

BC2001x: Lab week 8
Solutions, Salts, and Solubility



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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, $\text{Ba}(\text{IO}_3)_2$, 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}** ,
 $K_{sp}(\text{Ba}(\text{IO}_3)_2)$, in the solutions.

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Consider a different salt: $\text{PbI}_2(\text{s})$

Is lead iodide soluble?

What will happen if we mix aqueous
solutions of NaI and $\text{Pb}(\text{NO}_3)_2$?

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.



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$\text{PbI}_2(\text{s})$ dissolving in water

If $\text{PbI}_2(\text{s})$ is insoluble, does that mean that
no salt dissolves in water?

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

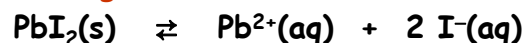
Is $\text{PbI}_2(\text{s})$ a strong electrolyte?

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

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Dissolving $\text{PbI}_2(\text{s})$: reaction

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



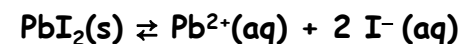
The solid is at equilibrium with a saturated solution.

How do we know if a solution is saturated?

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

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Dissolving $\text{PbI}_2(\text{s})$: K_{eq}



What is the equilibrium constant for this reaction?

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

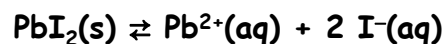
Equilibrium constants for poorly soluble solids are written as K_{sp} for "solubility product"

$$K_{\text{sp}}(\text{PbI}_2) = 1.4 \times 10^{-8}$$

Different sources of data have values which may differ slightly.

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Dissolving $\text{PbI}_2(\text{s})$: solubility



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

Let X = molar solubility of PbI_2 in water.

Is X large or small?

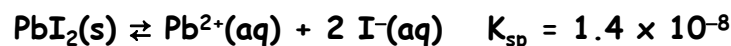
Small: the salt is insoluble

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

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

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K_{sp} and Molar Solubility



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

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

Substitute:

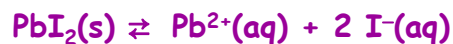
$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{I}^{-}]^2 = X(2X)^2 = 4X^3$$

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.)

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Determining Molar Solubility in H₂O



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

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

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

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

this is the molar solubility of PbI₂(s) in water

$$[\text{Pb}^{2+}] = 0.0015 \text{ M at } 25 \text{ }^\circ\text{C}$$

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Now for the common ions...

Suppose we add some KI(s) to the saturated solution of PbI₂ 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.

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the common ions...

Add some KI(s) to a saturated solution of PbI₂ in water. What happens?

We are adding ions K⁺ and I⁻. Iodide is the common ion: present in PbI₂(s) and KI(s)

Will the K⁺ do anything?

No, all potassium salts are soluble.

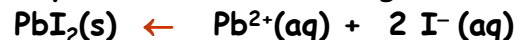
Will the I⁻ do anything?

Yes! We have disturbed the equilibrium.

What happens?

Use LeChatelier's principle:

The equilibrium shifts making more PbI₂(s):



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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 PbI₂ will increase, and [Pb²⁺] will decrease.

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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} .

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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):



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

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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.

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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?

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

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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}

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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?

$$[I^-] = 2Z$$

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The common ion is the cation: Equilibrium constant expression

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

Substitute into the the K_{sp} equation:

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

Summary:

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

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

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Today's experiment

Insoluble salt: **Barium iodate** $Ba(IO_3)_2(s)$
contains Ba^{2+} (barium) and IO_3^- (iodate)

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

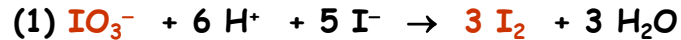
We choose to measure **[iodate]**

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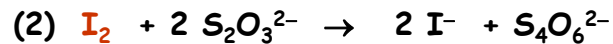
Determining $[\text{IO}_3^-]$ with a redox reaction

Pipet a precise **volume** of the solution.

Convert all the iodate to iodine:



Titrate the iodine with sodium thiosulfate:



mmoles of thiosulfate = (molarity)(mL)

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

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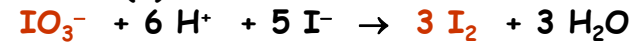
Determining iodate: endpoint

How is endpoint determined?

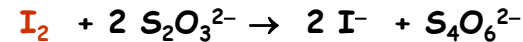
Iodate, iodide, and thiosulfate are all **colorless** (as are barium and sodium ions)

but I_2 in water is **yellow-brown** →

Reaction (1) creates brown color



Reaction (2) gets rid of it.



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



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Determining iodate: indicator

We take advantage of a special property of $\text{I}_2(\text{aq})$ molecules:

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

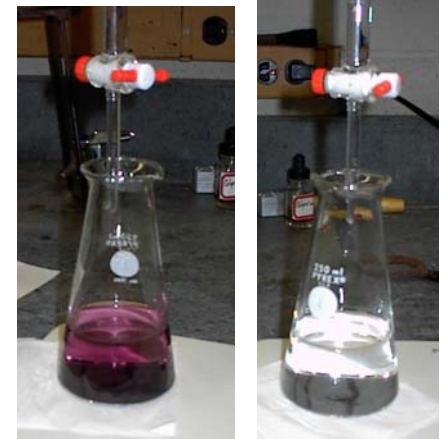
Add starch near the end...



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Determining iodate: colors

Continue titrating until the black color fades to **purple** and **disappears**. This is a VERY SHARP endpoint. Learn to **split drops**!



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