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.

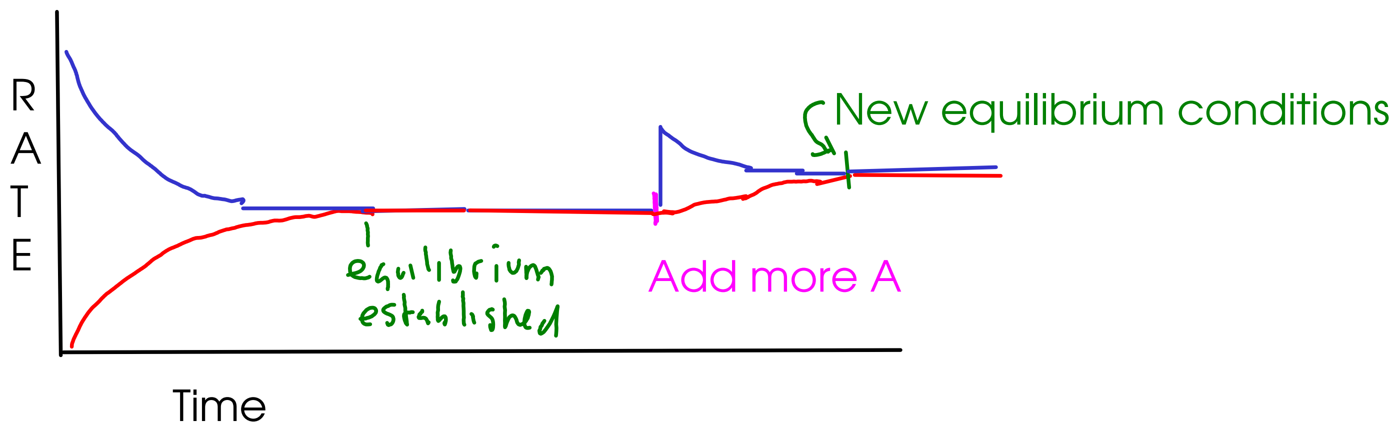
- If you do something to the reaction mixture that changes the rates of the forward or the reverse reaction (or sometimes BOTH), the mixture will no longer be at equilibrium.

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

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

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

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



- 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.

---

* 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.

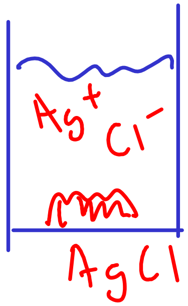
So how do we find out what the concentrations are at equilibrium if we initially know NONE of them?

- 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.

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



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

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

Assign a variable: We've let 'x' equal the change in concentration of silver(I) ion.

Each time we make a silver(I) ion, we also make a chloride ion

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

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

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

$$x = 1.34 \times 10^{-5} \; ; \; [Ag^+] = [Cl^-] = 1.34 \times 10^{-5} \, \underline{M}$$

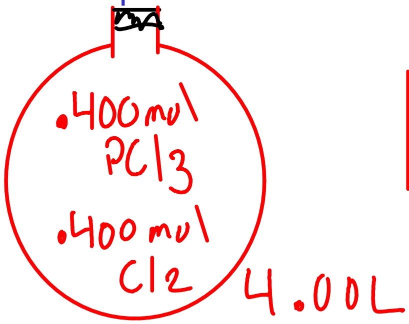
Substitute the equilibrium concentrations in terms of our variable 'x' into the equilibrium expression.

Since the concentration of dissolved AgCl equals the silver ion cocnentration (aka 'x'):

$$[AgCl]_{dissolved} = 1.34 \times 10^{-5} \frac{mol}{L} \times \frac{143.35 \, g}{mol} = \boxed{0.0019 \frac{g \, AgCl}{L}}$$

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

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



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

These concentrations are EQUILIBRIUM concentrations!

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

We've defined 'x' as the amount of change in the concentration of phosphorus trichloride

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

To solve this problem, we must solve this expression for 'x'

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

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

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

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

$$x = 49(0.0100 - .200x + x^2)$$

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

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

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

This equation is second order in 'x', so we can solve it simply by using the quadratic equation:

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

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

Each quadratic equation has TWO solutions. However, the chemical problem we're trying to solve has only ONE solution. One of the answers, therefore, will be chemically incorrect.

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

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

This value of 'x' results in NEGATIVE concentrations for both reactants. That's not physically possible, since you can't react away more molecules than you started with!

Species	[Equilibrium]
PCl_3	$0.100 - x$
Cl_2	$0.100 - x$
PCl_5	x

Species	[Equilibrium]
PCl_3	$0.100 - x$
Cl_2	$0.100 - x$
PCl_5	x

$x = 0.0639$

Now, calculate the composition of the equilibrium mixture. Since it's not specified, we'll give both concentrations and numbers of moles.

Equilibrium concentrations

moles at equilibrium

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

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

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

Quick comparison of initial and equilibrium states:

initial state:
- 0.400 mol PCl_3
- 0.400 mol Cl_2
- 0 mol PCl_5

$\xrightarrow{K_c = 49}$

equilibrium state:
- 0.144 mol PCl_3
- 0.144 mol Cl_2
- 0.256 mol PCl_5