Equilibrium

Le Châtelier's Principle

- ~whenever stress is applied to a system at equilibrium, a new equilibrium will be obtained to relieve this stress.
- stress is a change in temperature, pressure, or concentration of some component.
- This will change the rate of reaction of either the forward or backward reaction
- So you will see an increase in the concentration of the substances on one side of the equation, and a decrease on the other.
- This will "shift" the equation to the right or left.

Examples

- Endothermic reactions absorb heat, i.e. they need heat to react.
- If the solution is heated prior to the reaction (stress)…
- It will react more quickly
- So the equation will be forced to the right (product side)
- If the reaction is cooled, it will be forced to the left (reactant side)

Equilibrium

- Systems at equilibrium are still dynamic (changing). However, no NET CHANGE will be observed.
- A system is at equilibrium when the *rate of the* ***forward reaction*** *is* ***equal*** *to the rate of the* ***reverse reaction****.*

Changing concentration

- $CO + 2\ H_2 \rightleftharpoons CH_3OH$
- If I add more reactant material (increasing the concentration of either CO or H_2) that will speed up the forward reaction causing this equilibrium to shift right, adding more product subtracting reactant.
- If I add more product material (CH_3OH) that will speed up the reverse reaction causing this to shift left

Equilibrium

Add carbon monoxide

	CO	$+ 2\ H_2$	$\rightleftharpoons CH_3OH$
Stress	+ S	0	0
Shift	-x	-2x	+x
Final	↑	↓	↑

*where S is the amount of CO added to stress the equilibrium

Since the stress was added to the reactants, we will speed up the forward reaction subtracting reactant, adding product

*x is the amount that "shifts" to relieve the stress.

*S is bigger than x with any coefficient

What this means…

- By adding carbon monoxide

	CO	$+ 2\ H_2$	$\rightleftharpoons CH_3OH$
Stress	+ S	0	0
Shift	-x	-2x	+x
Final	↑	↓	↑

- The overall amount of carbon monoxide has increased because S is always larger than x (with any coefficient).
- We decreased H_2 by 2x
- We increased CH_3OH by x

$2\ H_2O \rightleftharpoons H_3O^+ + OH^-$

- If I remove hydroxide from the solution…

	$2\ H_2O$	$\rightleftharpoons H_3O^+$	$+ OH^-$
Stress	0	0	-S
Shift	-2x	+x	+x
Final	↓	↑	↓

- *Where S is larger than 2x
- So removing hydroxide increases $[H_3O^+]$, only slightly decreases $[OH^-]$, and decrease the water

Try This

- If I add an acid to the equilibrium…
- $2\ H_2O \rightleftharpoons H_3O^+ \quad + OH^-$
- Stress
- Shift
- Final

More Le Châtelier's

- If I add an acid to the equilibrium…
- $2\ H_2O \rightleftharpoons H_3O^+ + OH^-$
- Stress 0 +S 0
- Shift +2x -x -x
- Final ↑ ↑ ↓
- *Where S is larger than 2x
- so adding acid will decrease the $[OH^-]$, only slightly increase the$[H_3O^+]$, and increase water.

Different equation

- Adding ammonia, NH_3, to the equilibrium
- $2\ NH_3 \rightleftharpoons 3\ H_2 + N_2$
- Stress
- Change
- Final

Different equation

- Adding ammonia, NH_3, to the equilibrium
- $2\ NH_3 \rightleftharpoons 3\ H_2 + N_2$
- Stress +S
- Change -2x +3x +x
- Final ↑ ↑ ↑
- *where S is larger than 2x
- Everything increases
- Note that the amount H_2 increases 3x as much as N_2

With heat

- If I cool the following equilibrium
- $Heat + Co^{2+} + 4\ Cl^- \rightleftharpoons CoCl_4^{2-}$
- Stress
- Shift
- Final

With heat

- If I cool the following equilibrium
- $Heat + Co^{2+} + 4\ Cl^- \rightleftharpoons CoCl_4^{2-}$
- Stress -S 0 0 0
- Shift +x +4x -x
- Final ↑ ↑ ↓
- So cooling the solution will cause more Co^{2+} & Cl^- and less $CoCl_4^{2-}$ to form

Law of chemical equilibrium

- For an equilibrium
- $a\,A + b\,B \rightleftharpoons c\,C + d\,D$
- $K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$
- K is the equilibrium constant for that reaction.
- The [ ] mean concentration in molarity. Make sure those are square brackets and not parenthesis!!

So for the equilibrium

- $CS_2\,(g) + 3\ O_2\,(g) \rightleftharpoons CO_2\,(g) + 2\ SO_2\,(g)$
- The K expression is concentrations of products over the reactants
- Raised to the power of their coefficient.
- $K = \frac{[CO_2]\,[SO_2]^2}{[CS_2]\,[O_2]^3}$

Determine the equilibrium expression

- For the following:
- $Br_2(g) \rightleftharpoons 2Br(g)$
- $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
- $H_2\,(g) + Br_2(g) \rightleftharpoons 2\ HBr(g)$
- $HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$

Determine the equilibrium expression

- For the following:
- $K = \frac{[Br]^2}{[Br_2]}$
- $K = \frac{[NH_3]^2}{[N_2]\,[H_2]^3}$
- $K = \frac{[HBr]^2}{[H_2][Br_2]}$
- $K = \frac{[H^+][CN^-]}{[HCN]}$

Problem

- $2NH_{3\,(g)} \rightleftharpoons N_{2\,(g)} + 3H_{2\,(g)}$
- Calculate the equilibrium constant for the above reaction if it comes to equilibrium with the following concentrations: N_2 = .59 M, H_2 =3.1 M, and NH_3 = 1.03 M

Answer

- $K = \frac{[N_2][H_2]^3}{[NH_3]^2}$
- $K = \frac{[.59][3.1]^3}{[1.03]^2}$
- K = 17

Equilibrium by phase

- Equilibrium depends on the concentration of the reactants.
- We can calculate the concentration of a gas or of anything dissolved (aqueous).
- Insoluble solids or liquids won't have a concentration.
- They in essence are removed from the equilibrium.

So using that

- What would the equilibrium expression look like for the following reaction?
- $2\ H_2O_{2(l)} \rightleftharpoons 2\ H_2O_{(l)} + O_{2(g)}$
- We ignore the liquids (and solids).
- $K = [O_2]$

Water

- $2\ H_2O_{(l)} \rightleftharpoons H_3O^+_{\ (aq)} + OH^-_{\ (aq)}$
- $K_w = [OH^-]\ [H_3O^+] = 1x10^{-14}$
- K_w is the equilibrium constant for water, it equals 1×10^{-14} M
- This is the equation we were using earlier!