Theoretical Vs. Experimental Results

Thermodynamics and equilibrium chemistry are powerful theoretical approaches that allow us to model chemical reactions. Using these theories we can predict the favorability of a reaction and how that favorability depends on temperature, and predict the composition of a reaction mixture at equilibrium and how a system at equilibrium responds to a change in conditions. Our treatment of these theoretical models assumes what we might call “ideal”" conditions. Under non-ideal conditions, experimental results may not match theoretical predictions; the purpose of this worksheet is to understand why this is true for a system at equilibrium.

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

$$\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag}^{+}(aq) + \mathrm{Br}^{-}(aq)$$
$$K_{\mathrm{sp}} = 5.0 \times 10^{-13}$$

What are the expected equilibrium concentrations of Ag^+ and of Br^- in a saturated solution of AgBr prepared by adding solid AgBr to deionized water?

Answer. The concentrations of the two ions are equal to each other; thus

$$[\mathrm{Ag}^{+}] = [\mathrm{Br}^{-}] = \sqrt{K_{\mathrm{sp}}} = \sqrt{5.0 \times 10^{-13}} = 7.1 \times 10^{-7}$$

For each of the following, predict what will happen to the equilibrium concentration of Ag^+ in a saturated solution of AgBr if you add (a) a small amount of solid KBr, (b) a small amount of solid KNO_3. Explain how you arrived at each of your predictions.

Answers.

(a) From Le Châtelier’s Principle, adding a source of Br^- will increase its concentration and decreases the concentration of Ag^+.

(b) Adding KNO_3 should have no effect on the equilibrium concentration of Ag^+ because neither K^+ or KNO_3 will react with Ag^+ or with Br^-.

Experimental Results. The table below shows the equilibrium concentrations of Ag^+ and of Br^- in a saturated solution of AgBr after adding KNO_3; note that KNO_3 is a strong electrolyte that dissociates completely in solution.

KNO_3 (M)	Ag^+ (M)	Br^- (M)
0	7.1×10^{-7}	7.1×10^{-7}
1.0×10^{-6}	7.1×10^{-7}	7.1×10^{-7}
1.0×10^{-5}	7.1×10^{-7}	7.1×10^{-7}
1.0×10^{-4}	7.2×10^{-7}	7.2×10^{-7}
1.0×10^{-3}	7.3×10^{-7}	7.3×10^{-7}
1.0×10^{-2}	7.9×10^{-7}	7.9×10^{-7}
1.0×10^{-1}	9.5×10^{-7}	9.5×10^{-7}

To what extent are these results consistent with your theoretical predictions from the previous page?

Answer. The equilibrium concentrations of Ag^+ and of Br^- match the expected value for the first three entries in the table.

To what extent are these results inconsistent with your theoretical predictions from the previous page?

Answer. The equilibrium concentrations of Ag^+ and of Br^- do not match the expected value for the last four entries in the table.

What is the effect on the solubility of AgBr of increasing the concentration of KNO_3?

Answer. The solubility of AgBr increases when the concentration of KNO_3 is greater than 1.0×10^{-5} M.

Building a New Theoretical Model. AgBr is an ionic compound that is held together by the electrostatic attraction between the Ag^+ ions and the 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.

Answer. The strength of an ionic bond is directly proportional to the charges of the ions and inversely proportional to the distances separating the charges. This is Coulomb's law.

Given the strong attraction between oppositely charged ions, what might prevent some of the Ag^+ ions and some of the Br^- ions from recombining to form AgBr when solid AgBr is added to deionized water? Hint: the solvent, water, is a polar molecule. Explain your answer in terms of the factors that affect the electrostatic attraction between ions. To support your answer, draw a picture that shows how water molecules are arranged around the Ag^+ ions and the Br^- ions.

Answer. Polar water molecules are attracted to the ions. For a water molecule near a cation, for example, the partial negative charges on water's oxygen are oriented toward and attracted to the cations and the partial positive charge on water's hydrogens are oriented toward and attracated to the anions. In order for a Ag^+ and a Br^- ion to form an ionic bond, releasing energy, some energy goes into disrupting this interaction between the water molecules and the ions, which makes the overall ΔH less negative, making the formation of the bond a bit less likely and increasing the solubility of AgBr.

Now, consider what happens when you add a strong electrolyte such as KNO_3 to a saturated solution of AgBr. Sketch a picture that shows an Ag^+ ion in an aqueous solution that contains NO_3^- ions. Repeat for a Br^- ion in an aqueous solution that contains K^+ ions.

Answer. In the presence of inert electrolyte such as KNO_3, the Ag^+ cations are surrounded by a small excess of NO_3^- relative to K^+. The opposite is true for the Br^- ions, which are surrounded by a small excess of K^+ relative to NO_3^-. For the same reasons as above, the effect is to increase the solubility of AgBr.

Making a New Theoretical Prediction. Based on your answers above, why does the solubility of AgBr increase with an increasing concentration of KNO_3?

Answer. 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 Ag^+ and Br^- is less because each ion "sees" less of a charge on the other ion due to the interfering ions.

Do you expect that AgBr is more soluble, less soluble, or equally soluble in 0.1 M $Mg(NO_3)_2$ as it is in 0.1 M KNO_3? Explain your reasoning.

Answer. An equimolar solution of $Mg(NO_3)_2$ has a greater total concentration of ions relative to KNO_3 and has cations with a greater charge. Together, these suggest that $Mg(NO_3)_2$ has a greater impact on solubility, making AgBr even more soluble.

The molar solubility of AgBr in 0.1 M KNO_3 is 9.5×10^{-7} and its molar solubility in 0.1 M $Mg(NO_3)_2$ is 1.2×10^{-6}. Do these experimental results agree with your theoretical predictions? If your answer is no, then return to the previous page and reconsider your answers.

Answer. Yes; the solubility of AgBr is greater in equimolar $Mg(NO_3)_2$ than in KNO_3.

Based on the data considered in this worksheet, explain why a calculation for the pH of a solution of 0.10 M sodium acetate is not likely to agree exactly with an experimental determination of the solution's pH.

Answer. A solution of sodium acetate has Na^+ ions and acetate ions (as well as H_3O^+ and OH^- ions). The presence of these ions is likely to have some affect on the position of the equilibrium and, therefore, the pH of the solution.

Based on the data considered in this worksheet, explain why is it okay to make simplifying assumptions when solving equilibrium problems?

Answer. Because the concentration of dissolved ions affects the value of an equilibrium constant there is 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, we can tolerate some uncertainty in our calculations.

So Where Do Equilibrium Constants Come From if an Ideal Solution is Impossible? Most of the equilibrium constants in your textbook are reported for an ideal solution in which there are no interactions between ions. Interestingly, for a solubility reaction this constraint is impossible since the equilibrium reaction itself creates ions.

The effect of an ion on an equilibrium constant involves both the ion’s concentration and its charge. A common way to account for both concentration and charge is to calculate a solution’s ionic strength, μ, which is defined as

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

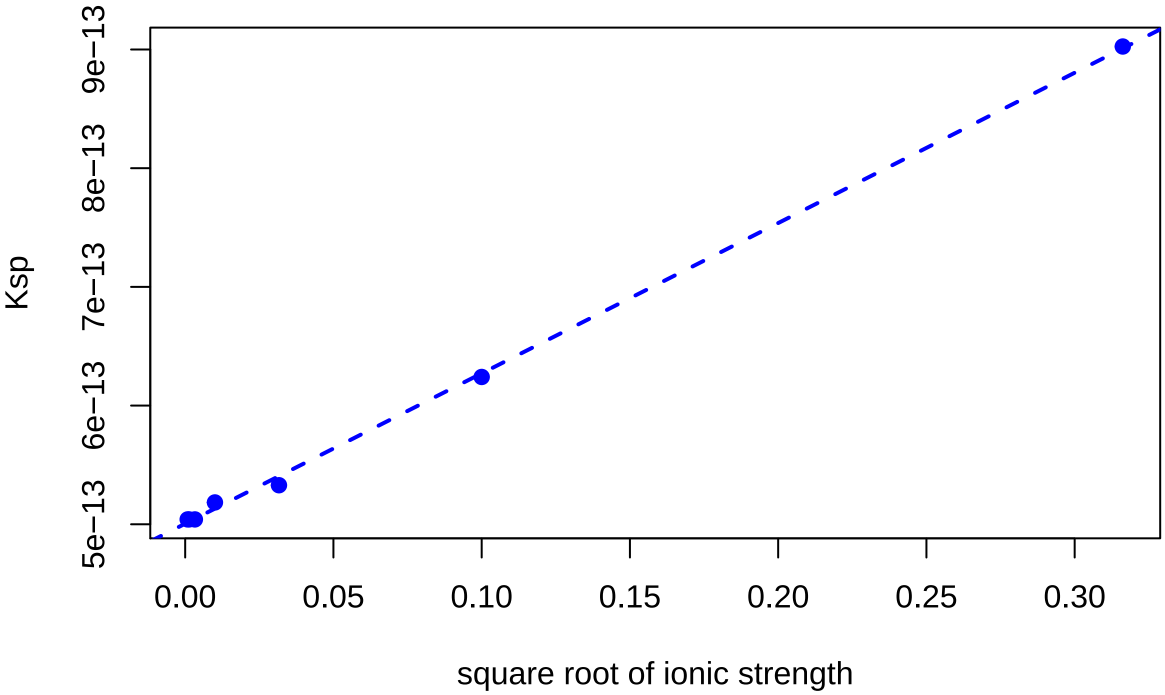
where n is the number of different types of ions, c_i is the concentration of an ion and z_i is the ion’s charge. The unit for ionic strength is molarity. Calculate the ionic strength for each of the solutions in the table on page 24. Be sure to include the concentrations of Ag^+ and Br^-, as well as the concentrations of the ions from the strong electrolyte.

Answer. The table below provides the ionic strengths. Note that the concentrations of the ions are rounded to the nearest power of 10 and the ionic strengths are reported to more significant figures than merited to show that the concentration of KNO_3 dominates the ionic strength for most solutions. Although the concentrations are rounded to the nearest power of 10, the actual concentrations were used to calculate the ionic strengths.

[K+] (M)	[NO3-] (M)	[Ag+] (M)	Br-] (M)	ionic strength
0e+00	0e+00	7e-07	7e-07	0.0000007
1e-06	1e-06	7e-07	7e-07	0.0000017
1e-05	1e-05	7e-07	7e-07	0.0000107
1e-04	1e-04	7e-07	7e-07	0.0001007
1e-03	1e-03	7e-07	7e-07	0.0010007
1e-02	1e-02	8e-07	8e-07	0.0100008
1e-01	1e-01	1e-06	1e-06	0.1000010

For a relatively small range of ionic strengths, a plot of K_{sp} (on the y-axis) as a function of $\sqrt{\mu}$ (on the x-axis) 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 2, using the ionic strengths determined above. Fit a straight-line to the data and report the value for the thermodynamic K_{sp} of AgBr.

Answer. The plot and regression results are shown below. The y-intercept of the regression line is 5.005×10^{-13}, which is the theoretical solubility product for AgBr.



A thermodynamic K_{sp} has limited use since it applies only to a solution with an ionic strength of zero. Any calculation that uses a thermodynamic equilibrium constant will give an expected value that differs from the experimental result and this difference is 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 (Chem 352: Analytical Equilibria).

Note: This worksheet is based on a worksheet created by Juliette Lantz, David Langhus and Shirley Fischer-Drowos for the POGIL project.