ASSUMPTIONS WITH EQUILIBRIUM

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Example #1

At 2000°C, K_{eq} is 6.40 x 10^{-7} for the decomposition of CO_2 into CO and O_2. Calculate all equilibrium concentrations if 0.250 mol of CO_2 is placed in a 1.00 L container at the given temperature.

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$$2CO_{2(g)} \Leftrightarrow 2CO_{(g)} + O_{2(g)}$$

	$2CO_{2(g)}$	$2CO_{(g)}$	$O_{2(g)}$
I	0.250	0	0
C			
E			

$$K_{eq} = \frac{[CO]^2[O_2]}{[CO_2]^2}$$

$$6.40\times10^{-7} = \frac{[2x]^2[x]}{[0.250-2x]^2}$$

$$6.40\times10^{-7} = \frac{4x^3}{0.0625-x+4x^2}$$

How do we solve this cubic equation?!

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	$2CO_{2(g)}$	$2CO_{(g)}$	$O_{2(g)}$
I	0.250	0	0
C	-2x	+2x	+x
E	0.250-2x	2x	x

Look at the K_{eq} (which is 0.000000640): VERY little of the CO_2 actually decomposes.

So x must be a VERY VERY small number.

So we assume that 0.250-2x = 0.250

It's **as if** we're assuming that x is 0.

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$$2CO_{2(g)} \Leftrightarrow 2CO_{(g)} + O_{2(g)}$$

	$2CO_{2(g)}$	$2CO_{(g)}$	$O_{2(g)}$
I	0.250	0	0
C	-2x	+2x	+x
E	0.250-2x	2x	x

$$K_{eq} = \frac{[CO]^2[O_2]}{[CO_2]^2}$$

$$6.40\times10^{-7} = \frac{[2x]^2[x]}{[0.250-2x]^2}$$

Assumption: 0.250-2x = 0.250

$$6.40\times10^{-7} = \frac{[2x]^2[x]}{[\mathbf{0.250}]^2}$$

$$6.40\times10^{-7} = \frac{4x^3}{0.0625}$$

$$4.00\times10^{-8} = 4x^3$$

$$1.00\times10^{-8} = x^3$$

$$\sqrt[3]{(1.00\times10^{-8})} = \sqrt[3]{(x^3)}$$

$$2.15\times10^{-3} = x$$

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Example #1

At 2000°C, K_{eq} is 6.40 x 10^{-7} for the decomposition of CO_2 into CO and O_2.

Calculate all equilibrium concentrations

if 0.250 mol of CO_2 is placed in a 1.00 L container at the given temperature.

	$2CO_{2(g)}$	$\Leftrightarrow$ $2CO_{(g)}$	+ $O_{2(g)}$
I	0.250	0	0
C	-2x	+2x	+x
E	0.250-2x	2x	x

$x = 2.15 \times 10^{-3}$

$= 0.250 - 2(2.15 \times 10^{-3})$
$= 0.247M$

$= 2(2.15 \times 10^{-3})$
$= 0.0043M$

.: $[CO_{2(g)}] = 2.47 \times 10^{-1}M$, $[CO_{(g)}] = 4.30 \times 10^{-3}M$, & $[O_{2(g)}] = 2.15 \times 10^{-3}M$

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Example #1

	$2CO_{2(g)}$ ⇔	$2CO_{(g)}$ +	$O_{2(g)}$
I	0.250	0	0
C	-2x	+2x	+x
E	0.250-2x	2x	x

0.247 and 0.250 are very close

The difference is 1.2%. As long as the difference is less than 5%, you can use the assumption.

You can also divide the initial concentration by k_{eq}. If the answer is AT LEAST 100, you can use the assumption.

$0.250/6.40 \times 10^{-7} = 3.91 \times 10^{5}$, which is MUCH bigger than 100

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Simplification of equilibrium equations may usually be used if K_{eq} values are:

1. greater than 10^3

2. less than 10^{-3}

Questions involving a lot of polynomial expansion is a good indication that an assumption should be used.

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Example #2

What is molar solubility of $PbCl_{2(s)}$ in a 0.2 mol / L $NaCl_{(aq)}$ solution? $K_{sp} = 1.7x10^{-5}$

K_{sp} = solubility product constant

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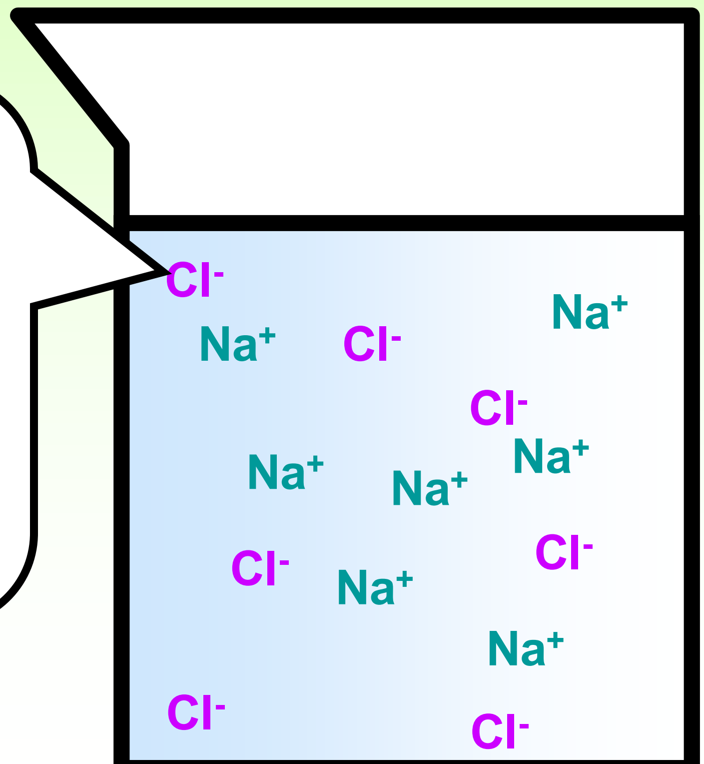
Example #2

What is molar solubility of $PbCl_{2(s)}$ in a 0.2 mol / L $NaCl_{(aq)}$ solution? $K_{sp} = 1.7 \times 10^{-5}$

$$PbCl_{2(s)} \Leftrightarrow Pb^{2+}_{(aq)} + 2Cl^{-}_{(aq)}$$

The Cl^- ions *ALREADY* in solution will limit the amount of $PbCl_2$ that can be dissolved



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Example #2

What is molar solubility of $PbCl_{2(s)}$ in a 0.2 mol / L $NaCl_{(aq)}$ solution? $K_{sp} = 1.7 \times 10^{-5}$

	$PbCl_{2(s)}$ ⇔	$Pb^{2+}_{(aq)}$ +	$2Cl^{-}_{(aq)}$
I	-	0	0.2
C	-	+x	+2x
E	-	x	0.2+2x

$$K_{sp} = [Pb^{2+}][Cl^{-}]^2$$

$$1.7 \times 10^{-5} = [x][0.2+2x]^2$$

Because K_{sp} is SO small, very little $PbCl_2$ actually dissolves

Assumption: $0.2+2x = 0.2$

$$1.7 \times 10^{-5} = [x][\mathbf{0.2}]^2$$

$$\frac{1.7 \times 10^{-5}}{0.04} = x$$

$$4.2 \times 10^{-4} = x$$

.: the molar solubility of $PbCl_2$ in 0.2M $NaCl_{(aq)}$ is 4.2×10^{-4} mol/L

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Net Ionic Equations

Do you remember what this is?

How does it affect equilibrium?

Chemical equation:

$$K_2CO_{3(aq)} + CuSO_{4(aq)} \rightarrow K_2SO_{4(aq)} + CuCO_{3(s)}$$

Ionic equation:

→ Anything that is aqueous must be separated into its component ions

$$\cancel{2K^{+}_{(aq)}} + CO_3^{2-}{}_{(aq)} + Cu^{2+}{}_{(aq)} + \cancel{SO_4^{2-}{}_{(aq)}} \rightarrow \cancel{2K^{+}_{(aq)}} + \cancel{SO_4^{2-}{}_{(aq)}} + \underline{CuCO_{3(s)}}$$

Net Ionic equation:

→ **Spectator ions** are eliminated

$$Cu^{2+}{}_{(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow CuCO_{3(s)}$$

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Common Ion Effect

For aqueous solutions, the addition of ions may or may not affect equilibrium.

The added ion will only affect equilibrium when it is one that is common with those involved in the net ionic equation.

Spectator ions will not affect equilibrium.