BC2001x: Lab week 8
Solutions, Salts, and Solubility

Investigating the COMMON ION EFFECT

This is the last QUANTITATIVE experiment (last uncertainty analysis)

Next week begins a four-week series on QUALITATIVE ANALYSIS.

TODAY'S EXPERIMENT

Measure and compare the molar solubility, s, of barium iodate, $Ba(IO_3)_2$, in three solutions:

(1) water

(2) a solution with a known amount of Ba^{2+}

(3) a solution with a known amount of IO_3^-

Calculate and compare the solubility product, $K_{sp}(Ba(IO_3)_2)$, in the solutions.

Consider a different salt: $PbI_2(s)$

Is lead iodide soluble?

What will happen if we mix aqueous solutions of NaI and $Pb(NO_3)_2$?

Use solubility rules:

Sodium salts? Nitrate salts?

both generally soluble

Are halides soluble?

Most, but there are exceptions

What are the important exceptions?

Halides of Ag^+, Cu^+, Pb^{2+}, and Hg_2^{2+}

Therefore PbI_2 is insoluble.

$PbI_2(s)$ dissolving in water

If $PbI_2(s)$ is insoluble, does that mean that no salt dissolves in water?

No! All salts dissolve to some extent. "insoluble" salts dissolve very little.

Is $PbI_2(s)$ a strong electrolyte?

Yes, almost all salts are strong electrolytes. The dissolved species are ions.

Dissolving $PbI_2(s)$: reaction

What is the chemical reaction which describes the dissolving of lead iodide?

$$PbI_2(s) \rightleftarrows Pb^{2+}(aq) + 2\ I^{-}(aq)$$

The solid is at equilibrium with a saturated solution.

How do we know if a solution is saturated?

It has had time to equilibrate, and there is undissolved salt present.

Dissolving $PbI_2(s)$: K_{eq}

$$PbI_2(s) \rightleftarrows Pb^{2+}(aq) + 2\ I^{-}(aq)$$

What is the equilibrium constant for this reaction?

$$K_{eq} = [Pb^{2+}][I^{-}]^2$$

Equilibrium constants for poorly soluble solids are written as K_{sp} for "solubility product"

$$K_{sp}(PbI_2) = 1.4 \times 10^{-8}$$

Different sources of data have values which may differ slightly.

Dissolving $PbI_2(s)$: solubility

$$PbI_2(s) \rightleftarrows Pb^{2+}(aq) + 2\ I^{-}(aq)$$

$$K_{sp} = [Pb^{2+}]\ [I^{-}]^2 = 1.4 \times 10^{-8}$$

Let X = molar solubility of PbI_2 in water.

Is X large or small?

Small: the salt is insoluble

When X moles/L dissolve, what is the $[Pb^{2+}]$ in solution?

$[Pb^{2+}] = X$

K_{sp} and Molar Solubility

$PbI_2(s) \rightleftarrows Pb^{2+}(aq) + 2\ I^{-}(aq)$ $K_{sp} = 1.4 \times 10^{-8}$

When X moles/L of PbI_2 dissolve, what is $[I^{-}]$?

$[I^{-}] = 2X$

Substitute:

$K_{sp} = [Pb^{2+}][I^{-}]^2 = X\ (2X)^2 = 4X^3$

This equation relates the solubility product (an equilibrium constant), to the molar solubility in water.

From X, we can determine K_{sp} (or vice versa.)

Determining Molar Solubility in H_2O

$PbI_2(s) \rightleftarrows Pb^{2+}(aq) + 2\ I^-(aq)$

$K_{sp} = [Pb^{2+}][\ I^-]^2 = 4X^3 = 1.4 \times 10^{-8}$

$X = \{K_{sp}/4\}^{1/3}$

$= \{\ 1.4 \times 10^{-8}\ /4\ \}^{1/3} = 0.0015281\ M$

$X = 1.5 \times 10^{-3}\ M$

this is the molar solubility of $PbI_2(s)$ in water

$[Pb^{2+}] = 0.0015\ M$ at 25 °C

Now for the common ions...

Suppose we add some KI(s) to the saturated solution of PbI_2 in water. What happens?

Some preliminary questions.

Is KI(s) soluble?

Yes, all potassium salts are soluble.

Is KI(s) a strong electrolyte?

Yes, almost all ionic salts are strong electrolytes.

the common ions...

Add some KI(s) to a saturated solution of PbI_2 in water. What happens?

We are adding ions K^+ and I^-. Iodide is the common ion: present in $PbI_2(s)$ and KI(s)

Will the K^+ do anything?

No, all potassium salts are soluble.

Will the I^- do anything?

Yes! We have disturbed the equilibrium.

What happens?

Use LeChatelier's principle:

The equilibrium shifts making more $PbI_2(s)$:

$PbI_2(s) \leftarrow Pb^{2+}(aq) + 2\ I^-(aq)$

Common ions: change K?

Will K_{sp} change?

No, it is an equilibrium *constant*.

So long as the temperature is fixed, it is constant, however the solution is prepared.

So after the KI has been added, the amount of solid PbI_2 will increase, and $[Pb^{2+}]$ will decrease.

Common ions: Stoichiometry

Does K_{sp} depend on whether the ratio of Pb^{2+} to I^- in solution is 1:2 or not?

NO! So long as there is solid PbI_2 and both Pb^{2+} and I^- ions in the solution in any proportions, the same K_{sp} value applies.

There is nothing that requires that Pb^{2+} and I^- be present in a 1:2 ratio, or any particular ratio.

Many different sets of concentrations give the same numerical value of K_{sp}.

Common ions: Q and K

Add K^+ and I^- to saturated $PbI_2(s)$:
$[I^-]$ increases.
At the instant of mixing, before anything happens, $Q = [Pb^{2+}][I^-]^2$ is too large.

Q must become smaller. How?

Reduce both ion concentrations by making more ppt (according to stoichiometry):

$$PbI_2(s) \leftarrow Pb^{2+} + 2\,I^-$$

Net effect: less Pb^{2+} is in solution at end than initially: $[Pb^{2+}]$ is less than 0.0015 M.

Common ions: does order of adding reagents matter?

Would the final conditions be different if we added the KI first, then PbI_2?

No: if the system is at equilibrium, it doesn't matter how it got that way.

Let's think about a solution of KI with molarity c_I. If we add some $PbI_2(s)$, will its molar solubility here be the same, larger, or smaller than it was in water?

Smaller: adding I^- increased solid.

Equations including the common ion

Let Y = molar solubility of $PbI_2(s)$ in a c_I molar solution of KI.

Is $Y = X$, $< X$, or $> X$?

$Y < X$ This is the common ion effect: the molar solubility is less in a solution which contains a common ion.

What is $[Pb^{2+}]$ in the saturated solution?

$[Pb^{2+}] = Y$

What is $[I^-]$ in this solution?

$[I^-] = c_I + 2Y$

Equations: a chart helps keep track….

		$[Pb^{2+}]$	$[I^-]$
initial	(KI in solution)	0	c_I
change	(PbI_2 dissolves)	+Y	+2Y
final		Y	c_I +2Y

Substitute into the the K_{sp} equation:

$$K_{sp} = (Y)(c_I + 2Y)^2$$

The equation also implies $Y < X$ when $c_I > 0$.

If we know c_I and measure Y, we can calculate an experimental K_{sp}

Suppose the common ion is the cation

Let Z = molar solubility of $PbI_2(s)$ in a c_L molar solution of $Pb(NO_3)_2$.

$Z < X$ ← also the common ion effect

What is $[Pb^{2+}]$ in this saturated solution?

$[Pb^{2+}] = c_L + Z$

What is $[I^-]$ in this solution?

$[I^-] = 2Z$

The common ion is the cation: Equilibrium constant expression

$[Pb^{2+}] = c_L + Z$ and $[I^-] = 2Z$

Substitute into the the K_{sp} equation:

$$K_{sp} = (c_L + Z)(2Z)^2$$

Summary:

Y and Z are both less that X: this is the common ion effect.

The values of K_{sp} are the same within experimental uncertainty, which may be quite large..

Today's experiment

Insoluble salt: Barium iodate $Ba(IO_3)_2(s)$

contains Ba^{2+} (barium) and IO_3^- (iod<u>ate</u>)

How much salt dissolves?

Since both ions come from the same salt, we need to measure concentration of only one of the two: stoichiometry tells us the other.

Still true when the common ion is present, since we know how much was present before the barium iodate dissolved

We choose to measure [iodate]

Determining $[IO_3^-]$ with a redox reaction

Pipet a precise volume of the solution.

Convert all the iodate to iodine:

(1) $IO_3^- + 6\ H^+ + 5\ I^- \rightarrow 3\ I_2 + 3\ H_2O$

Titrate the iodine with sodium thiosulfate:

(2) $I_2 + 2\ S_2O_3^{2-} \rightarrow 2\ I^- + S_4O_6^{2-}$

mmoles of thiosulfate = (molarity)(mL)

from this find mmoles iodate in original solution, combine with volume to get molarity.

Determining iodate: endpoint

How is endpoint determined?

Iodate, iodide, and thiosulfate are all colorless (as are barium and sodium ions)

but I_2 in water is yellow-brown ➔

Reaction (1) creates brown color

$IO_3^- + 6\ H^+ + 5\ I^- \rightarrow 3\ I_2 + 3\ H_2O$

Reaction (2) gets rid of it.

$I_2 + 2\ S_2O_3^{2-} \rightarrow 2\ I^- + S_4O_6^{2-}$

But it becomes very pale: hard to see exact disappearance of yellow.

Determining iodate: indicator

We take advantage of a special property of $I_2(aq)$ molecules:

They readily (and reversibly) form an intensely colored purple-black complex ➔ with *starch*.

Add starch near the end...

Determining iodate: colors

Continue titrating until the black color fades to purple and disappears

This is a VERY SHARP endpoint.

Learn to split drops!