

Theoretical vs. Experimental Results Key

(or why the result of an equilibrium calculation might not agree with an experimental result)

Thermodynamics and equilibrium chemistry are powerful theoretical tools for modeling a chemical reaction. Using these theories we can predict a reaction's favorability, predict the reaction's composition at equilibrium, and, when it is at equilibrium, predict how the reaction will respond to a change in conditions. Such models assume what we might call "ideal conditions;" when conditions are not ideal, our experimental results may not agree with our theoretical predictions. In this exercise we seek to define what we mean by ideal conditions.

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



and answer the following questions:

What are the concentrations of Ag^+ and Br^- in a saturated solution of $\text{AgBr}(s)$?

In the saturated solution we know that $[\text{Ag}^+] = [\text{Br}^-]$; thus

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

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

Will the concentration of Br^- increase, decrease, or remain the same if you add $\text{AgNO}_3(s)$ to this saturated solution? Why?

We expect that the concentration of Br^- will decrease. Adding Ag^+ increases Q so that it is larger than K_{sp} , pushing the reaction to the left and decreasing the concentration of Br^- .

Will the concentration of Ag^+ increase, decrease, or remain the same if you add $\text{KBr}(s)$ to this saturated solution? Why?

We expect that the concentration of Ag^+ will decrease. Adding Br^- increases Q so that it is larger than K_{sp} , pushing the reaction to the left and decreasing the concentration of Ag^+ .

Will the concentration of Br^- increase, decrease, or remain the same if you add $\text{KNO}_3(s)$ to this saturated solution? Why?

We expect that the concentration of Br^- will remain the same as neither K^+ or NO_3^- is involved in the equilibrium reaction and, therefore, that neither ion will affect the value of Q .

Will the concentration of Ag^+ increase, decrease, or remain the same if you add $\text{KNO}_3(s)$ to this saturated solution? Why?

We expect that the concentration of Ag^+ will remain the same as neither K^+ or NO_3^- is involved in the equilibrium reaction and, therefore, that neither ion will affect the value of Q .

Review your answers with at least two classmates and, if your answers are not the same, work to resolve your differences.

Experimental Results. The table below shows experimental results for $[\text{Ag}^+]$ and $[\text{Br}^-]$ in saturated solutions of $\text{AgBr}(s)$ that contain different concentrations of KNO_3 , a strong electrolyte that dissolves completely to form equal concentrations of K^+ and NO_3^- .

$[\text{KNO}_3], \text{M}$	$[\text{Ag}^+], \text{M}$	$[\text{Br}^-], \text{M}$
0	7.1×10^{-7}	7.1×10^{-7}
1×10^{-5}	7.1×10^{-7}	7.1×10^{-7}
1×10^{-4}	7.2×10^{-7}	7.2×10^{-7}
1×10^{-3}	7.3×10^{-7}	7.3×10^{-7}
1×10^{-2}	7.9×10^{-7}	7.9×10^{-7}
1×10^{-1}	9.5×10^{-7}	9.5×10^{-7}

To what extent do these experimental results agree with and to what extent do they disagree with your theoretical predictions?

The data show that solubility of AgBr is not affected by KNO_3 when its concentration is $1 \times 10^{-5} \text{ M}$ as the solubility of AgBr , at least to two significant figures, is identical to the solubility of AgBr in pure water; this is consistent with our prediction that KNO_3 should not affect the solubility of AgBr . For higher concentrations of KNO_3 , however, it is clear that the concentration of KNO_3 does affect the solubility of AgBr .

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

The molar solubility of AgBr increases as the concentration of KNO_3 increases.

What is the effect on the K_{sp} for AgBr of increasing the concentration of KNO_3 ?

We know that $K_{\text{sp}} = [\text{Ag}^+][\text{Br}^-]$; thus, the value of K_{sp} becomes larger as the concentration of KNO_3 increases.

Review your answers with at least two classmates and, if your answers are not the same, work to resolve your differences.

Building a New Theoretical Model. AgBr is an ionic compound held together by the electrostatic attraction between the Ag^+ ions and the Br^- ions. What factors affect this force of attraction?

From Coulomb's law we know that the force of attraction between two ions of opposite charge is directly proportional to the charge of the ions, Q_+ and Q_- , and inversely proportional to the square of the distance, r , between the ions.

$$\text{force of attraction} \propto \frac{Q_+ Q_-}{r^2}$$

Given the strong attraction between ions of opposite charge, what might prevent all the Ag^+ ions and Br^- ions from recombining to form $\text{AgBr}(s)$? Explain your answer in terms of the factors that affect the formation of an ionic bond. [*Hint: the solvent, water is a polar molecule.*]

Polar water molecules are attracted to the Ag^+ and Br^- ions. For a water molecule near a Ag^+ ion, for example, the molecule's partial negative charge on the oxygen will orient itself toward and be attracted to the cation's positive charge. This somewhat structured layer of water around the Ag^+ ion increases its size and, from Coulomb's law, the greater the distance between the ions, the weaker the force of attraction between Ag^+ and Br^- , and the greater the solubility of AgBr.

What happens at the level of individual ions when you add an inert, strong electrolyte, such as KNO_3 , to a saturated solution of $\text{AgBr}(s)$. Sketch a picture that shows a Ag^+ ion in a solution that contains NO_3^- ions. Repeat for Br^- ions in a solution that contains K^+ ions.

In the presence of an inert, electrolyte, such as KNO_3 , the Ag^+ cations are surrounded by an excess of NO_3^- ions relative to K^+ , and the Br^- anions are surrounded by an excess of K^+ ions. We call these clouds of charge that surround Ag^+ and Br^- ionic atmospheres.

Explain why the molar solubility of $\text{AgBr}(s)$ is greater in solutions with higher concentrations of KNO_3 .

There are two important effects of an ionic atmosphere on the solubility of AgBr. First, as noted above for water, the ionic atmospheres around Ag^+ and Br^- increase the distance between the ions. Second, because a Ag^+ cation is surrounded by a slightly negative ionic atmosphere, the charge "seen" by a Br^- anion is slightly less than +1 (and, for the same reason, the charge on Br^- "seen" by a Ag^+ cation is slightly less than -1. From Coulomb's law, smaller charges separated by greater distance results a smaller force of attraction; thus, the greater the concentration of KNO_3 , the greater the molar solubility of AgBr.

Making a New Theoretical Prediction. Do you expect that AgBr is more soluble, less soluble, or equally soluble in 0.1 M $\text{Mg}(\text{NO}_3)_2$ than in 0.1 M KNO_3 ? Explain your reasoning.

An equimolar solution of $\text{Mg}(\text{NO}_3)_2$ will have a greater concentration of ions relative to KNO_3 , and will have cations with a greater charge. Both suggest that $\text{Mg}(\text{NO}_3)_2$ will have a greater impact on the solubility of AgBr.

Review your answers with at least two classmates and, if your answers are not the same, work to resolve your differences.

Experimental Results. The table below shows K_{sp} values for $\text{AgBr}(s)$ in deionized water and in several different solutions of strong electrolytes.

Solution	[electrolyte], M	$[\text{Ag}^+] = [\text{Br}^-]$	K_{sp}
Deionized water	0	7.1×10^{-7}	5.0×10^{-13}
KNO_3	1×10^{-5}	7.1×10^{-7}	5.0×10^{-13}
	1×10^{-4}	7.2×10^{-7}	5.2×10^{-13}
	1×10^{-3}	7.3×10^{-7}	5.3×10^{-13}
	1×10^{-2}	7.9×10^{-7}	6.2×10^{-13}
	1×10^{-1}	9.5×10^{-7}	9.0×10^{-13}
$\text{Mg}(\text{NO}_3)_2$	1×10^{-5}	7.1×10^{-7}	5.0×10^{-13}
	1×10^{-4}	7.2×10^{-7}	5.2×10^{-13}
	1×10^{-3}	7.6×10^{-7}	5.8×10^{-13}
	1×10^{-2}	8.7×10^{-7}	7.6×10^{-13}
	1×10^{-1}	1.2×10^{-7}	1.4×10^{-12}

Do these experimental results agree with your theoretical predictions? If your answer is no, then return to the previous page and reconsider your answers to the questions found there. Do not proceed until you understand why $\text{AgBr}(s)$ is more soluble in a solution of $\text{Mg}(\text{NO}_3)_2$ than in an equimolar solution of KNO_3 .

Yes, the solubility of AgBr is greater in equimolar $\text{Mg}(\text{NO}_3)_2$ relative to KNO_3 .

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

A solution of sodium acetate will have Na^+ ions and acetate ions (as well as H_3O^+ and OH^- ions). The presence of these ions will have some effect on the the position of acetate's base dissociation reaction for acetate and, therefore, on the solution's pH.

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

Because the concentration of dissolved ions affects the value of an equilibrium constant, there must be some uncertainty as to whether a reaction's published thermodynamic equilibrium constant is "correct" for the solution in question. Given this uncertainty in the value of the equilibrium constant, we can tolerate some uncertainty in our calcluations.

Review your answers with at least two classmates and, if your answers are not the same, work to resolve your differences.

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 ions and, therefore, 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 to account for both an ion's concentration and its charge is ionic strength, μ , which we define 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 that 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 Ag^+ and Br^- , as well as the concentrations of the ions from the strong electrolyte. Feel free to divide the work with other classmates.

Solution	[electrolyte], M	$[\text{Ag}^+] = [\text{Br}^-]$	K_{sp}	μ , M
Deionized water	0	7.1×10^{-7}	5.0×10^{-13}	7.10×10^{-7}
KNO_3	1×10^{-5}	7.1×10^{-7}	5.0×10^{-13}	1.07×10^{-5}
	1×10^{-4}	7.2×10^{-7}	5.2×10^{-13}	1.01×10^{-4}
	1×10^{-3}	7.3×10^{-7}	5.3×10^{-13}	1.00×10^{-3}
	1×10^{-2}	7.9×10^{-7}	6.2×10^{-13}	1.00×10^{-2}
	1×10^{-1}	9.5×10^{-7}	9.0×10^{-13}	1.00×10^{-1}
$\text{Mg}(\text{NO}_3)_2$	1×10^{-5}	7.1×10^{-7}	5.0×10^{-13}	3.07×10^{-5}
	1×10^{-4}	7.2×10^{-7}	5.2×10^{-13}	3.01×10^{-4}
	1×10^{-3}	7.6×10^{-7}	5.8×10^{-13}	3.00×10^{-3}
	1×10^{-2}	8.7×10^{-7}	7.6×10^{-13}	3.00×10^{-2}
	1×10^{-1}	1.2×10^{-6}	1.4×10^{-12}	3.00×10^{-1}

For a relatively small range of ionic strengths, a plot of K_{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 using the data in the table above. Fit a straight-line to the data and report the thermodynamic K_{sp} for $\text{AgBr}(s)$.

A plot of K_{sp} vs. $\sqrt{\mu}$ (not shown) is linear with a y -intercept of 5.0×10^{-13} , which is the thermodynamic K_{sp} for AgBr .

The Moral of the Story. A thermodynamic K_{sp} applies only to a solution with an ionic strengths of zero. Calculations that use a thermodynamic equilibrium constant will give a predicted result different from an 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; however, that is a topic for another day and another course.