MODIFYING EQUILIBRIUM

- Remember, at equilibrium the reaction has not actually STOPPED. Both forward and reverse processes are still happening - just at the same rate so there's no overall concetration change.

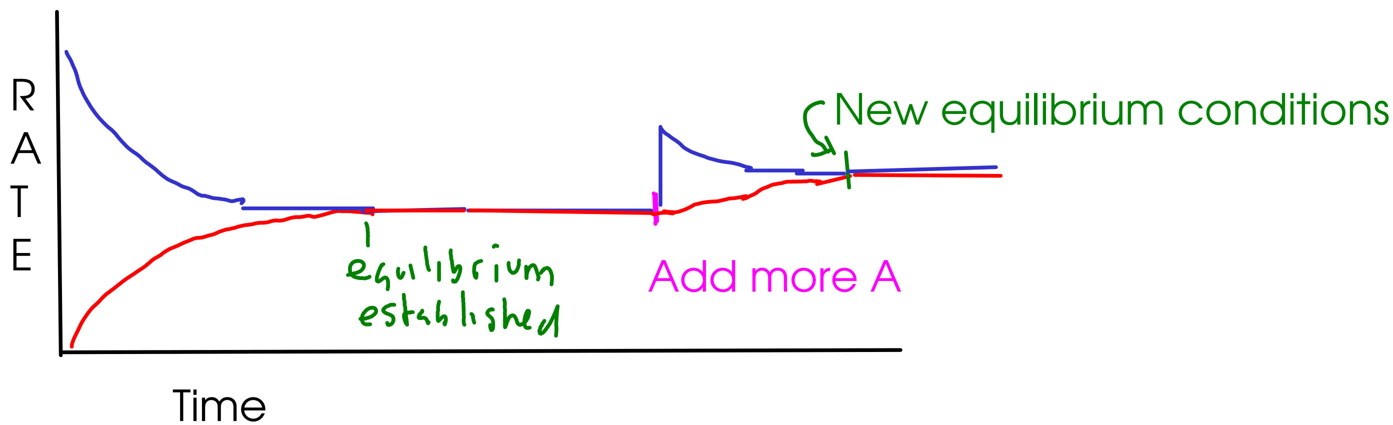
- If you do something to the reaction mixture that changes the rates of the forward or the reverse reaction (or sometimes BOTH), the mixture will no longer be at equilibrium.

Simplest case is to add or remove a substance, changing its concentration.

$$A + B \rightleftarrows C + D$$

$$Rate_{,fwd} = k_f [A][B]$$

$$Rate_{,rev} = k_r [C][D]$$



- After adding A, the rate of the forward reaction increased. As more C and D were produced by the (faster) forward reaction, the forward reaction and reverse reaction came back to equilibrium, but at a new set of conditions.

- The addition of A caused our equilibrium to SHIFT towards the RIGHT - consuming some of the extra A to form more products (C and D).

- 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...

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

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

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

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

Define "x" as the change in Ag+ concentration

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

Each time we make an Ag+, we also make a Cl- ... 1:1 ratio of Ag+ to Cl- in chem. eqn.

Substitute into the Kc expression

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

$$x^2 = 1.8 \times 10^{-10}\ ;\ so\ x = 1.3 \times 10^{-5} = [Ag^+] = [Cl^-]$$

Since every silver ion comes from dissolving one formula unit of AgCl, the dissolved AgCl concentration just equals the silver ion concentration. $[AgCl]_{dissolved} = [Ag^+] = 1.3 \times 10^{-5}\ M$

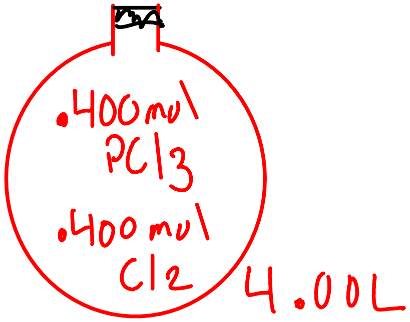
$$\frac{1.3 \times 10^{-5}\ mol\ AgCl}{L} \times \frac{143.35\ g\ AgCl}{mol\ AgCl} = \boxed{0.0019\ g\ AgCl/L}$$

formula weight of AgCl

A common solubility unit: ppm (parts per million) For dilute aqueous solutions, ppm is equivalent to mg/L. So the AgCl concentration is 1.9 ppm ...

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

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?



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

We need to relate the three concentrations to a single variable so we can solve the problem!

Initial conditions

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

Let "x" equal the decrease in the phosphorus trichloride concentration

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

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

This is a second-order equation ...