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 equilibrium expression and solve.

$$A + B \rightleftharpoons C + D$$

$$K_c = \frac{[C][D]}{[A][B]} \quad \text{... at equilibrium}$$

> 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 moles of Cl- ion in a solution where solid AgCl has been mixed with distilled water and allowed to come to equilibrium.

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

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

We need to relate the silver and chloride concentrations in order to solve the problem!

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

Let "x" equal the change in silver ion concentration

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

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

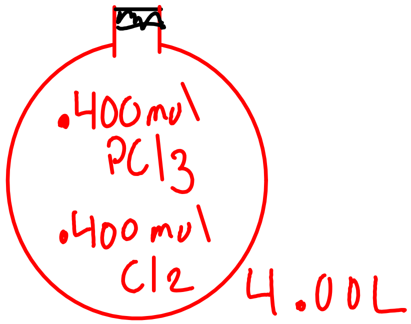
$$x^2 = 1.8 \times 10^{-10}$$

$$x = 1.3 \times 10^{-5} = [Ag^+] = [Cl^-]$$

$$[Cl^-] = \boxed{1.3 \times 10^{-5} \, \underline{M} \; Cl^-}$$

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

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



Initial conditions

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

We need to relate these concentrations to a single variable. Use an equilibrium chart!

Species	[Initial]	Δ	[Equilibrium]
PCl_5	0	$+x$	$0 + x = x$
PCl_3	$\frac{0.400 \text{ mol}}{4.00 \text{ L}} = 0.100$	$-x$	$0.100 - x$
Cl_2	$\frac{0.400 \text{ mol}}{4.00 \text{ L}} = 0.100$	$-x$	$0.100 - x$

Lex "x" equal the change in phosphorus pentachloride concentration

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

Now, we need to solve for "x"

$$\frac{(x)}{(0.100-x)(0.100-x)} = 49$$

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

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

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

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

$0 = \underbrace{0.49}_{c} \underbrace{- 10.8x}_{b} + \underbrace{49}_{a}x^2$

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

$x = 0.157$ OR $x = 0.0639$

The QUADRATIC EQUATION:

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

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

Each quadratic has two solutions (see the +/- part of the equation), but only one of them will be the correct chemical solution.

A quadratic equation has two solutions, BUT only one of them is correct chemically.

HOW DO WE CHOOSE?

Species	[Initial]	Δ	[Equilibrium]
PCl_5	0	$+x$	$0+x = x$
PCl_3	$\frac{0.400 \text{ mol}}{4.00 L} = 0.100$	$-x$	$0.100-x$
Cl_2	$\frac{0.400 \text{ mol}}{4.00 L} = 0.100$	$-x$	$0.100-x$

$x = 0.157$ OR $x = 0.0639$

This solution would give NEGATIVE concentrations of both phosphorus trichloride and chlorine gas, which is physically impossible! Use the other solution (0.0639) instead.

$[PCl_5] = x = 0.0639\ M\ PCl_5$

$[PCl_3] = 0.100 - x = 0.0361\ M\ PCl_3$

$[Cl_2] = 0.100 - x = 0.0361\ M\ Cl_2$

The equilibrium constant is 49, which is significantly larger than 1. That means the amount of product should be large compared to the amount of reactant left over at equilibrium.