

Reactions

WAT-E2120 Physical and Chemical Treatment of Water and Waste

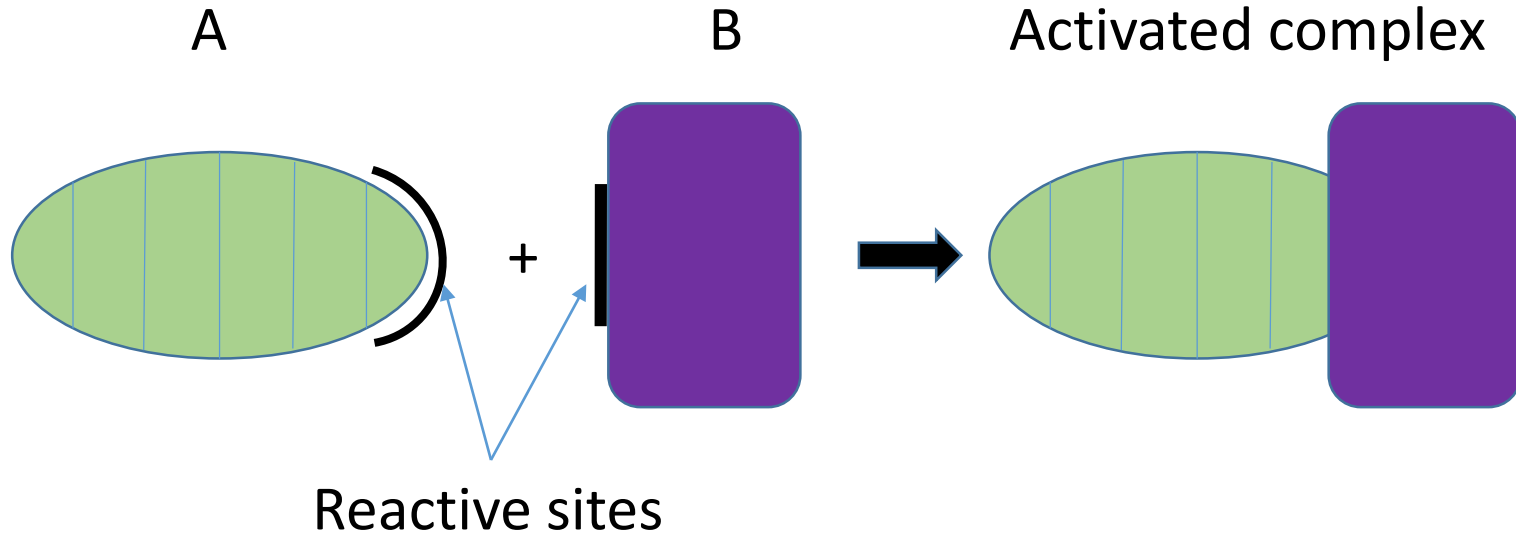
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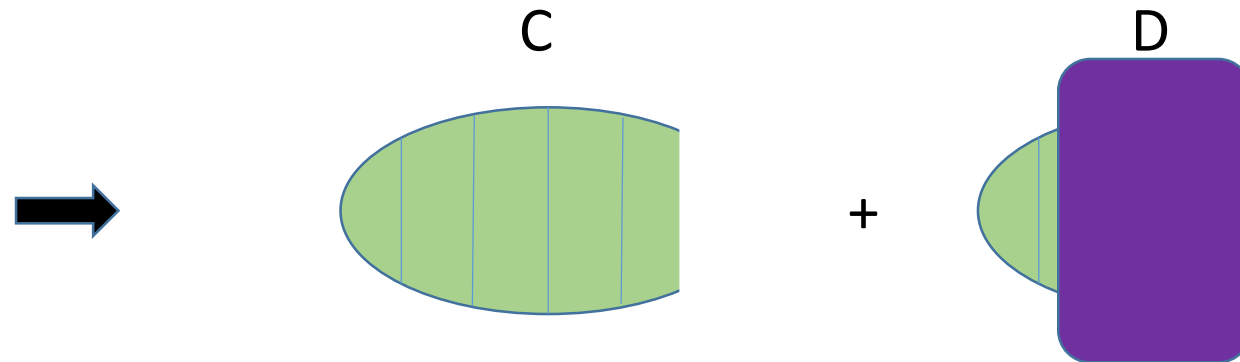
Reaction types

- Mixing – no reaction
- Oxidation-reduction reactions
- Acid-base reactions
- Catalytic reactions
- Exothermic and endothermic reactions
- Precipitation reactions
- Electrochemical reactions
- ...

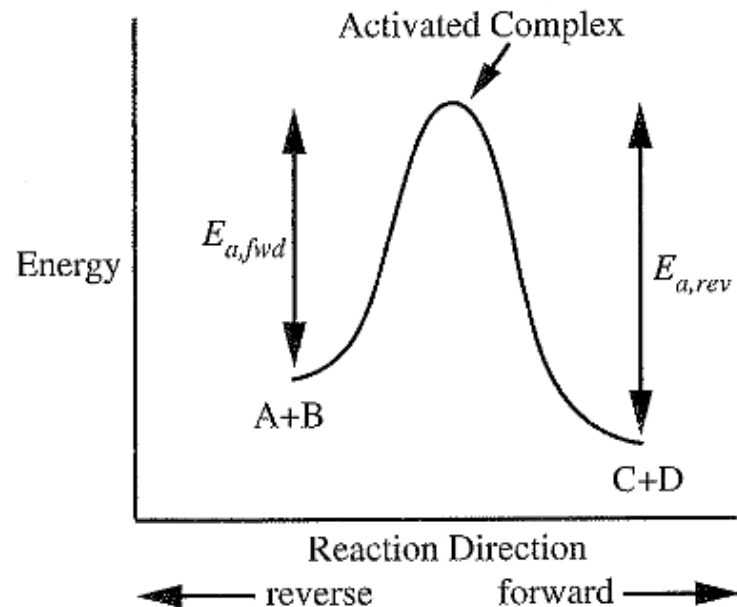
Reactions



- Collisions of A and B enable the reaction
- Collisions of C and D enable the backwards reaction



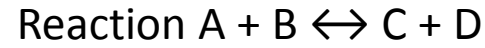
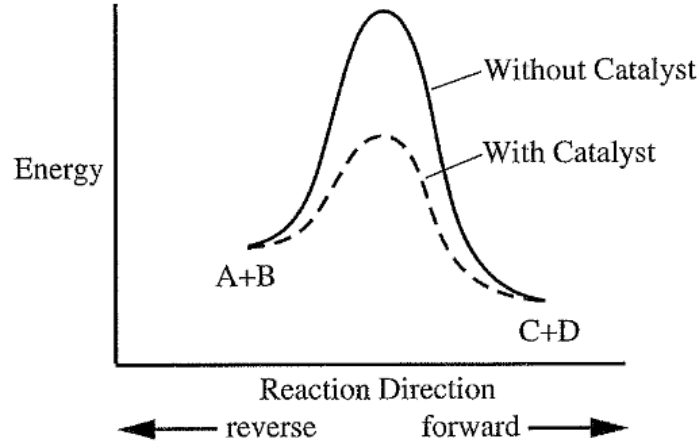
Activation energy



Reaction $A + B \leftrightarrow C + D$

- E_a = activation energy = difference in energies of separate A and B and the energy of the activated complex
- $E_{a,\text{fwd}}$ = The energy needed to to produce the forward reaction
- $E_{a,\text{rev}}$ = The energy needed to to produce the reverse reaction
- In this example the forward reaction is more favourable because $E_{a,\text{fwd}} < E_{a,\text{rev}}$
 - This is not always the case, depends on each reaction
- Reaction goes mostly forward: irreversible reaction
- Reaction goes forward and reverse: reversible reaction

Activation energy in catalyzed reactions



- Catalyst provides a surface for the reactants and alters them so that they are more likely to react or a chemical that is not consumed in the reaction, but makes the reactants more likely to react
- Catalysts lower activation energy => reactions are more rapid
 - Which makes it possible to use smaller reactors
- Reactions are enabled in lower temperatures and pressures with catalysts

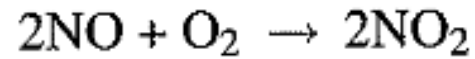
Reaction rate

- Reaction: $A + B \leftrightarrow C + D$
- Reaction rate in liquid phase =

$$r_{\text{reaction, A}} = k_r c_A^n c_B^m$$

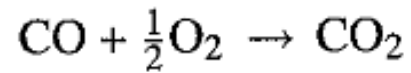
- $r_{\text{reaction, A}}$ units are moles or mass of A / time * volume
- c_A = concentration of A (moles or mass / volume)
- c_B = concentration of B (moles or mass / volume)
- k_r = reaction rate constant (units depend on the form of the rate equation)
- n, m = order of the reaction, the general case
 - n^{th} order, m^{th} order, $n+m^{\text{th}}$ order
 - Most common orders of reaction 0, $\frac{1}{2}$, 1, 2, 3
 - In water engineering the reaction order is usually already known (unless you are doing research)

Examples of reaction rates



$$r_{\text{reaction,NO}} = k_r c_{\text{NO}}^2 c_{\text{O}_2}$$

- Oxidation of nitric oxide to nitrogen peroxide
- Elementary reaction: the order of the reaction matches the stoichiometry of the reaction



$$r_{\text{reaction,CO}} = k_r c_{\text{CO}} c_{\text{H}_2\text{O}}^{0.5} c_{\text{O}_2}^{0.25}$$

- In many cases the order of the reaction rate equation does not match the stoichiometry:
- Oxidation of carbon monoxide to carbon dioxide
- The reaction mechanism is complex including water molecules, which are not shown in the total reaction equation

Reaction rates

- For gases:

$$r_{\text{reaction, A}} = k_r p_A^n p_B^m$$

- p_A = partial pressure of A (atm)
- p_B = partial pressure of B (atm)
- The units of $r_{\text{reaction, A}}$ are atm/time
 - Can be converted to mol/time volume with ideal gas law

Reaction rate constant k_r

- k_r is a constant but it depends on temperature
- Arrhenius equation:

$$k_r = k_0 \exp(-E_a/RT)$$

- k_0 = frequency factor, units the same as k_r
 - Includes collisions and their direction
- E_a = activation energy (in units of energy per mole)
- R = universal gas constant, 8.31 J / mol K
- T = temperature (K)

Determining the reaction rate coefficient

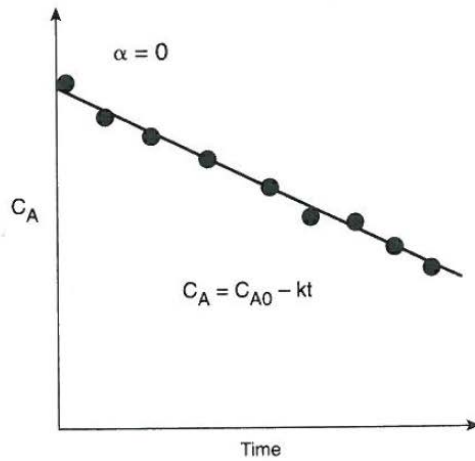


Figure 5-3 Zero-order reaction.

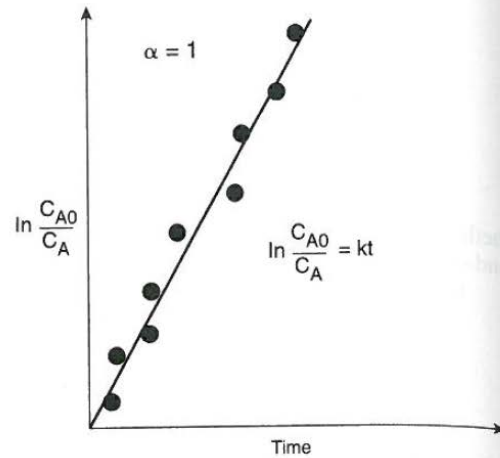


Figure 5-4 First-order reaction.

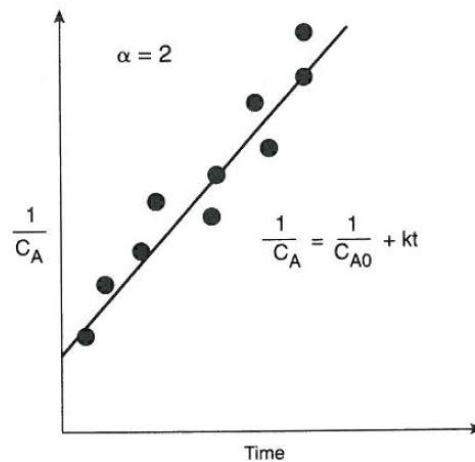


Figure 5-5 Second-order reaction.

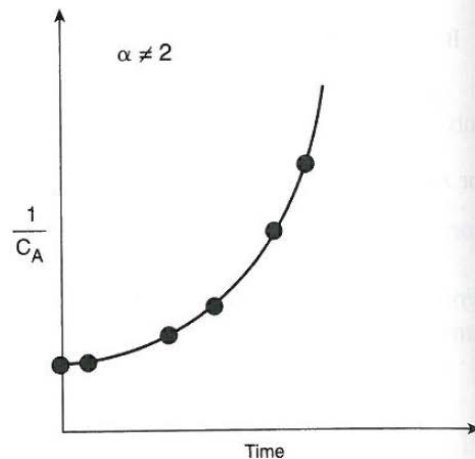


Figure 5-6 Plot of reciprocal concentration as a function of time.

- Experimental methods
 - The order of reaction cannot be deduced from the reaction equation
- Differential method
- Integral method:
 - A → reaction products
 - Zeroth order reaction
 - $C_A = C_{A0} - kt$
 - First order reaction
 - $\ln(C_{A0}/C_A) = kt$
 - Second order reaction
 - $1/C_A - 1/C_{A0} = kt$

Common reaction rate equations

Reaction	Order	Differential form	Integrated form
$A \rightarrow P$	zeroth	$\frac{d[A]}{dt} = -k$	$[A] = [A]_0 - kt$
$A \rightarrow P$	first	$\frac{d[A]}{dt} = -k [A]$	$\ln[A] = \ln[A]_0 - kt$
$A + A \rightarrow P$	second	$\frac{1}{2} \frac{d[A]}{dt} = -k [A]^2$	$\frac{1}{[A]} = \frac{1}{[A]_0} + 2kt$
$A + B \rightarrow P$	second	$\frac{d[A]}{dt} = -k [A][B]$	$kt = \frac{1}{[B]_0 - [A]_0} \ln \frac{[B]_0 [A]}{[A]_0 [B]}$

Equilibrium constant

- Equilibrium constant of a reaction, K (K_a , K_c , K_p)

- For a reversible reaction: $aA + bB \leftrightarrow cC + dD$

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

- Concentrations of reaction products above, reactants below, coefficients as powers
- K changes with temperature (reference temp 25 °C)

- If the concentration of the reactants or products is changed, the other concentrations change according to the equilibrium constant

- E.g. If you constantly remove C from the system, reaction balance moves towards the products

- Equilibrium constant is a link between reaction kinetics to chemical thermodynamics

$$\Delta G^\circ = -RT \ln K$$

- ΔG° = standard Gibbs free energy change of the reaction (the driving force of the reaction)

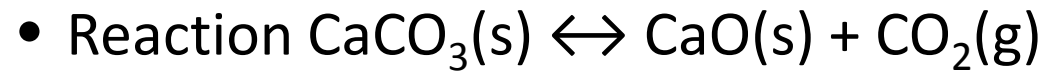
Special equilibrium constants

- Gas reactions



- Use partial pressures: $K_p = P_C^c \times P_D^d / P_A^a \times P_B^b$

- Heterogenous reactions involving solid substances



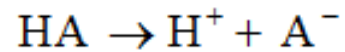
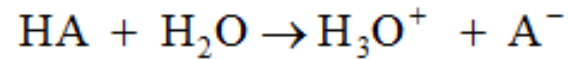
- Equilibrium constant does not include solids: $K_p = P_{CO_2}$

Acids and water

Acid – base reactions

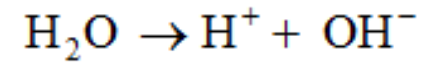
K_a = dissociation constant

HA = acid, A^- = base



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

Dissociation of water, K_w



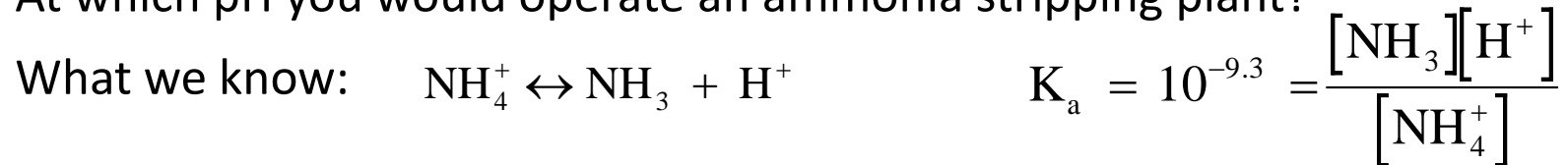
$$K_w = \frac{[H^+][OH^-]}{[H_2O]}$$

$$K_w = [H^+][OH^-] = 10^{-14}$$

$$pH = -\log[H^+]$$

Equilibrium constant - example of use

At which pH you would operate an ammonia stripping plant?



First we try at pH 7: $\% \text{NH}_3 = \frac{[\text{NH}_3]}{[\text{NH}_4^+] + [\text{NH}_3]} \cdot 100$

We need to express NH_4^+ in terms of NH_3 : $10^{-9.3} = \frac{[\text{NH}_3][10^{-7}]}{[\text{NH}_4^+]} \Rightarrow [\text{NH}_4^+] = 200 \cdot [\text{NH}_3]$

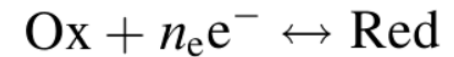
Substituting in the %- equation: $\% \text{NH}_3 = \frac{[\text{NH}_3]}{200 \cdot [\text{NH}_3] + [\text{NH}_3]} \cdot 100 = 0.5\%$

For pH 6 : 0.052%, 8: 4.8%, 9: 33 %, 10: 83%, 11: 98%.

Answer: An alkaline pH would be best. Because NH_3 is removed from the system by stripping, pH 9-10 could be sufficient. The exact answer depends on the required yield and cost optimization of alkali addition.

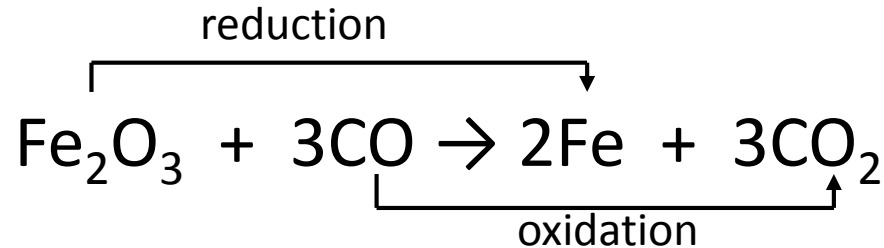
Reduction –oxidation reactions

- Also called redox reactions
- Transfer of electrons between reactants
- Oxidation can be thought as:
 - Loss of electron(s)
- Reduction can be thought as:
 - Gaining electron(s)



Redox-reactions

- An oxidising agent oxidises something else when it is reduced itself
- A reduction agent reduces something else when it is oxidized itself
- In redox-reactions both reduction and oxidation happen the same time
 - Be careful with the terms!



- Fe_2O_3 is the oxidizing agent and is reduced in the reaction.
- CO is the reducing agent and is oxidized in the reaction.