

VI. Equilibria in specific chemical systems

- One of the decisive objectives of thermodynamics is the exact description of chemical equilibria.
- Our general contexts apply to all types of equilibria.
- The issue of chemical equilibrium covers almost the entire chemistry, so, many different phenomena can and should be studied, described and utilized.
- Here are just some of the most important types, groups, and examples.

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VI. Equilibria in specific chemical systems

1. **Forms of chemical equilibria:**
- a. simple, one-step equilibria,
  - b. parallel equilibria,
  - c. serial (stepwise, consecutive) equilibria,
  - d. cyclic equilibria,
  - e. equilibrium relations of connected (complex) reactions,
  - f. macroscopic and microscopic equilibria,
  - g. cooperative equilibria,
  - h. ...

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2. **Types of equilibria:**
- A. Homogeneous (one-phase) equilibria:
    - acid-base equilibria
    - redox equilibria
    - equilibria for metal complexes
    - dissociation of gas molecules
    - equilibria in complex systems
    - the thermodynamics of ATP
  - B. Heterogeneous equilibria:
    - solubility (product)
    - thermal decomposition of solids
    - electrodes and galvanic cells (electrochemistry)
    - adsorption on solid surfaces (colloids)

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V. Connection between the formal and thermodynamic description of an equilibrium

- so  $\Delta_r G = \Delta_r G^\circ + RT \ln Q_p$  equation in equilibrium:
- If  $\Delta_r G = 0$ ,  $Q_p$  is identical to the equilibrium constant  $K_p$ :
$$Q_{p, \text{equilibrium}} = K_p = \frac{p_{B, \text{equilibrium}}}{p_{A, \text{equilibrium}}}$$
  - Result:  $\Delta_r G^\circ = -RT \ln K_p$
  - The negative sign is important!
    - negative  $\Delta_r G^\circ \rightarrow K$  is higher than 1 (product-dominance)
    - positive  $\Delta_r G^\circ \rightarrow K$  is lower than 1 (reactant-dominance)

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**K** equilibrium constant,  $\xi$  extent of reaction\*, degree of conversion\*

$K_a$  stability (association) constant

$\gamma$  fractional occupancy\*

adsorption constant, fractional coverage\*

$K_d$  dissociation constant, degree of dissociation\*

Adsorption Process

adsorbent + adsorptive	adsorbate
molecule (acid, base)	cation + anion

\* the actual equilibrium state is given, not the equilibrium constant value!

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$\Delta_r G^\circ$ (kJ/mol)	K	equilibrium composition
-50	$6 \times 10^8$	the reaction is almost complete
-10	57	there is a lot of products
-5	7.5	more products than reactants
0	1	products = reactants
+5	0.13	more reactants than products
+10	0.02	there is a lot of reactants left
+50	$1.7 \times 10^{-9}$	almost no products at all

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1.a Simple, one-step equilibria:

- A ⇌ P
- aA + bB ⇌ cC + dD

$$K_a = \prod_j a_{j,\text{equilibrium}}^{v_j}$$

$$K_x = \prod_j x_{j,\text{equilibrium}}^{v_j}$$

$$K_p = \prod_j \left( \frac{p_{j,\text{equilibrium}}}{p^\ominus} \right)^{v_j}$$

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- One of the reactants (L) is in large excess:
  - ligand is in excess of metal ion,
  - the substrate is in excess of the enzyme, etc.:

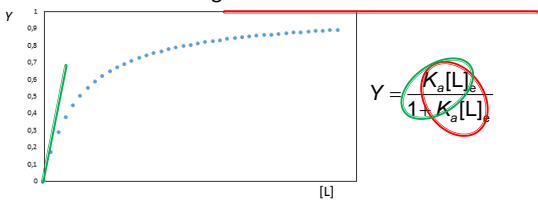
$$M + L \rightleftharpoons ML \quad K_a = [ML]_e / [M]_e [L]_e \quad \text{and} \quad K_d = [M]_e [L]_e / [ML]_e, \text{ so} \quad K_d = 1 / K_a.$$

- The degree of ML formation: Y fractional occupancy (elsewhere average ligand number, extent of reaction):  
 $Y = [ML]_e / ([M]_e + [ML]_e)$
- Since  $[ML]_e = K_a [M]_e [L]_e$ ,  
$$Y = \frac{K_a [M]_e [L]_e}{[M]_e + K_a [M]_e [L]_e} = \frac{K_a [L]_e}{1 + K_a [L]_e}$$

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- The excess L (ligand, substrate) concentration influences the degree of ML formation as follows:

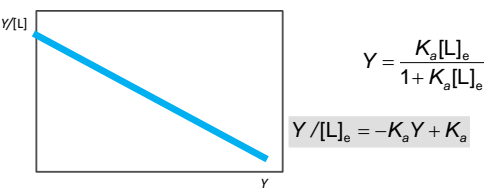


- This is the Langmuir-Hill equation: a binding isotherm.
- Shape: saturation curve, which is almost linear at low [L].
- This is very similar to ES formation and adsorption of gases.

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- The excess L (ligand, substrate) concentration influences the degree of ML formation as follows:
  - This can also be linearized by simple rearrangement:



- This is the Scatchard equation. In enzyme kinetics, the same is called the Lineweaver–Burk equation.

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1.b Parallel equilibria:



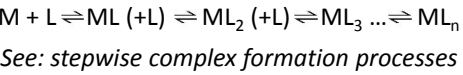
- In equilibrium:  $\frac{[M_1A]}{[M_2A]} = \frac{K_{a,1}}{K_{a,2}}$



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1.c Consecutive equilibria:

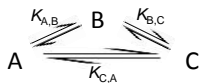


- See: stepwise complex formation processes

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1.d Cyclic equilibria:



$K_{A,B} = \frac{[B]_e}{[A]_e}$     $K_{B,C} = \frac{[C]_e}{[B]_e}$     $K_{C,A} = \frac{[A]_e}{[C]_e}$

- When (n-1) equilibrium constants are known, the „missing” one can be calculated:

$$K_{A,B} K_{B,C} K_{C,A} = \frac{[B]_e}{[A]_e} \frac{[C]_e}{[B]_e} \frac{[A]_e}{[C]_e} = 1$$

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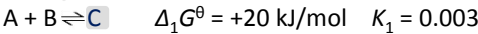
1.e Equilibria of combined reactions:

- Another non-spontaneous reaction can be achieved by using the enthalpy of a spontaneous reaction. (E.g. combustion heat of propane can oxidize copper.)
- How can one use the Gibbs free energy of a reaction to force another non-spontaneous one?

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1.e Equilibria of combined reactions:



- There is hardly any product formation, reaction (1) does not take place.
- Find a suitable spontaneous reaction that removes C:  
 $C(+F) \rightleftharpoons E$     $\Delta_2 G^\circ = -30 \text{ kJ/mol}$     $K_2 = 18100$ 
  - In this, C is almost completely transformed into E. The necessary formation of the "missing" C "pulls" the reaction (1), and it is practically complete.

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- Combining the two reactions:  
 $A + B (+F) \rightleftharpoons E$     $\Delta_{1,2} G^\circ = -10 \text{ kJ/mol}$     $K_{1,2} = 56.$ 
  - The condition of such coupling is the C in both.
  - This is basically the „Le Chatelier’s principle”: the system (reaction 1) tries to compensate the the external stress – the removal of C – by producing more and more C.
- Examples:
  - two inorganic (important industrial) systems;
  - a biological system (the thermodynamics of ATP);
  - ...

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Producing copper from copper(I) sulfide

- $Cu_2S \rightarrow 2Cu + S$     $\Delta_1 G^\circ = +86 \text{ kJ/mol}$ 
  - non-spontaneous process! Only traces of Cu and S.
- Remove sulfur continuously by oxidizing it:  
 $S + O_2 \rightarrow SO_2$     $\Delta_2 G^\circ = -214 \text{ kJ/mol}$ 
  - spontaneous!
- Coupling of the two reactions (using S as a „common” reactant):  
 $Cu_2S + O_2 \rightarrow 2Cu + SO_2$     $\Delta_{1,2} G^\circ = -128 \text{ kJ/mol}.$ 
  - This coupled reaction already happens spontaneously. The Gibbs free energy of the oxidation of sulfur provides the Gibbs free energy for copper formation (from copper sulfide).

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Producing iron from iron(III) oxide

- $Fe_2O_3 \rightarrow 2Fe + 1.5 O_2$     $\Delta_1 G^\circ = 742 \text{ kJ/mol}$ 
  - non-spontaneous process!
- $1.5 C + 1.5 O_2 \rightarrow 1.5 CO_2$     $\Delta_1 G^\circ = -1.5 \cdot 394 \text{ kJ/mol}$ 
  - spontaneous!
- The two reactions coupled:  
 $Fe_2O_3 + 1.5 C \rightarrow 2Fe + 1.5 CO_2$     $\Delta_{1,2} G^\circ = 150 \text{ kJ/mol}$ 
  - At room temperature, the reaction is still non-spontaneous,
  - but there is gas formation in the coupled reaction,  $\Delta_{1,2} S$  is a large positive value. Since  $\Delta G = \Delta H - T\Delta S$ , at higher temperatures (in this case, at 826 K)  $\Delta_{1,2} G$  changes its sign from + to –.

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## The thermodynamics of ATP

- Living systems are powered by energy in food. Part of this energy is used as it is produced, but some of them is stored for later use.
- A complicated mechanism works in which there are energy storing and energy utilizing steps.
- Important: energy stored in exergonic reactions my drive other, endergonic processes.
- It is practicable to use a **biological standard state**.

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## The thermodynamics of ATP

- Biological standard state:** pH = 7
  - $a_{H^+} = 1$  (pH = 0) would be too acidic.
  - Designation:  $^{\circ}$
- Example:  $A + \nu H^+(aq) \rightarrow P$ 

$$\Delta_r G = \mu_P - \mu_A - \nu \mu_{H^+}$$
- After some derivations:
 
$$\Delta_r G^{\circ} = \Delta_r G^{\circ} + 7 \cdot \nu RT \ln 10$$
  - (The two standard  $\Delta_r G$  values are only different if  $H^+$  participates in the process.)

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## The thermodynamics of ATP

- Particular example (nicotine amide dinucleotide):  
 $NADH(aq) + H^+(aq) \rightarrow NAD^+(aq) + H_2(g)$ 
  - $\Delta_r G^{\circ} = -21.8 \text{ kJ/mol}$  (exergonic for  $a_{H^+} = 1$ )
  - But at pH = 7,  $\Delta_r G^{\circ} = +19.7 \text{ kJ/mol}$  **endergonic**, so free energy is needed to „feed“ the reaction.
- Endergonic reactions:** do not proceed spontaneously (protein biosynthesis, muscle contractions, vision etc.)

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## The thermodynamics of ATP

- Endergonic reactions:** do not proceed spontaneously (protein biosynthesis, muscle contractions, vision etc.)
- Exergonic reactions:** energy is stored in adenosine triphosphate (ATP) molecules. Its hydrolysis is exergonic and can drive other, endergonic reactions. *[These are usually catalyzed by enzymes, but this is a kinetic phenomenon.]*

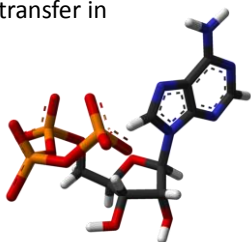
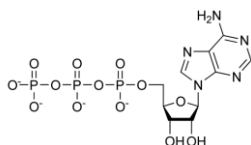
$$ATP + H_2O \rightarrow ADP + P_i + H^+$$

$$\begin{aligned} \Delta_r G^{\circ} &= -30 \text{ kJ/mol} \\ \Delta_r H^{\circ} &= -20 \text{ kJ/mol} \\ \Delta_r S^{\circ} &= +34 \text{ J/(molK)} \end{aligned}$$
- Where does the energy of ATP (hydrolyzable phosphate ester bonds) come from? Its origin is the oxidation (burning) of food (carbohydrate, fat) in complicated, coupled processes.

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## The thermodynamics of ATP

- ATP (adenosine-5'-triphosphate): the common unit of energy transfer in biological systems.



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## The thermodynamics of ATP

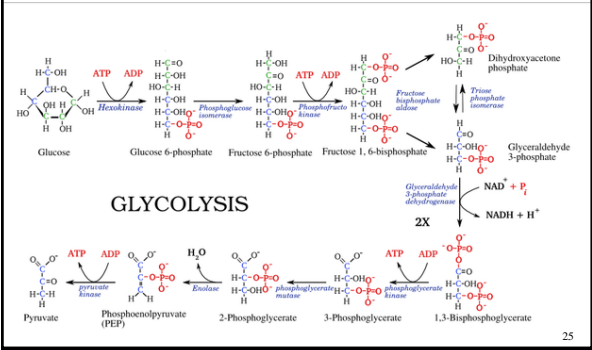
### Anaerobic cell metabolism (in the absence of $O_2$ ).

- Insufficient  $O_2$  (at birth; long-distance running):  

$$\text{glucose} + 2 P_i + 2 ADP \rightarrow 2 \text{lactate}^- + 2 ATP + 2 H_2O$$
- Source of energy: partial oxidation of glucose to lactate.
- Exergonic process:  $\Delta_r G^{\circ} = -218 \text{ kJ/mol}$ .
- Two molecules of ADP converted to ATP :  $2 \times (+30)$ .
- $\Delta_r G^{\circ} = -218 + 2 \times 30 = -158 \text{ kJ/mol}$  is available.
- Food is both a source of direct energy and energy stored for later use by  $ADP \rightarrow ATP$  transformation.
- Poor efficiency. *[Aerobic respiration is better, the burning of glucose in total oxidation yields  $-2880 \text{ kJ/mol}$ .]*

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The thermodynamics of ATP



The thermodynamics of ATP

**Aerobic cell metabolism (with oxygen).**

- Energy source: the total oxidation of glucose to carbon dioxide and water:  $\Delta_r G^0 = -2880 \text{ kJ/mol}$  ( $\text{CO}_2$  is exhaled.)
- Schematically (as the mechanism is very complicated):  
**glucose +  $\text{O}_2$  + 38 ADP  $\rightarrow$   $\text{CO}_2$  +  $\text{H}_2\text{O}$  + 38 ATP**
- For 38 ATP,  $38 \times 30 = 1140 \text{ kJ}$  is needed. Available 1740 kJ
- To produce sucrose from glucose and fructose ( $\Delta_r G^0 = 23 \text{ kJ/mol}$ ), one molecule of ATP ( $-30 \text{ kJ}$ ) is sufficient.
- For protein synthesis, a lot of ATP is needed: a single peptide bond is  $\Delta_r G^0 = 17 \text{ kJ/mol}$  endergonic, but its indirect biosynthesis needs 3 molecules of ATP. In myoglobin (relatively small protein)  $\sim 150$  peptide bonds require 450 molecules of ATP, i.e. 12 molecules of glucose in aerobic oxidation.

Solubility of salts

- Introducing the solubility product:  
 $\text{KA(s)} \rightleftharpoons \text{K}^+(\text{sol}) + \text{A}^-(\text{sol})$
- For saturated solutions (at given  $T$  and  $p$ ):  
$$K_{\text{sol}} = \frac{a_{\text{K}^+} a_{\text{A}^-}}{a_{\text{KA}}} = \frac{a_{\text{K}^+} a_{\text{A}^-}}{1}$$

ZnS	$1.6 \times 10^{-24}$	AgCl	$1.6 \times 10^{-10}$
AgBr	$7.7 \times 10^{-13}$	$\text{CaCO}_3$	$8.9 \times 10^{-6}$
$\text{BaSO}_4$	$1.1 \times 10^{-10}$	$\text{PbBr}_2$	$7.9 \times 10^{-5}$

Thermal decomposition of  $\text{CaCO}_3$

- $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$**
- Reaction Gibbs free energy:  
$$\Delta_r G = \mu_{\text{CaO}}^0 + \mu_{\text{CO}_2} - \mu_{\text{CaCO}_3}^0 = \mu_{\text{CaO}}^0 + \mu_{\text{CO}_2} + RT \ln \frac{p_{\text{CO}_2}}{p^0} - \mu_{\text{CaCO}_3}^0$$
- In equilibrium:  $\Delta_r G = 0$ , so  
$$\Delta_r G^0 = \mu_{\text{CaO}}^0 + \mu_{\text{CO}_2}^0 - \mu_{\text{CaCO}_3}^0 = -RT \ln \frac{p_{\text{CO}_2}}{p^0}$$
- As a conclusion:  $K_p = \frac{p_{\text{CO}_2}}{p^0}$

Thermal decomposition of NiO

- $\text{NiO} + \text{H}_2(\text{g}) \rightleftharpoons \text{Ni} + \text{H}_2\text{O}(\text{g})$**
- Reaction Gibbs free energy :  
$$\Delta_r G = G_{\text{m,Ni}} + \mu_{\text{H}_2\text{O}}^0 + RT \ln \frac{p_{\text{H}_2\text{O}}}{p^0} - \left( G_{\text{m,NiO}} + \mu_{\text{H}_2}^0 + RT \ln \frac{p_{\text{H}_2}}{p^0} \right)$$
- In equilibrium:  $\Delta_r G = 0$ , so (as before)  
$$\Delta_r G^0 = G_{\text{m,Ni}} + \mu_{\text{H}_2\text{O}}^0 - (G_{\text{m,NiO}} + \mu_{\text{H}_2}^0) = -RT \ln \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}}$$
- As a conclusion:  $K_p = \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}}$
- For example, the removal of the water vapor can shift the equilibrium until the total reduction of Ni.

Equilibria in acid and base solutions

- The most important type of equilibrium, it is everywhere!
- Aqueous solutions are the most common (laboratory, biological systems, nature, industry etc.)
- In essence: electrolytic dissociation.
- Acid-base theories and classifications :**
- Arrhenius:** produce  $\text{H}^+$  or  $\text{OH}^-$  in aqueous dissociation
- Brønsted-Lowry:**
  - proton donor acids:  $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$
  - proton acceptor bases:  $\text{B} + \text{H}^+ \rightleftharpoons \text{BH}^+$
- Lewis:** electron pair acceptor or donor.
- There are always conjugate acid-base pairs.

Equilibria in acid and base solutions

- Application of the known concepts:  
 $HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$ 
    - HA: acid
    - A<sup>-</sup>: conjugate base of the acid
- $$K_a = \frac{a_{H_3O^+} \cdot a_{A^-}}{a_{HA} \cdot a_{H_2O}}$$
- As  $a_{H_2O}$  is constant:  $K_a = \frac{a_{H_3O^+} \cdot a_{A^-}}{a_{HA}}$
- $$pK_a = -\lg K_a$$

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Equilibria in acid and base solutions

- Water also takes part in acid-base reactions!  
 $B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$ 
  - B: base
  - BH<sup>+</sup>: the conjugated acid

$$K_b = \frac{a_{BH^+} \cdot a_{OH^-}}{a_B}$$

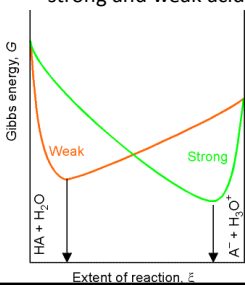
$$pK_b = -\lg K_b$$

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Equilibria in acid and base solutions

Classification of acids and bases:

- strong and weak acids/bases (superacids)
  - Determined by the degree of dissociation – dependent on c.
  - Continuous transition:
    - from very strong mineral acids to very weak organic acids,
    - the same for bases.
  - Superacids (Nobel prize for George Olah).
  - K is in strong connection with the reaction Gibbs free energy.



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Equilibria in acid and base solutions

Classification of acids and bases:

- strong and weak acids/bases (superacids)

Acid	conjugate base	$K_a$	$pK_{a(1)}$	$pK_{a(2,3)}$
HI	I <sup>-</sup>	$10^{11}$	-11	
HCl	Cl <sup>-</sup>	$10^7$	-7	
H <sub>2</sub> SO <sub>4</sub>	HSO <sub>4</sub> <sup>-</sup>	$10^2$	-2	
HSO <sub>4</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	$1.2 \times 10^{-2}$		1.92
acetic acid	Ac <sup>-</sup>		4.75	
carbonic acid	HCO <sub>3</sub> <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup>		6.37	10.25
phosphoric acid	...		2.12	7.21
NH <sub>4</sub> <sup>+</sup>	NH <sub>3</sub>		9.25	12.67

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Equilibria in acid and base solutions

Classification of acids and bases:

- strong and weak acids/bases (superacids)
- mono-, by-, triprotic acids/bases
- diluted and concentrated acids (Hammett function)

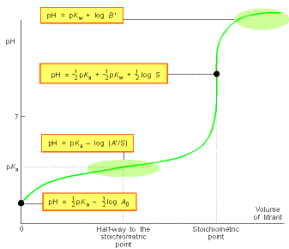
pH scale  
measurement of pH  
calculation of pH

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Equilibria in acid and base solutions

Acid/base titrations

- Henderson–Hasselbach equation:  $pH = pK_a - \lg([HA]/[A])$
- Versions :
  - strong acid + strong base
  - strong acid + weak base
  - weak acid + strong base
  - (weak acid + weak base)
  - polyprotic acid + strong base
- End point detection:
  - hydrogen electrode
  - indicator (colored organic compound with suitable  $pK_a$ ).



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Redox equilibria and titrations

- They are formally similar to acid-base equilibria – but here there is electron transfer instead of proton transfer.
- In general:  $A_{red} + B_{ox} \rightleftharpoons A_{ox} + B_{red}$   $K = \frac{a_{A_{ox}} \cdot a_{B_{red}}}{a_{A_{red}} \cdot a_{B_{ox}}}$
- Their description is discussed in electrochemistry using standard redox potentials.
- The endpoints of the redox titrations may be indicated by an electrode or by a colored redox indicator (with appropriate  $E^0$ ).

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Equilibria of metal complexes

- Metal complexes: central metal ion + ligands (solv)
- composition, stoichiometry: (1:1 – 1:8)
    - mono- and bimetallic complexes, aqua complexes, mixed ligand complexes
  - equilibrium description:
    - stepwise complex formation equilibria
  - structure, bindings:
    - the crystal field and ligand field theory was introduced to explain the color and the magnetic properties of the complexes.
  - kinetic properties:
    - ligand substitution (labile/inert);
    - complex catalysts
  - practical importance (industry, agriculture, living organisms ...)

Equilibria of metal complexes

- Net reaction (charges:  $Me^{m+}$ ,  $L^-$  and/or  $0$ )  
 $Me(H_2O)_6(aq) + 6 L(aq) \rightleftharpoons MeL_6(aq) + 6 H_2O$ 
  - Thermodynamic equilibrium constant:  $K = \frac{a_{MeL_6} \cdot a_{H_2O}^6}{a_{Me(H_2O)_6} \cdot a_L^6}$
  - The activity of water can be incorporated into  $K$ .
  - The equilibria can be described separately for the stepwise coordination of each ligand:  
 $Cd^{2+} \xrightleftharpoons{L^-} [CdL]^+ \xrightleftharpoons{L^-} [CdL_2] \xrightleftharpoons{L^-} [CdL_3]^- \xrightleftharpoons{L^-} [CdL_4]^{2-}$
  - To describe these processes, stepwise equilibrium constants or net stability products should be given.

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Equilibria of metal complexes

- Some colorful examples:
- $[Fe(SCN)_x]^{(3-x)+}$  – blood red (in acidic medium)
  - $[Fe(phen)_3]^{2+}$  – red
  - $[Fe(phen)_3]^{3+}$  – blue
  - $[Fe(mioglobin)_4]^{2+}$  – deep red (hemoglobine)
  - $[Cu(H_2O)_4]^{2+}$  – light blue
  - $[Cu(NH_3)_4]^{2+}$  – deep blue
  - $[Cu(en)_2]^{2+}$  – green
  - $[Cu(Br)_4]^{2-}$  – violet
  - $[Cr(H_2O)_6]^{3+}$  – violet
  - $[Co(H_2O)_6]^{2+}$  – pink
  - $[Co(NH_3)_5(ONO)]^{2+}$  – red

Equilibria of metal complexes



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Overview of electrochemistry

	Equilibrium electrochemistry (no current flows)	Dynamic electrochemistry (current does flow)
Homogeneous	Thermodynamics of electrolyte solutions: <ul style="list-style-type: none"><li>electrolytic dissociation</li><li>thermodynamics and activities of ions</li></ul>	Conductance of electrolytes: <ul style="list-style-type: none"><li>electrolytic conduction</li><li>mobilities of ions</li><li>Kohlrausch laws</li></ul>
Heterogeneous	Thermodynamics of electrodes and Galvanic cells: <ul style="list-style-type: none"><li>electrochemical cells</li><li>cell and electrode potential</li><li>types of electrodes</li></ul>	Kinetics of electrode reactions: <ul style="list-style-type: none"><li>exchange current</li><li>overpotential</li><li>Tafel equation</li><li>Butler-Volmer equation</li><li>electrolysis</li><li>batteries</li></ul>

# HOMOGENEOUS EQUILIBRIUM ELECTROCHEMISTRY: THERMODYNAMICS OF ELECTROLYTES

- I. Thermodynamics of electrolytes.
  - A. Characterization of electrolytes
  - B. Thermodynamic formation functions of ions
  - C. Activities of ions in solution, the Debye-Hückel theory

# I. Thermodynamics of electrolytes A. Characterization of electrolytes

- Electrolytes are special types of **solutions**: **homogeneous**, **multicomponent** systems
- Ionic compounds dissociate into **anion**(s) and **cation**(s) in polar solvents ([Svante Arrhenius, Nobel prize in 1903](#))
- Mostly the same general properties as for other (dilute) solutions:
  - colligative properties (freezing point depression, boiling point elevation, osmosis, distribution...)
  - may both be ideal and real
- Unique property:
  - conduction of electricity

# I. Thermodynamics of electrolytes A. Characterization of electrolytes

- Electroneutrality – there are no solutions containing **cation** only, or **anion** only!
- The electric conduction is an ion conduction where  $\kappa$  increases with increasing temperature (versus metals).
- Molten electrolytes (e.g. NaCl(l)) also conduct electricity.

# I. Thermodynamics of electrolytes A. Characterization of electrolytes

- Acids, bases, salts are electrolytes:
  - Salts: practically complete dissociation
  - Acids and bases: weak or strong
- Dissociation is an equilibrium:
  - $K_d$  dissociation constant or
  - $\alpha$  degree of dissociation
- Electrolytic dissociation:  
 $HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$   
 $K_a = \frac{a_{H_3O^+} \cdot a_{A^-}}{a_{HA}}$ 
  - (acid-base equilibria, pH, buffers, indicators, pH-titration,  $pK_a$ )
  - complexation)

# I. Thermodynamics of electrolytes A. Characterization of electrolytes

- Dissociation of **weak acids**:  
 $HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$ 
  - $K_a$  dissociation constant ( $K_a = \frac{a_{H_3O^+} \cdot a_{A^-}}{a_{HA}}$ ) or
  - $\alpha$  degree of dissociation.
    - $0 < \alpha < 1$
    - $\alpha = \frac{A_m}{A_m^0}$  (more later)
    - $[A^-(aq)]_e = [H_3O^+(aq)]_e = c\alpha$
    - $[HA(aq)]_e = c(1-\alpha)$

$K_a = \frac{c\alpha^2}{1-\alpha}$


- Ostwald's dilution law.**

# I. Thermodynamics of electrolytes A. Characterization of electrolytes

- Complete dissociation in the saturated solutions of **solid salts**.
- Ions are in equilibrium with a solid phase rather than individual molecules:  
 $KA(s) \rightleftharpoons K^+(sol) + A^-(sol)$   
 $K_{sol} = \frac{a_{K^+} \cdot a_{A^-}}{a_{KA}} = a_{K^+} \cdot a_{A^-}$

Exception: e.g.  $HgCl_2$  ( $S = 1.3 \times 10^{-5} \text{ mol/dm}^3$ )

 $HgCl_2(s) \rightleftharpoons HgCl_2(aq) \rightleftharpoons Hg^{2+}(aq) + 2 Cl^-(aq)$





B. Thermodynamic formation functions of ions

- Thermodynamic formalism:
  - behavior is close to *ideal* until ca.  $10^{-3}$  mol/dm<sup>3</sup>,
  - above: *real* solutions.
  - Activity (*a*) is used instead of concentration (*c* or *m*).

B. Thermodynamic formation functions of ions

- Problem: solutions never contain one type of ion (e.g. cation) only, there is always at least one other oppositely charged ion.
- Arbitrary conventions (but widely agreed on):
  - $\Delta_f H^\circ(\text{H}^+, \text{aq}) = 0$  J/mol and
  - $\Delta_f G^\circ(\text{H}^+, \text{aq}) = 0$  J/mol.
- What's more:
  - $\Delta_f S^\circ(\text{H}^+, \text{aq}) = 0$  J/(K mol) at every temperature. This entropy is measured on a relative scale!
  - Absolute entropy (third law of thermodynamics)  
 $\Delta_f S^\circ(\text{H}^+, \text{aq}) = -21$  J/(K mol).

B. Thermodynamic formation functions of ions

- Example:  $\text{Ag(s)} + \frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq})$   
 $\Delta_f H^\circ = \Delta_f H^\circ(\text{Ag}^+, \text{aq}) + \Delta_f H^\circ(\text{Cl}^-, \text{aq}) = -61.5$  kJ/mol,  
but  $\Delta_f H^\circ$  for the processes  $\text{Ag(s)} \rightarrow \text{Ag}^+(\text{aq}) + \text{e}^-$   
and  $\frac{1}{2}\text{Cl}_2(\text{g}) + \text{e}^- \rightarrow \text{Cl}^-(\text{aq})$  are not measurable separately.
- Solution: start from  $\text{H}^+(\text{aq})$  and proceed to other ions:
  - $\frac{1}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$   $\Delta_f H^\circ = \Delta_f H^\circ(\text{H}^+, \text{aq}) + \Delta_f H^\circ(\text{Cl}^-, \text{aq}) = -167$  kJ/mol, and thus  $\Delta_f H^\circ(\text{Cl}^-, \text{aq}) = -167$  kJ/mol.
  - Now  $\Delta_f H^\circ(\text{Ag}^+, \text{aq})$  is available.

B. Thermodynamic formation functions of ions

- Example: Born–Haber cycle for ion formation:  
 $\frac{1}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$

	$\Delta G^\circ$ (kJ/mol)
dissociation of $\text{H}_2$ : $\frac{1}{2}\text{H}_2(\text{g}) \rightarrow \text{H}(\text{g})$	+203
ionization of H: $\text{H}(\text{g}) \rightarrow \text{H}^+(\text{g}) + \text{e}^-$	+1318
hydration of $\text{H}^+$ : $\text{H}^+(\text{g}) \rightarrow \text{H}^+(\text{aq})$	$x = 0$
dissociation of $\text{Cl}_2$ : $\frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{Cl}(\text{g})$	+106
electron affinity of Cl: $\text{Cl}(\text{g}) + \text{e}^- \rightarrow \text{Cl}^-(\text{g})$	-355
hydration of $\text{Cl}^-$ : $\text{Cl}^-(\text{g}) \rightarrow \text{Cl}^-(\text{aq})$	$y$

  - $\Delta_f G^\circ(\text{Cl}^-, \text{aq}) = x + y + 1272$  kJ/mol.
  - This is an indirect method for determining the directly not measurable **Gibbs free energy of hydration (or solvation)**.

B. Thermodynamic formation functions of ions

- Example: Born–Haber cycle for ion formation:  
 $\frac{1}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{X}_2(\text{g}) \rightarrow \text{H}^+(\text{aq}) + \text{X}^-(\text{aq})$
  - Comparison of Cl and I
- 
- (a)  $\text{H}^+(\text{g}) + \text{Cl}(\text{g}) + \text{e}^- \rightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$   
 $-(\Delta_f G^\circ(\text{H}^+, \text{aq}) + \Delta_f G^\circ(\text{Cl}^-, \text{aq}))$
- (b)  $\text{H}^+(\text{g}) + \text{I}(\text{g}) + \text{e}^- \rightarrow \text{H}^+(\text{aq}) + \text{I}^-(\text{aq})$   
 $-(\Delta_f G^\circ(\text{H}^+, \text{aq}) + \Delta_f G^\circ(\text{I}^-, \text{aq}))$

B. Thermodynamic formation functions of ions

- $\Delta_{\text{hyd}} G^\circ$  cannot be measured experimentally, but can be calculated from the Born–Haber cycle.
- The **Born equation** can be used for estimating the electrostatic component of Gibbs free energy of solvation of an ion:
$$\Delta_{\text{hyd}} G^\circ = \frac{-z^2 \cdot e^2 \cdot N_A}{8\pi \cdot \epsilon_0 \cdot r_i} \left(1 - \frac{1}{\epsilon_r}\right)$$
  - $z$ : charge of ion
  - $e$ : elementary charge,  $1.6022 \times 10^{-19}$  C
  - $\epsilon_0$ : vacuum permittivity
  - $\epsilon_r$ : dielectric constant of the solvent
  - $r_i$ : effective radius of ion

C. Activities of ions in solution

- Solutions containing ions (electrolytes) are not ideal because of electrostatic interactions. Therefore, **activities** are used instead of concentrations (e.g. equilibria or electrode potentials).
  - So far:
    - $\mu = \mu^\ominus + RT \ln a$
    - $a = \gamma \cdot m / m^\ominus$
    - where  $m$  is molality.
- $\mu = \mu^\ominus + RT \ln m / m^\ominus + RT \ln \gamma$   
 $= \mu^\ominus + RT \ln \gamma$

where  $\mu^\ominus$  is the chemical potential of an ideal dilute solution with the same molality.

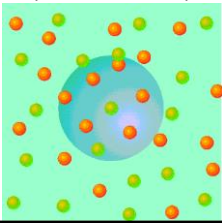
C. Activities of ions in solution

- Free energy in an ideal 1:1 electrolyte:
  - $G_m^\ominus = \mu_+^\ominus + \mu_-^\ominus$ , and
  - $G_m = \mu_+ + \mu_- = \mu_+^\ominus + \mu_-^\ominus + RT \ln \gamma_+ + RT \ln \gamma_- = G_m^\ominus + RT \ln \gamma_\pm$
- $\gamma_+$  and  $\gamma_-$  are not separable experimentally,  $\gamma_\pm$  **mean activity coefficients** are used instead:  $\gamma_\pm = \sqrt{\gamma_+ \gamma_-}$
- Generally (in a  $p:q$  electrolyte):  $\gamma_\pm = \sqrt[p+q]{\gamma_+^p \gamma_-^q}$ 
  - geometric mean
  - for any  $i$  ion:  $\mu_i = \mu_i^\ominus + RT \ln \gamma_\pm$

C. Activities of ions in solution

- Questions:
  - Value of  $\gamma_\pm$ .
  - Can it be measured?
    - YES. See next week's lecture (Nernst equation).
  - Can it be calculated?
    - YES. Debye-Hückel theory

C. Debye-Hückel theory

- Debye-Hückel limiting law:**
- Non-ideal behavior is caused by the electrostatic interaction between ions and it is sufficient to consider this one only in the theory.
    - Values of  $\gamma_\pm$  can be obtained.
  - Model:
    - Around any given ion, counter ions form a spherical cloud and are in excess.
    - This ion cloud reduces the chemical potential of the ion in the center.
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C. Debye-Hückel theory

- $\gamma_\pm$  **based on the Debye-Hückel theory:**
- Result:  $\lg \gamma_\pm = -A |z_+ z_-| \sqrt{I}$ 
    - $A$ : a combination of constants (in water at 25 °C, 0.509 (mol/kg)<sup>1/2</sup>)
    - $I$ : ionic strength of the solution:  $I = \frac{\sum z_i^2 m_i}{2}$
    - $I$  involves all ions!
  - This formula is only valid at low concentrations, so, it is called the **Debye-Hückel limiting law**.
  - An **extension** can be used at higher concentrations:  
 $\lg \gamma_\pm = \frac{-A |z_+ z_-| \sqrt{I}}{1 + B \sqrt{I}}$

C. Debye-Hückel theory

- The limiting and the extended Debye-Hückel laws:**
- $\lg \gamma_\pm = -A |z_+ z_-| \sqrt{I}$  $\lg \gamma_\pm = \frac{-A |z_+ z_-| \sqrt{I}}{1 + B \sqrt{I}}$
- What to do?
  - Use an indifferent salt (KCl, NaCl, NaClO<sub>4</sub>) to keep the ionic strength of the solution high and thereby constant. Determine and give the thermodynamic constants (e.g.  $K$ ,  $E^\ominus$ ,  $G^\ominus$ ) under these conditions.
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