EQUILIBRIUM CALCULATIONS

- We're often interested in figuring out what happens at equilibrium BEFORE we do an experiment!

- What's the problem? Initially, we know only ... INITIAL concentrations. Since these are NOT equilibrium concentrations, we cannot simply plug them into an equilbrium expression and solve.

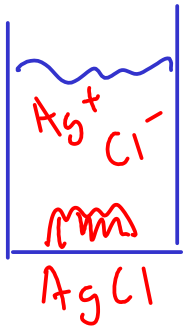
- So how do we find out what the concentrations are at equilibrium if we initially know NONE of them?

- To solve an equilibrium problem, write out the equilibrium constant expression. Then, try to RELATE ALL THE EQUILIBRIUM CONCENTRATIONS TO ONE ANOTHER using the chemical equation.

- It helps to assign a variable based on one of the substances in the reaction, then write the concentrations of the other substances based on that variable. How to do this? Take a look at the following examples...

EXAMPLE: Calculate the grams per liter of silver(i) chloride (AgCl) in a solution that is at equilibrium with solid AgCl.

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



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

Assign a VARIABLE, x, to be equal to the change in silver concentration...

	[initial]	Δ	[equilibrium]
Ag^+	0	+x	x
Cl^-	0	+x	x

Since the concentrations of silver ion and chloride ion are related, we can solve this problem!

$$[Ag^+][Cl^-] = 1.8 \times 10^{-10}$$

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

$$x = 1.34 \times 10^{-5} = [Ag^+] = [Cl^-]$$

'x' ALSO equals the nominal concentration of DISSOLVED AgCl

$$[AgCl]_{dissolved} = 1.34 \times 10^{-5} \, \underline{M}$$

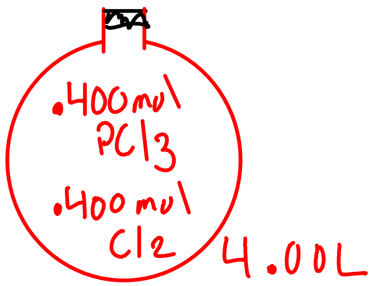
143.321 g AgCl / mol

$$\frac{1.34 \times 10^{-5} \text{ mol AgCl}}{L} \times \frac{143.321 \text{ g}}{\text{mol}} = \boxed{0.0019 \text{ g/L}}$$

Equivalent to 1.9 ppm (parts per million) - mg/L

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g) \quad K_c = 49$$

If you add 0.400 moles of each reactant to a 4.00 L reaction vessel, what is the composition of the equilibrium mixture?



Initial conditions

Start with the equilibrium expression:

$$K_c = 49 = \frac{[PCl_5]}{[PCl_3][Cl_2]}$$

These concentrations are EQUILIBRIUM concentrations

SPECIES	INITIAL CONCENTRATION	Δ	EQUILIBRIUM CONCENTRATION
PCl_3	$\frac{.400\ mol}{4.00\ L} = 0.100\ M$	$-x$	$0.100 - x$
Cl_2	$\frac{.400\ mol}{4.00\ L} = 0.100\ M$	$-x$	$0.100 - x$
PCl_5	0	$+x$	x

Define 'x' as the change in concentration of phosphorus pentachloride

$$\frac{[PCl_5]}{[PCl_3][Cl_2]} = \boxed{\frac{x}{(0.100 - x)(0.100 - x)} = 49}$$

To solve the problem, we must first solve this equation for 'x'.

$$\frac{x}{(.100-x)(.100-x)} = 49$$

$$\frac{x}{(.100-x)^2} = 49$$

$$(a-b)^2 = a^2 - 2ab + b^2$$

$$\frac{x}{0.0100 - 0.200x + x^2} = 49$$

$$x = 49(0.0100 - 0.200x + x^2)$$

$$x = 0.49 - 9.8x + 49x^2$$

$$0 = 49x^2 - 10.8x + 0.49$$

$a = 49$ $b = -10.8$ $c = 0.49$

$$x = \frac{10.8 \pm \sqrt{(-10.8)^2 - 4(49)(0.49)}}{2(49)} = \frac{10.8 \pm \sqrt{20.6}}{98}$$

$x = \cancel{0.157}$ OR 0.0639

This value for 'x' results in NEGATIVE concentrations for both reactants. This is physically impossible (conservation of mass), so we throw this answer out!

This equation is a QUADRATIC equation:

$$ax^2 + bx + c = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Each quadratic equation has TWO solutions. However, only ONE of these solutions makes chemical sense!

	Initial	Δ	Equilibrium
$[PCl_5]$	0	$+x$	x
$[Cl_2]$	$\frac{.400\text{ mol}}{4.00\text{ L}} = .100$	$-x$	$0.100 - x$
$[PCl_3]$	$\frac{.400\text{ mol}}{4.00\text{ L}} = .100$	$-x$	$0.100 - x$

$x = 0.0639\ \underline{M}$

To change from molarity to moles, multiply by the volume (in liters)

$[PCl_5] = x = 0.0639\ \underline{M} \times 4.00\text{ L} = .286\text{ mol } PCl_5$

$[Cl_2] = 0.100 - x = 0.0361\ \underline{M} \times 4.00\text{ L} = .144\text{ mol } Cl_2$

$[PCl_3] = 0.100 - x = 0.0361\ \underline{M} \times 4.00\text{ L} = .144\text{ mol } PCl_3$

Concentrations at equilibrium

Number of moles in reaction vessel at equilibrium

Quick comparison of initial and equilibrium states:

$$\boxed{\begin{array}{l} 0.400\text{ mol } PCl_3 \\ 0.400\text{ mol } Cl_2 \\ 0\text{ mol } PCl_5 \end{array}} \xrightarrow{\quad} \boxed{\begin{array}{l} 0.144\text{ mol } PCl_3 \\ 0.144\text{ mol } Cl_2 \\ 0.286\text{ mol } PCl_5 \end{array}}$$

$K_c = 49$

INITIAL STATE

EQUILIBRIUM STATE