

Chapter 6 HW: #1, 4, 9, 21, 27, 30, 33, 34, 36-39

1)	<u>ACID</u>	<u>BASE</u>
a.	AlBr ₃	Br ⁻
b.	HClO ₄	CH ₃ CN
c.	Ni ²⁺	NH ₃
d.	ClF	NH ₃
e.	SO ₂	ClO ₃ ⁻
f.	HF	C ₃ H ₇ COOH

4) $2 \text{BrF}_3 \leftrightarrow \text{BrF}_2^+ + \text{BrF}_4^-$ Autoionization equilibrium for BrF₃



Addition of either AgF or SnF₄ results in increasing ion concentrations and increasing conductivity. (In the former case, BrF₃ acts as an acid; in the latter, it acts as a base. This is possible because BrF₃ is an ionizing solvent.)

9) On the basis of inductive effects, one would expect triphenylamine, N(Ph)₃, to be the stronger base. Both N(Ph)₃ and P(Ph)₃ have electron-donating phenyl groups (where Ph = C₆H₅), but the greater electronegativity of nitrogen means that it has more electron density to donate than phosphorus does. The experimental observation that triphenylphosphine is more basic in the gas phase must therefore result from steric considerations. As we learned in Ch. 3, bond angles are smaller in PPh₃ than in NPh₃ due to the larger size and lower electronegativity of the central atom. The smaller bond angles (and longer P-Ph bonds) must promote better interaction with reacting acids.

21) NO⁻ has a double bond with two lone pairs on each atom, putting the -1 formal charge on N. With more electron density on this atom, it is predicted that H⁺ will bind to N, forming HNO.

Recall that this can also be justified based on MO Theory, as you did for similar interactions in Chapter 5 (Problems 5.8 and 5.10) and as is requested here in Problem 6.43 (not assigned).

27)

a. pyridine + BF_3

$$\Delta H = -[E_p E_B + C_p C_B] = -[(1.17)(9.88) + (6.40)(1.62)] = -21.9 \text{ kcal/mol} * (4.184 \text{ J/cal}) = \mathbf{-91.6 \text{ kJ/mol}}$$

(approx. 10% low compared to -105 kJ/mol)

pyridine + $\text{B}(\text{CH}_3)_3$

$$\Delta H = -[(1.17)(6.14) + (6.40)(1.70)] = -18.1 \text{ kcal/mol} * (4.184 \text{ J/cal}) = \mathbf{-75.7 \text{ kJ/mol}}$$

(approx. 5-18% high)

b. F is electron-withdrawing; CH_3 is electron-donating. B can more easily accept electrons from pyridine when F atoms are present, so adduct formation is more favorable between BF_3 and pyridine.

c. (As it turns out), the harder acid, BF_3 , interacts more strongly with the borderline base pyridine. [Because pyridine is a borderline base, HSAB Theory is not clearly predictive here.]

30) Solubility in water is related to how favorably the ions interact with H_2O molecules as compared to how strongly they are attracted to each other. The interactions between Cs^+ and I^- are more favorable than those between Cs^+ and F^- , because F^- is much harder than I^- . As a result, CsF is more easily dissolved in water. For the lithium compounds, interaction between (hard) Li^+ and (hard) F^- is much more favorable than that between Li^+ and (soft) I^- , so LiI is more soluble.

33) Al^{3+} is a hard acid; the tungsten ion (formally, W^+) is softer. As such, the harder "end" of CO will bind to Al and the softer "end" will bind to W: **Al-OC-W**

34)

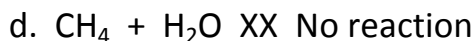
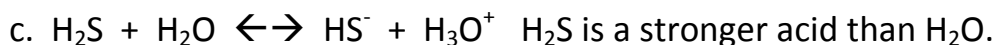
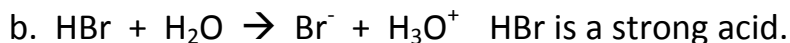
a. **TeH_2** – Te is the most electronegative, making the H atoms most electropositive.

b. **NH_3** – N is the most electronegative and the most successful in competing to accept H^+

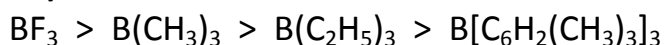
c. **$(\text{CH}_3)_3\text{N}$** – With (small) H^+ in the gas phase, sterics are not an issue. The three electron-donating methyl groups increase electron density on N, increasing basicity.

d. 4-Mepy > py > 2-Mepy (Draw these.) – The methyl group is e-donating, increasing electron density on N. For 2-Mepy, however, with the methyl group on the carbon adjacent to the N, steric hindrance makes it harder for N to donate electrons to BMe_3 .

36)



37)



F is electron-withdrawing, reducing e⁻ density on B and making it easier for B to accept e⁻ from the base NH₃. Alkyl groups are electron-donating and therefore decrease the acidity of the borane. Of these alkyl groups, C₆H₂(CH₃)₃ is the most bulky, making that borane the poorest acid: steric hindrance will hamper the formation of tetrahedral geometry around B in the product.

38)

a. **CH₃NH₂** – stronger base due to electron donation from methyl group

b. 2-Mepy is a stronger base due to e⁻-donation, but is also more sterically hindered. Adduct formation is therefore more favorable for **pyridine**.

c. **Trimethylboron** forms a stronger adduct with NH₃ because the phenyl rings of B(C₆H₅)₃ do not readily bend back into tetrahedral geometry (steric hindrance)

39)

