

# **Models of Acid-Base Chemistry**

Chapter 6

Friday, October 30, 2015

# Models of Acid-Base Chemistry

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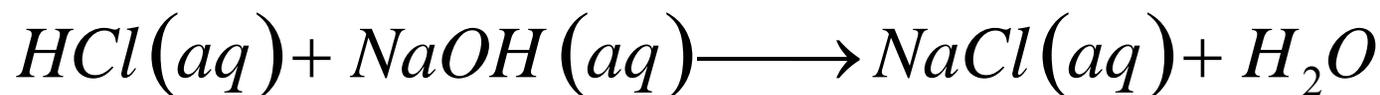
Several models have been developed to classify, rationalize and predict the reactivity of acid-base pairs (or donor-acceptor pairs).

- ***Arrhenius Model*** – acids give hydrogen ions in aqueous solution and bases give hydroxide in aqueous solution
- ***Brønsted-Lowry Model*** – acids are hydrogen ion donors and bases are hydrogen ion acceptors
- ***Lewis Model*** – acids are electron pair acceptors and bases are electron-pair donors
- ***Electrophile-Nucleophile Model*** – acids are electrophilic reagents and bases are nucleophilic reagents
- ***Lux-Flood Model*** – acids are oxide ( $O^{2-}$ ) acceptors and bases are oxide donors
- ***Usanovich Model*** – an acid-base reaction is a reaction leading to formation of a salt

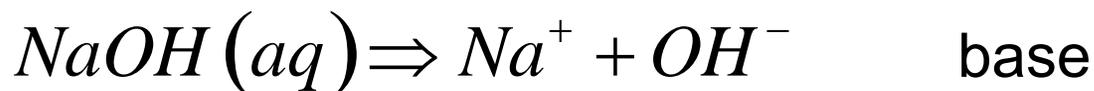
# Arrhenius Acid-Base Model

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Acids form hydrogen ions in aqueous solution and bases form hydroxide in aqueous solution



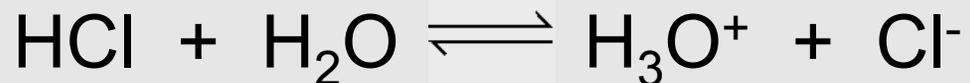
really more  
like  $H_3O^+$



- **Good fundamental definition of acids and bases for aqueous solution**
- **Of limited use in non-aqueous solvents or the gas phase where dissociation doesn't occur**
- **Also fails to capture analogous reactivity of substances that don't dissociate into  $H^+$  or  $OH^-$ , e.g., what do you do about  $NH_3$ ?**

# Brønsted-Lowry Model

Acids release hydrogen ions and bases take up hydrogen ions



acid

base

acid

base

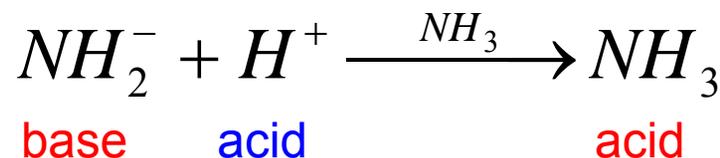
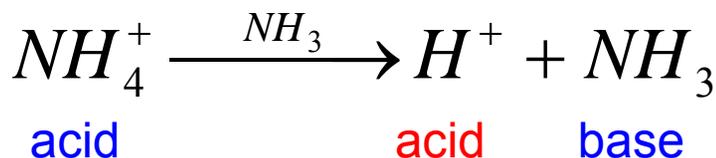
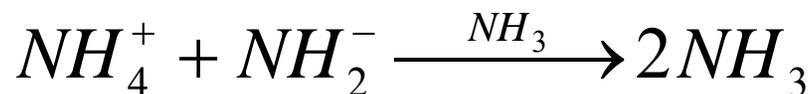
*strong*

*weak*

*weaker*

*very weak*

- **Conjugate acids and bases** – when an acid gives up a hydrogen ion, it forms the conjugate base
- **Acid-base reactions always proceed to form the weaker acid/base pair**
- **The Brønsted-Lowry Model accommodates non-aqueous solvents and gas-phase reactions**

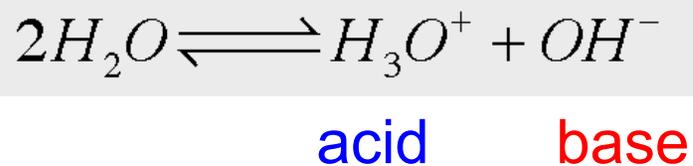


# Solvent System Model

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This model for acid-base reactivity was developed for solvents that can dissociate into cations (acid) and anions (base)

- The classic example is water:



- Now we can say that sulfuric acid is an acid because it increases the concentration of  $H_3O^+$ :

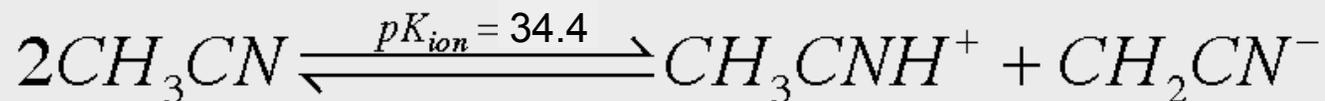
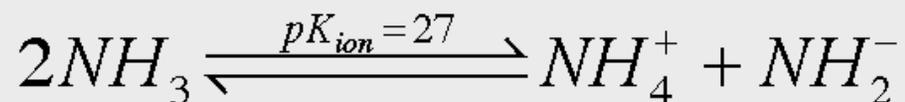
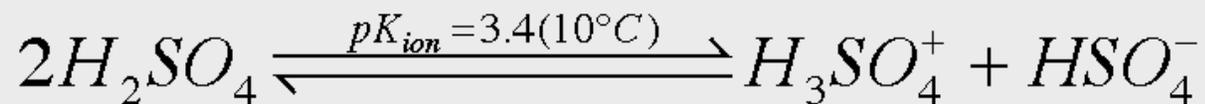
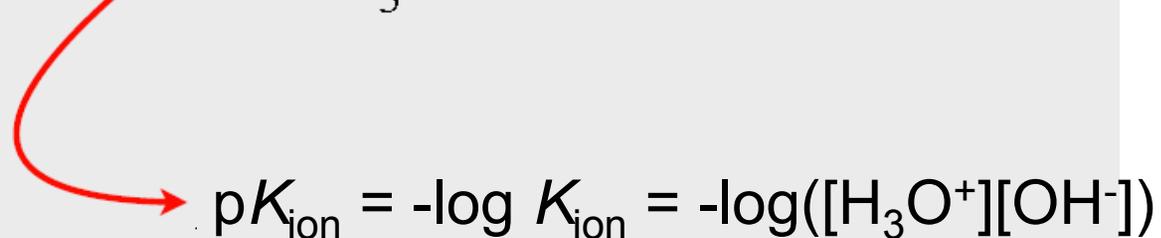
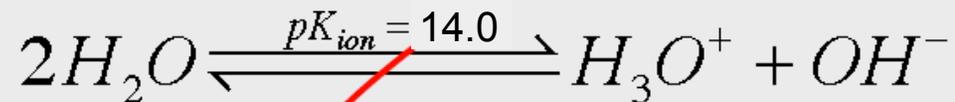


- On the other hand, ammonia is a base because it increases the concentration of  $OH^-$ :



# Solvent System Model

Many solvents dissociate to some degree:

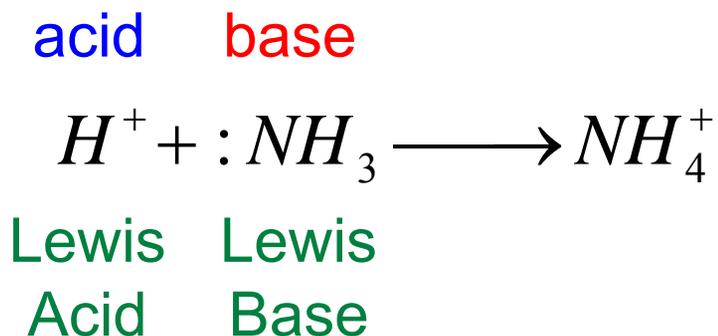


# The Lewis Concept

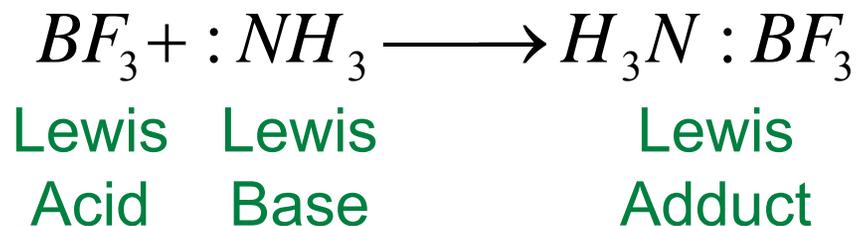
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A base is an electron-pair donor and an acid is an electron-pair acceptor

- This model is consistent with the Arrhenius and Brønsted-Lowry Models:

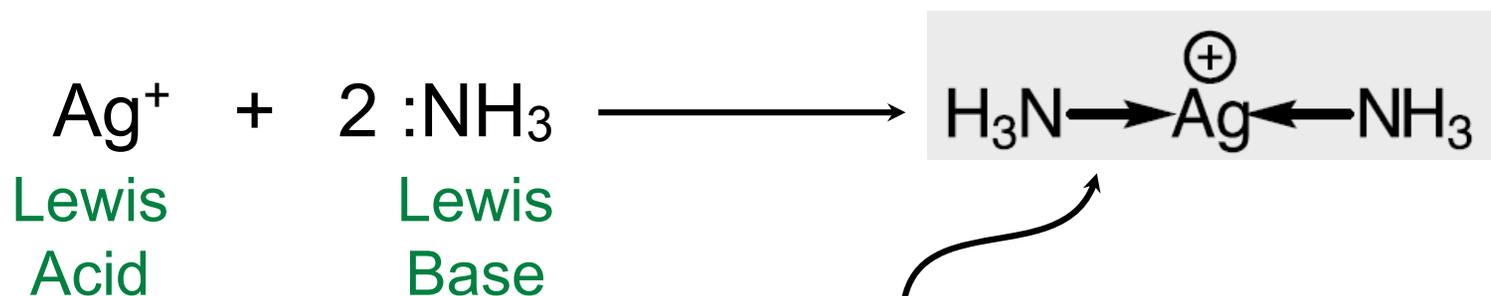


- It also works with molecules that neither give up nor accept a hydrogen ion



# The Lewis Concept

The Lewis concept also allows us to describe coordination complexes within an acid-base framework.

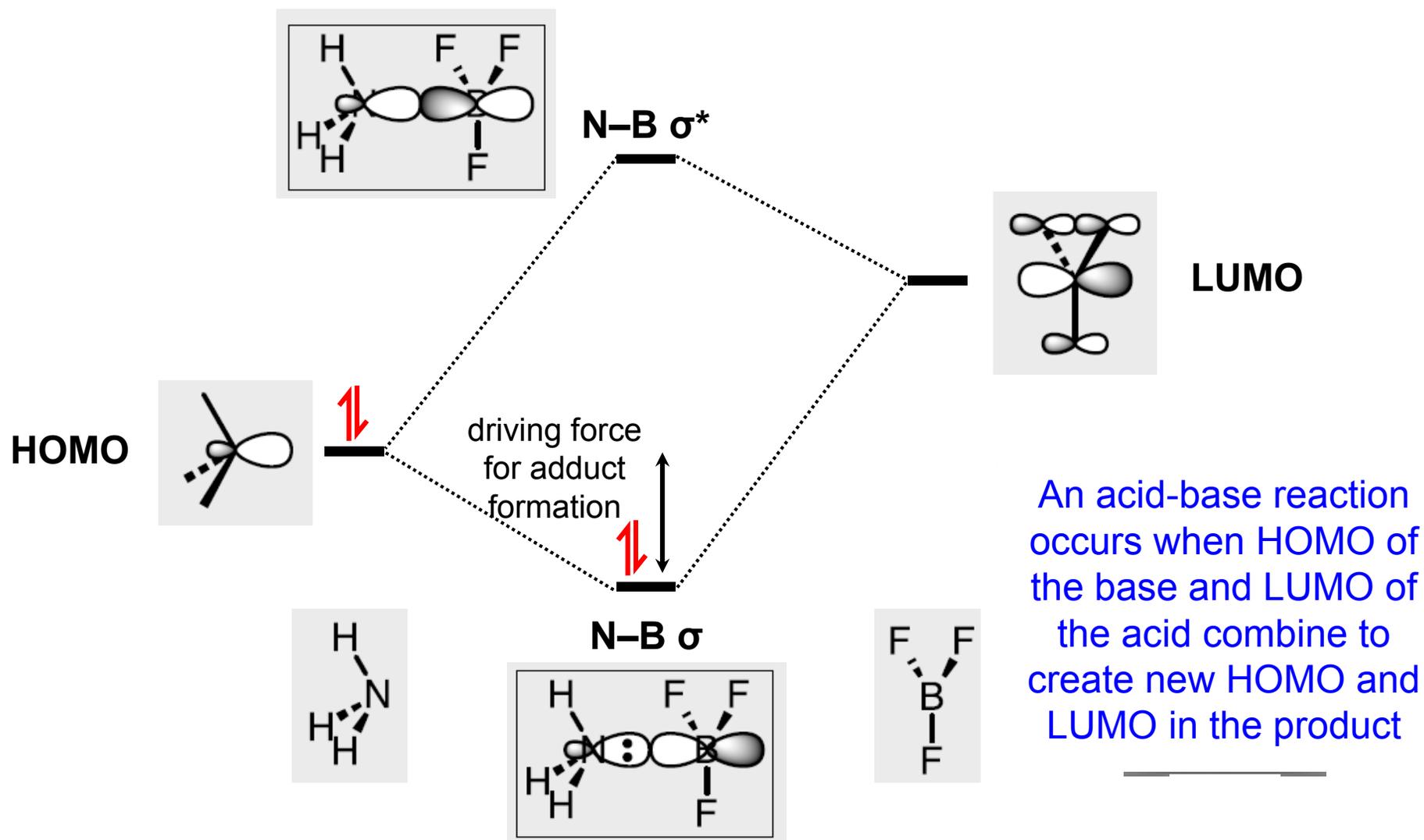
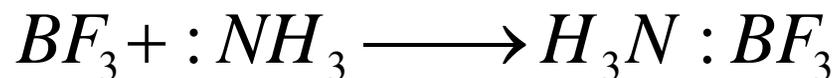


Coordinate covalent or dative bond –  
used to show that both electrons in the  
bond come from a Lewis base

- Lewis Acid-Base adducts in which the Lewis acid is a metal ion are typically called *coordination compounds*

# The Lewis Concept and Molecular Orbitals

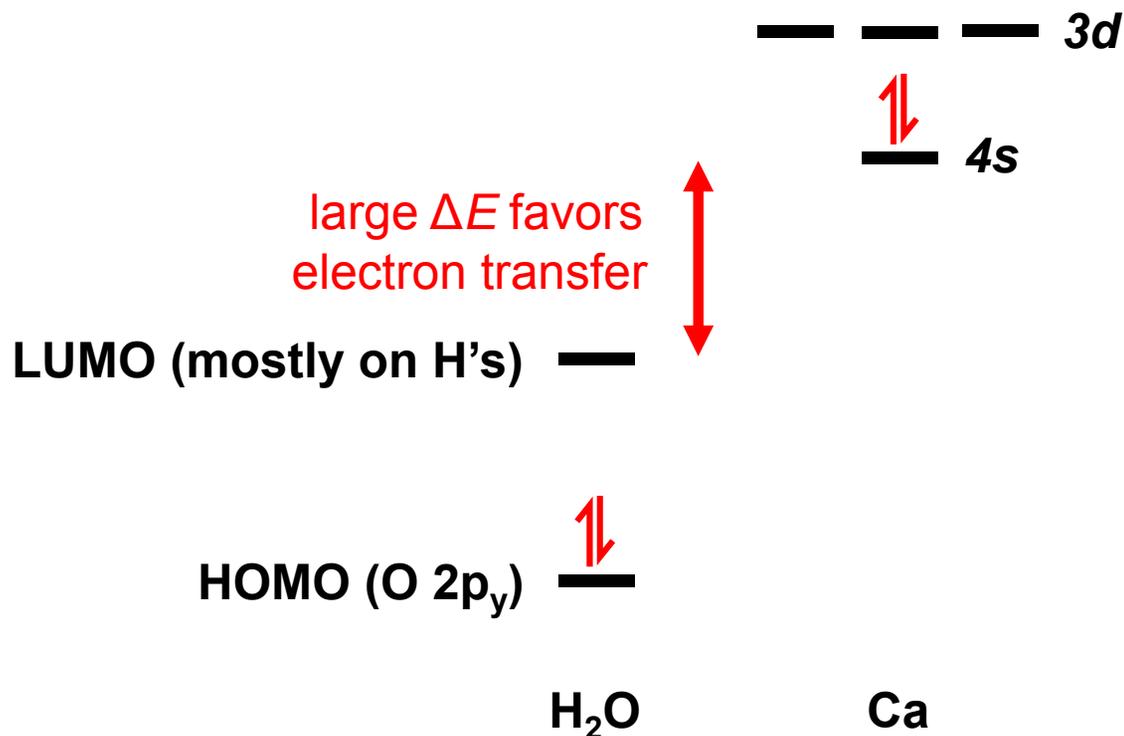
The Lewis concept of acids and bases is readily interpreted using molecular orbital theory.



# The Lewis Concept and Molecular Orbitals

The MO perspective on Lewis acids/bases is versatile and can help us understand many types of reactions. Consider water:

water as oxidizing agent



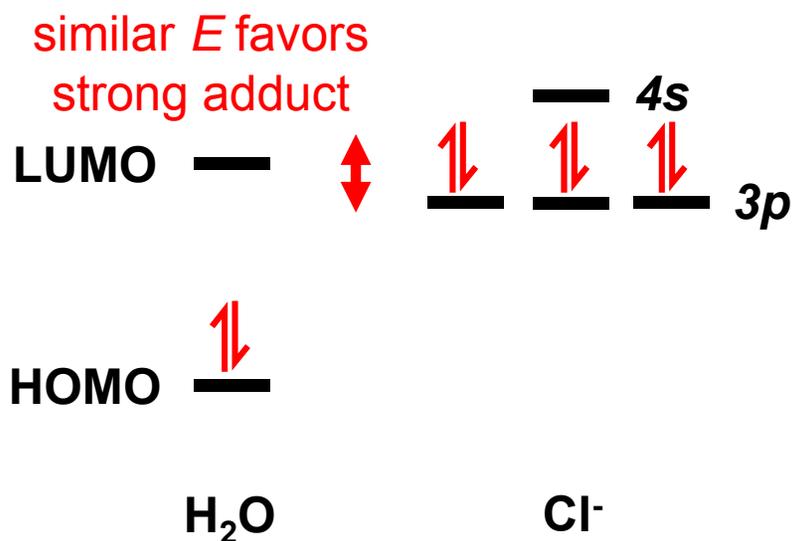
*Here, water acts as an “extreme Lewis acid” to oxidize Ca to Ca<sup>2+</sup> (complete electron transfer)*



# The Lewis Concept and Molecular Orbitals

The MO perspective on Lewis acids/bases is versatile and can help us understand many types of reactions. Consider water:

solvation of an anion



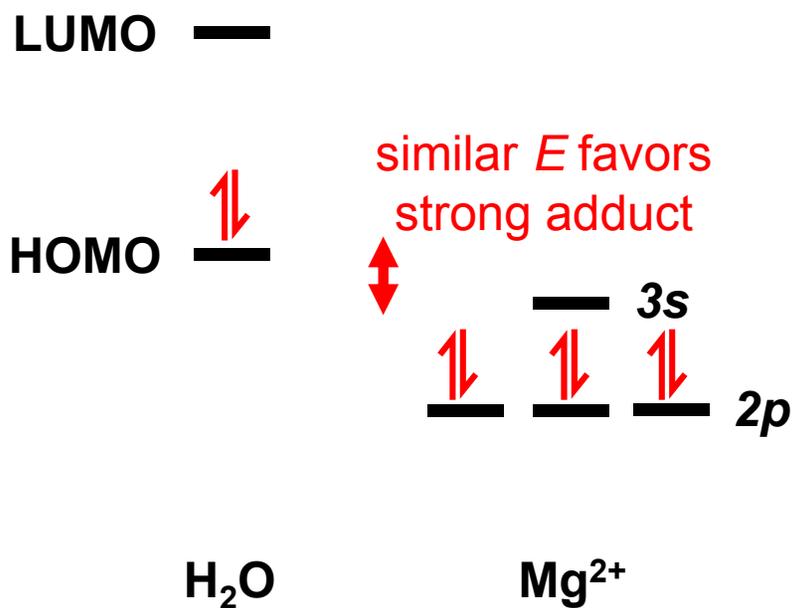
*Here, water acts as a Lewis acid to form an adduct with an anion*



# The Lewis Concept and Molecular Orbitals

The MO perspective on Lewis acids/bases is versatile and can help us understand many types of reactions. Consider water:

## solvation of a cation



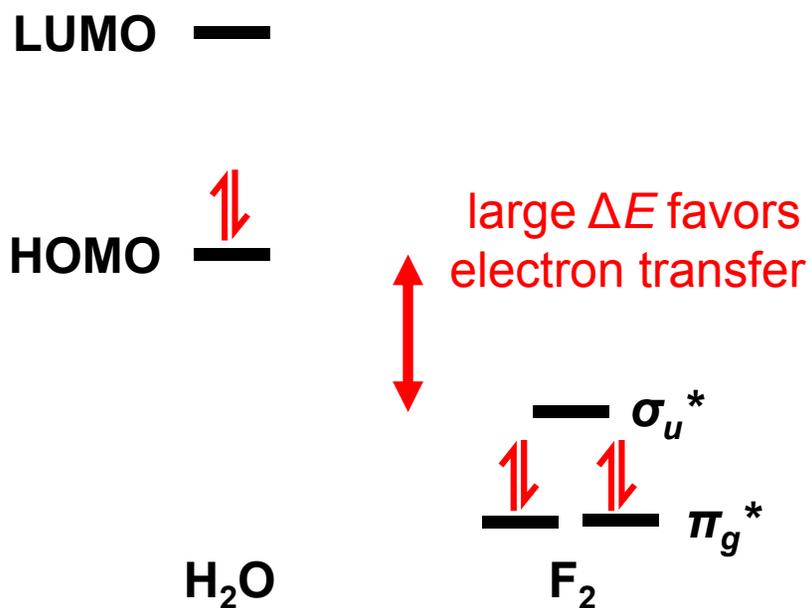
*Here, water acts as a Lewis base to form an adduct with a metal cation*



# The Lewis Concept and Molecular Orbitals

The MO perspective on Lewis acids/bases is versatile and can help us understand many types of reactions. Consider water:

water as reducing agent



*Here, water acts as an “extreme Lewis base” to reduce F<sub>2</sub> to 2 F<sup>-</sup> (complete transfer)*



# HSAB Model

The Hard-Soft Acid-Base concept seeks to understand the reactivity of Lewis acids and bases according to the polarizability of their valence electrons (i.e., their deformability by other molecules/ions).

- hard Lewis acids are small acids with a high positive charge
- soft Lewis acids are larger and typically have a lower positive charge

Hard Acids	Borderline Acids	Soft Acids
H <sup>+</sup> , Li <sup>+</sup> , Na <sup>+</sup> , K <sup>+</sup> Be <sup>2+</sup> , Mg <sup>2+</sup> , Ca <sup>2+</sup> , Sr <sup>2+</sup> BF <sub>3</sub> , BCl <sub>3</sub> , B(OR) <sub>3</sub> Al <sup>3+</sup> , AlCl <sub>3</sub> , AlH <sub>3</sub> Cr <sup>3+</sup> , Mn <sup>2+</sup> , Fe <sup>3+</sup> , Co <sup>3+</sup> M <sup>n+</sup> (n ≥ 4) H-bonding molecules	B(CH <sub>3</sub> ) <sub>3</sub> Fe <sup>2+</sup> , Co <sup>2+</sup> , Ni <sup>2+</sup> Cu <sup>2+</sup> , Zn <sup>2+</sup> Rh <sup>3+</sup> , Ir <sup>3+</sup> , Ru <sup>3+</sup> , Os <sup>2+</sup>	BH <sub>3</sub> , Tl <sup>+</sup> , Tl(CH <sub>3</sub> ) <sub>3</sub> Cu <sup>+</sup> , Ag <sup>+</sup> , Au <sup>+</sup> , Cd <sup>2+</sup> , Hg <sub>2</sub> <sup>2+</sup> , Hg <sup>2+</sup> , CH <sub>3</sub> Hg <sup>+</sup> [Co(CN) <sub>5</sub> ] <sup>2-</sup> , Pd <sup>2+</sup> , Pt <sup>2+</sup> Br <sub>2</sub> , I <sub>2</sub> M <sup>n+</sup> (n = 0) π-acceptor molecules

# HSAB Model

The Hard-Soft Acid-Base concept seeks to understand the reactivity of Lewis acids and bases according to the polarizability of their valence electrons (i.e., their deformability by other molecules/ions).

- hard Lewis bases are small bases with highly electronegative donor atoms
- soft Lewis bases are larger and typically have smaller electronegativities

Hard Bases	Borderline Bases	Soft Bases
F <sup>-</sup> , Cl <sup>-</sup> H <sub>2</sub> O, OH <sup>-</sup> , O <sup>2-</sup> , ROH, RO <sup>-</sup> , R <sub>2</sub> O, RCOO <sup>-</sup> NO <sub>3</sub> <sup>-</sup> , ClO <sub>4</sub> <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup> , SO <sub>4</sub> <sup>2-</sup> , PO <sub>4</sub> <sup>3-</sup> NH <sub>3</sub> , RNH <sub>2</sub> , N <sub>2</sub> H <sub>4</sub>	Br <sup>-</sup> NO <sub>2</sub> <sup>-</sup> , N <sub>3</sub> <sup>-</sup> SO <sub>3</sub> <sup>2-</sup> C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> , C <sub>5</sub> H <sub>5</sub> N, N <sub>2</sub>	H <sup>-</sup> I <sup>-</sup> H <sub>2</sub> S, SH <sup>-</sup> , S <sup>2-</sup> , RSH, RS <sup>-</sup> , R <sub>2</sub> S SCN <sup>-</sup> , CN <sup>-</sup> , RNC, CO S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> PR <sub>3</sub> , P(OR) <sub>3</sub> , AsR <sub>3</sub> , C <sub>2</sub> H <sub>4</sub> , C <sub>6</sub> H <sub>6</sub> , R <sup>-</sup>

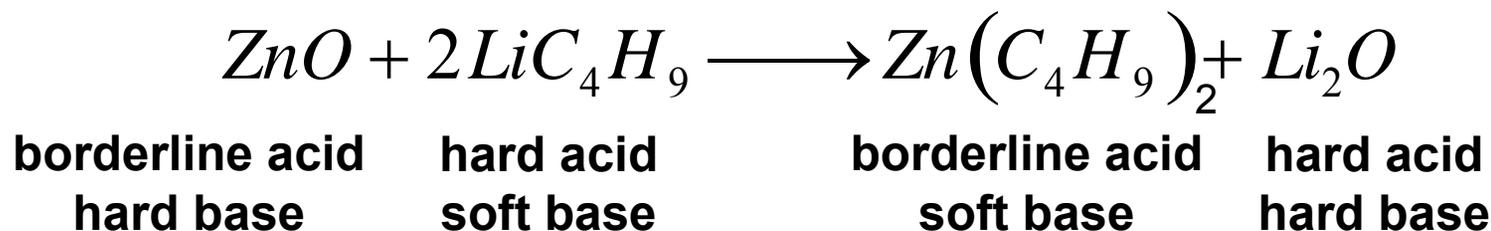
# HSAB Theory

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The Hard-Soft Acid-Base concept seeks to understand the reactivity of Lewis acids and bases according to the polarizability of their valence electrons (i.e., their deformability by other molecules/ions).

- hard Lewis acids are small acids with a high positive charge, soft Lewis acids are larger and typically have a lower positive charge
- hard Lewis bases are small bases with electronegative donor atoms, soft Lewis bases are larger and typically have smaller electronegativities

**Hard acids prefer to interact with hard bases, soft acids prefer to interact with soft bases.**



# HSAB Theory and Exchange Reactions

HSAB theory is consistent with the large differences in  $K_{eq}$  for simple exchange reactions:

**TABLE 6.3** Equilibrium Constants for Reactions of Mercury Complexes<sup>25</sup>

Reaction	$K$
1. $[\text{CH}_3\text{Hg}(\text{H}_2\text{O})]^+ + \text{HF} \rightleftharpoons \text{CH}_3\text{HgF} + \text{H}_3\text{O}^+$	$4.5 \times 10^{-2}$
2. $[\text{CH}_3\text{Hg}(\text{H}_2\text{O})]^+ + \text{HCl} \rightleftharpoons \text{CH}_3\text{HgCl} + \text{H}_3\text{O}^+$	$1.8 \times 10^{12}$
3. $[\text{CH}_3\text{Hg}(\text{H}_2\text{O})]^+ + \text{HBr} \rightleftharpoons \text{CH}_3\text{HgBr} + \text{H}_3\text{O}^+$	$4.2 \times 10^{15}$
4. $[\text{CH}_3\text{Hg}(\text{H}_2\text{O})]^+ + \text{HI} \rightleftharpoons \text{CH}_3\text{HgI} + \text{H}_3\text{O}^+$	$1 \times 10^{18}$

**$\text{Hg}^{2+}$  is a soft acid. As the halide becomes softer, the reaction becomes increasingly favorable.**

# HSAB Theory and Solubilities

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Because the dissolution of salts in water typically requires the replacement of a Lewis base with water, HSAB can predict trends in solubilities. Consider the silver halides:



very  
soluble

insoluble

- $F^-$  and  $Cl^-$  are hard bases; however, so is water. It turns out that water is softer than  $F^-$  but harder than  $Cl^-$
- $Br^-$  and  $I^-$  are soft bases
- Because  $Ag^+$  is a soft acid, it is less prone to give up the halide as we move down the series

# HSAB Theory and Solubilities

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Because the dissolution of salts in water typically requires the replacement of a Lewis base with water, HSAB can predict trends in solubilities. Lithium halides show the opposite trend:



insoluble

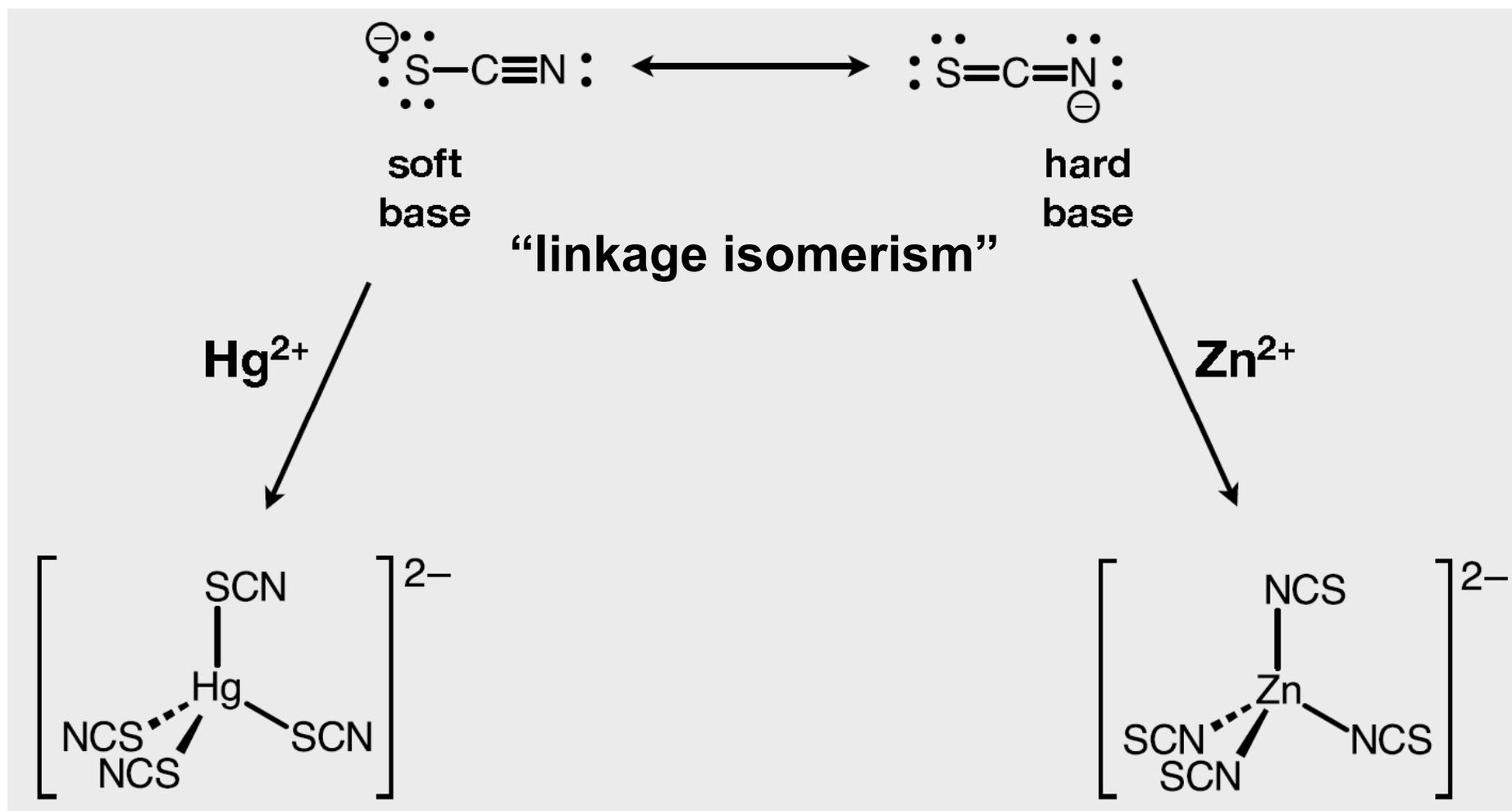
very  
soluble

- $F^-$  and  $Cl^-$  are hard bases; however, so is water. It turns out that water is softer than  $F^-$  but harder than  $Cl^-$
- $Br^-$  and  $I^-$  are soft bases
- In this case,  $Li^+$  is a hard acid and it prefers to interact with the hardest base available

# HSAB Theory and Metal Thiocyanate Complexes

In coordination complexes the metal is the Lewis acid. The Lewis base is normally called a *ligand*.

- Thiocyanate ( $\text{SCN}^-$ ) is an interesting ligand because there are two Lewis base sites:



# Pearson's Absolute Hardness Scale

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The absolute hardness is defined as

$$\eta = \frac{I - A}{2}$$

- $I$  is the ionization energy of the molecule in eV, approximately equal to  $-E_{\text{HOMO}}$
- $A$  is the electron affinity of the molecule in eV, approximately equal to  $-E_{\text{LUMO}}$
- So the absolute hardness is just half the HOMO-LUMO difference (i.e., half the band gap!)
- Hard acids have large values for  $\eta$ , soft acids have smaller values for  $\eta$
- Softness of a donor atom is given by the inverse of hardness, i.e.,

$$\sigma = \frac{1}{\eta}$$

# Pearson's Absolute Hardness Scale

**TABLE 6.16** Hardness Parameters (eV)

Ion	$I$	$A$	$\chi$	$\eta$
$\text{Al}^{3+}$	119.99	28.45	74.22	45.77
$\text{Li}^+$	75.64	5.39	40.52	35.12
$\text{Na}^+$	47.29	5.14	26.21	21.08
$\text{K}^+$	31.63	4.34	17.99	13.64
$\text{Au}^+$	20.5	9.23	14.90	5.6
$\text{BF}_3$	15.81	-3.5	6.2	9.7
$\text{H}_2\text{O}$	12.6	-6.4	3.1	9.5
$\text{NH}_3$	10.7	-5.6	2.6	8.2
$\text{PF}_3$	12.3	-1.0	5.7	6.7
$\text{PH}_3$	10.0	-1.9	4.1	6.0
$\text{F}^-$	17.42	3.40	10.41	7.01
$\text{Cl}^-$	13.01	3.62	8.31	4.70
$\text{Br}^-$	11.84	3.36	7.60	4.24
$\text{I}^-$	10.45	3.06	6.76	3.70

NOTE: The anion values are approximated as the same as the parameters for the corresponding neutral radicals or atoms.  
Data from R. G. Pearson, *Inorg. Chem.*, **1988**, 27, 734.

# The Nature of the Adduct

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**Hard acid/hard base adducts tend to have more ionic character in their bonding. These are generally more favored energetically.**

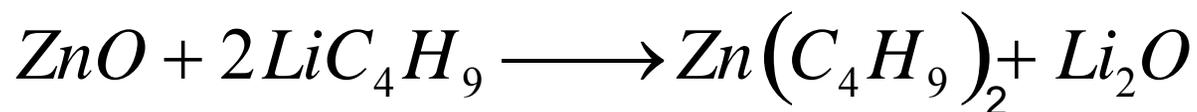
**Soft acid/soft base adducts are more covalent in nature.**

# Acid/Base Strength

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It is important to realize that hard/soft considerations have nothing to do with acid or base strength. An acid or a base may be hard or soft and also be either weak or strong.

In a competition reaction between two bases for the same acid, one must consider both the relative strength of the bases, and the hard/soft nature of each base and the acid.



borderline acid  
hard base

hard acid  
soft base

borderline acid  
soft base

hard acid  
hard base

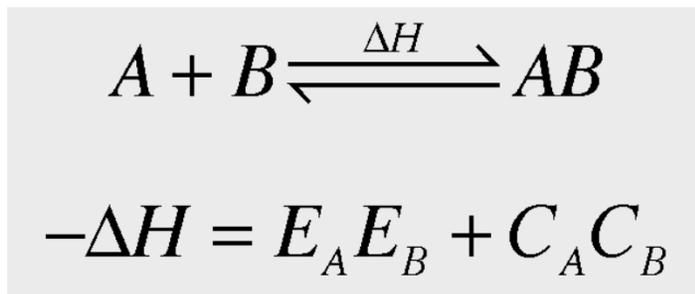
Zinc ion is a strong Lewis acid, and oxide ion is a strong Lewis base, suggesting the reaction is unfavorable as written.

However, the reaction proceeds to the right ( $K > 1$ ), because hard/soft considerations override acid-base strength considerations.

# Drago's EC Approach

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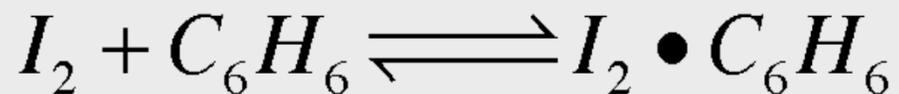
A quantitative system for calculating the thermodynamics of acid-base reactions takes account of both covalent and ionic components of the acid-base interaction. For the reaction,



- $E_A$  and  $E_B$  are the capacity for electrostatic (ionic) interactions of the acid and base
- $C_A$  and  $C_B$  are the capacity for covalent interactions of the acid and base
- $I_2$  is the reference acid with  $C_A = E_A = 1.00$  kcal/mol
- Reference bases are  $MeC(O)NMe_2$  ( $E_B = 1.32$ ) and  $SEt_2$  ( $C_B = 7.40$ )

# Using the EC Model

The enthalpy of a given Lewis acid-base reaction can be determined using tabulated values (see Table 6.17 in your textbook).



Lewis  
acid

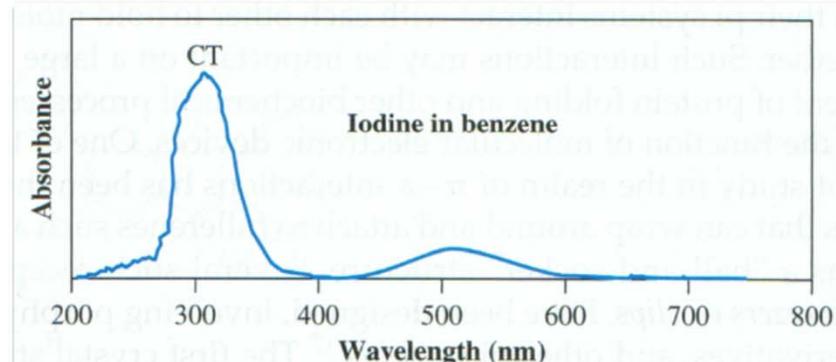
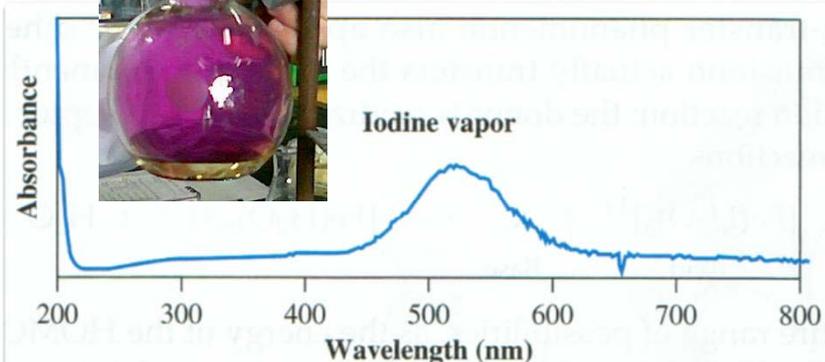
Lewis  
base

Lewis  
adduct

$$-\Delta H = E_A E_B + C_A C_B$$

$$-\Delta H = \left(1.00 \frac{\text{kcal}}{\text{mol}}\right) \left(0.525 \frac{\text{kcal}}{\text{mol}}\right) + \left(1.00 \frac{\text{kcal}}{\text{mol}}\right) \left(0.681 \frac{\text{kcal}}{\text{mol}}\right)$$

$$\Delta H = -1.21 \frac{\text{kcal}}{\text{mol}} \quad \text{within 9\% of experimental value}$$



# Summary

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- There are several models to describe acids and bases. The Lewis model is one of the most general since it does not depend on the transfer of a hydrogen ion.
- A dative bond (coordinate covalent bond) is often used to denote a bond between a neutral Lewis base and a Lewis acid:



- The Lewis model is readily interpreted using MO theory: the HOMO of the Lewis base interacts with the LUMO of the Lewis acid.
- HSAB provides a semi-quantitative method for understanding trends in acid-base reactivity: hard acids like hard bases and soft acids like soft bases.
- The Drago EC model provides a more quantitative method for understanding the thermodynamics of an acid-base reaction.