

**Chemical reactions: diverse classifications**

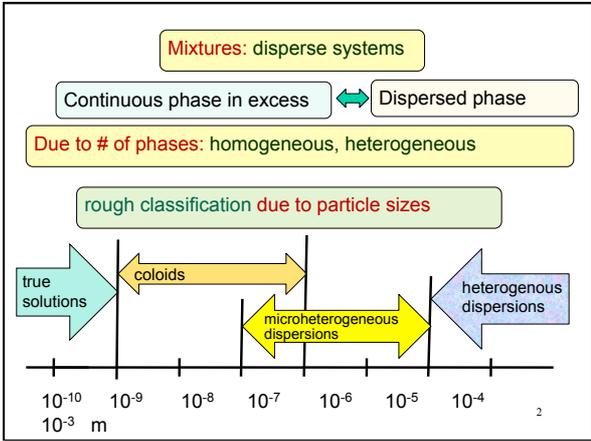
**stoichiometric changes:** combination or synthesis, decomposition, substitution or single replacement, metathesis or double displacement

**Involved particles (entities):** molecular, ionic, radical

**initialization:** photochemical, electrochemical .....

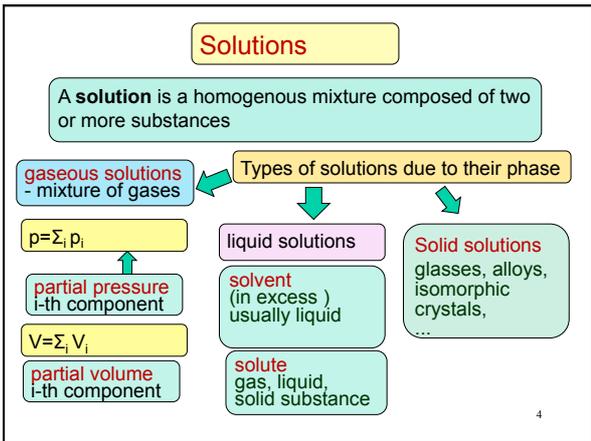
**From the chemical nature view are important:**

- protolytic reactions (proton exchange)
- oxidation-reduction or redox reactions (electron exchange)
- precipitation reactions (products are insoluble)
- reactions composition and decomposition of complexes



**Classification of disperse systems**

Medium/Phase	Dispersed phase		
	Gas	Liquid	Solid
<b>Gas</b>	None (All gases are mutually miscible)	Liquid aerosol (fog, hair sprays)	Solid aerosol (smoke cloud, air particles)
<b>Liquid</b>	Foam (whipped cream, shaving cream)	Emulsion (milk, mayonnaise)	Sol (blood, pigmented ink)
<b>Solid</b>	Solid foam (aerogel, pumice, polystyrene foam)	Gel (agar, gelatine, jelly, opal)	Solid sol (gemstone, jewel)



Veličiny vyjadrujúce zloženie roztokov (výpočtový seminár)

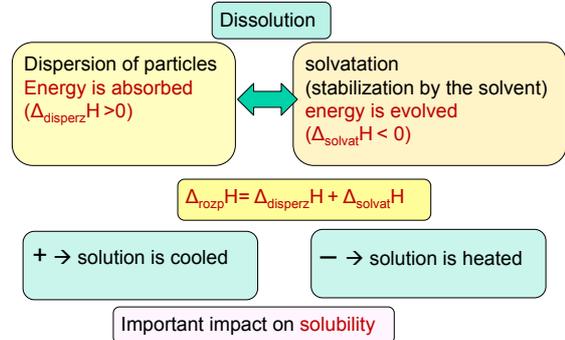
fraction, symbol	Definition	units
mass, w	$w_B = m_B / \sum_i m_i$	1, %, g/g, mg/g, g/t (hm. %)
volume, $\varphi$	$\varphi_B = V_B / \sum_i V_i$	1, %, cm <sup>3</sup> /cm <sup>3</sup> , mL/L (obj. %, vol. %)
molar, x	$x_B = n_B / \sum_i n_i$	1, mol/mol, mmol/mol (mol. %)

Concentration, symbol	Definition	units
Molarity, c	$c_B = n_B / V_R$	mol/dm <sup>3</sup> , mol/L (M = mol/L, mM = mmol/L)
Mass, $\gamma$ ( $\rho$ )	$\gamma_B = m_B / V_R$	g/dm <sup>3</sup> , g/L, mg/L, mg/mL [% (m/v) = % (w/v) = g/dL]
Number of particles (molecular), C	$C_B = N_B / V_R$	dm <sup>-3</sup> , L <sup>-1</sup> , mL <sup>-1</sup>
Volume, $\sigma$	$\sigma_B = V_B / V_R$	1, cm <sup>3</sup> /dm <sup>3</sup> , mL/L, mL/dL (nie v %!!!)

Molality (m) (mol.kg<sup>-1</sup>) Moles of solute/kg of solvent

5

solutions: solvation and heat of solution



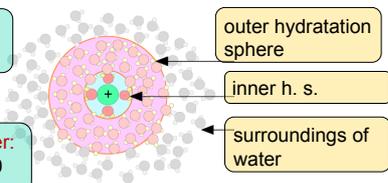
6

Most frequently used solvent **water**: ions are hydrated

Smaller cations  
more hydrated

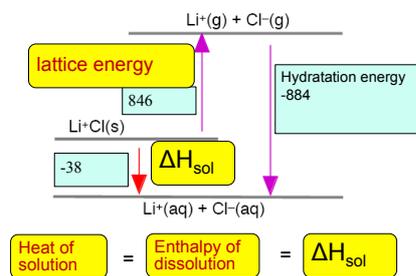
Hydration number:  
Li<sup>+</sup> 4, K<sup>+</sup> 2, Mg<sup>2+</sup> 10

anions less:  
F<sup>-</sup> 2-4

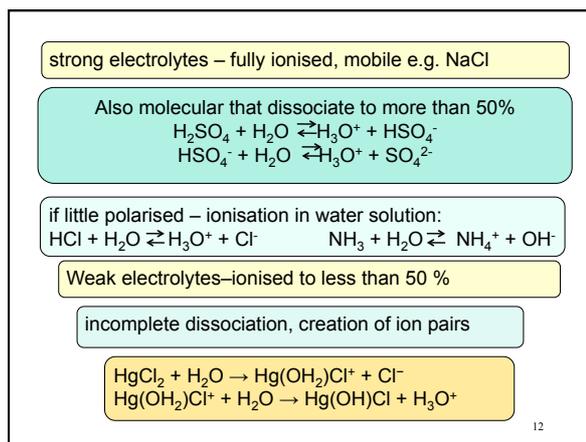
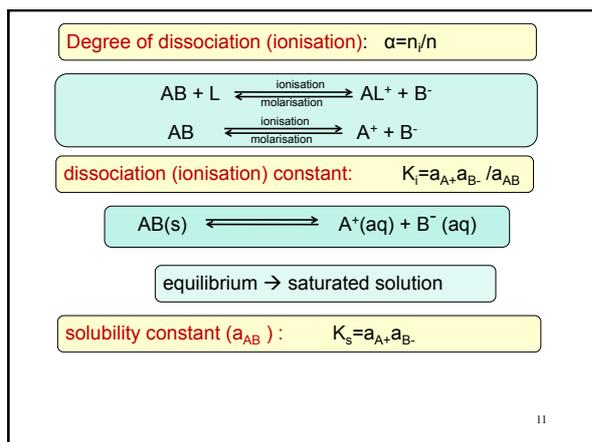
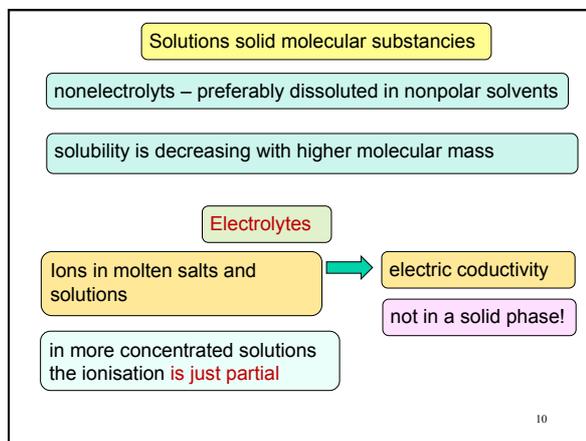
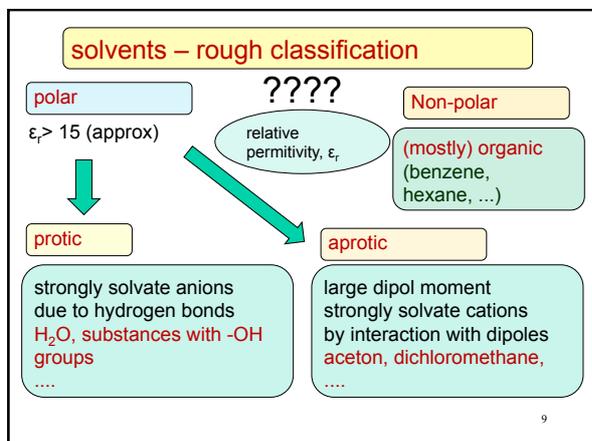


7

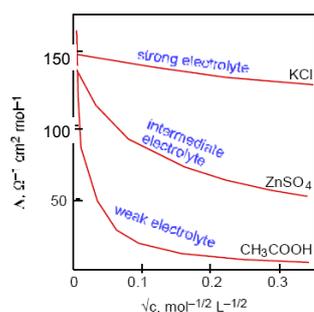
Example ( $\Delta H$  v kJ/mol)



8



conductivity – depends on  $\alpha$  and mobility – viscosity!



Molar conductivity (normed to a mole of charge)

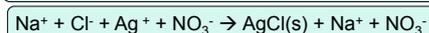
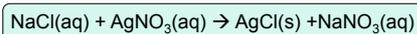
conductivity  
molarity

13

## Precipitation reactions

Product – a substance with very low solubility constant

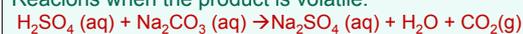
solubility constant ( $a_{AB}$ ):  $K_s = a_{A^+} a_{B^-}$



$$K_s(\text{AgCl})^{18^\circ\text{C}} = [\text{Ag}^+][\text{Cl}^-] = 1.1 \times 10^{-18}$$

$$K_s(\text{Ag}_2\text{S})^{20^\circ\text{C}} = [\text{Ag}^+]^2[\text{S}^{2-}] = 6 \times 10^{-50}$$

Reactions when the product is volatile:



## Acids and Bases

The term acid was first used in the seventeenth century; it comes from the Latin root ac-, meaning "sharp", as in acetum, vinegar. Some early writers suggested that acidic molecules might have sharp corners or spine-like projections that irritate the tongue or skin.

Acids have long been recognized as a distinctive class of compounds whose aqueous solutions exhibit the following properties:

- A characteristic sour taste (think of lemon juice!);
- ability to change the color of litmus\* from blue to red;
- react with certain metals to produce gaseous H<sub>2</sub>;
- react with bases to form a salt and water.

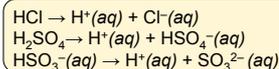
\*Litmus is a natural dye found in certain lichens. The name is of Scandinavian origin, e.g. lit (color) + mosi (moss) in Icelandic. "Litmus test" has acquired a meaning that transcends both Chemistry and science to denote any kind of test giving a yes/no answer.

The name **base** has long been associated with a class of compounds whose aqueous solutions are characterized by:

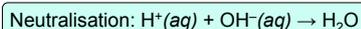
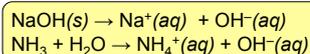
- a bitter taste;
- a "soapy" feeling when applied to the skin;
- ability to restore the original blue color of litmus that has been turned red by acids;
- ability to react with acids to form salts.
- react with certain metals to produce gaseous  $H_2$ ;

Acids and bases: Arrhenius theory (1884-1890)  
Svante Arrhenius, Swedish

Acids are substances whose molecules contain at least a single hydrogen atom that can dissociate and at dissolution a hydrated hydrogen cation and an anion are created.



**Bases:** substances that after a dissolution increase the amount of hydroxide anions ( $\text{OH}^-$ )

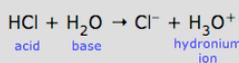


## Proton donors and acceptors

Brønsted-Lowry theory

an **acid** is a **proton donor**; a **base** is a **proton acceptor**.

These definitions carry a very important **implication**: a substance cannot act as an acid without the presence of a base to accept the proton, and vice versa.



**Hydrogen ions cannot exist in water!**

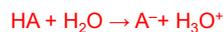
central role of hydronium  $\text{H}_3\text{O}^+$

Instead of dissociation

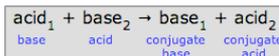
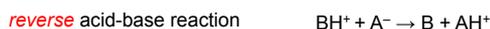


acid base reactions

According to the Brønsted concept, the process that was previously written as a simple dissociation of a **generic acid** HA (" $\text{HA} \rightarrow \text{H}^+ + \text{A}^-$ ") is now an acid-base reaction in its own right:



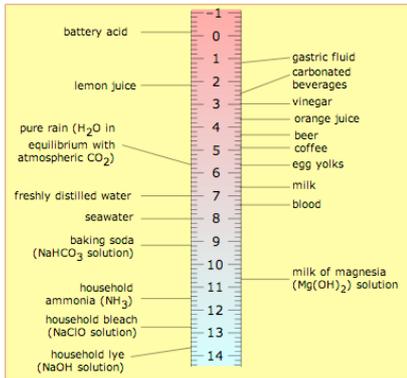
The idea, again, is that the proton, once it leaves the acid, must end up somewhere; it cannot simply float around as a free hydrogen ion. A reaction of an acid with a base is thus a **proton exchange reaction**



**conjugate pairs**



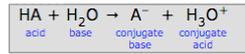
$\text{pH} = -\log(c_{\text{H}_3\text{O}^+})$  : pH values for selected compounds



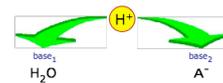
25

### Strong acids and weak acids

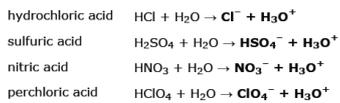
We can look upon the generalized acid-base reaction



as a competition of two bases for a proton:



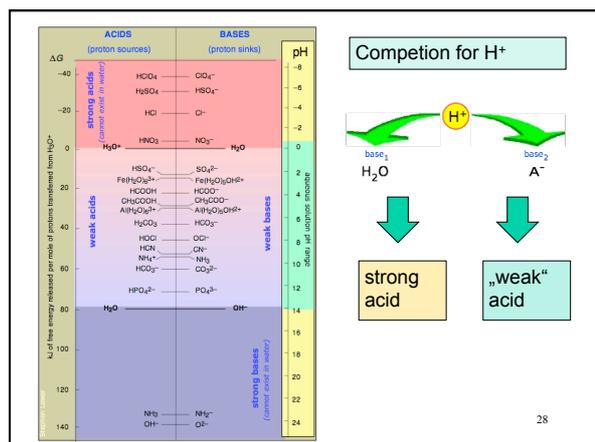
If the base  $\text{H}_2\text{O}$  overwhelmingly wins this tug-of-war, then the acid  $\text{HA}$  is said to be a **strong acid**.



Solutions of these acids in water are really solutions of the ionic species shown in heavy type on the right. This being the case, it follows that what we call a 1 M solution of "hydrochloric acid" in water, for example, does not really contain a significant concentration of HCl at all; the only real acid present in such a solution is  $\text{H}_3\text{O}^+$ !



$\text{H}_3\text{O}^+$  is the strongest acid that can exist in water;  
 All strong acids appear to be equally strong in water.



**Strength of acids and bases**

Depends on the ionisation degree  $\longleftrightarrow$  Impact of a solvent

Ionisation constants:  $K_a$  acidity;  $K_b$  basicity

$A + H_2O \rightleftharpoons B + H_3O^+$        $B + H_2O \rightleftharpoons A + OH^-$

$K_a = \frac{a_{H_3O^+} \cdot a_B}{a_A}$        $K_b = \frac{a_{OH^-} \cdot a_A}{a_B}$        $\longrightarrow$        $K_a \cdot K_b = K_w$

Strong acid  $\longrightarrow$  Weak conjugated base

acids/bases:  $K_a$  or  $K_b$        $[pK_x = -\log(K_x)]$

$10^{-6}$	$10^{-5}$	$10^{-4}$	$10^{-2}$	$10^{-1}$	$10^0$	$10^1$
6	5	4	2	1	0	-1
very weak	weak	intermediate	strong	very strong		

29

**Kyseliny:  $XO_m(OH)_n$**

$X(OH)_n$  [ $HClO, H_3BO_3, H_4SiO_4 \dots$ ]: very weak

$XO(OH)_n$  [ $HNO_2, H_2SO_3, H_3PO_4 \dots$ ]: weak

$XO_2(OH)_n$  [ $HNO_3, H_2SO_4, HClO_3 \dots$ ]: strong (to very strong)

$XO_3(OH)_n$  [ $HClO_4, HMnO_4, \dots$ ]: strong (very strong)

Oxidation state of X: high > ... > ... > low

acids  $H_nX$  ( $pK_a$ ):

$NH_3$ (35)	<	$H_2O$ (14)	<	$HF$ (3)
		$H_2S$ (7)	<	$HCl$ (-7)
		$H_2Se$ (4)	<	$HBr$ (-9)
		$H_2Te$ (3)	<	$HI$ (-10)

important factors: bond energy  $HX$ ,  $EA(X)$ ,  $\Delta_{hydr}H$  (anion)

$H_nA > H_{n-1}A^- > H_{n-2}A^{2-} \dots$

$H_3PO_4$	>	$H_2PO_4^-$	>	$HPO_4^{2-}$
$pK_a$ : 2		7		12

30

**Orientation tests of pH: ACID-BASE INDICATORS**

Dyes changing colour in a narrow pH range

Weak acids/bases – ionised and non-ionised forms are of different colors

$H_{Ind} + H_2O \rightleftharpoons Ind^- + H_3O^+$

Indicator constant  $K_I'$

$$K_I' = \frac{a_{H_3O^+} \cdot a_{Ind^-}}{a_{Ind}}$$

indicator	transition pH	pH <	$pK_I'$	>	pH
Methyl orange	3.0–4.4	red			yellow
Litmus	4.4–6.2	red			blue
Phenolphthalein	8.5–10.5	colorless			red

Accurate measurements: pH-meter based on electrode potentials 31

**Neutralisation**

Stoichiometrically – reaction of acids with bases  $\rightarrow$  salts

$HCl + NaOH \rightarrow NaCl + H_2O$   
 $H_2SO_4 + 2 KOH \rightarrow K_2SO_4 + 2 H_2O$

$HCl + H_2O \rightleftharpoons Cl^- + H_3O^+$   
 $NaOH \rightleftharpoons Na^+ + OH^-$

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

Adjusting of  $c_{H_3O^+}, c_{OH^-}$  to  $K_w$  [ $c_{H_3O^+} = c_{OH^-} = 10^{-7}$ ]

when  $Y^+, X^-$  interact with  $H_2O/OH^-/H_3O^+$   $\rightarrow$  hydrolysis

32

**Hydrolysis (solvolyis for other than protic solvents)**

Acidic cations:  $c_{H_3O^+} > c_{OH^-}$  → pH < 7

$NH_4^+ Cl^-$  →  $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

Hydrolytic constant  
 $K_{hydr} = K_a(NH_4^+)$

$$K'_{hydr} = \frac{a_{H_3O^+} a_{NH_3}}{a_{NH_4^+}}$$

hydrated cations  $M^{2+}, M^{3+}$

$[Be(H_2O)_4]^{2+} + H_2O \rightleftharpoons [Be(H_2O)_3(OH)]^+ + H_3O^+$

Hydrolysis control: acid supresses /base deepens

33

**Hydrolysis (solvolyis for other than protic solvents)**

basic anions:  $c_{H_3O^+} < c_{OH^-}$  → pH > 7

KCN →  $CN^- + H_3O^+ \rightleftharpoons HCN + H_2O$

Hydrolytic constant  
 $K_{hydr} = K_b(CN)$

$$K'_{hydr} = \frac{a_{HCN} a_{OH^-}}{a_{CN^-}}$$

Hydrolysis control: acid deepens base supresses

acidic cations and basic anions:  $c_{H_3O^+} \approx c_{OH^-}$

$NH_4^+ + CH_3COO^- \rightleftharpoons CH_3COOH + NH_3$

34

$K_a = \frac{a_{H_3O^+} a_{A^-}}{a_{AH}}$  →  $c_{H^+} = K_a c_{AH} / c_{A^-}$

$-\log c_{H^+} = -\log K_a + \log c_{A^-} / c_{AH}$

$pH = pK_a + \log c_{A^-} / c_{AH}$

35

**acids and bases: Lewis theory**  
 (Gilbert Newton Lewis, USA, 1923)

$A + :B \rightarrow A-B$       proton is not needed

Lewis base – nucleophile, donor of an electron pair

Lewis acid – electrophile, acceptor of an electron pair

$H^+ + :NH_3 \rightarrow NH_4^+$        $B_2H_6 + 2H^- \rightarrow 2BH_4^-$

$AlF_3 + 3F^- \rightarrow AlF_6^{3-}$        $BF_3 + :NH_3 \rightarrow H_3N-BF_3$

coordination compounds: central atom – L. acid  
 ligand – L. base

36

