



**SEMMELWEIS  
UNIVERSITY**



**PÁZMÁNY PÉTER  
CATHOLIC UNIVERSITY**



**Development of Complex Curricula for Molecular Bionics and Infobionics Programs within a consortial\* framework\*\***

Consortium leader

**PÁZMÁNY PÉTER CATHOLIC UNIVERSITY**

Consortium members

**SEMMELWEIS UNIVERSITY, DIALOG CAMPUS PUBLISHER**

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# WORLD OF MOLECULES

(Molekulák világa)

## CHEMICAL EQUILIBRIA, ACID-BASE THEORIES

(Kémiai egyensúlyok, sav-bázis elméletek)

**KRISTÓF IVÁN**





## Previously – Chemical compounds, stoichiometry

1. Compounds
2. Chemical composition
3. Ambiguity of the chemical formula
4. Stoichiometry
5. Main groups of chemical compounds
6. Grouping of inorganic compounds
7. Salts
8. Properties of water



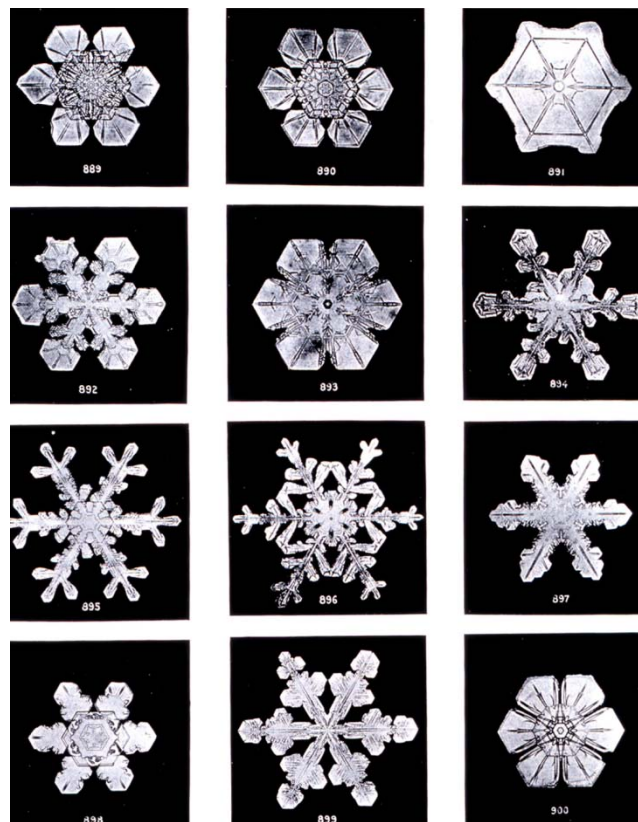


## Previously - Grouping of chemical compounds

- organic, which has – C – C – bonds
- inorganic, which lacks – C – C – bonds
  - acids
    - the reaction result of water and oxydes of non-metallic compounds
  - bases
    - the reaction result of water and oxydes of metallic compounds
  - salts
    - produced from the reaction of acids and bases
  - metal complexes
    - a central, metallic atom or ion is bonded to the surrounding molecules/ligands, which usually donate dative bond to the metal



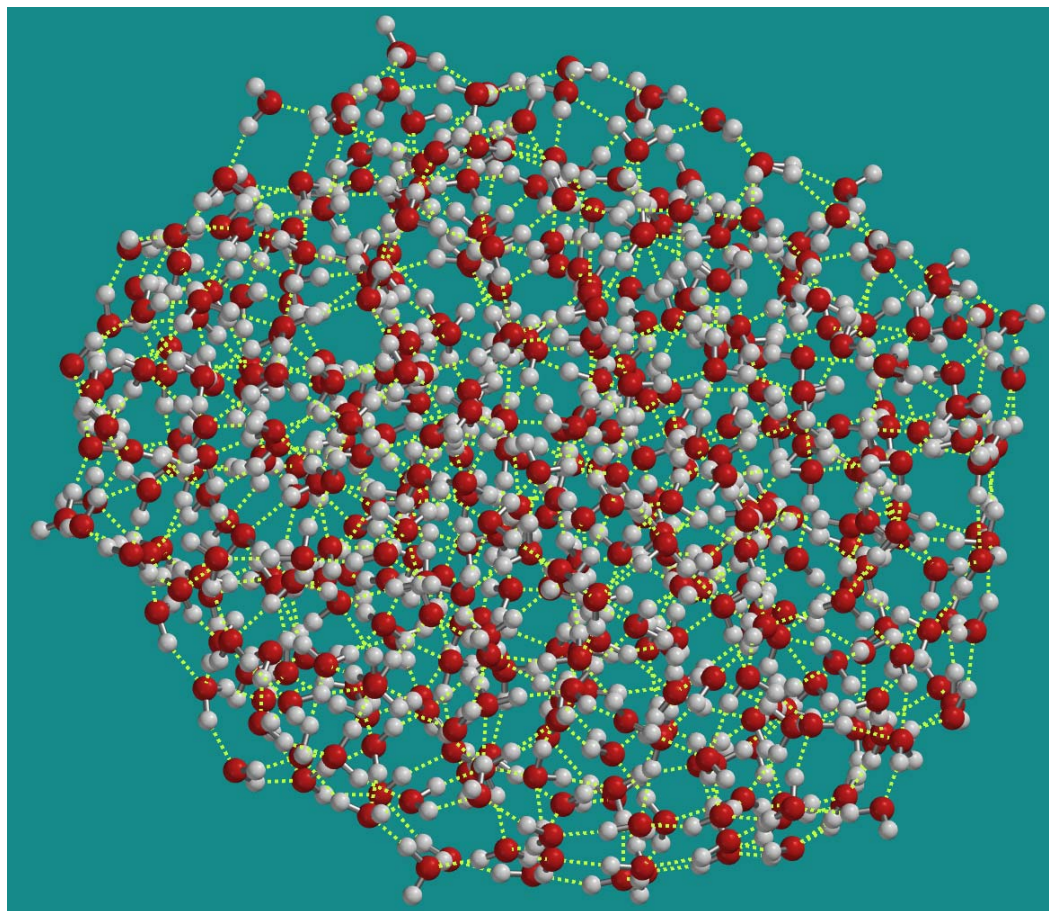
# Previously - Different phases of crystalline water



<http://en.wikipedia.org/wiki/File:IceBlockNearJoekullsarlon.jpg> | <http://en.wikipedia.org/wiki/File:SnowflakesWilsonBentley.jpg>



## Previously - Network of Hydrogen bonds with 500 molecules





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  - Lewis theory
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3. Superacids and superbases



## Chemical equilibria

- regarding reversible reactions in gaseous or liquid phase
- e.g.  $\text{H}_2 + \text{I}_2 \rightleftharpoons 2 \text{HI}$
- the equilibrium is *dynamic*
  - reaching the equilibrium means the rate of the two opposing reactions become equal
  - the ratio between reactants and products remain fixed (concentrations are constants)
  - description of equilibrium (for simple reactions): law of mass action (by Guldberg and Waage, 1867)







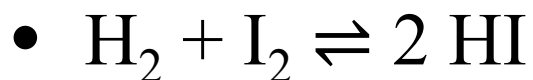
## Law of mass action (1867)

- can be derived from the equality of the forward and backward reaction rates
- the product of the equilibrium concentrations of the reaction products raised to a power according to their stoichiometric constant *divided by* the product of the equilibrium concentrations of the reactants raised to their respective stoichiometric power *is* constant ( $K$ ) in equilibrium.
- (under the same conditions: **p**ressure, **V**olume, **T**emperature )
- e.g. for the above reaction ( $H_2 + I_2 \rightleftharpoons 2 HI$ )

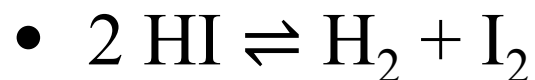
$$K = \frac{[HI]^2}{[H_2] \cdot [I_2]} = \text{constant}$$



## Chemical equilibria



$$\vec{K} = \frac{[HI]^2}{[H_2] \cdot [I_2]}$$



$$\vec{K} = \frac{[H_2] \cdot [I_2]}{[HI]^2} = \frac{1}{\vec{K}}$$

- the relationship of the equilibrium constant to the direction of the reaction is evident
- to be more precise instead of the concentration, the more accurate *activity value* of each molecule should be substituted into the law of mass action
- the activity can be approximated with the concentration in ideal gases or solutions





## Le Châtelier - Braun's principle

- If a chemical system at equilibrium experiences a change in its status, then the equilibrium shifts to counteract the imposed change and a new equilibrium is established.
- status:
  - concentration,
  - temperature,
  - volume,
  - pressure,
  - ...





## Le Châtelier - Braun's principle - example

- $PCl_5 \rightleftharpoons PCl_3 + Cl_2$
- $\begin{matrix} \uparrow & \uparrow & \downarrow \\ PCl_5 & PCl_3 & Cl_2 \end{matrix}$  direction of concentration changes

$$\vec{K} = \frac{[PCl_3] \cdot [Cl_2]}{[PCl_5]}$$

- increasing the *concentration of  $PCl_3$* 
  - the equilibrium will favor the production of reactants
  - since the equilibrium constant remains constant, increasing the  $PCl_3$  concentration, decreases the concentration of  $Cl_2$ , and increases the concentration of  $PCl_5$  reactant.





## Le Châtelier - Braun's principle - example

- $PCl_5 \rightleftharpoons PCl_3 + Cl_2$
- $\downarrow \quad \quad \downarrow \quad \quad \uparrow$  direction of concentration changes

$$\vec{K} = \frac{[PCl_3] \cdot [Cl_2]}{[PCl_5]}$$

- decreasing the *concentration of  $PCl_3$* 
  - the equilibrium will favor the production of the products
  - decreasing the  $PCl_3$  concentration, increases the concentration of  $Cl_2$ , and decreases the concentration of  $PCl_5$  reactant.





## Le Châtelier - Braun's principle - example

- $PCl_5 \rightleftharpoons PCl_3 + Cl_2$
- $\begin{matrix} \uparrow & & \uparrow & & \uparrow \\ PCl_5 & & PCl_3 & & Cl_2 \end{matrix}$  direction of concentration changes

$$\vec{K} = \frac{[PCl_3] \cdot [Cl_2]}{[PCl_5]}$$

- increasing the *concentration of  $PCl_5$* 
  - the equilibrium will favor the production of products
  - basically, we introduce fresh amounts of the reactant, thus this will increase the concentration of both products  $Cl_2$  and  $PCl_3$ .





## Le Châtelier - Braun's principle - example

- $PCl_5 \rightleftharpoons PCl_3 + Cl_2$
- $\begin{matrix} \downarrow & & \downarrow & \downarrow \end{matrix}$  direction of concentration changes

$$\vec{K} = \frac{[PCl_3] \cdot [Cl_2]}{[PCl_5]}$$

- decreasing the *concentration of  $PCl_5$* 
  - the equilibrium will favor the production of the reactant
  - basically, we remove reactant, therefore the products will favor the reverse direction.





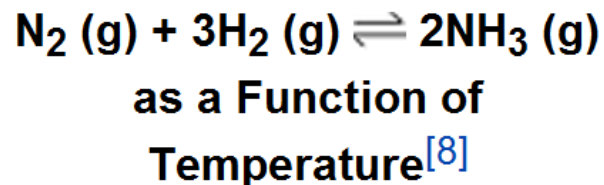
## Chemical equilibria

- Haber-Bosch process
- $N_2 + 3H_2 \rightleftharpoons 2NH_3$

$$\vec{K} = \frac{[NH_3]^2}{[N_2] \cdot [H_2]^3}$$

- hard to manage industrially
- requires
  - 150-250 bar pressure
  - 300-550 °C

### Variation in $K_{eq}$ for the Equilibrium



Temperature (°C)	$K_{eq}$
300	$4.34 \times 10^{-3}$
400	$1.64 \times 10^{-4}$
450	$4.51 \times 10^{-5}$
500	$1.45 \times 10^{-5}$
550	$5.38 \times 10^{-6}$
600	$2.25 \times 10^{-6}$





## Le Châtelier - Braun's principle - example



$$\vec{K} = \frac{[\text{NH}_3]^2}{[\text{N}_2] \cdot [\text{H}_2]^3} \quad \vec{K}_p = \frac{p_{\text{NH}_3}^2}{p_{\text{N}_2} \cdot p_{\text{H}_2}^2} \quad p'_{\text{NH}_3} = 2p_{\text{NH}_3}, \quad Q = \frac{4p_{\text{NH}_3}^2}{2p_{\text{N}_2} \cdot 8p_{\text{H}_2}^2} = \frac{1}{4}\vec{K}$$

$Q \rightarrow \vec{K}$

- $K_p$  is the equilibrium constant with partial pressures
- $p'$  is the new partial pressure of the compound
- $Q$  is the non equilibrium reaction quotient
- increasing the *pressure* of the system
  - the compression will enforce fewer molecules to form
  - therefore the reaction will favor the products to form





## Le Châtelier - Braun's principle - example

- increasing the *pressure* of reversible gas reactions in equilibrium will cause the reaction to remove molecules from the system
  - in case of reactions where the total number of molecules change the equilibrium will shift
    - e.g.  $1\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$  where  $1+3=4$  molecules react to result in 2 molecules
  - in case of reaction where there is no molecule number change such an effect cannot be observed
    - e.g.  $1\text{H}_2 + 1\text{I}_2 \rightleftharpoons 2\text{HI}$ , where 2 molecules react to produce 2





## Le Châtelier - Braun's principle - example

- increasing the *temperature* of reversible gas reactions in equilibrium will favor
  - *endothermic* reactions, where heat is required for the reaction to take place
- decreasing the *temperature* of an equilibrium
  - will favor *exothermic* reaction, where heat removal is required for the reaction to take place

e.g. a dimerization,  $2 \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$

$2 \text{NO}_2 \rightarrow \text{N}_2\text{O}_4$  is an exothermic process

$2 \text{NO}_2 \leftarrow \text{N}_2\text{O}_4$  is an endothermic process

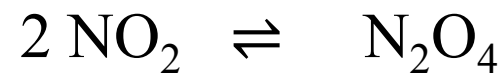
$\text{NO}_2$  is brown,  $\text{N}_2\text{O}_4$  is colorless



## Le Châtelier - Braun's principle - example



the equilibrium reaction  
of



left: hot, more  $\text{NO}_2$

right: cold, more  $\text{N}_2\text{O}_4$

<http://commons.wikimedia.org/wiki/File:NO2-N2O4.jpg>



## Homogenous and heterogenous equilibria

- in the case of homogenous equilibrium both the reactants and the products are in the same phase (gas, liquid)
- in the case of inhomogenous equilibrium some of the reactants or products are in a different phase
  - e.g.  $\text{C(s)} + \text{CO}_2(\text{g}) \rightleftharpoons 2\text{CO}(\text{g})$ 
$$\vec{K} = \frac{P_{\text{CO}}^2}{P_{\text{CO}_2}}$$
  - $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ 
$$\vec{K} = P_{\text{CO}_2}$$
  - thus the equilibrium constants are modified accordingly



## Acid dissociation equilibrium

- in case of a general acid, the dissociation reaction is
- $HA \rightleftharpoons H^+ + A^-$
- the equilibrium constant can be written

$$K_a = \frac{[H^+] \cdot [A^-]}{[HA]}, \quad pK_a = -\log(K_a)$$

- it is called the acid dissociation constant ( $K_a$ )
- for water
- $2H_2O \rightleftharpoons H_3O^+ + OH^- \quad pK_w = 14$

$$K_a = \frac{[H_3O^+] \cdot [OH^-]}{[H_2O]^2} \rightarrow K_w = [H_3O^+] \cdot [OH^-] = 10^{-14} \text{ M}^2$$





## Acid dissociation constant of some compounds

name	$pK_a$
benzoic acid	4.204
formic acid	3.751
hydrofluoric acid	3.17
hydrocyanic acid	9.21
hydrogen peroxide	11.7
nitric acid	-1.64
acetic acid	4.76
nitrous acid	3.37



## Base dissociation equilibrium

- in case of a general base, the dissociation reaction is
- $BOH \rightleftharpoons B^+ + OH^-$
- the equilibrium constant can be written

$$K_b = \frac{[B^+] \cdot [OH^-]}{[BOH]}, \quad pK_b = -\log(K_b)$$

- it is called the base dissociation constant ( $K_b$ )
- connection between  $K_b$  and  $K_a$ :  $pK_a + pK_b = pK_w = 14$
- $B + H_2O \rightleftharpoons BH^+ + OH^-$

$$K_b = \frac{[BH^+] \cdot [OH^-]}{[B]} \quad \text{and} \quad K_w = [H_3O^+] \cdot [OH^-] \Rightarrow K_b = \frac{K_w}{K_a}$$







## Base dissociation constant of some compounds

name	$pK_b$
ammonia	4.775
methylamine	3.355
thiethylamine	3.28
aniline	4.6
pyrrolidine	2.6
pyridine	8.8





## Grouping of chemical compounds

- organic, which has – C – C – bonds
- inorganic, which lacks – C – C – bonds
  - acids
    - the reaction result of water and oxydes of non-metallic compounds
  - bases
    - the reaction result of water and oxydes of metallic compounds
  - salts
    - produced from the reaction of acids and bases
  - metal complexes
    - a central, metallic atom or ion is bonded to the surrounding molecules/ligands, which usually donate dative bond to the metal





## Arrhenius – Ostwald acid base theory

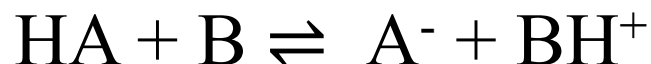
- acid: dissociates to produce proton
  - $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$
  - increases the number of protons in water
- base: dissociates to produce hydroxide ions
  - $\text{BOH} \rightleftharpoons \text{B}^+ + \text{OH}^-$
  - increases the number of hydroxide ions in water
- **aqueous** acids and bases (only aqueous is considered!)
  - neutralize according:  $\text{H}^+_{(\text{aq})} + \text{OH}^-_{(\text{aq})} \rightleftharpoons \text{H}_2\text{O}$
  - acid + base  $\rightarrow$  salt + water
    - e.g.  $2 \text{NaOH} + \text{H}_2\text{SO}_4 \rightarrow 2 \text{H}_2\text{O} + \text{Na}_2\text{SO}_4$





## Brønsted – Lowry acid base theory

- Brønsted acid (HA): proton donor
  - $HA \rightleftharpoons H^+ + A^-$
- Brønsted base (B): proton acceptor
  - $B + H^+ \rightleftharpoons BH^+$



- the resulting ions can also be classified
  - $A^-$  : conjugate **base**,
    - in the reverse direction this can accept a proton
  - $BH^+$  : conjugate **acid**,
    - in the reverse direction this can donate a proton





## Brønsted – Lowry acid base theory

- according to this theory
  - the autoprotolysis/self dissociation of water
  - $\text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$
  - can be classified both
    - $\text{H}_2\text{O}$ : Brønsted acid
    - $\text{H}_2\text{O}$ : Brønsted base } amphoteric property
  - furthermore
    - $\text{H}_3\text{O}^+$  : conjugate acid
    - $\text{OH}^-$  : conjugate base





## Brønsted – Lowry acid base theory

- examples (water acts as the counterpart)
  - Brønsted acids – proton donors
    - $\text{HCl} + \text{H}_2\text{O} \rightleftharpoons \text{Cl}^- + \text{H}_3\text{O}^+$
    - $\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+$
  - Brønsted bases – proton acceptors
    - $\text{H}_2\text{O} + \text{NH}_3 \rightleftharpoons \text{OH}^- + \text{NH}_4^+$
- these acids and bases can always be defined by the reaction
  - **acid + base  $\rightleftharpoons$  conjugate base + conjugate acid**



## Lewis acid base theory

- Lewis acid (**A**)
  - electron pair acceptor
- Lewis base (**:B**)
  - electron pair donor
- through an acid – base reaction a dative covalent bond is created



- the product is called a Lewis adduct
- e.g.:  $(\mathbf{CH_3})_3\mathbf{B} + \mathbf{:NH_3} \rightleftharpoons (\mathbf{CH_3})_3\mathbf{B-NH_3}$





## Lewis acid base theory

- examples (Lewis acid (**A**), Lewis base (**:B**))
  - $\text{H}^+ + \text{:NH}_3 \rightarrow \text{NH}_4^+$
  - $\text{BF}_3 + \text{F}^- \rightarrow \text{BF}_4^-$
  - $\text{PCl}_5 + \text{Cl}^- \rightarrow \text{PCl}_6^-$
  - $\text{SF}_4 + \text{F}^- \rightarrow \text{SF}_5^-$
  - $\text{CO} + \text{BF}_3 \rightarrow \text{COBF}_3$
  - $\text{H}_2\text{O}$
  - molecules with non-bonding electron pairs
  - two non-bonding electrons on HOMO orbitals









## Brønsted – Lewis compatibility

- Lewis base = Brønsted base
  - the electron pair can be donated to the proton
- conjugate base = Lewis base
  - an electron pair remains after donating a proton
  - BUT: Lewis base cannot be protonated easily
- acid-base strength do not compare in the two theories
- Brønsted –Lowry theory is useful in non-aqueous solvents (proton is still required)
- Lewis theory is useful in complex/coordination chemistry



## HSAB theory (Pearson, 1963)

- Hard and Soft Acids and Bases
- hard acids and bases
  - small atomic and ionic radius
  - high oxidation state
  - low polarizability
  - high electronegativity
  - low energy HOMOs (in case of bases)
  - high energy LUMOs (in case of acids)
    - hard acids:  $\text{H}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , ...
    - hard bases:  $\text{OH}^-$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ , ...





## HSAB theory (Pearson, 1963)

- soft acids and bases
  - large atomic and ionic radius
  - low or zero oxidation state
  - high polarizability
  - low electronegativity
  - soft bases have higher energy HOMOs than hard bases
  - soft acids have lower energy LUMOs than hard acids
    - soft acids:  $\text{Hg}^{2+}$ ,  $\text{Pt}^{2+}$ ,  $\text{Ag}^+$ , ...
    - soft bases:  $\text{H}^-$ ,  $\text{SCN}^-$ ,  $\text{I}^-$ , ...





# HSAB theory - examples

Acids				Bases			
hard		soft		hard		soft	
Hydronium	H <sup>+</sup>	Mercury	CH <sub>3</sub> Hg <sup>+</sup> , Hg <sup>2+</sup> , Hg <sub>2</sub> <sup>2+</sup>	Hydroxide	OH <sup>-</sup>	Hydride	H <sup>-</sup>
Alkali metals	Li <sup>+</sup> , Na <sup>+</sup> , K <sup>+</sup>	Platinum	Pt <sup>2+</sup>	Alkoxide	RO <sup>-</sup>	Thiolate	RS <sup>-</sup>
Titanium	Ti <sup>4+</sup>	Palladium	Pd <sup>2+</sup>	Halogens	F <sup>-</sup> , Cl <sup>-</sup>	Halogens	I <sup>-</sup>
Chromium	Cr <sup>3+</sup> , Cr <sup>6+</sup>	Silver	Ag <sup>+</sup>	Ammonia	NH <sub>3</sub>	Phosphine	PR <sub>3</sub>
Boron trifluoride	BF <sub>3</sub>	borane	BH <sub>3</sub>	Carboxylate	CH <sub>3</sub> COO <sup>-</sup>	Thiocyanate	SCN <sup>-</sup>
Carbocation	R <sub>3</sub> C <sup>+</sup>	P-chloranil		Carbonate	CO <sub>3</sub> <sup>2-</sup>	carbon monoxide	CO
		bulk Metals	M <sup>0</sup>	Hydrazine	N <sub>2</sub> H <sub>4</sub>	Benzene	C <sub>6</sub> H <sub>6</sub>
		Gold	Au <sup>+</sup>				

[http://en.wikipedia.org/wiki/HSAB\\_theory](http://en.wikipedia.org/wiki/HSAB_theory)



## HSAB theory – hardness values of acids and bases (in eV)

Acids			Bases		
Hydrogen	H <sup>+</sup>	infinite	Fluoride	F <sup>-</sup>	7
Aluminum	Al <sup>3+</sup>	45.8	Ammonia	NH <sub>3</sub>	6.8
Lithium	Li <sup>+</sup>	35.1	hydride	H <sup>-</sup>	6.8
Scandium	Sc <sup>3+</sup>	24.6	carbon monoxide	CO	6.0
Sodium	Na <sup>+</sup>	21.1	hydroxyl	OH <sup>-</sup>	5.6
Lanthanum	La <sup>3+</sup>	15.4	cyanide	CN <sup>-</sup>	5.3
Zinc	Zn <sup>2+</sup>	10.8	phosphane	PH <sub>3</sub>	5.0
Carbon dioxide	CO <sub>2</sub>	10.8	nitrite	NO <sub>2</sub> <sup>-</sup>	4.5
Sulfur dioxide	SO <sub>2</sub>	5.6	Hydrosulfide	SH <sup>-</sup>	4.1
Iodine	I <sub>2</sub>	3.4	Methane	CH <sub>3</sub> <sup>-</sup>	4.0

[http://en.wikipedia.org/wiki/HSAB\\_theory](http://en.wikipedia.org/wiki/HSAB_theory)



## HSAB theory (Pearson, 1963)

- this theory is the extension of the Lewis acid - base theory
- the theory predicts that the interaction between hard acids bases (ionogenic), and soft acids and bases (covalent character) are more stable
- useful for reaction mechanism descriptions
- softness of a base (B) is described by determining the equilibrium constant for the following
  - $\text{BH} + \text{CH}_3\text{Hg}^+ \rightleftharpoons \text{H}^+ + \text{CH}_3\text{HgB}$ 
    - where  $\text{CH}_3\text{Hg}^+$  is a soft acid and  $\text{H}^+$  is a strong acid





## Superacids

- special acids that have acidity greater than pure sulfuric acid ( $\text{pK}_a \sim -3$ )
- used to create and maintain organic cations for certain reactions
- usually prepared by the combination of a strong Lewis acid and a strong Brønsted acid
  - e.g.  $\text{SO}_3 + \text{HF} \rightarrow \text{FSO}_3\text{H}$  (fluorsulfuric acid)
- trifluoromethanesulfonic acid,  $\text{CF}_3\text{SO}_3\text{H}$ ,  $\text{pK}_a \sim -15$
- Fluoroantimonic acid,  $\text{HSbF}_6$ ,  $\text{pK}_a \sim -25$







## Superacids – György Oláh, Nobel prize in chemistry, 1994

### György Oláh

- used magic acid (which has a  $pK_a \sim -20$ ) to protonate hydrocarbons,
- magic acid: fluorsulfonic acid and antimony pentafluoride ( $\text{HSFO}_3 \cdot \text{SbF}_5$ )
- protonated hydrocarbons, i.e. organic cations are useful in many synthetic reactions
- $\text{CH}_4 + \text{H}^+ \rightarrow \text{CH}_5^+$



[http://upload.wikimedia.org/wikipedia/commons/6/68/Ol%C3%A1h\\_Gy%C3%B6rgy\\_el%C5%91ad%C3%A1sa\\_8299.jpg](http://upload.wikimedia.org/wikipedia/commons/6/68/Ol%C3%A1h_Gy%C3%B6rgy_el%C5%91ad%C3%A1sa_8299.jpg)



## Superbases

- a compound that has a high affinity to protons in non-aqueous solutions
- destroyed by water, carbon dioxide, and oxygen
- used in organic synthesis for deprotonation
  - e.g. lithium diisopropylamide,  $\text{LiN}(\text{C}_3\text{H}_7)_2$ ,  $\text{pK}_b \sim -16$  (in tetrahydrofuran),
  - e.g. proton sponge: 1,8-Bis(dimethylamino)-naphthalene,  $\text{C}_{14}\text{H}_{18}\text{N}_2$ ,  $\text{pK}_b \sim 1.9$ ,
- classes: organic, organometallic, inorganic





## Next – Case studies

1. Hydrogen,
2. Oxygen,
3. Carbon,
4. Nitrogen,
5. Sulphur,
6. Sodium,
7. Silicon,
8. Boron,
9. ...

