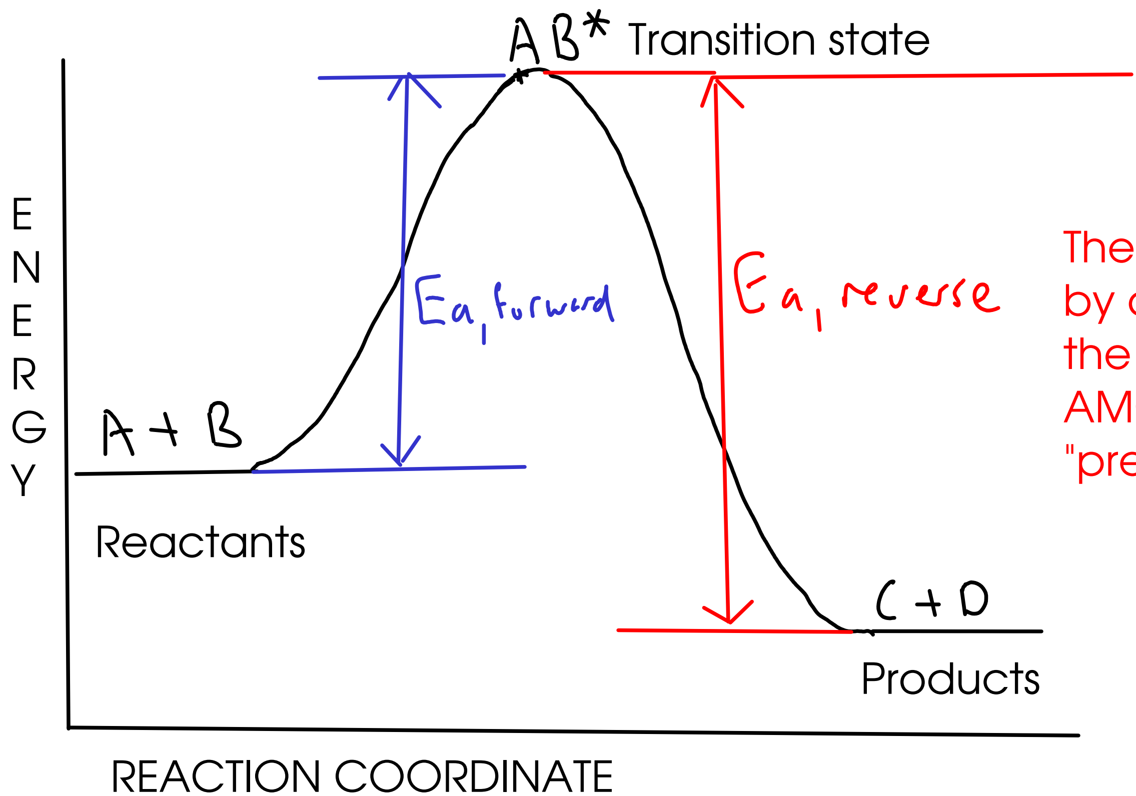
WHAT KEEPS A REACTION FROM GOING BACKWARDS?

$A + B \rightarrow C + D$ (reactants → products) | $C + D \rightarrow A + B$ (reactants → products)

... what keeps the reaction on the right from occurring?

$$A + B \rightarrow C + D$$



The reverse reaction is "prevented" by an activation energy barrier - the same thing (if not the same AMOUNT of energy) that "prevents" the forward reaction!

So what really happens during a reaction? Both forward and reverse reactions occur!

$A + B \longrightarrow C + D$

reactants products

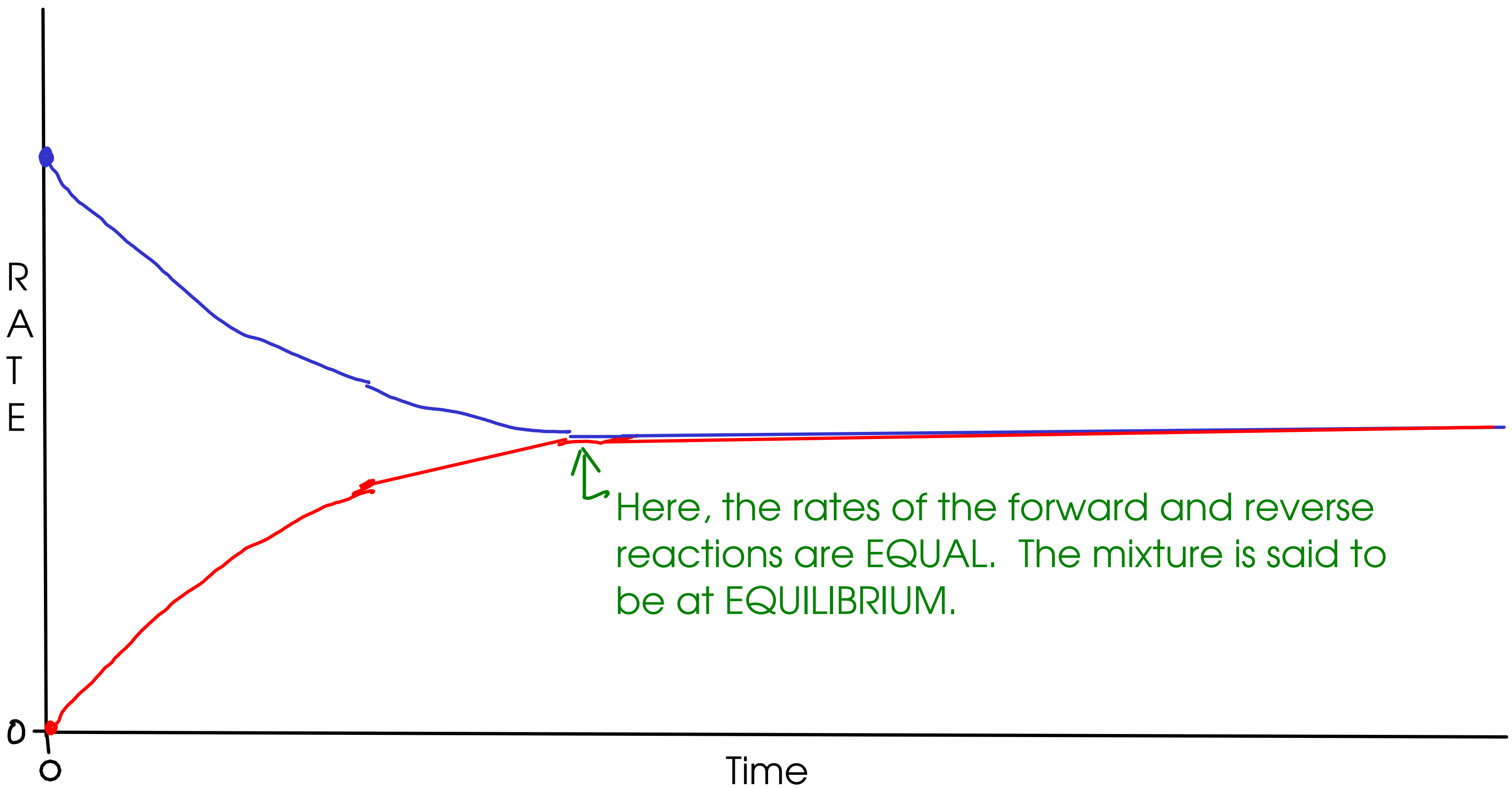
$Rate = k_F[A][B]$

$C + D \longrightarrow A + B$

reactants products

$Rate = k_r[C][D]$

- Let's look at the RATES of both the forward and reverse reactions over time.



- Initially, the mixture is all A and B. As C and D are formed, the rate of the reverse reaction increases while the rate of the forward reaction decreases. Eventually, these rates become equal.

- At EQUILIBRIUM, the concentrations of A, B, C, and D stop CHANGING. The reaction doesn't stop, but it appears stopped to an outside observer.

DESCRIBING EQUILIBRIUM

$$\underbrace{a}A + \underbrace{b}B \rightleftarrows \underbrace{c}C + \underbrace{d}D$$

Stoichiometric coefficients

- Double-headed arrow is often used to show that both the forward and reverse reactions are important.

[ ] : molar concentrations of reactants and products AT EQUILIBRIUM.

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Equilibrium constant (concentration based)

- At equilibrium, the ratio above equals a constant number - the EQUILIBRIUM CONSTANT. The equilibrium constant depends on TEMPERATURE, but not on other factors.

- Not all reactants and products are included in the equilibrium constant expression!

$$PbI_2(s) \rightleftarrows Pb^{2+}(aq) + 2I^-(aq)$$

$$K_c = \frac{[Pb^{2+}][I^-]^2}{[PbI_2]}$$

Since the concentration of SOLID lead(II) iodide is fixed by the crystal structure of the solid and does not change over the course of the reaction, we "fold it" into the equilibrium constant.

$$K_c = [Pb^{2+}][I^-]^2 = 6.5 \times 10^{-9}$$

- Species whose CONCENTRATIONS do not change do not appear in the equilibrium constant expression. PURE SOLIDS and PURE LIQUIDS. Also, bulk SOLVENTS (like water when dealing with a reaction that takes place in water).

$$HC_2H_3O_2(aq) + H_2O(\ell) \rightleftarrows H_3O^+(aq) + C_2H_3O_2^-(aq)$$

$$K_c = \frac{[H_3O^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = 1.7 \times 10^{-5}$$

Since water is the solvent, there's enough of it so that the reaction doesn't really change the concentration of the water itself.

$[H_2O] = ?$ $\quad 1\,g/mL$, $\quad 1\,L$ water $= 1000\,g\ H_2O$

$$1000\,g\ H_2O \times \frac{mol}{18.02\,g} = 55.5\,mol\ H_2O/1L = 55.5\ \underline{M}$$

WHAT DOES AN EQUILIBRIUM CONSTANT TELL US?

1 - Whether the final reaction mixture consists of mainly products or mainly reactants. In other words, which side of the reaction is "favored". ("extent" of reaction)

2 - Whether a reaction will proceed to the left or to the right when the reaction is not yet at equilibrium.

3 - With more math, we can actually determine the final composition of an equilibrium mixture from the initial amount of reactant present WITHOUT doing an experiment!

WHICH IS FAVORED? PRODUCT OR REACTANT?

$$aA + bB \rightleftarrows cC + dD$$

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$$HC_2H_3O_2(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + C_2H_3O_2^-(aq)$$

$$K_c = \frac{[H_3O^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = 1.7 \times 10^{-5}$$

To get a small value like this one, the DENOMINATOR of the equilibrium expression must be a lot larger than the NUMERATOR.

Since REACTANTS are the denominator of this fraction, this reaction favors REACTANTS at equilibrium!

- If Kc is small (<<1), then REACTANTS are favored at equilibrium
- If Kc is large (>>1), then PRODUCTS are favored at equilibrium.

HOW TO TELL IF A REACTION IS AT EQUILIBRIUM?

- Use REACTION QUOTIENT (Q)

$$aA + bB \rightleftharpoons cC + dD$$

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Reaction quotient = equilbrium expression using NON-EQUILIBRIUM concentrations.

- If Q = Kc, then reaction is at equiilibrium.
- If Q < Kc, then reaction is NOT at equilibrium and proceeds to the right, forming more products.
- If Q > Kc, then reaction is NOT at equilibrium and proceeds to the left, forming more reactants.

$$2\,NOBr(g) \rightleftharpoons 2\,NO(g) + Br_2(g)\ ;\ K_c = 3.07\times10^{-4}$$

$[NOBr] = 0.0720\ \underline{M}$, $[NO] = 0.0162\ \underline{M}$, $[Br_2] = 0.0123\ \underline{M}$

Is mix at equilibrium? If not, which direction will reaction proceed?

$$Q = \frac{[NO]^2[Br_2]}{[NOBr]^2} = \frac{(0.0162)^2(0.0123)}{(0.0720)^2} = 6.23\times10^{-4}$$

$$6.23\times10^{-4} > 3.07\times10^{-4}$$

$$Q > K_c$$

... So the reaction is NOT at equilibrium and will proceed to the left (makes more NOBr)

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.

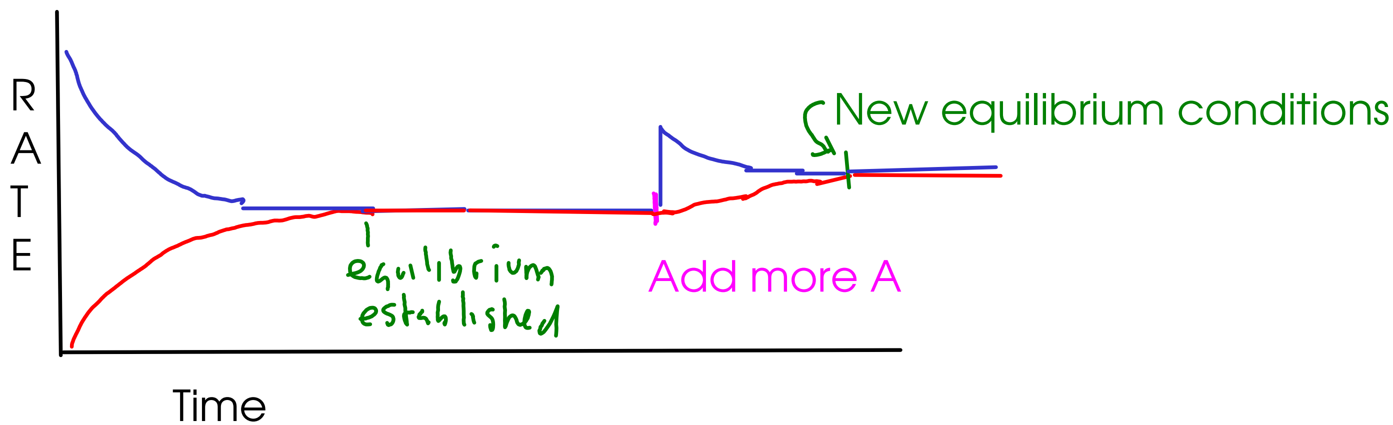
- If you do something to the reaction mixture that changes the rates of the forward or the reverse reaction (or sometimes BOTH), the mixture will no longer be at equilibrium.

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.

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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' = change in Ag^+ concentration...

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

Each time we make an Ag+ ion, we also make a Cl- ion. See the equation - there's a 1:1 ratio of Ag+ to Cl-!

Substitute 'x' into the expression and solve ...

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

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

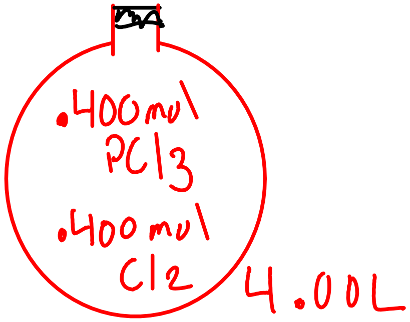
Since every silver ion comes from dissolving 1 formula unit of AgCl, the dissolved AgCl concentration must equal the silver ion concentration: $[AgCl]_{dissolved} = [Ag^+]$

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

ppm (parts per million). Equivalent to mg/L ... so the AgCl would be 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 concentraiton of each species in the equilibrium mixture?



Initial conditions

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

We need to relate all these concentrations to a single variable to solve this problem!

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 must now solve for 'x'

This is a second order equation in 'x' ...

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

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

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

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

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

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

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

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

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

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

This value of 'x' gives us negative concentration of both phosphorus trichloride and chlorine gas. That's physically impossible, so the value of 0.0639 must be the correct value for 'x'.

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 onlu one of them will be the correct chemical solution.

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

$x = 0.0639$

Now plug the value of 'x' into the expressions above to get the equilibrium concentrations.

$[PCl_3] = 0.100 - 0.0639 = \underline{0.036\ M}\ PCl_3$

$[Cl_2] = 0.100 - 0.0639 = \underline{0.036\ M}\ Cl_2$

$[PCl_5] = \underline{0.0639\ M}\ PCl_5$