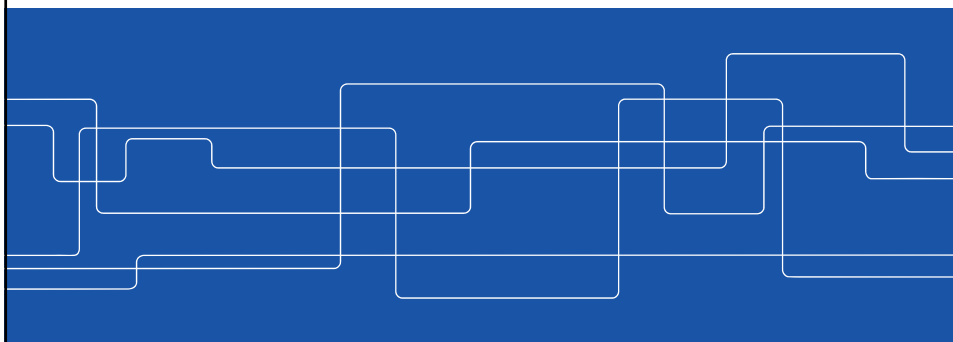




Reactor Chemistry

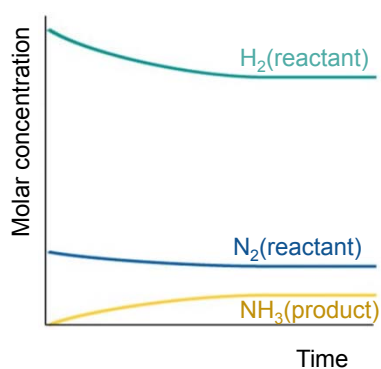
Chemical equilibrium

Mats Jansson



Chemical Equilibrium

Consider the reaction $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightarrow 2 \text{NH}_3(\text{g})$



All N_2 is not consumed
 \Rightarrow The reaction is not complete

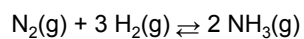
WHY?

The reverse reaction takes place
 $2 \text{NH}_3(\text{g}) \rightarrow \text{N}_2(\text{g}) + 3 \text{H}_2(\text{g})$

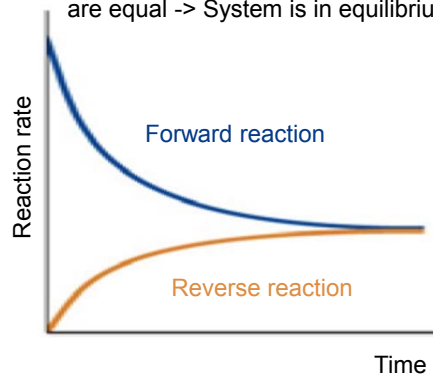
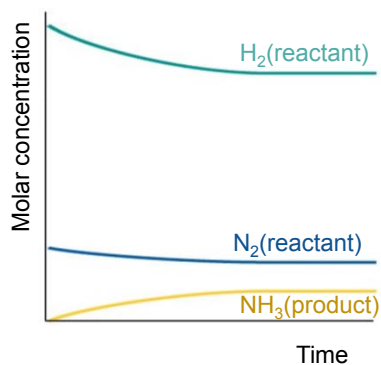
The reaction is hence written
 $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$



Chemical Equilibrium, continued



After a certain time the rate of the forward and reverse reactions are equal -> System is in equilibrium



Law of Mass Action (Guldberg Waage's law)

For any equilibrium reaction $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$

The rate expression for the forward reaction = $k_f [\text{A}]^a \cdot [\text{B}]^b$
(more about reaction rates next lecture)

Reverse reaction rate = $k_r [\text{C}]^c \cdot [\text{D}]^d$

[A] = concentration of species A

A constant for the reaction at equilibrium is defined as:

$$K = \frac{k_r}{k_f} = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

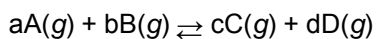
Large K => The reaction driven far to the right
The opposite for small K

Unit: $\text{M}^{c+d-a-b}$ (M = moles / liter)



The equilibrium constant

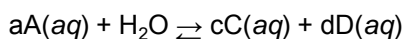
Gas reactions:



$$K = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

Unit: (Pa)^{c+d-a-b}

Reactions in water:

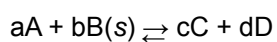


$$K = \frac{[C]^c [D]^d}{[A]^a}$$

Unit: (M)^{c+d-a}



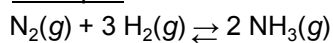
Reactions with a solid phase



$$K = \frac{[C]^c [D]^d}{[A]^a}$$

Unit: (M)^{c+d-a}

Example:

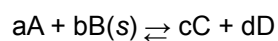


Calculate the equilibrium pressure of $N_2(g)$ at 500K if the equilibrium pressures of $H_2(g)$ and $NH_3(g)$ are 13.3 and 32.7 atm, respectively and the equilibrium constant $K_p = 0.0362 \text{ atm}^{-2}$.

What is the total pressure?



Le Chatelier's principle (The equilibrium law)

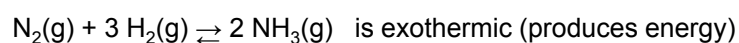


$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

When a system in equilibrium is changed in some way (concentration, temperature, volume or pressure), the equilibrium will be shifted to counteract the change and a new equilibrium will be established.



Le Chatelier's principle Examples



An addition of N_2 would lead to that more NH_3 is produced. Since H_2 is consumed, the concentration of H_2 would decrease slightly.

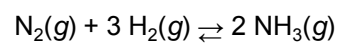
What would happen if the temperature was lowered?

- More NH_3 would be produced
- The process would be slower

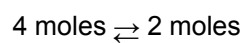
⇒ The Haber process is kept at a reasonable temperature to have sufficient ammonia produced at reasonable rate



More Le Chatelier's principle



What would happen if the volume is decreased (*i.e.* the pressure of the system increased)?

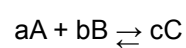


What would happen if an inert gas like Helium was added?

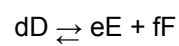
What would happen if a catalyst (in this case Mo or Fe) was added?



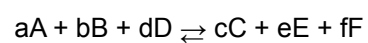
Adding reactions



$$K_1 = \frac{[C]^c}{[A]^a[B]^b}$$



$$K_2 = \frac{[E]^e[F]^f}{[D]^d}$$



$$K_3 = \frac{[C]^c[E]^e[F]^f}{[A]^a[B]^b[D]^d}$$

$$K_3 = K_1K_2$$

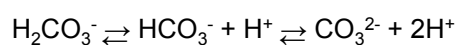


Acids and bases

An acid is a molecule or ion that can donate a proton (H^+)

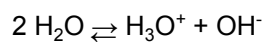
A base is a molecule or ion that can accept a proton (H^+)

An amphoteric molecule or ion can act both as an acid or a base (HCO_3^-)

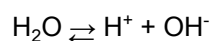


Autodissociation of water

In water some of the molecules will dissociate forming oxonium- and hydroxide ions (that's why water has a conductivity of $0.055 \mu S/cm$)



Chemists often write H^+ instead of H_3O^+ :



$$K_w = [H^+] [OH^-]$$

$$-\log K_w = -\log [H^+] + -\log [OH^-] \quad p = -\log_{10}$$

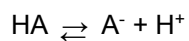
$$pK_w = pH + pOH$$

$$K_w = 10^{-14} M^2 \text{ (for reasonably pure water)}$$



Acid-base equilibria

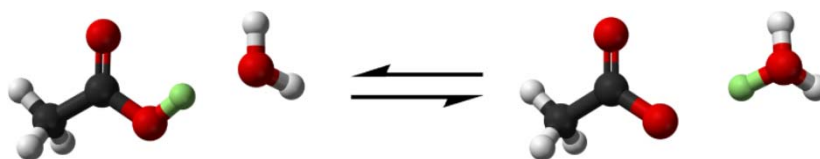
HA as an acid



“HA” is an acid with one proton;
HNO₃, CH₃COOH or whatever

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

K_a is the acid dissociation
constant

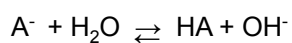


HA and A⁻ is a conjugated acid-base pair.
A⁻ is the conjugate base of the acid HA.



Acid-base equilibria

A⁻ as a base



$$K_b = \frac{[\text{OH}^-][\text{HA}]}{[\text{A}^-]}$$

K_b is the base association
constant

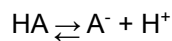
$$\text{p}K_w = \text{p}K_a + \text{p}K_b$$

A strong acid always conjugates with a weak base.

HNO₃: strong acid. NO₃⁻ so weak base it's often not considered a base

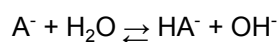


Le Chatelier vs Acid-base equilibria



Adding a strong acid to the system will push the equilibrium to the left.

=> The system will not have a large increase in hydrogen ions (pH will not decrease that much)



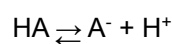
Adding a strong base to the system will push the equilibrium to the left.

=> The system will not have a large increase in hydroxide ions (pH will not increase that much)

=> The system is not sensitive to changes in $[\text{H}^+]$; A buffer



The Henderson–Hasselbalch equation



$$K_a = \frac{[\text{A}^-][\text{H}^+]}{[\text{HA}]}$$

$$\log K_a = \log \frac{[\text{A}^-][\text{H}^+]}{[\text{HA}]} = \log[\text{H}^+] + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$pK_a = pH - \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$pH = pK_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$



Example of buffer

What will the pH be if one drop of conc. HCl is added to

- 1) Water, normal pH = 7
- 2) Blood, normal pH = 7.4 (buffered by HCO_3^-), $[\text{HCO}_3^-] = 0.024\text{M}$

1) One drop $\sim 0.05\text{ ml} = 5 \cdot 10^{-5}\text{ l}$.
Concentrated HCl is 12 M (mol/l)

$6 \cdot 10^{-4}$ moles H^+ added to 1 l.
 $[\text{H}^+] = 6 \cdot 10^{-4}\text{ M} \Rightarrow -\log(6 \cdot 10^{-4}) = 3.22$

$\Rightarrow \text{pH} = 3.22$ (a change in ~ 4 magnitudes)