Solubility as an equilibrium process

SOLUTION: Homogeneous mixture of substances Solutions contain:

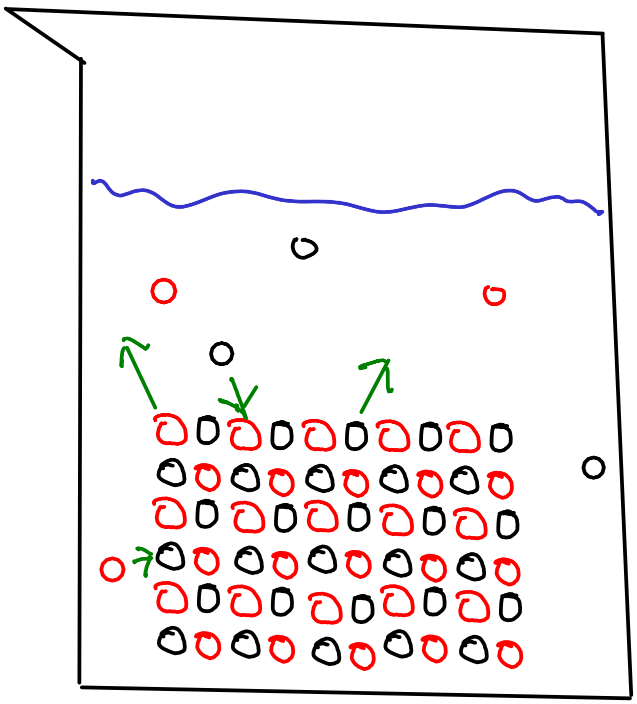
SOLUTE: Component(s) of a solution present in small amount
SOLVENT: Component of a solution present in greatest amount

We usually call water the solvent in aqueous mixtures, even if the water is present in smaller amount than another component

SOLUBILITY: The amount of a solute that will dissolve in a given volume of solvent

SATURATED SOLUTION: Contains the maximum amount of solute that it is possible to dissolve in a given volume of solvent!

A SATURATED SOLUTION is a solution where dissolved solute exists in an EQUILIBRIUM with undissolved solute!



Example: Consider a saturated solution of silver chloride:

$$AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq)$$

At equilibrium, the rate of dissolving equals the rate of crystallization!

$$AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq)$$

$$K_c = [Ag^{+}][Cl^{-}] = \boxed{1.8\times10^{-10}}$$

... what does this equilibrium constant tell us? That silver chloride isn't very soluble!

$$AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq)$$

$$K_{sp} = [Ag^{+}][Cl^{-}]$$

This equilibrium constant is given a special name - the SOLUBILITY PRODUCT CONSTANT - because the equilibrium expression for the dissolving of a salt always appears as a PRODUCT of the concentrations of the ions in the compound!

Remember, Ksp is an equilibrium constant, so everything that applies to equilibrium constants applies to the solubility constant - including what to do with coefficients:

What is the solubility product constant expression for calcium phosphate?

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$$

Solubility calculations and Ksp

You can calculate the solubility of a compound if you know Ksp!

Calculate the solubility (in g/L) of lead(II) iodide at 25C. (see p A-15 in book)

$K_{sp} = 6.5 \times 10^{-9}$; $FW = 461.0\ g/mol$

$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$; $K_{sp} = [Pb^{2+}][I^-]^2 = 6.5 \times 10^{-9}$

Species	[Initial]	Δ	[Equilibrium]
Pb^{2+}	0	+x	x
I^-	0	+2x	2x

Let "x" equal the change in lead ion concentration

$(x)(2x)^2 = 6.5 \times 10^{-9}$

$4x^3 = 6.5 \times 10^{-9}$

$x = 0.001175673\ M = [Pb^{2+}] = [PbI_2]_{dissolved}$

Express the answer in units of grams per liter...

$$\frac{0.001175673\ mol\ PbI_2}{L} \times \frac{461.0\ g\ PbI_2}{mol\ PbI_2} = \boxed{0.54\ g\ PbI_2/L} = 540\ ppm$$

*ppm = "parts per million". For dilute aqueous solutions, ppm is the same thing as milligrams per liter (mg/L)

Precipitation - also known as the reaction quotient

To predict whether a salt at a given concentration will precipitate out, calculate the reaction quotient Q and compare it to the Ksp

Example: $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$; $K_{sp} = 1.8 \times 10^{-10}$

$Q = [Ag^+][Cl^-]$

IF...

* Q < Ksp ; the reaction proceeds to produce more products (dissolved ions), so more solid is able to dissolve: NO PRECIPITATION

* Q > Ksp ; the reaction proceeds to produce more reactants (solid), so solid falls out of solution: PRECIPITATION OCCURS

* Q = Ksp ; the reaction is at equilibrium. PRECIPITATION IS JUST BEGINNING

Would a solution with (Ag+) = 0.014 M and (Cl-) = 0.00042 M precipitate?

$Q = [Ag^+][Cl^-] = (0.014)(0.00042) = 5.88 \times 10^{-6}$

$5.88 \times 10^{-6} > 1.8 \times 10^{-10}$

$Q > K_{sp}$

SInce Q > Ksp, precipitation would occur with these concentrations.

Le Chateleir's Principle

The "common ion effect" affects the solubility of a compound in solution. The presence of one of the ions in a salt in the solution will REDUCE THE SOLUBILITY of that salt!

$$AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq)$$

Silver chloride is much less soluble in a solution of 0.1 M NaCl than it is in distilled water. Why? The presence of CHLORIDE ION forces the solubility equilibrium back to the left, meaning less silver chloride can dissolve!

Solubility can also be affected by pH - depending on the acidic or basic properties of the salt!

A second example: Salicylic acid in the characterization lab

Calculate the solubility of AgCl (FW = 143.35 g/mol) in distilled water. Then, calculate the solubility of AgCl in 0.10 M NaCl solution. Report both answers in parts per million (mg/L)

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)\ ;\ K_{sp} = [Ag^+][Cl^-] = 1.8 \times 10^{-10} \quad (pA\text{-}15)$$

For distilled water...

Species	[Initial]	Δ	[Equilibrium]
Ag^+	0	+x	x
Cl^-	0	+x	x

Let "x" equal the change in dissolved Ag+ concentration.

$$(x)(x) = 1.8 \times 10^{-10}$$

$$x^2 = 1.8 \times 10^{-10}$$

$$x = 1.341640786 \times 10^{-5}\ M = [Ag^+] = [AgCl]_{dissolved}$$

Convert answer's units to ppm (mg/L)...

$$\frac{1.341640786 \times 10^{-5}\ mol\ AgCl}{L} \times \frac{143.35\ g\ AgCl}{mol\ AgCl} \times \frac{mg}{10^{-3}\ g} = \boxed{1.9\ ppm\ AgCl\ \text{in distilled}\ H_2O}$$

converts mol to g

converts g to mg

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq);\ K_{sp} = 1.8\times10^{-10}$$
$$[Ag^+][Cl^-] = 1.8\times10^{-10}$$

For solubility in 0.10 M NaCl solution...

Species	[Initial]	Δ	[Equilibrium]
Ag^+	0	$+x$	x
Cl^-	0.10	$+x$	$0.10+x$

$$(x)(0.10+x) = 1.8\times10^{-10}$$

We know that x << 0.10 , so $0.10 + x \approx 0.10$

$$(x)(0.10) = 1.8\times10^{-10}$$
$$x = 1.8\times10^{-9}\ M = [Ag^+] = [AgCl]_{dissolved}$$

$$\frac{1.8\times10^{-9}\ mol\ AgCl}{L} \times \frac{143.35\ g\ AgCl}{mol\ AgCl} \times \frac{mg}{10^{-3}\ g} = \boxed{2.6\times10^{-4}\ ppm\ AgCl\ in\ 0.10\ M\ NaCl}$$

(0.00026 ppm)

Compare:
1.9 ppm AgCl in distilled water vs
0.00026 ppm AgCl in 0.10 M NaCl

Conclusion: The presence of a common ion greatly decreases solubility

pH AND SOLUBILITY

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\,OH^-(aq)\ ;\ K_{sp} = 1.8 \times 10^{-11}$$

This compound's solubility is pH dependent. How?

* In a BASIC solution, the concentration of hydroxide ion in solution is high. , so solubility is LOWER than in pure water.

* In an ACIDIC solution, we have a significant amount of hydronium, which can react with hydroxide. This lowers the hydroxide concentration and makes magnesium hydroxide MORE SOLUBLE

Generalizing

If a compound is BASIC, then it will be LESS SOLUBLE in basic solutions, and MORE SOLUBLE in acidic solutions!

If a compound is ACIDIC, then it will be MORE SOLUBLE in basic solutions, and LESS SOLUBLE in acidic solutions!

If a compound is NEUTRAL (neither acidic nor basic), then its solubility will be UNAFFECTED by pH