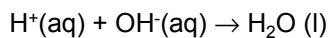


Chemistry 475

Acids and Bases

Acid-Base Models

- Arrhenius-Ostwald
 - Only for water
 - Acid increases $[H^+]$ or decreases $[OH^-]$
 - Base increases $[OH^-]$
 - Base can also decrease $[H^+]$ by *hydrolysis* (e. g. NH_3)
 - Neutralization reaction



Acid-Base Models

- Arrhenius-Ostwald generalized to *Solvent Theory*
 - Acid produces positive ions derived from solvent
 - Base produces negative ions derived from solvent
 - Neutralization combines these ions giving solvent molecules

Acid-Base Models

- Brønsted-Lowry
 - Acid is a proton donor
 - Base is a proton acceptor
 - Neutralization reaction
$$\text{HA} + \text{B} \rightarrow \text{A}^- + \text{HB}^+$$

acid \leftrightarrow conjugate
base

base \leftrightarrow conjugate
acid

Acid-Base Models

- Lewis
 - Acid is electron-pair acceptor
 - Base is electron-pair donor
 - Neutralization leads to formation of a coordinate covalent bond
 - *Solvation* (hydration)
- Basis for Coordination Chemistry
 - Metal is Lewis acid, *ligand* is Lewis base

Acid-Base Models

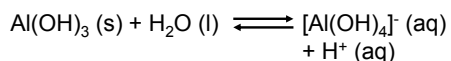
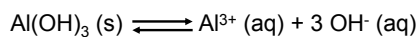
- Lux-Flood
 - Acid accepts oxide ion
 - Base is an oxide ion donor
 - Neutralization is transfer of oxide ion from base to acid
 - Can be generalized to transfer of any negative ion
 - Useful in ceramics and metallurgy

Amphoterism

- Ability of a Chemical Species to behave as both an Acid and a Base

- Definition is independent of model
- Chemistry is not independent of model

- Example



Protonic Solvent Systems

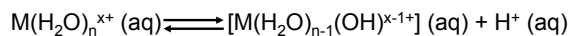
	H ₂ O	ROH	NH ₃	HOAc	H ₂ SO ₄
Lyate ion	OH ⁻	RO ⁻	NH ₂ ⁻	OAc ⁻	HSO ₄ ⁻
Lyonium ion	H ₃ O ⁺	ROH ₂ ⁺	NH ₄ ⁺	H ₂ OAc ⁺	H ₃ SO ₄ ⁺

- Any Amphoteric Liquid can be Solvent System for Acid-Base Reactions
 - Must undergo autoionization (autoprotolysis)
- Define Autoprotolysis Constant, K_s
 - This defines acidity range of solvent

Acid-Base Strength

- Extent of Dissociation ($K_{a/b} \Leftrightarrow \Delta G$)
 - Not constant!
- Substrate Effects (ΔG_f of Reactants)
 - Inductive effects
 - Resonance effects
 - Steric effects
- Solvent Effects (ΔG_f of Products)
 - Solvation of products
 - Leveling effect

Hydrolysis and Metal Ions



- Aquated Metal Ions behave as weak Acids
 - Deprotonation of OH^- also possible
- K_a depends on
 - Charge
 - Size
 - Electronic configuration (transition metals)
- Leads to Multiple Species in Solution

Pearson Classification of Lewis Acids and Bases

- Two Groupings
 - *Hard*: high charge or large charge to size ratio
 - *Soft*: low charge or low charge to size ratio
 - *Borderline*: intermediate hardness/softness
- Pearson Classification is *Qualitative* and *Relative*
 - See section 7.4.3 in the text

Hard/Soft Lewis Acids

Hard	Soft
$H^+, Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Al^{3+}, Sc^{3+}, Ga^{3+}, In^{3+}, Fe^{3+}, Cr^{3+}, La^{3+}, Zr^{4+}, BF_3, AlH_3, AlCl_3, CO_2$	$Cu^+, Ag^+, Au^+, Hg^+, Hg^{2+}, Tl^+, Pd^{2+}, Pt^{2+}, Cd^{2+}, BH_3, Br_2, I_2, \text{metals with formal charges } \leq 0$

Borderline: $Fe^{2+}, Ru^{2+}, Os^{2+}, Rh^{3+}, Ir^{3+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+}, Sn^{2+}, SO_2, NO^+, BMe_3$

See Table 7.5 in text.

Notes:

- Higher charges and smaller ions are hard
- Larger ions are softer (except highly charged)

Hard/Soft Lewis Bases

Hard	Soft
CO_3^{2-} , RCO_2^- , NH_3 , NH_2^- , O^{2-} , H_2O , OH^- , ROH , RO^- , R_2O , F^- , Cl^- , NO_3^- , ClO_4^- , PO_4^{3-} , SO_4^{2-} , N_2H_4 , RCONR^-	CO , CN^- , RNC , C_2H_4 , C_6H_6 , R_3P , R_2S , RSH , RS^- , H^- , R^- , SCN^- , I^-

Borderline: $\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_5\text{H}_5\text{N}$, N_3^- , N_2 , NO_2^- , SO_3^{2-} , Br^-

See Table 7.5 in text.

Notes:

- N, O donors tend to be hard
- C, S, P donors tend to be soft
- Hard/soft not related to acid/base strength

General Rule for Pearson Classification

- Lewis Acids-Base Interaction strongest when "Hardness" similar
 - Hard/hard and soft/soft are more stable than hard/soft (electronegativity and MO)
 - Can form hard/soft combinations
- Examples
 - Which is stronger R-S- Fe^{3+} or R-O- Fe^{3+} ?
 - Will Al^{3+} form a stronger bond with RNH_2 or R-O?
