- TEMPERATURE can also cause equilibrium shifts. These temperature-caused shifts can be easily illustrated with Le Chaleleir's principle.

endothermic reaction:

$$A + B + \text{heat} \rightleftarrows C + D$$

- Heat, here, is represented as if it's a reactant!
- If temperature INCREASES, the equilibrium shifts to the RIGHT, making more products.
- If temperature DECREASES, the equilibrium shifts to the LEFT, making more reactants.

exothermic reactions:

$$A + B \rightleftarrows C + D + \text{heat}$$

- In the exothermic case, heat is a product!
- If temperature INCREASES, then the equilibrium shifts to the LEFT, making more reactants.
- If temperature DECREASES, then the equilibrium shifts to the RIGHT, making more products.

- Optimization:

* For ENDOTHERMIC reactions, run as hot as possible. You make MORE products FASTER.
* For EXOTHERMIC reactions, you want to run the reaction cooler (for more products), but not so cool as to make the reaction slow!

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.

$\boxed{\text{So how do we find out what the concentrations are at equilibrium if we initially know NONE of them?}}$

- 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...

AgCl: $107.9 + 35.45 = 143.35$ g/mol

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

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

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

We need to solve the equilibrium expression for either the (Ag+) or the (Cl-), but there are two variables. Let's see if we can relate them.

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

Define "x" as the increase in the concentration of Ag+ ...

Now that we've expressed all the concentrations in terms of a single variable (x), we can solve!

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

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

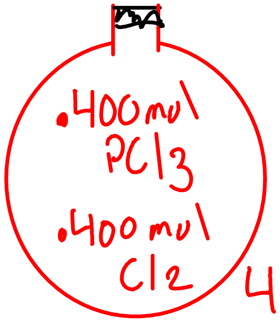
$$x = 1.34 \times 10^{-5}\,M = [Ag^+] = [Cl^-] = [AgCl]_{dissolved}$$

Convert molar solubility of AgCl to grams per liter...

$$\frac{1.34 \times 10^{-5} \text{ mol AgCl}}{L} \times \frac{143.35 \text{ g AgCl}}{\text{mol AgCl}} = \boxed{0.0019 \text{ g AgCl}/L}$$

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

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



4.00L

Initial conditions

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

We'll need to solve this expression.

Like the last example, we'll want to try to relate these concentrations to one variable...

Let "x" equal the increase in phosphorus pentachloride concentration!

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

Substitute (Equilibrium) concentrations back into the equilibrium expression...

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

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

$$\frac{x}{(0.100-x)^2} = 49$$

$$x = 49(0.100-x)^2$$

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

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

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

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

$$c = 0.49, \quad b = -10.8, \quad a = 49$$

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

$$x = \cancel{0.157} \quad \underline{\text{or}} \quad x = 0.0639$$

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.

The quadratic has TWO solutions, but only ONE of those is possible checmically. Which?

(x = 0.157 doesn't work because it would lead to impossible concentrations of phosphorus trichloride and chlorine! See the chart on the previous page!)