

Stoichiometric coefficients

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

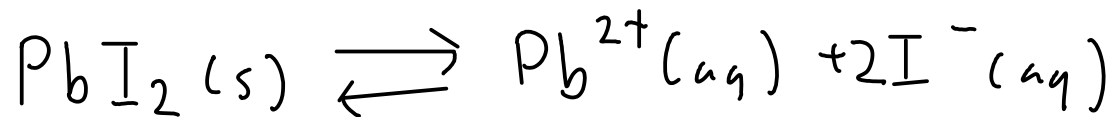
$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

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

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!



$$K_c = \frac{[\text{Pb}^{2+}][\text{I}^{-}]^2}{[\text{PbI}_2]}$$

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.

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

- 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).



$$K_c = \frac{[\text{H}_3\text{O}^{+}][\text{C}_2\text{H}_3\text{O}_2^{-}]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 1.7 \times 10^{-5}$$

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

$[\text{H}_2\text{O}] = ?$

1 g/mL, 1 L water \approx 1000 g H_2O

$$1000 \text{ g } \text{H}_2\text{O} \times \frac{\text{mol}}{18.02 \text{ g}} \approx 55.5 \text{ mol } \text{H}_2\text{O} / \text{L} \approx 55.5 \text{ M}$$

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".
- 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?



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



$$K_c = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 1.7 \times 10^{-5}$$

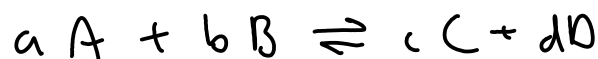
To get a small value like this one, the DENOMINATOR of the equilibrium expression must be a lot larger than the NUMERATOR.

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

- If K_c is small ($\ll 1$), then REACTANTS are favored at equilibrium
- If K_c is large ($\gg 1$), then PRODUCTS are favored at equilibrium.

HOW TO TELL IF A REACTION IS AT EQUILIBRIUM?

- Use REACTION QUOTIENT (Q)



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

Reaction quotient = equilibrium expression using NON-EQUILIBRIUM concentrations.

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



$$[\text{NOBr}] = 0.0720 \text{ M}, [\text{NO}] = 0.0162 \text{ M}, [\text{Br}_2] = 0.0123 \text{ M}$$

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

$$K_c = \frac{[\text{NO}]^2 [\text{Br}_2]}{[\text{NOBr}]^2} = 3.07 \times 10^{-4} \quad \bigg| \quad Q = \frac{(0.0162)^2 (0.0123)}{(0.0720)^2} = 6.23 \times 10^{-4}$$

$$6.23 \times 10^{-4} > 3.07 \times 10^{-4}$$

$$Q > K_c ;$$

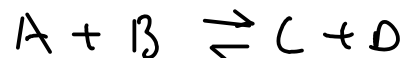
Since $Q > K_c$, the reaction is NOT at equilibrium, and will proceed to the LEFT, forming more NOBr at the expense of the two products.

¹¹⁴ 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 concentration change.

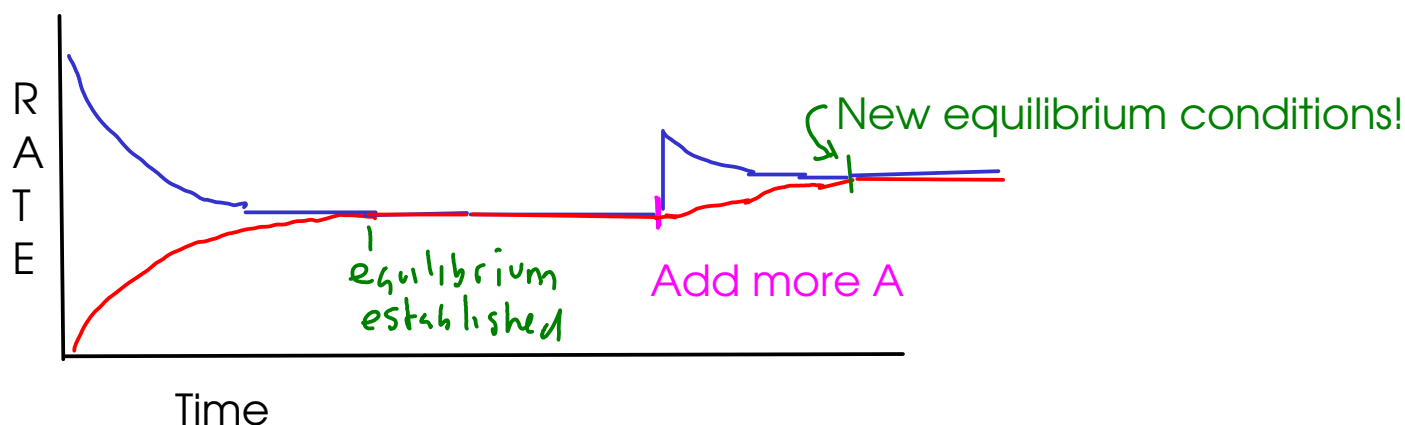
- If you do something to the reaction mixture that changes the rates of the forward or the reverse reaction (or sometimes BOTH), the mixture will no longer be at equilibrium.

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



$$\text{Rate}_{\text{fwd}} = k_{\text{F}}[A][B]$$

$$\text{Rate}_{\text{rev}} = k_{\text{r}}[C][D]$$



- 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 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...

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



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

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 Ag, we make the same amount of Cl ... 1:1 ratio!

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

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

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

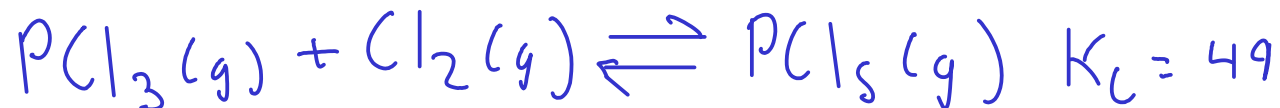
$$x = 1.34 \times 10^{-5} ; [\text{Ag}^+] = [\text{Cl}^-] = 1.34 \times 10^{-5} \text{ M}$$

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

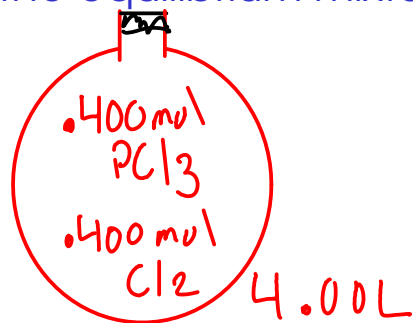
Equivalent to 1.9 ppm (parts per million). Same as mg/L for dilute aqueous solutions

The concentration of DISSOLVED AgCl also equals 'x'!

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



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



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

These concentrations are molar concentrations AT EQUILIBRIUM!

Initial conditions

Species	[Initial]	Δ	[Equilibrium]
PCl ₃	$\frac{0.400 \text{ mol}}{4.00 \text{ L}} = 0.100 \text{ M}$	-x	0.100 - x
Cl ₂	$\frac{0.400 \text{ mol}}{4.00 \text{ L}} = 0.100 \text{ M}$	-x	0.100 - x
PCl ₅	0 M	+x	x

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

$$\frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = \frac{(x)}{(0.100 - x)(0.100 - x)} = 49$$

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

Rearrange this expression to make it easier to solve. Usually, we try to isolate 'x'.

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

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

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

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

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

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

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

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

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

$$x = \cancel{0.157} \quad \underline{\underline{0.0639}}$$



This value of 'x' results in NEGATIVE concentrations for both reactants. This is not possible, so this value for 'x' must be discarded. It does not make chemical sense.

This equation is second-order in 'x', or QUADRATIC.

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

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

Each quadratic equation 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	$\frac{0.400 \text{ mol}}{4.00 \text{ L}} = 0.100 \text{ M}$	$-x$	$0.100 - x$
Cl_2	$\frac{0.400 \text{ mol}}{4.00 \text{ L}} = 0.100 \text{ M}$	$-x$	$0.100 - x$
PCl_5	0 M	$+x$	x

Number of moles of each substance at equilibrium

$$x = 0.0639$$

Equilibrium concentrations

$$[\text{PCl}_3] = 0.100 - x = 0.036 \text{ M} \times 4.00 \text{ L} = 0.144 \text{ mol PCl}_3$$

$$[\text{Cl}_2] = 0.100 - x = 0.036 \text{ M} \times 4.00 \text{ L} = 0.144 \text{ mol Cl}_2$$

$$[\text{PCl}_5] = 0.0639 \text{ M} \times 4.00 \text{ L} = 0.256 \text{ mol PCl}_5$$

Quick comparison of initial and equilibrium states:

