction, by mixing together either the reactants or the products, clearly indicating that chemical reactions can go either forward or backward. Adding or removing a component, in an equilibrium system, will disturb the dynamic balance between two rates by forcing the forward and reverse reaction rates to become unequal. In order for the chemical system to reestablish equilibrium the concentration of all components must change. One way of predicting these concentration shifts is through the use of Le Chatelier's principle: *When a stress is applied to a system at equilibrium (a change in concentrations, temperature, pressure, volume), the system will shift in the direction that reduces the stress and return unaided to a new equilibrium.*

This introductory experiment is designed to show qualitatively several important features of chemical equilibria. In subsequent experiments, you will learn about the quantitative aspects of chemical equilibria, measuring the equilibrium constants for a variety of reactions, and making calculations of equilibrium concentrations from previously measured equilibrium constants.

Experimental Procedure

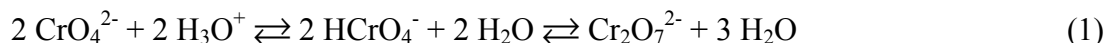
Supplies: Electric hot plate; crushed ice; polyethylene transfer pipets (25 drops/mL).

Chemicals: 1 M K_2CrO_4 ; 3 M H_2SO_4 ; 6 M NaOH; 0.1% methyl orange indicator; 0.1% phenolphthalein indicator; 6 M HCl; 0.1 M CH_3COOH (acetic acid); 1 M $NaCH_3COO$ (sodium acetate); 0.1 M NH_3 ; 1 M NH_4Cl ; 0.1 M $Fe(NO_3)_3$; 0.1 M KSCN (potassium thiocyanate); 0.15 M anhydrous $CoCl_2$, in methanol (20 g anhydrous $CoCl_2$ per liter of methanol; if only the hydrated salt $CoCl_2 \cdot 6H_2O$ is available, it must be dried before use); concentrated (12 M) HCl; saturated (5.4 M) NaCl; 0.1 M $BaCl_2$; 0.1 M $CaCl_2$; 0.5 M $H_2C_2O_4$ (oxalic acid); 0.5 M $K_2C_2O_4$ (potassium oxalate); 6 M NH_3 .

1. The Shifting of Equilibria in Acid–Base Reactions; The Common Ion Effect

(a) The Chromate Ion–Dichromate Ion Equilibrium.

Yellow chromate ion reacts with hydrogen ion first to form hydrogen chromate ion and then, by condensation and loss of H_2O , orange dichromate ion:



Examples of Chemical Equilibria

For this experiment we need consider only the overall equilibrium,

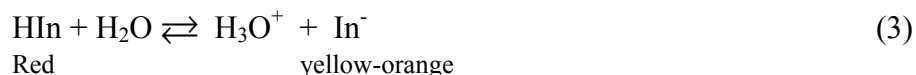


CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ are known to be carcinogenic. Rinse them off immediately if they contact your skin. Dispose of them in waste containers in the fume hood. Do not pour them down the drain.

To 3 mL of 1 M K_2CrO_4 in a test tube, add several drops of 3 M H_2SO_4 . Mix this and observe any change. Now add several drops of 6 M NaOH, stirring continuously, until a change occurs. Again add H_2SO_4 . Interpret the observed changes. How did the equilibrium shift in response to the added reagents—toward the formation of yellow chromate ion or toward the formation of orange dichromate ion? Explain how the addition of hydroxide ion exerts an effect, even though it doesn't appear in the overall equation.

(b) Weak Acid–Base Indicator Equilibria.

First we will observe the effects of strong acid and strong base on indicators, which are themselves weak acids and bases. The chemical equation for the dissociation of the indicator methyl orange can be written as



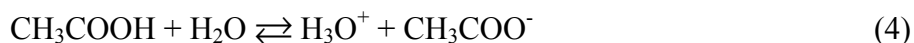
where HIn represents the protonated (acid) form of the indicator (red in color) and In^- represents the deprotonated (or base) form of the indicator (yellow-orange in color). Methyl orange indicator changes color around pH 4, which corresponds to a hydronium ion concentration of 10^{-4} M. (For a more complete discussion of indicators and the pH scale, see your text.)

Other acid–base indicators change color at different hydronium ion concentrations. Phenolphthalein, whose acid form is colorless, changes to the pink base form around pH 9, which corresponds to a hydronium ion concentration of 10^{-9} M.

First, in order to observe the effects of acid and base on indicators, add a drop of methyl orange to 3 mL of water. Then add 2 drops of 6 M HCl, record your observations, followed by 4 drops of 6 M NaOH. Repeat the experiment, using phenolphthalein indicator in place of the methyl orange. Record your observations.

(c) Weak Acid–Weak Base Equilibria.

Now we will use the indicators to observe changes involving weak acids and bases that are themselves colorless. To each of two 3-mL samples of 0.1 M CH_3COOH (acetic acid), add a drop of methyl orange. To one of the samples, add 1 M NaCH_3COO (sodium acetate), a few drops at a time, with mixing. Compare, then record the colors in the two test tubes. The added salt, sodium acetate, has an ion in common with acetic acid, a weak acid that dissociates in water to give acetate ion:



Note that adding acetate ion produces a change in the color of the indicator. The color change indicates that the indicator has been changed from its acid to its base form, which in turn must mean that the hydrogen ion concentration became smaller when the sodium acetate was added. Explain your observations in terms of the equilibria shown in Equations (3) and (4). The effect on the dissociation of acetic acid that is produced by adding sodium acetate is called the common ion effect. To each of two 3-

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mL samples of 0.1 M NH_3 , add a drop of phenolphthalein indicator. Note and record the color. To one sample, add 1 M NH_4Cl , a few drops at a time, with mixing. To the other add 6 M HCl , a drop at a time, with mixing. In each case, note any changes in the solution's color and odor.

Write the equation for the reaction of NH_3 with water to form NH_4^+ and OH^- . Interpret the results in terms of the changes of H_3O^+ concentration (shown by the color change of the indicator) and the equilibrium for the reaction of NH_3 with water. Explain clearly how the equilibria shift when NH_4^+ ions (from NH_4Cl) and H_3O^+ (from HCl) are added. Write the net ionic equation for the reaction of NH_3 with HCl .

2. Complex Ion Equilibria

It is common for cations (especially those with +2 or +3 charge) to attract negatively charged ions (or neutral molecules with lone pairs of electrons) to form aggregates called *complexes*. If the resulting aggregate has a net charge, it is called a *complex ion*. The composition of these complexes may vary with the proportion and concentration of reactants.

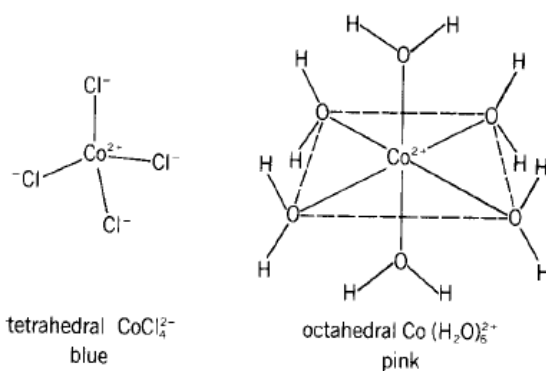
(a) The Thiocyanatoiron(III) Complex Ion.

This ion, sometimes called the ferric thiocyanate complex ion, is formed as a blood-red substance described by the equilibrium equation.



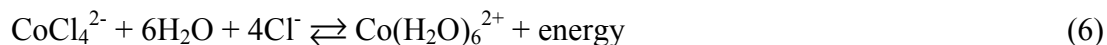
In a 100-mL beaker, add 1 mL of 0.1 M $\text{Fe}(\text{NO}_3)_3$ to 1 mL of 0.1 M KSCN . Dilute by adding 15 to 20 mL of water until the deep-red color is reduced in intensity, making further changes (either increases or decreases in color) easy to see. Put 5 mL of this solution in a test tube; add 1 mL (about 25 drops) of 0.1 M $\text{Fe}(\text{NO}_3)_3$. To a 5-mL portion in a second test tube, add 1 mL of 0.1 M KSCN . To a third 5-mL portion, add 5 to 6 drops of 6 M NaOH . [$\text{Fe}(\text{OH})_3$ is very insoluble.] Put remainder (a fourth 5-mL portion) in a tube to *serve as a control*. Compare the relative intensity of the red color of the thiocyanato complex in each of the first three test tubes to that of the original solution in the fourth tube. Interpret your observations, using Le Châtelier's principle and considering the equilibrium shown in Equation (5).

(b) The Temperature-Dependent Equilibrium of Co(II) Complex Ions.



The chloro complex of cobalt(II), CoCl_4^{2-} , is tetrahedral and has a blue color. The aquo complex of cobalt(II), $\text{Co}(\text{H}_2\text{O})_6^{2+}$, is octahedral and has a pink color. (Figure-1 shows the geometry of the tetrahedral and octahedral complexes.) There is an equilibrium between the two forms in aqueous solution, and because the conversion of one form to another involves a considerable energy change, the equilibrium is temperature dependent:

Figure-1: The cobalt(II) complexes with chloride ion and water have different molecular geometries and different colors.



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Le Châtelier's principle applied to Equation (6) predicts that, if energy is removed (by cooling the system), the equilibrium tends to shift toward the aquo complex, because a shift in this direction produces some energy, thus partly offsetting the change.

Put 3 mL of 0.15 M CoCl_2 (in methanol) into a 13 x 100 mm test tube. (Methanol is used as a solvent so that you can observe the effects of adding water.) Using a dropper, add just enough water to the blue methanol solution to change the color to that of the pink aquo complex. Divide the pink solution into two equal portions in two 13 x 100 mm test tubes. Add concentrated (12 M) HCl one drop at a time to one test tube until you observe a color change. Record your observations. Heat the test tube containing the other portion of the pink solution in a beaker of hot water (65 to 70 °C) on a hot plate in a fume hood.

Take care when heating the methanol solution of CoCl_2 . Methanol vapors are toxic and flammable, so the heating must be done by placing the test tube in a beaker of hot water at 65 to 70 °C on a hot plate in the *fume hood*.

You should note a color change. (If you do not, you probably added too much water to the original methanol solution. Try again.) The color change is reversible. Cooling the solution in an ice bath will restore the original pink color. Repeat the cycle of heating and cooling to verify this. Record your observations, and interpret them by applying Le Châtelier's principle to the equilibrium shown in Equation (6).

3. The Equilibria of Saturated Solutions

(a) Saturated Sodium Chloride.

To 4 mL of saturated (5.4 M) sodium chloride in a 13 x 100 mm test tube, add 2 mL of concentrated (12 M) HCl. Mix, observe, and record your observations. The Cl^- concentration in the original solution is 5.4 M (the same as the NaCl concentration). Calculate the total Cl^- concentration that the solution would have immediately after adding 2 mL of 12 M HCl (before anything happens), and explain what you observed in terms of the saturated solution equilibrium.

(b) Saturated Barium Chromate.

To 3 mL of 0.1 M BaCl_2 , add 5 to 6 drops of 1 M K_2CrO_4 , stir, and then add 10 to 12 drops of 6 M HCl. Record your observations. Write an equation for the reaction of Ba^{2+} with CrO_4^{2-} . Using the equation you have written, explain how the addition of HCl shifts the equilibrium of the reaction. [Recall your observations in part 1 as summarized by Equation (2).]

Ba^{2+} is toxic. Rinse them off immediately if they contact your skin. Dispose of them in waste containers. Do not pour them down the drain.

4. Application of the Law of Chemical Equilibrium to Solubility Equilibria

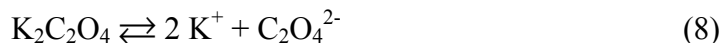
In qualitative analysis (QA), Ca^{2+} is usually precipitated as insoluble calcium oxalate:



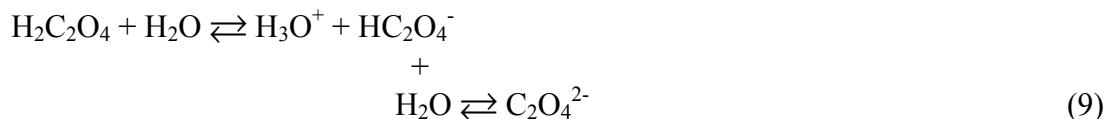
What conditions will make the precipitation as complete as possible? Since Ca^{2+} is the unknown ion in QA, it is desirable to drive the reaction (7) as far as possible to the right by obtaining the maximum $\text{C}_2\text{O}_4^{2-}$ concentration possible. Would it be better to use a substance that completely dissociates, such as the soluble salt $\text{K}_2\text{C}_2\text{O}_4$, or a substance that forms only a slight amount of oxalate ion, such as the weak acid $\text{H}_2\text{C}_2\text{O}_4$?

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The dissociation equilibria are



and



Would it be better to make the solution acidic or basic to achieve the maximum $\text{C}_2\text{O}_4^{2-}$ concentration? Test your reasoning by the following experiments. Mix 4 mL of 0.1 M CaCl_2 with 4 mL of deionized water and place equal portions in three 13 x 100 mm test tubes. To tube 1, add 0.3 mL (6 to 7 drops) of 0.5 M $\text{H}_2\text{C}_2\text{O}_4$; to tube 2, add 0.3 mL (6 to 7 drops) of 0.5 M $\text{K}_2\text{C}_2\text{O}_4$. Compare the results. In your notebook (records), refer to these experiments as solution 1 and solution 2, respectively. To tube 1, add 0.5 mL (10 drops) of 6 M HCl and mix well. (For purposes of your recorded data, refer to this new mixture as solution 3.) Explain the results. Now, again to the solution in tube 1, add a slight excess of 6 M NH_3 , and mix well. (Refer to this mixture as solution 4.) Is the precipitate that forms $\text{Ca}_2\text{C}_2\text{O}_4$ or $\text{Ca}(\text{OH})_2$? { $\text{Ca}(\text{OH})_2$ could be a possible product because the reaction of NH_3 with water generates some OH^- ion.}

To find out if the precipitate is $\text{Ca}(\text{OH})_2$, add a few drops of 6 M NH_3 to the third tube that you prepared (the one that contains diluted 0.1 M CaCl_2 solution). (For reference, call this solution 5.) Does a precipitate form? From this result, what conclusion can you draw about the identity of the precipitate in solution 4? Explain all of your results in terms of the equilibria shown in Equations (7), (8), and (9) and the reaction with acid of NH_3 :



In Chapter 16 we will consider the properties and reaction of weak acid/bases and their anions/cations in greater detail. For now contemplate whether the acidity of the solution be more important in the precipitation of the salt of a strong acid or in the precipitation of the salt of a weak acid? To put this question another way, is H_3O^+ more effective in competing with the metal ion for the anion of a strong acid or the anion of a weak acid?



Chemical Equilibria: Le Chatelier's Principle Report Form

Name: _____

Partner's Name: _____ (if any) Lab Section: MW/TTH/M-TH/F
(circle)

Observations and Data

1. Shifting of equilibria in acid-base reactions; Stress due to common ion.

(a) The Chromate Ion-Dichromate Ion Equilibrium

(i) Observation when H_2SO_4 is added to the K_2CrO_4 solution

Use net ionic equation and write out the pertinent equilibrium that illustrates what happened when H_2SO_4 was added to the K_2CrO_4 solution.

Indicate the stress applied, the shift in equilibrium and the concentration changes of all reactants and products in the resulting equilibrium.

Equation:	<input type="text"/>	+	<input type="text"/>	\rightleftharpoons	<input type="text"/>	+	<input type="text"/>
	yellow				orange		
Stress.....	<input type="text"/>						
Shift	<input type="text"/>						
New Equilibrium: {Increase (I), Decrease (D)}	<input type="text"/>	+	<input type="text"/>	\rightleftharpoons	<input type="text"/>	+	<input type="text"/>

(ii) Observation when NaOH is added to the K_2CrO_4 solution. _____

(iii) Briefly explain how OH^- exert an effect on the $\text{CrO}_4^{2-}/\text{Cr}_2\text{O}_7^{2-}$ equilibrium? _____

Provide a balanced net ionic equation to support your argument.



(iv) Interpret your observations in terms of the equilibrium described in part (i) and Le Châtelier's principle.

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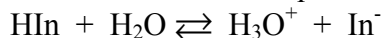
(b) Weak Acid–Base Indicator Equilibria

(i) Describe the effects of adding...

HCl to methyl orange _____ HCl to phenolphthalein _____

NaOH to methyl orange _____ NaOH to phenolphthalein _____

Interpret these effects in terms of the indicator equilibrium equation given below and Le Châtelier's principle.



(c) Weak Acid–Weak Base Equilibria

(i) Complete the equation for the dissociation equilibrium of acetic acid in water.



Predict the direction of the shift in the above equilibrium when 1 M sodium acetate is added to 0.1 M acetic acid containing methyl orange indicator. _____

Are the observed changes to the methyl orange indicator consistent with Le Châtelier's principle upon the addition of 1 M sodium acetate? Briefly explain.

(ii) Complete the equation for the reaction of ammonia with water: $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons$

Describe any *observed odor or color changes* when you add the following to 0.1 M $\text{NH}_3(\text{aq})$ containing phenolphthalein indicator:

NH_4Cl - _____

HCl - _____

Indicate in which direction, left (\leftarrow) or right (\rightarrow), does each reagent above shift the equilibrium for the reaction of NH_3 with water?

Adding NH_4Cl =	adding HCl =
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Explain clearly the shift indicated in the ammonia with water equilibrium using Le Châtelier's principle and the observed color change in the phenolphthalein indicator.

When NH_4Cl is added -

_____.

When HCl is added – Start with the net ionic equation between HCl and NH_3 .

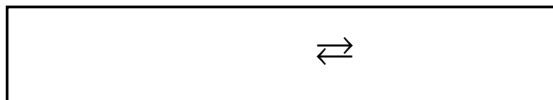
_____.

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2. Complex ion equilibria

(a) The Thiocyanatoiron(III) Complex Ion

Write the equation for this equilibrium {Eq'n (5)}.



The complex ion, $[\text{Fe}(\text{H}_2\text{O})_5(\text{SCN})]^{2+}$, is responsible for the observed red color. Compare the intensity of the red color upon addition of each of the following with the intensity of the color in tube 4. Interpret your observations in terms of the equation describing the equilibrium and Le Châtelier's principle.

$\text{Fe}(\text{NO}_3)_3$ - lighter / darker **-red; equilibrium shifts-** left right {circle your choices}

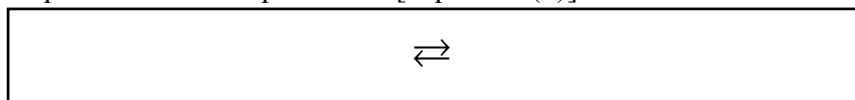
KSCN - lighter / darker **-red; equilibrium shifts-** left right {circle your choices}

NaOH – {The brown precipitate formed is due to the reaction: $\text{Fe}^{3+} + 3 \text{OH}^- \rightleftharpoons \text{Fe}(\text{OH})_3(\text{s})$.}

Red color lighter / darker / disappears; **equilibrium shifts-** left right {circle your choices}

(b) The Temperature-Dependent Equilibrium of Co(II) Complex Ions

Write the equation for this equilibrium [Equation (6)].



What happens when you add 12 M HCl (or Cl^-) to the pink (aquo) complex?

solution turns blue-purple / pink; **equilibrium shifts-** left right {circle your choices}

What happens when you heat the pink (aquo) complex and when you cool it?

heat solution turns blue-purple / pink; **cool** solution turns blue-purple / pink {circle}

Explain *why* these results occur in terms of the equation describing the equilibrium and Le Châtelier's principle.

3. The equilibria of saturated solutions

(a) Saturated Sodium Chloride

What happens when 12 M HCl is added to saturated (5.4 M) NaCl?

nothing solution turn transparent a precipitate forms {circle your choice}

The $[\text{Cl}^-]$ in the original saturated solution is 5.4 M. What is the Cl^- concentration

(i) just after addition of the 12 M HCl (before anything occurs)?

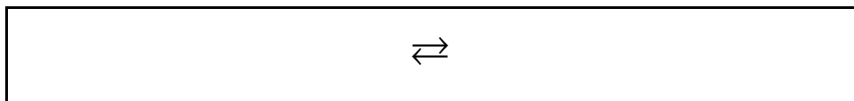
Explain this behavior in terms of the $[\text{Cl}^-]$ in the two solutions, and in terms of the equilibrium equation $\text{NaCl}(\text{s}) \rightleftharpoons \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$.

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(b) *Saturated Barium Chromate*

Write a balanced equation for the reaction that occurs when K_2CrO_4 and $BaCl_2$ solutions are mixed.

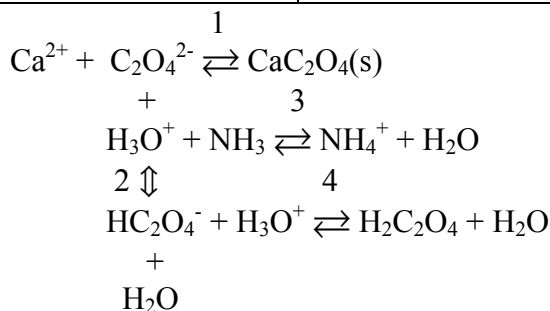
Write a balanced equation describing the equilibrium that is established upon mixing K_2CrO_4 and $BaCl_2$ solutions.



Explain the changes observed when this equilibrium (above) is treated with 6 M HCl.

4. Application of the law of chemical equilibrium to solubility equilibria

Solutions mixed	Relative amounts of precipitate, if any
(1) $CaCl_2(aq) + H_2C_2O_4(aq)$	
(2) $CaCl_2(aq) + K_2C_2O_4(aq)$	
(3) Results of (1) + 6 M HCl	
(4) Results of (3) + 6 M NH_3	
(5) $CaCl_2(aq) + 6 M NH_3$	



Answer questions (a) and (d), relating these data on the relative amounts of $CaC_2O_4(s)$ formed, or dissolved, under various conditions to the following coupled equilibrium equations. *The equilibria are said to be coupled because each equilibrium shares at least one species in common with another equilibrium.*

(a) Account for the difference in behavior of $H_2C_2O_4$ and $K_2C_2O_4$ in tubes 1 and 2 toward $CaCl_2$. Specifically, why does one solution form so much more $CaC_2O_4(s)$? {Hint: Consider the nature of the electrolytes.}

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(b) From this array of coupled equilibria, explain the effect of adding HCl on these equilibria. {Note that H_3O^+ participates in equilibria 2, 3, and 4.} Why does the addition of HCl change the amount of $\text{CaC}_2\text{O}_4(\text{s})$?

(c) Consider solutions 4 and 5, where NH_3 was added. How does ammonia affect the amount of $\text{CaC}_2\text{O}_4(\text{s})$ present in solution 4?

(i) Does $\text{Ca}(\text{OH})_2(\text{s})$ form when NH_3 is added to a Ca^{2+} solution (solution 5)? _____

(d) Why does the H_3O^+ concentration have more influence on the precipitation of the salt of a weak acid, such as $\text{CaC}_2\text{O}_4(\text{s})$, than on the precipitation of the salt of a strong acid, such as $\text{AgCl}(\text{s})$ or $\text{CaSO}_4(\text{s})$?