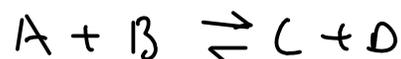


MODIFYING EQUILIBRIUM

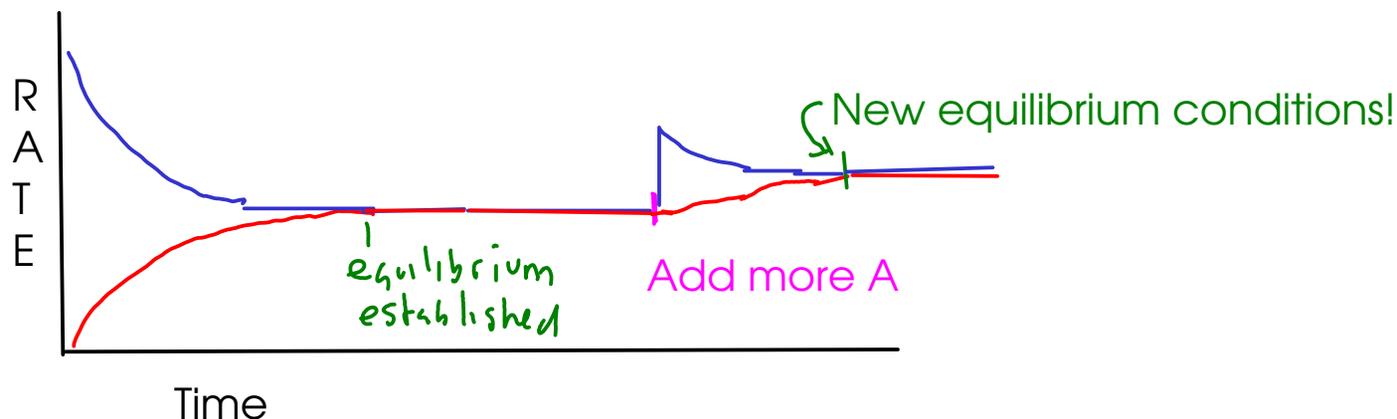
- Remember, at equilibrium the reaction has not actually STOPPED. Both forward and reverse processes are still happening - just at the same rate so there's no overall concentration change.
- If you do something to the reaction mixture that changes the rates of the forward or the reverse reaction (or 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.
-
- * 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.



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

We need to solve the equilibrium expression above, but we know neither the silver ion nor chloride ion concentrations at equilibrium. Let's try to assign a single variable ...

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

Let "x" equal the concentration change of silver ions...

Plug the equilibrium concentrations from the table into the K_c expression...

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

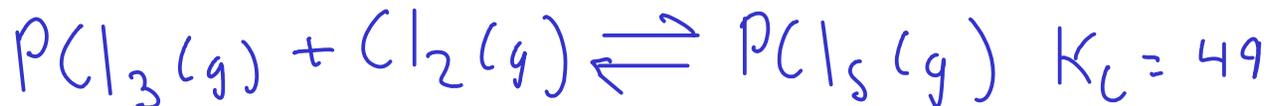
$$X^2 = 1.8 \times 10^{-10}$$

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

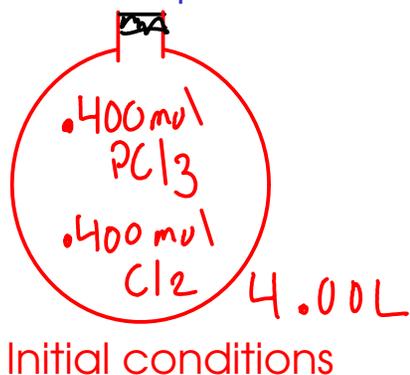
All we need to do now is to convert the (AgCl) dissolved units from mol/L to g/L ...

$$= [\text{AgCl}]_{\text{dissolved}}$$

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



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?



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

We need to solve the equilibrium expression, but we don't know any of the three equilibrium concentrations. So let's assign a variable...

Species	[Initial]	Δ	[Equilibrium]
PCl_5	0	+x	x
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	$0.100 - x$

Let "x" equal the change in concentration of phosphorus PENTACHLORIDE

Substitute into the K_c expression...



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

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

Now we need to solve for "x" ...

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

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

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

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

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

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

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

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

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

$x = 0.157$ or 0.0639 ... but only one of these answers works chemically!

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.