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Activity and Activity Coefficients

Learning Objectives:

- To differentiate the use of activities vs. concentrations in calculations involving solutions
- To understand the effect of ionic strength on equilibrium concentrations
- To introduce strategies for calculating ionic strength, activity coefficients and activities

Performance Criteria:

- Be able to recognize when activities must be used in calculations
- Be able to calculate the ionic strength of a solution and predict its effect on equilibrium concentrations
- Be able to calculate activity coefficients and activities
- Be able to write equilibrium expressions using activities and to solve equilibrium problems using activities

Prior Knowledge:

- Calculate equilibrium concentrations for solution species using equilibrium constants
- Familiarity with precipitation reactions and the solubility of sparingly-soluble compounds.
- Familiarity of the basic properties of an electrolyte

CONCEPT:

SOLUBILITY: amount of solid that dissolves in a solution, given in mol/L or g/L

MODEL 1: Consider the following equilibrium



$$K_{\text{sp}} = 5.0 \times 10^{-13}$$

TABLE 1:

SOLUTION	electrolyte concentration	[Ag ⁺] = [Br ⁻]
Distilled water	0	7.07 x 10 ⁻⁷ M
KNO ₃	1 x 10 ⁻⁵ M	7.10 x 10 ⁻⁷ M
	1 x 10 ⁻⁴ M	7.15 x 10 ⁻⁷ M
	1 x 10 ⁻³ M	7.33 x 10 ⁻⁷ M
	1 x 10 ⁻² M	7.88 x 10 ⁻⁷ M
	1 x 10 ⁻¹ M	9.50 x 10 ⁻⁷ M
MgC ₂ O ₄	1 x 10 ⁻⁵ M	7.12 x 10 ⁻⁷ M
	1 x 10 ⁻⁴ M	7.24 x 10 ⁻⁷ M
	1 x 10 ⁻³ M	7.59 x 10 ⁻⁷ M
	1 x 10 ⁻² M	8.65 x 10 ⁻⁷ M
	1 x 10 ⁻¹ M	1.15 x 10 ⁻⁶ M

Critical Thinking Questions:

- 1) Look at Table 1. Note the [Ag⁺] and [Br⁻] in distilled water, where the electrolyte concentration is zero. Quickly show (via calculation) how this value was obtained.

2) Consider the equilibrium of AgBr(s) in an aqueous solution. According to Le Chatelier's Principle,

a) **adding** some additional Ag^+ ions would cause $[\text{Br}^-]$ to

INCREASE

DECREASE

NEITHER

Explain briefly:

b) **removing** some Ag^+ ions would cause $[\text{Br}^-]$ to

INCREASE

DECREASE

NEITHER

Explain briefly:

c) **adding** some KNO_3 would cause $[\text{Br}^-]$ to

INCREASE

DECREASE

NEITHER

Explain briefly:

3) Now, consider the data in Table 1.

a) as $[\text{KNO}_3]$ increases, $[\text{Ag}^+]$ and $[\text{Br}^-]$

INCREASE

DECREASE

NEITHER

b) as $[\text{MgC}_2\text{O}_4]$ increases, $[\text{Ag}^+]$ and $[\text{Br}^-]$

INCREASE

DECREASE

NEITHER

4) Which substance has the larger effect on $[\text{Ag}^+]$ and $[\text{Br}^-]$?

KNO_3

MgC_2O_4

- 5) In a grammatically correct sentence, summarize the effect of increasing either the KNO_3 or the MgC_2O_4 concentration on the solubility of AgBr :

Ionic strength is a measure of the total ion concentration of a solution. It is given the symbol μ and has units of molarity. The total number of ions in a solution changes the behavior of the ions in equilibrium (in this case $[\text{Ag}^+]$ and $[\text{Br}^-]$).

- 6) What two properties of an ion in solution affect its ability to contribute to the ionic strength of the overall solution? (Hint – the ionic strength of MgC_2O_4 is greater than the ionic strength of KNO_3 at the same concentration.)

Consider the Ag^+ ion. Since it has a positive charge it will tend to attract any negatively charged ions present in solution. When it appears in a solution of distilled water in which there aren't many other ions available, you can imagine that it is surrounded by polar water molecules, with the negative end of several water molecules in close proximity to the positively charged ion.

When the ion is in a solution containing other ions, some of the oppositely charged ions are attracted to it, just like one end of the polar water molecule. The ions that closely surround the equilibrium ion are referred to as the “ionic atmosphere” for that ion. The whole assembly is called the “solvated ion”.

- 7) When Ag^+ appears in a solution of KNO_3 , which ions will surround it?
- 8) When Br^- appears in a solution of KNO_3 , which ions will surround it?

- 9) Draw a picture below showing Ag^+ surrounded by the ions that comprise its ionic atmosphere. Draw another picture below showing Br^- surrounded by its ionic atmosphere.

Consider Ag^+ in water. It carries roughly a full +1 charge. When it is surrounded by a negatively charged ionic atmosphere, the overall charge of the solvated Ag^+ is reduced to something less than a full +1 charge. Likewise, Br^- in water carries roughly a full -1 charge, but when surrounded by its positively charged ionic atmosphere, its overall charge is diminished to something less (that is, a little bit more positive!) than -1.

The solubility of AgBr depends upon the strength of the attraction between the Ag^+ ion and the Br^- ion.

- 10) If the charges on the Ag^+ and Br^- ions are diminished due to the ionic atmosphere, do you expect the solubility of AgBr to

INCREASE

DECREASE

NEITHER

Explain.

- 11) A higher ionic strength solution causes a larger ionic atmosphere around each equilibrium ion. As the ionic strength of solution increases, do you expect the solubility of AgBr to

INCREASE

DECREASE

NEITHER

Verify your answer by looking at Table 1 – what happens to the $[\text{Ag}^+]$ and $[\text{Br}^-]$ as the concentration of the inert salts increases?

- 12) In Table 1, look at the solubility of AgBr at the same concentration of the two different electrolytes (say $1 \times 10^{-3} \text{ M}$). In which case is AgBr more soluble? Offer an explanation for this.

The ionic strength of a solution (μ) is (where z is the charge on an ion and C is its concentration in units of molarity):

$$\mu = \frac{1}{2} \sum_{\text{ions}} C_i z_i^2$$

- 13) Calculate the ionic strength of 1×10^{-3} M KNO_3 . Why would the ionic strength of 1×10^{-3} M MgC_2O_4 be higher than this?

TABLE 2:

SOL'N	electrolyte conc.	μ (Ionic strength) **	γ_{Ag^+} (Activity coefficient for Ag^+)	γ_{Br^-} (Activity coefficient for Br^-)	$[\text{Ag}^+] = [\text{Br}^-]$
Distilled water	0		1	1	7.07×10^{-7} M
KNO₃	1×10^{-5} M	1×10^{-5} M	0.996	0.996	7.10×10^{-7} M
	1×10^{-4} M	1×10^{-4} M	0.988	0.988	7.15×10^{-7} M
	1×10^{-3} M	1×10^{-3} M	0.964	0.964	7.33×10^{-7} M
	1×10^{-2} M	1×10^{-2} M	0.897	0.897	7.88×10^{-7} M
	1×10^{-1} M	1×10^{-1} M	0.745	0.745	9.50×10^{-7} M
MgC₂O₄	1×10^{-5} M	4×10^{-5} M	0.993	0.993	7.12×10^{-7} M
	1×10^{-4} M	4×10^{-4} M	0.977	0.977	7.24×10^{-7} M
	1×10^{-3} M	4×10^{-3} M	0.932	0.932	7.59×10^{-7} M
	1×10^{-2} M	4×10^{-2} M	0.817	0.817	8.65×10^{-7} M
	1×10^{-1} M	4×10^{-1} M	0.613	0.613	1.15×10^{-6} M

**Note that the ionic strength of solutions containing +2 and -2 charges can only be estimated by the equation for μ given above, due to the strong ion pairing of species carrying these charges.

Critical Thinking Questions:

14) Examine Table 2, and verify that your answers to CTQ #13 are correct.

If the effectiveness of the charges on the Ag^+ and Br^- ions are diminished due to the ionic atmosphere generated largely by the ions of the electrolyte, it is sort of like diminishing their “effective concentration”. The **activity** of each ion, or its “effective concentration” due to the presence of an electrolyte is given as:

$$A_i = [i]\gamma_i$$

where A_i is the activity of an ion, $[i]$ is its molar concentration and γ_i is the activity coefficient associated with each ion. Note that γ values are dependent upon the overall ionic strength of a solution.

We used to write the solubility product for $\text{AgBr}(s)$ like this:

$$K_{sp} = [\text{Ag}^+][\text{Br}^-]$$

Now, if we use the activities of Ag^+ and Br^- to correctly represent their behavior in a solution where many ions are present, the expression becomes

$$K_{sp} = [\text{Ag}^+]\gamma_{\text{Ag}^+}[\text{Br}^-]\gamma_{\text{Br}^-} = A_{\text{Ag}^+} A_{\text{Br}^-}$$

15) Examine the activity coefficients for Ag^+ in Table 2. What happens to their magnitude as the concentration of KNO_3 increases?

16) What happens to the magnitude of γ_{Br^-} as the concentration of the KNO_3 increases?

17a) In low ionic strength solutions –

⇒ μ becomes small. What value will γ approach?

⇒ Under these conditions would activity be (less than) (greater than) (about equal to) concentration?

17b) In high ionic strength solutions -

⇒ μ becomes large. What happens to γ ?

⇒ Would activity be (less than) (greater than) (about equal to) concentration?

18) In complete, grammatically correct sentences explain a) the dependence of the ionic strength on the presence of an electrolyte in solution and b) the effect of ionic strength on solubility.

19) To a good approximation, $\gamma = 1$ for species neutral species in solution. Explain why this makes sense.

To solve an equilibrium problem using activities, a γ value is needed for each ion in solution. Recall that the ionic strength (μ) of a solution can be calculated by taking into account the concentration of all ions present in appreciable amounts and their corresponding charges. As the ionic strength increases, we know that γ decreases. There are two ways to obtain γ for an ion in solution:

A) Tables exist that list γ values for many common ions in solutions of varying ionic strength – one is likely to be found in your textbook.

B) γ can be calculated using the Extended Debye-Huckel (EDH) equation, as long as $\mu < 0.1$ M.

$$\log \gamma = \frac{-0.51z^2\sqrt{\mu}}{1 + \frac{\alpha\sqrt{\mu}}{305}}$$

where μ is the ionic strength of the solution, z is the charge on the ion of interest, and α is the hydrated ionic radius in pm, which is also likely available in a table in your textbook.

20) For a solution of 1×10^{-3} M KNO_3 , calculate γ for Ag^+ using the EDH equation. Does it agree with the γ value found in Table 2?

21) For a solution of 1×10^{-3} M MgC_2O_4 , calculate γ for Ag^+ using the EDH equation. Does it agree with the γ value found in Table 2?

22) Now, using the new equilibrium expression

$$K_{\text{sp}} = [\text{Ag}^+]\gamma_{\text{Ag}^+}[\text{Br}^-]\gamma_{\text{Br}^-}$$

a) Calculate $[\text{Ag}^+]$ and $[\text{Br}^-]$ in a 1×10^{-3} M solution of KNO_3 . Compare your results to those found in Table 2.

b) Calculate $[\text{Ag}^+]$ and $[\text{Br}^-]$ in a 1×10^{-3} M solution of MgC_2O_4 . Compare your results to those found in Table 2.

23) Summarize:

a) In what electrolyte concentration regime is it wise to use activities?

b) What impact does increasing a solution's ionic strength have on the solubility of slightly soluble compounds?

24) Can you think of any circumstances where adding an electrolyte to a solution is necessary?