

## Theoretical vs. Experimental Results

Thermodynamics and equilibrium chemistry provide powerful theoretical approaches to modeling chemical reactions. Using these theories we can model chemical systems by predicting the favorability of reactions, predicting the composition of the reaction mixture at equilibrium and predicting how a system at equilibrium responds to a change in conditions. Such models assume what we might call “ideal” conditions and, under non-ideal conditions, experimental results do not always match theoretical predictions.

**Theoretical Predictions.** Consider the equilibrium reaction and equilibrium constant for the solubility of AgBr



Equilibrium theory tells us that for a saturated solution of AgBr in deionized water, the concentrations of  $\text{Ag}^+$  and  $\text{Br}^-$  are equal; thus

$$K_{\text{sp}} = [\text{Ag}^+][\text{Br}^-] = [\text{Ag}^+]^2 = 5.0 \times 10^{-13}$$

$$[\text{Ag}^+] = [\text{Br}^-] = 7.1 \times 10^{-7} \text{ M}$$

Before continuing, make sure that everyone in your group can explain why this is true.

According to Le Châtelier's principle...

...adding additional  $\text{Ag}^+$  ions in the form of  $\text{AgNO}_3$  will cause the  $[\text{Br}^-]$  to

*Decrease; adding  $\text{Ag}^+$  will increase  $Q$  so that it is larger than  $K_{\text{sp}}$ , pushing the reaction back to the left and decreasing the concentration of  $\text{Br}^-$ .*

... adding additional  $\text{Br}^-$  ions in the form of  $\text{KBr}$  will cause the  $[\text{Ag}^+]$  to

*Decrease; same reason as above*

... adding  $\text{KNO}_3$  will cause the  $[\text{Ag}^+]$  to

*Stay the same; neither  $\text{K}^+$  or  $\text{NO}_3^-$  is involved in the equilibrium reaction and, therefore, should not affect  $Q$ .*

... adding  $\text{KNO}_3$  will cause the  $[\text{Br}^-]$  to

*Stay the same; same reason as above.*

**Experimental Results.** The table below shows experimental determinations of the  $[\text{Ag}^+]$  and  $[\text{Br}^-]$  in solutions containing different amounts of  $\text{KNO}_3$ . Calculate the  $K_{\text{sp}}$  values.

$[\text{KNO}_3], \text{M}$	$[\text{Ag}^+], \text{M}$	$[\text{Br}^-], \text{M}$	$K_{\text{sp}}$
0	$7.1 \times 10^{-7}$	$7.1 \times 10^{-7}$	$5.0 \times 10^{-13}$
$1 \times 10^{-5}$	$7.1 \times 10^{-7}$	$7.1 \times 10^{-7}$	$5.0 \times 10^{-13}$
$1 \times 10^{-4}$	$7.2 \times 10^{-7}$	$7.2 \times 10^{-7}$	$5.2 \times 10^{-13}$
$1 \times 10^{-3}$	$7.3 \times 10^{-7}$	$7.3 \times 10^{-7}$	$5.3 \times 10^{-13}$
$1 \times 10^{-2}$	$7.9 \times 10^{-7}$	$7.9 \times 10^{-7}$	$6.2 \times 10^{-13}$
$1 \times 10^{-1}$	$9.5 \times 10^{-7}$	$9.5 \times 10^{-7}$	$9.0 \times 10^{-13}$

To what extent do these experimental results agree with the theoretical predictions?

*The  $K_{\text{sp}}$  values for concentrations of 0 and  $1 \times 10^{-5} \text{ M KNO}_3$  agree with the theoretical value for  $K_{\text{sp}}$  of  $5.0 \times 10^{-13}$ .*

To what extent do these experimental results disagree with the theoretical predictions?

*The  $K_{\text{sp}}$  values for concentrations of  $\text{KNO}_3$  greater than  $1 \times 10^{-5}$  increase as the concentration of  $\text{KNO}_3$ . This disagrees with the prediction that  $\text{KNO}_3$  should not affect the position of the equilibrium reaction.*

What is the effect on the solubility of  $\text{AgBr}$  of increasing the concentration of  $\text{KNO}_3$ ?

*The greater the concentration of  $\text{KNO}_3$ , the greater the solubility of  $\text{AgBr}$ .*

**Building a New Theoretical Model.** AgBr is an ionic compound, which is held together by the electrostatic attraction between the  $\text{Ag}^+$  ions and the  $\text{Br}^-$  ions. What factors affect the strength of an ionic bond? Feel free to use your textbook if you need to review ionic bonding and electrostatic attraction.

*The strength of an ionic bond is directly proportional to the charges of the ions and inversely proportional to the distances separating the charges.*

Given the strong attraction between oppositely charged ions, what might prevent all of the  $\text{Ag}^+$  ions and  $\text{Br}^-$  ions from recombining to form AgBr? Hint: the solvent, water, is a polar molecule. Explain your answer in terms of the factors affecting the electrostatic attraction between ions.

*Polar water molecules will be attracted to the ions. For a water molecule near an cation, for example, the partial negative charges on the oxygen atom will become oriented toward and attracted to the positive charge. In order for a  $\text{Ag}^+$  and a  $\text{Br}^-$  ion to form an ionic bond, releasing energy, some energy must go into disrupting this interaction between the water molecules and the ions, decreasing the overall  $\Delta H$  for the reaction and making the formation of the bond a bit less likely.*

What happens at molecular level when you add a strong electrolyte such as  $\text{KNO}_3$  to a saturated solution of AgBr. Sketch a picture showing an  $\text{Ag}^+$  ion in an aqueous solution containing  $\text{NO}_3^-$  ions. Repeat for  $\text{Br}^-$  ions in an aqueous solution containing  $\text{K}^+$  ions.

*In the presence of inert electrolyte such as  $\text{KNO}_3$ , the  $\text{Ag}^+$  cations are surrounded by a small excess of  $\text{NO}_3^-$  relative to  $\text{K}^+$ . The opposite is true for the  $\text{Br}^-$  ions, which are surrounded by a small excess of  $\text{K}^+$  relative to  $\text{NO}_3^-$ .*

Explain, in words, why the solubility of AgBr increases with an increasing concentration of  $\text{KNO}_3$ .

*As noted above, disrupting the attractive interactions between the ions requires some energy, which makes the formation of the Ag-Br ionic bond less likely. In addition, the force of attraction between  $\text{Ag}^+$  and  $\text{Br}^-$  is less because each ion “sees” less of a charge on the other ion due to the interfering ions.*

**Making a New Theoretical Prediction.** Will AgBr be more soluble, less soluble, or equally soluble in 0.1 M  $\text{Mg}(\text{NO}_3)_2$  than in 0.1 M  $\text{KNO}_3$ ? Explain your reasoning.

*An equimolar solution of  $\text{Mg}(\text{NO}_3)_2$  will have a greater concentration of ions relative to  $\text{KNO}_3$  and will have cations with a greater charge. Together, these suggest that  $\text{Mg}(\text{NO}_3)_2$  will have a greater impact on solubility, making AgBr even more soluble.*

**Experimental Results.** The table below shows  $K_{sp}$  values for AgBr in several different solutions.

Solution Electrolyte	[electrolyte], M	$[Ag^+] = [Br^-]$	$K_{sp}$
Deionized water	0	$7.1 \times 10^{-7}$	$5.0 \times 10^{-13}$
KNO <sub>3</sub>	$1 \times 10^{-5}$	$7.1 \times 10^{-7}$	$5.0 \times 10^{-13}$
	$1 \times 10^{-4}$	$7.2 \times 10^{-7}$	$5.2 \times 10^{-13}$
	$1 \times 10^{-3}$	$7.3 \times 10^{-7}$	$5.3 \times 10^{-13}$
	$1 \times 10^{-2}$	$7.9 \times 10^{-7}$	$6.2 \times 10^{-13}$
	$1 \times 10^{-1}$	$9.5 \times 10^{-7}$	$9.0 \times 10^{-13}$
Mg(NO <sub>3</sub> ) <sub>2</sub>	$1 \times 10^{-5}$	$7.1 \times 10^{-7}$	$5.0 \times 10^{-13}$
	$1 \times 10^{-4}$	$7.2 \times 10^{-7}$	$5.2 \times 10^{-13}$
	$1 \times 10^{-3}$	$7.6 \times 10^{-7}$	$5.8 \times 10^{-13}$
	$1 \times 10^{-2}$	$8.7 \times 10^{-7}$	$7.6 \times 10^{-13}$
	$1 \times 10^{-1}$	$1.2 \times 10^{-6}$	$1.4 \times 10^{-12}$

Do these experimental results agree with the theoretical predictions? If your answer is no, then return to the previous page and reconsider your answers. Do not proceed until everyone in your group understands why AgBr is more soluble in a solution of Mg(NO<sub>3</sub>)<sub>2</sub> than in an equimolar solution of KNO<sub>3</sub>.

*Yes; the solubility of AgBr is greater in equimolar Mg(NO<sub>3</sub>)<sub>2</sub>.*

Given what you have learned in completing this worksheet, explain why a calculation for the pH of a solution of 0.10 M sodium acetate is not likely to be exactly the same as an experimental determination of the pH of the same solution.

*A solution of sodium acetate will have Na<sup>+</sup> ions (as well as H<sub>3</sub>O<sup>+</sup> and OH<sup>-</sup>). The presence of the ions is likely to have some effect on the position of the equilibrium and, therefore, the pH of the solution.*

Why is it okay to make simplifying assumptions when solving equilibrium problems?

*Because the concentration of dissolved ions affects the value of an equilibrium constant, there must be some uncertainty in whether the published, thermodynamic equilibrium constant is "correct" for the solution being considered. Given that there is some uncertainty in the value for  $K_{eq}$ , we can tolerate some uncertainty in our calculations.*

**So, Where Do Equilibrium Constants Come From?** The equilibrium constants in your textbook are for ideal solutions; that is, for solutions in which there are no interactions between ions. Interestingly, for a solubility reaction this constraint is impossible since the equilibrium reaction itself involves ions.

The effect of an ion on an equilibrium constant involves both the ion's concentration and its charge. A common method for accounting for both concentration and charge is ionic strength,  $\mu$ , which is defined as

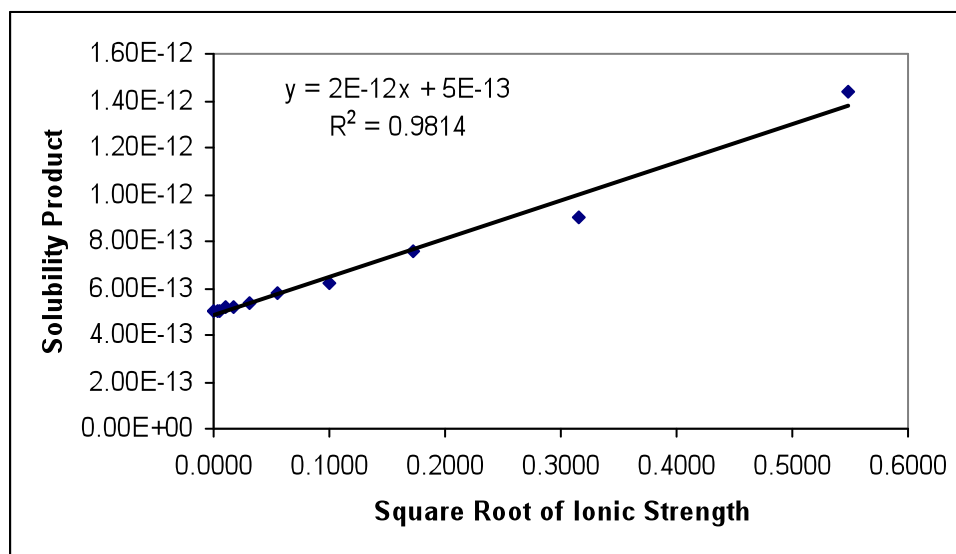
$$\mu = \frac{1}{2} \sum_{i=1}^n c_i z_i^2$$

where  $n$  is the number of different types of ions,  $c_i$  is the concentration of an ion and  $z_i$  is the ion's charge. The unit for ionic strength is molarity. Calculate the ionic strength for each of the solutions in the table on page 4. Be sure to include the concentrations of  $\text{Ag}^+$  and  $\text{Br}^-$ , as well as the concentrations of the ions from the strong electrolyte.

For a relatively small range of ionic strengths, a plot of  $K_{\text{sp}}$  (on the y-axis) as a function of  $\sqrt{\mu}$  is a straight-line. Extrapolating this line to an ionic strength of zero gives the thermodynamic equilibrium constant. Construct such a plot for the data in table on page 4, using the ionic strengths determined above. Fit a straight-line to the data and report the value for the thermodynamic  $K_{\text{sp}}$ .

Solution Electrolyte	[electrolyte], M	$[\text{Ag}^+] = [\text{Br}^-]$	$K_{\text{sp}}$	$\mu$
Deionized water	0	$7.1 \times 10^{-7}$	$5.0 \times 10^{-13}$	$7.10 \times 10^{-5}$
$\text{KNO}_3$	$1 \times 10^{-5}$	$7.1 \times 10^{-7}$	$5.0 \times 10^{-13}$	$1.07 \times 10^{-5}$
	$1 \times 10^{-4}$	$7.2 \times 10^{-7}$	$5.2 \times 10^{-13}$	$1.01 \times 10^{-4}$
	$1 \times 10^{-3}$	$7.3 \times 10^{-7}$	$5.3 \times 10^{-13}$	$1.00 \times 10^{-3}$
	$1 \times 10^{-2}$	$7.9 \times 10^{-7}$	$6.2 \times 10^{-13}$	$1.00 \times 10^{-2}$
	$1 \times 10^{-1}$	$9.5 \times 10^{-7}$	$9.0 \times 10^{-13}$	$1.00 \times 10^{-1}$
$\text{Mg}(\text{NO}_3)_2$	$1 \times 10^{-5}$	$7.1 \times 10^{-7}$	$5.0 \times 10^{-13}$	$3.07 \times 10^{-5}$
	$1 \times 10^{-4}$	$7.2 \times 10^{-7}$	$5.2 \times 10^{-13}$	$3.01 \times 10^{-4}$
	$1 \times 10^{-3}$	$7.6 \times 10^{-7}$	$5.8 \times 10^{-13}$	$3.00 \times 10^{-3}$
	$1 \times 10^{-2}$	$8.7 \times 10^{-7}$	$7.6 \times 10^{-13}$	$3.00 \times 10^{-2}$
	$1 \times 10^{-1}$	$1.2 \times 10^{-6}$	$1.4 \times 10^{-12}$	$3.00 \times 10^{-1}$

A plot of  $K_{\text{sp}}$  vs.  $\mu^{1/2}$  is shown below.



*The thermodynamic equilibrium constant is the y-intercept, or  $5.0 \times 10^{-13}$ .*

*A thermodynamic  $K_{sp}$  has limited use since it applies only to a solution with an ionic strengths of zero. Any calculation that uses a thermodynamic equilibrium constant will give a prediction that will differ from the experimental result and this difference will be greater for larger ionic strengths. The relationship between  $K_{sp}$  and  $\sqrt{\mu}$ , however, suggests that appropriate corrections are possible; that, however, is a topic for another day and another course.*