

- LE CHATELEIR'S PRINCIPLE states that if an equilibrium 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  $K_c$  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:



- 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:



- 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 equilibrium 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...

$$\text{AgCl: } 107.9 + 35.45 = 143.35 \text{ g/mol}$$

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



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

To solve the equilibrium expression, we need to express BOTH concentrations in terms of a single variable. Let

Species	[Initial]	$\Delta$	[Equilibrium]
$\text{Ag}^+$	0	+x	x
$\text{Cl}^-$	0	+x	x

Let "x" equal the change in silver ion concentration

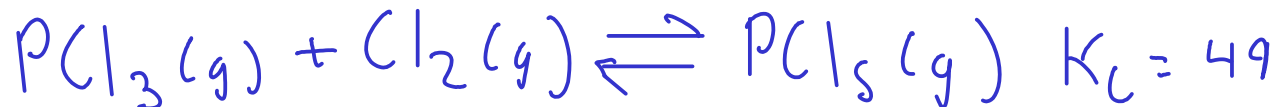
Plug our equilibrium expressions for silver ion and chloride ion back into the  $K_c$  equation, then solve.

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

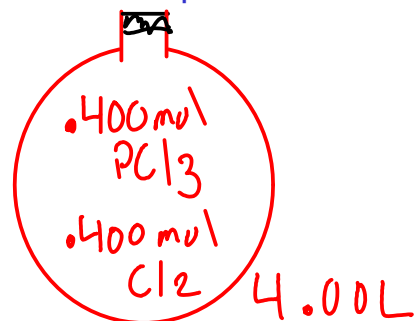
$$x = 1.3416 \times 10^{-5} = [\text{Ag}^+] = [\text{Cl}^-] = [\text{AgCl}]_{\text{dissolved}}$$

The dissolved AgCl concentration just equals the concentration of either the silver or chloride ions. So all we need to do is change the units from MOLES/L to g/L ...

$$\frac{1.3416 \times 10^{-5} \text{ mol AgCl}}{\text{L}} \times \frac{143.35 \text{ g AgCl}}{\text{mol AgCl}} = \boxed{0.0019 \text{ g AgCl/L}}$$



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?



Start by writing the equilibrium expression:

$$K_c = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = 49$$

Make a chart to try to tie the three unknown concentrations together!

Species	[Initial]	$\Delta$	[Equilibrium]
PCl <sub>5</sub>	0	+ X	X
PCl <sub>3</sub>	$\frac{0.400 \text{ mol}}{4.00 \text{ L}} = 0.100$	- X	0.100 - X
Cl <sub>2</sub>	$\frac{0.400 \text{ mol}}{4.00 \text{ L}} = 0.100$	- X	0.100 - X

Let "x" equal the change in phosphorus pentachloride concentration

Plug back into K<sub>c</sub> equation ...

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

... now solve for "x".

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

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

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

$$x = 49(0.01 - 0.200x + x^2)$$

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

$$0 = \underbrace{0.49}_c - \underbrace{10.8x}_b + \underbrace{49x^2}_a$$

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

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

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 equation has two solutions, but only one of them is CHEMICALLY possible. How can we tell which one is correct?