Relationship between Solubility Product (K_s) and Solubility (S) for Sparingly Soluble Electrolytes
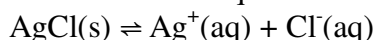
One method of dealing with this is to approach it via the "ICE" table, but in terms of moles rather than molarity.

1. Case A: a 1:1 Electrolyte in Water (no "common ion")

Examples include $CaSO_4$ and CuCl.
Consider the example of silver chloride, AgCl:
The dissolution equilibrium is:
$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$
The equilibrium constant for this equilibrium is known as the solubility product of silver chloride and may be written K_s(AgCl). Its solubility is a measure of the equilibrium concentration of AgCl, i.e. the final concentration of dissolved AgCl in the presence of undissolved solid. Both are dependent on temperature.

We may build up the "ICE" table for an arbitrary number of moles of AgCl(s), say 1 for convenience, as follows:

	AgCl(s)	$\rightleftharpoons$	Ag^+(aq)	+	Cl^-(aq)
Initial /mol	1		0		0
Change /mol	-x		+x		+x
Equilibrium /mol	1-x		x		x
Volume of solution /L	V		V		V
Equilibrium molarities /M	N/a (the solid is not in solution)		$\dfrac{x}{V}$		$\dfrac{x}{V}$

Note that x denotes the number of moles of AgCl that have passed into solution at equilibrium, and so, if V is the volume of the solution in litres, $\dfrac{x}{V}$ represents the solubility of AgCl in terms of molarity. Hence

$$K_s = [Ag^+][Cl^-] = \left(\frac{x}{V}\right)^2 = S^2$$

$$\therefore S = \sqrt{K_s}$$

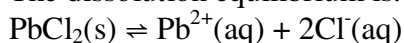Since K_s(AgCl) = 1.8×10^{-10} @ 25°C, S(AgCl) = $\sqrt{1.8 \times 10^{-10}} = 1.3 \times 10^{-5}$ M to 2 s.f.

2. Case B: a 1:2 (or 2:1) Electrolyte in Water (no "common ion")

Examples include Ag_2SO_4 (2:1) and $Ca(OH)_2$ (1:2).
Here we consider lead(II) chloride, $PbCl_2$, a 1:2 electrolyte:
The dissolution equilibrium is:
$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$
and the "ICE" table becomes:

	$PbCl_2$(s)	$\rightleftharpoons$	Pb^{2+}(aq)	+	$2Cl^-$(aq)
Initial /mol	1		0		0
Change /mol	-x		+x		+2x
Equilibrium /mol	1-x		x		2x
Volume of solution /L	V		V		V
Equilibrium molarities /M	N/a (the solid is not in solution)		$\dfrac{x}{V}$		$\dfrac{2x}{V}$

Once again, x denotes the number of moles of $PbCl_2$ that have passed into solution at equilibrium, and so $\dfrac{x}{V}$ represents the solubility of $PbCl_2$, S($PbCl_2$), in terms of molarity. This time, however, $[Cl^-] = \dfrac{2x}{V} = 2S(PbCl_2)$.

Hence

$$K_s = [Pb^{2+}][Cl^-]^2 = x\left(\frac{2x}{V}\right)^2 = S(2S)^2 = 4S^3$$

$$\therefore S = \sqrt[3]{\frac{K_s}{4}}$$

Give that $K_s(PbCl_2) = 1.7 \times 10^{-5}$ @25°C, $S(PbCl_2) = \sqrt[3]{\frac{1.7 \times 10^{-5}}{4}} = 1.6 \times 10^{-2}\ M$ @25°C

The same results is obtained for a 2:1 electrolyte.

3. Case C: a 1:1 Electrolyte in Solution where a "common ion" is present.

Examples include silver chloride dissolved in sodium chloride solution, or in silver nitrate solution. The "common ion" in the first case is the chloride ion, and in the second case is the silver ion.
Consider the case of silver chloride dissolved in 0.10 M sodium chloride solution. Le Chatelier's Principal tells us that increasing the concentration of a product will shift equilibrium position to the left, in favour of reactants. In this case that means a decrease in solubility. A quantitative treatment follows.
It is now better to build up the "ICE" table in terms of molarities:

	AgCl(s)	$\rightleftharpoons$	Ag^+(aq)	+	Cl^-(aq)
Initial /M	N/a		0		0.1
Change /M	N/a		+x		+x
Equilibrium /M	N/a		x		0.1+x

Again x represents the solubility of the silver chloride and we note that since the AgCl is only sparingly soluble, We assume that $x \ll 0.1$, and so $0.1 + x \approx 0.1$.

$$K_s = [Ag^+][Cl^-] = x(0.1 + x) \approx 0.1x = 0.1S$$

$$\therefore S = \frac{K_s}{0.1} = 10K_s$$

Since $K_s = 1.8 \times 10^{-10}$ at 25°C, the solubility of silver chloride in 0.1 M sodium chloride solution is 1.8×10^{-9} M.

(This value confirms the assumption as true since $\frac{1.8 \times 10^{-9}}{0.1} = 1.8 \times 10^{-8} = 1.8 \times 10^{-6}\%$ and $1.8 \times 10^{-6}\% \ll 5\%$.)

The above value (1.8×10^{-9} M) is much smaller than the solubility in pure water (1.3×10^{-5} M @ 25°C). We conclude that the presence of a common ion greatly reduces solubility. This can be employed to aid precipitation i.e. make it more nearly complete.

4. Case D: a 1:2 (or 2:1) Electrolyte in Solution where a "common ion" is present.

Consider lead(II) chloride in the presence of 0.10 M lead(II) nitrate.
The "ICE" table becomes:

	$PbCl_2$(s)	$\rightleftharpoons$	Pb^{2+}(aq)	+	$2Cl^-$(aq)
Initial /M	N/a		0.1		0
Change /M	N/a		+x		+2x
Equilibrium /M	N/a		0.1+x		2x

The solubility of lead(II) chloride is again represented by x.
Once again we assume that $x \ll 0.1$, and so $0.1 + x \approx 0.1$.

$$K_s = [Pb^{2+}][Cl^-]^2 = (0.1 + x)(2x)^2 \approx 0.1(2x)^2 = 0.4S^2$$

$$\therefore S = \sqrt{\frac{K_s}{0.4}}$$

At 25°C, $K_s(PbCl_2) = 1.7 \times 10^{-5}$ and so

$$S(PbCl_2) = \sqrt{\frac{1.7 \times 10^{-5}}{0.4}} = 6.519 \times 10^{-3} = 6.5 \times 10^{-3}\ M\ \text{to 2 s.f.}$$

In this case the assumption is unsatisfactory since $\frac{6.5 \times 10^{-3}}{0.1} = 6.5 \times 10^{-2} = 6.5\%$ which is greater than 5%.

Another step or two of calculation is required.

We may construct a polynomial:

$$K_s = 1.7 \times 10^{-5} = (0.1 + x)(2x)^2 = 0.4x^2 + 4x^3$$

$$\therefore 4x^3 + 0.4x^2 - K_s = 0$$

and solve it, but since this is a cubic it is difficult to solve, although a graphical method is quite simple. (See the graph at the end of this article.)

Alternatively, we may rearrange the expression that we had previously,

$$1.7 \times 10^{-5} = (0.1 + x)(2x)^2 \ldots \text{①},$$

to give

$$x = \sqrt{\frac{1.7 \times 10^{-5}}{4(0.1 + x)}}$$

and substitute our (un-rounded) approximate value for x, 6.519×10^{-3}, in the right hand side of the expression, to give:

$$x = \sqrt{\frac{1.7 \times 10^{-5}}{4(0.1 + 6.5 \times 10^{-3})}}$$

$$\therefore x = 6.317 \times 10^{-3}$$

This is very conveniently done with a spread sheet (e.g. Microsoft Excel). Repeating the procedure by substituting $x = 6.317 \times 10^{-3}$ in ① gives $x = 6.323 \times 10^{-3}$, and then substituting $x = 6.323 \times 10^{-3}$ gives successively $6.322, \times 10^{-3}$, 6.322×10^{-3} etc. Once the value does not changes we know we have the correct value for x.

(We could have rearranged the expression in other ways too. For example:

$$x = \frac{1.7 \times 10^{-5}}{4x^2} - 0.1$$

If we use this expression we get, successively, 0, 6.51920×10^{-3}, 6.31656×10^{-3}, 6.32258×10^{-3}, 6.32240×10^{-3}, 6.32240×10^{-3}. We get the right answer, but a little slower.)

It is therefore clear that, to 2 s.f., the solubility is 6.3×10^{-3} M)

We note that the reduction in solubility caused by the introduction of a common ion (1.6×10^{-2} M to 6.3×10^{-3} M) is not nearly so significant as with silver chloride (1.3×10^{-5} M to 1.8×10^{-9} M).

The following graph was produced with "Speq Math", a neat little program which is a free download from . The function plotted is shown in the top right hand corner. It may be seen that the value of x that makes the function equal to 0 is about 0.0063, in agreement with the solution produced above.

$4*x^3+0.4*x^2-1.7*10^-5$