- LE CHATELEIR'S PRINCIPLE states that if an equilbrium is disturbed, it will SHIFT in such a way as to counteract the disturbance and restore equilibrium.

For concentrations:

* Increasing the concentration of a REACTANT will cause the equilibrium to shift to the RIGHT, making more products.
* Decreasing the concentration of a REACTANT will cause the equilibrium to shift to the LEFT, making more reactants.

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* Increasing the concentration of a PRODUCT will cause the equilibrium to shift to the LEFT, making more reactants.
* Decreasing the concentration of a PRODUCT will cause the equilibrium to shift to the RIGHT, making more products.

This one can be used to DRIVE a reaction to produce product, even if the Kc value is NOT favorable.

- 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.

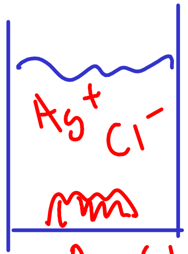
So how do we find out what the concentrations are at equilibrium if we initially know NONE of them?

- 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.

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



AgCl

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

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

Assign a variable: Let 'x' equal the change in concentration of silver(I) ion!

Each time we make Ag+, we also make Cl- ion ... They form in a 1:1 ratio.

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

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

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

$$x = 1.3416 \times 10^{-5}\ ;\ [Ag^+] = [Cl^-] = 1.3416 \times 10^{-5}\ \underline{M}$$

Sub stitute the variable into the equilibrium expression, then solve for 'x'.

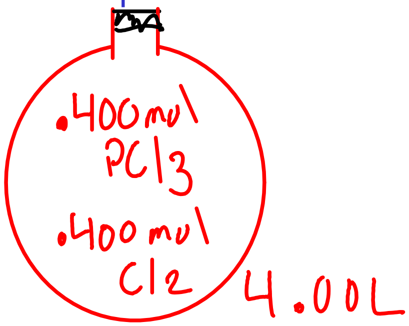
The concentration of dissolved AgCl also equals 'x':

$$[AgCl]_{dissolved} = [Ag^+] = 1.3416 \times 10^{-5} \frac{mol}{L} \times \frac{143.35\,g}{mol} = \boxed{0.0019\ g/L}$$

Equivalent to 1.9 ppm ("parts per million"). Same as mg/L for dilute aqueous solutions.

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

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



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

These concentration are EQUILIBRIUM concentrations.

Initial conditions

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

We've defined 'x' to be the change in concentration of phosphorus trichloride

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

To solve the problem, we need to solve this expression for 'x'.

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

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

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

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

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

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

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

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

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

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

This value of 'x' results in negative concentrations for both reactants, which is not possible. This value for 'x' must be discarded - it doesn't make chemical sense.

This is a second-order QUADRATIC equation:

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

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

Each quadratic has TWO SOLUTIONS. Only ONE of these solutions will be the real chemical solution. (The other will not make chemical sense!)

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

$0.0639 = x$

Equilibrium concentrations

Number of moles of each substance at equilibrium

$[PCl_3] = 0.100 - x = 0.036 M \times 4.00 L = 0.144 \text{ mol } PCl_3$

$[Cl_2] = 0.100 - x = 0.036 M \times 4.00 L = 0.144 \text{ mol } Cl_2$

$[PCl_5] = x = 0.0639 M \times 4.00 L = 0.256 \text{ mol } PCl_5$

Quick comparison of initial and equilibrium states:

0.400 mol PCl_3
0.400 mol Cl_2
0 mol PCl_5

$\xrightarrow{K_c = 49}$

(We expect products to be favored at equilibrium)

0.144 mol PCl_3
0.144 mol Cl_2
0.256 mol PCl_5