## **Chem 241**

#### Lecture 7

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#### Recap

- Finished Off MO Theory
- Bronsted Acids and Bases



#### Lewis Acids and Bases

Lewis acids are electron pair acceptors (electron deficient; BH<sub>3</sub>)

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• Lewis bases are electron pair donors.

# $[Ag-C_6H_6]^+$ $H_3B-NMe_3$







 $SiF_{6}^{2}$  [SiF<sub>4</sub> + 2 :F<sup>-</sup>]

#### Group 13

- B(CH<sub>3</sub>)<sub>3</sub> + :NH<sub>3</sub> → CH<sub>3</sub>B:NH<sub>3</sub> Trend for acidity of BX<sub>3</sub> is: X = F < CI < Br<I BF<sub>3</sub> has better B-F π-bonding
- AICl<sub>3</sub> is a dimer.

AICl<sub>3</sub> is used as a Lewis acid catalyst (e.g., Freidel-Crafts alkylation)





#### Group 14

- Elements that can expand their octet are good Lewis acids. (e.g., group 14)
  - $SiF_4 + 2F^- \rightarrow SiF_6^{2-}$
  - Sn(II) is both a Lewis acid and a Lewis base
    SnCl<sub>2</sub> + Cl<sup>-</sup> → SnCl<sub>3</sub><sup>-</sup>



Structure 4-21 Shriver & Atkins Inorganic Chemistry, Fourth Edition © 2006 by D.F. Shriver, P. W. Atkins, T.L. Overton, J. P. Rourke, M. T. Weller, and F. A. Armstrong



Sn(IV) is a good Lewis acid

Acidity of SnXor SiX<sub>4</sub>: F > CI > Br > I

 $SnCl_4 + 2 Cl^- \rightarrow SnCl_6^{2-}$ 

#### Group 15 & 16

- Group 15 Lewis acids include "super acids" which use the Lewis acidity of SbF<sub>5</sub> to form SbF<sub>6</sub><sup>-</sup> and a "solvated proton" that is acidic enough to protonate hydrocarbons.
- SbF<sub>5</sub> + 2HF → SbF<sub>6</sub><sup>-</sup> + H<sub>2</sub>F<sup>+</sup> SbF<sub>5</sub> + 2HSO<sub>3</sub>F → SbF<sub>5</sub>SO<sub>3</sub>F<sup>-</sup> + H<sub>2</sub>SO<sub>3</sub>F<sup>+</sup>

Sulfur oxides can be Lewis acids or bases:  $SO_2 + NR_3 \rightarrow O_2S-NR_3$ Can coordinate to metals via S or O



#### Lewis Acids and Bases

- $A + : B \rightarrow A B$
- A Lewis acid has a low-lying LUMO;
- A Lewis base has a high-lying HOMO





#### HSABT

Hard acids tend to bind best to hard bases and vice versa.

| Table 4.3 The classification of Lewis acids and bases*  |   |   |  |
|---|---|---|--|
| Hard  | Borderline  | Soft  |  |
| Acids H <sup>+</sup> , Li <sup>+</sup> , Na <sup>+</sup> , K <sup>+</sup><br>Be <sup>2+</sup> , Mg <sup>2+</sup> , Ca <sup>2+</sup><br>Cr <sup>2+</sup> , Cr <sup>3+</sup> , Al <sup>3+</sup><br>SO <sub>3</sub> , BF <sub>3</sub>                            | Fe <sup>2+</sup> , Co <sup>2+</sup> , Ni <sup>2+</sup><br>Cu <sup>2+</sup> , Zn <sup>2+</sup> , Pb <sup>2+</sup><br>SO <sub>2</sub> , BBr <sub>3</sub>                              | Cu <sup>+</sup> , Au <sup>+</sup> , Ag <sup>+</sup> , Tl <sup>+</sup> , Hg <sup>+</sup><br>Pd <sup>2+</sup> , Cd <sup>2+</sup> , Pt <sup>2+</sup> , Hg <sup>2+</sup><br>BH <sub>3</sub> |  |
| Bases F <sup>-</sup> , OH <sup>-</sup> , H <sub>2</sub> O, NH <sub>3</sub><br>CO <sub>3</sub> <sup>2-</sup> , NO <sub>3</sub> <sup>-</sup> , O <sup>2-</sup><br>SO <sub>4</sub> <sup>2-</sup> , PO <sub>4</sub> <sup>3-</sup> , ClO <sub>4</sub> <sup>-</sup> | NO <sub>2</sub> <sup>-</sup> , SO <sub>3</sub> <sup>2-</sup> , Br <sup>-</sup><br>N <sub>3</sub> <sup>-</sup> , N <sub>2</sub><br>C <sub>6</sub> H <sub>5</sub> N, SCN <sup>-</sup> | H <sup>-</sup> , R <sup>-</sup> , <u>C</u> N <sup>-</sup> , CO, I <sup>-</sup><br>SCN <sup>-</sup> , R <sub>3</sub> P, C <sub>6</sub> H <sub>5</sub><br>R <sub>2</sub> S                |  |

\* The underlined element is the site of attachment to which the classification refers.

Hard-hard interactions max. ionic character; soft-soft max. covalency.

#### HSABT

E and C parameters predict bond enthalpies

• 
$$-\Delta H^0(A-B) = E_A E_B + C_A C_B$$

 Strong bonds can be highly ionic, highly covalent, or have contributions from both.

| Table 4.4 Drago-Waylandparameters for some acids and bases* |      |       |  |
|---|------|-------|--|
|   | Ε    | С     |  |
| Acids   |      |       |  |
| Antimony pentachloride                                      | 15.1 | 10.5  |  |
| Boron trifluoride   | 20.2 | 3.31  |  |
| lodine  | 2.05 | 2.05  |  |
| lodine monochloride   | 10.4 | 1.70  |  |
| Phenol  | 8.86 | 0.90  |  |
| Sulfur dioxide  | 1.88 | 1.65  |  |
| Trichloromethane  | 6.18 | 0.32  |  |
| Trimethylboron  | 12.6 | 3.48  |  |
| Bases   |      |       |  |
| Acetone   | 2.02 | 4.67  |  |
| Ammonia   | 2.78 | 7.08  |  |
| Benzene   | 0.57 | 1.21  |  |
| Dimethylsulfide   | 0.70 | 15.26 |  |
| Dimethylsulfoxide   | 2.76 | 5.83  |  |
| Methylamine   | 2.66 | 12.00 |  |
| <i>p</i> -Dioxane   | 2.23 | 4.87  |  |
| Pyridine  | 2.39 | 13.10 |  |
| Trimethylphosphine  | 17.2 | 13.40 |  |

\* *E* and *C* parameters are often reported to give  $\Delta H$  in kcal mol<sup>-1</sup>; we have multiplied both by  $\sqrt{(4.184)}$  to obtain  $\Delta H$  in kJ mol<sup>-1</sup>.



#### Homework

- Chapter 4 Exercises: 4, 11, 20, 22
- Start reading Chapter 7



#### Symmetry

- Learning to recognize symmetry properties of molecules is a great help in qualitative MOT, assigning spectral properties, predicting reactions, etc.
- The line, plane, or point is the **symmetry element**
- The movement is a **symmetry operation**
- Classification of the symmetry properties of a molecule leads to the assignment to one of 32 crystallographic **point groups**, denoted by Schoenflies Symbols.
- In crystallography, crystals are assigned to one of 230 space groups based on the point group + the relationship of the molecules in space.



### E, identity

- Every Molecule has a E
- Simply do nothing
- Snap shot technique



#### C<sub>n</sub>, proper rotation

• n-fold rotation (proper rotation,  $C_n$ ) is a proper rotation if the molecule appears unchanged after rotation by 360<sup>0</sup> /n

a.  $H_2O$  has a 2-fold rotation axis. (n = 2;  $C_2$  axis) one rotation,  $C_2^{-1}$ , 360/2 degrees.  $C_2^{-2} = E$ .

b. Consider  $BCI_3$  has one 3-fold and 3 perpendicular 2-fold rotation axes ( $C_3$  and  $C_2$ ). The higher order axis becomes the principle rotation axis.  $C_3^1$  = rotation by 120 degrees,  $C_3^2$  = rot. By 240 degrees.  $C_3^3$  = E.

c. Consider  $PtCl_4$ . Principal rotation axis =  $C_4$ ; 4 perpendicular  $C_2$  axes, in two classes, one set along bonds (C2') and one between bonds (C2'').

Highest order rotational axis is principle axis  $C_1 = E$ 



#### $\sigma$ , mirror planes

Reflection (mirror planes, σ)

a. H<sub>2</sub>O has two mirror planes. Both contain the principle rotation axis, and are therefore vertical planes ( $\sigma_v$ ), one contains the bonds ( $\sigma_v$ ') and one does not ( $\sigma_v$ ).

b.  $BCI_3$  has three  $\sigma_v$  and one plane that is perpendicular to the principal rot. axis ( $\sigma_h)$ 

c.  $PtCl_4$  has a  $\sigma_h$  and four  $\sigma_v$  of two classes; containing bonds ( $\sigma_v$ ) and between bonds ( $\sigma_d$ ).



#### i, Inversion

- Inversion (inversion center)
  - a.  $SF_6$



Figure 7-5 Shriver & Atkins Inorganic Chemistry, Fourth Edition © 2006 by D. F. Shriver, P. W. Atkins, T. L. Overton, J. P. Rourke, M. T. Weller, and F. A. Armstrong



#### S<sub>n</sub>, Improper rotation

- Rotation followed by a reflection in the perpendicular plane. (C<sub>n</sub> then  $\sigma_{\rm h})$
- S<sub>2</sub> = i, S<sub>1</sub> = σ



#### Flow chart



#### Figure 7-9

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#### Practice

 $NH_3$   $CO_2$   $[Co(en)_3]^{3+}$  (ignore hydrogens) Cyclohexane (conformation) chair  $[Fe(H_2O)_6]^{3+}$ 



#### Symmetry

- B. Molecules may possess several symmetry elements, the sum of which define their point group.
  - 1. There is a difference between octahedral symmetry and octahedral geometry. Be careful.

