
### General References


### Problems

Additional acid–base problems are at the end of Chapter 8.

**6.1** For each of the following reactions, identify the acid and the base. Also indicate which acid–base definition (Lewis, Brønsted–Lowry) applies. In some cases, more than one definition may apply.

a. AlBr₃ + Br⁻ → AlBr₅⁻

b. HClO₄ + CH₂CN → CH₃CNH⁺ + ClO₄⁻

c. Ni²⁺ + 6 NH₃ → [Ni(NH₃)₆]²⁺

d. NH₃ + ClF → H₃N···ClF

e. 2 ClO₃⁻ + SO₂ → 2 ClO₂ + SO₄²⁻

f. C₃H₇-COOH + 2 HF → [C₃H₇-C(OH)₂]⁺ + HF₂⁻

**6.2** For each of the following reactions, identify the acid and the base. Also indicate which acid–base definition (Lewis, Brønsted–Lowry) applies. In some cases, more than one definition may apply.

a. XeO₃ + OH⁻ → [HXeO₄]⁻

b. Pt + XeF₄ → PtF₄ + Xe

c. C₂H₇OH + H₂SeO₄ → C₂H₇OH₂⁺ + HSeO₄⁻
d. \([\text{CH}_3\text{Hg(H}_2\text{O})]^+ + \text{SH}^- \rightleftharpoons [\text{CH}_3\text{HgS}]^- + \text{H}_2\text{O}^+
\)
e. \((\text{benzyl})_2\text{N} + \text{CH}_3\text{COOH} \rightarrow (\text{benzyl})_2\text{NH}^+ + \text{CH}_3\text{COO}^-
\)
f. \(\text{SO}_2 + \text{HCl} \rightarrow \text{OSO}^\cdot \cdot \cdot \text{HCl}
\)

6.3 Baking powder is a mixture of aluminum sulfate and sodium hydrogencarbonate, which generates a gas and makes bubbles in biscuit dough. Explain what the reactions are.

6.4 The conductivity of BrF$_3$ is increased by adding KF. Explain this increase, using appropriate chemical equations.

6.5 The following reaction can be conducted as a titration in liquid BrF$_5$:

\[2\text{Cs}^- + [\text{SbF}_3]^{-} \rightarrow 3\text{BrF}_3 + 2\text{CsSbF}_6\]

a. The ions in brackets contain both bromine and fluorine. Fill in the most likely formulas of these ions.

b. What are the point groups of the cation and anion identified in part a?

c. Is the cation in part a serving as an acid or base?

6.6 Anhydrous H$_2$SO$_4$ and anhydrous H$_3$PO$_4$ both have high electrical conductivities. Explain.

6.7 The gas-phase basicities for the nitrogen bases listed in Table 6.6 are uniformly less positive than the corresponding proton affinities. Explain.

6.8 The proton affinities of acetonite, diethylketone, and benzophenone are 812.0, 836.0, and 882.3 kJ/mol, respectively. Rationalize the ranking of these values. (Data from C. Laurence and J.-F. Gal, *Lewis Basicity and Affinity Scales Data and Measurement*, John Wiley and Sons, United Kingdom, 2010, p. 5.)

6.9 The gas-phase basicity of triphenylamine (876.4 kJ/mol) is less than that of triphenylphosphine (940.4 kJ/mol). Do you expect electronic or steric factors to contribute more to this difference? Explain. (Data from C. Laurence and J.-F. Gal, *Lewis Basicity and Affinity Scales Data and Measurement*, John Wiley and Sons, United Kingdom, 2010, p. 5.)

6.10 Correlation of gas-phase and aqueous-solution basicity data is instructive. Construct a graph of gas-phase basicity vs. \(pK_a\) of conjugate acids in water (like Figures 6.2 and 6.3) for the following Brønsted–Lowry bases using these data from C. Laurence and J.-F. Gal, *Lewis Basicity and Affinity Scales Data and Measurement*, John Wiley and Sons, United Kingdom, 2010, p. 5. Label each point clearly with the identity of the base.

<table>
<thead>
<tr>
<th>Lewis base</th>
<th>Formula</th>
<th>BF$_3$ Affinity (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diphenylsulfoxide</td>
<td>Ph$_2$SO</td>
<td>90.34</td>
</tr>
<tr>
<td>Methyl phenyl sulfoxide</td>
<td>PhSOMe</td>
<td>97.37</td>
</tr>
<tr>
<td>Dimethyl sulfoxide</td>
<td>Me$_2$SO</td>
<td>105.34</td>
</tr>
<tr>
<td>Di-n-butyl sulfoxide</td>
<td>(n-Bu)$_2$SO</td>
<td>107.60</td>
</tr>
<tr>
<td>Tetramethylene sulfoxide</td>
<td>cyclo-(CH$_2$)$_4$SO</td>
<td>108.10</td>
</tr>
</tbody>
</table>


a. Qualitatively, how well do the gas phase and solution data correlate for the two ethers and the two alcohols? Are these trends the result of inductive or steric effects? Explain.

d. Rationalize the seemingly paradoxical location of water in your graph relative to the other bases.


a. What are the ideal characteristics of a reference acid discussed by these authors?

b. Compare the relative Lewis basicities of quinuclidine and pyridine found by these authors to the BF$_3$ affinity for pyridine (Table 6.10) and the value for quinuclidine (150.01 kJ/mol). To what feature do these authors attribute the high basicities of these two nitrogen bases to their zinc(II) reference?

c. What general trends do these authors report for alicyclic (that is, aliphatic and cyclic) and acyclic amines? How are these trends rationalized?

6.13 If an equimolar mixture of P(t-C$_4$H$_9$)$_3$ and B(t-C$_4$F$_3$)$_3$ is mixed with 1 bar of the gas N$_2$O in bromobenzene solution, a white product is formed in good yield. A variety of NMR evidence has been gathered on the product: there is a single $^{31}$P NMR resonance; $^{11}$B and $^{19}$F NMR are consistent with a 4-coordinate boron atom; and $^{15}$N NMR indicates two nonequivalent nitrogen atoms. In addition, no gas is released in the reaction.

a. Suggest the role of N$_2$O in this reaction.


6.15 The ability of frustrated Lewis pairs to capture NO (nitric oxide) to afford aminoxyl radicals is a recent triumph of FLP chemistry (M. Sajid, A. Stute, A. J. P. Cardenas, B. J. Culotta, J. A. M. Hepperle, T. H. Warren, B. Schirmer, S. Grimm, A. Studer, C. G. Daniliuc, R. Fröhlich, J. L. Peterson, G. Kehr, G. Erker, J. Am. Chem. Soc., 2012, 134, 10156.) Use a molecular orbital argument to hypothesize why the N—O bond lengthens in complex 2b relative to nitric oxide (HINT: Which orbital is likely the acceptor?).

6.16 Use the pK_a, Slide Rule in P. Gilli, L. Pretto, V. Bertolasi, G. Gilli, Acc. Chem. Res., 2009, 42, 33 to answer these questions:

a. Which forms a stronger hydrogen bond with water, HCN or HSCN?

b. Identify two inorganic acids that are predicted to form strong hydrogen bonds with organic nitriles.

c. Which organic acid in the Slide Rule is predicted to form the strongest hydrogen bond to organic sulfides?

d. Water is a prototypical hydrogen bond donor. Classify the strengths of A···H_2O hydrogen bonds (for example, as strong, medium strong, medium, medium weak, or weak) with the following classes of acceptors: amines, triphosphines, sulfoxides, ketones, and nitro compounds.

6.17 The X-ray structure of Br_3As···C_6Et_6·AsBr_3 (Et = ethyl) has been reported (H. Schmidbaur, W. Bublak, B. Huber, G. Müller, Angew. Chem., Int. Ed., 1987, 26, 234).

a. What is the point group of this structure?

b. Propose an explanation of how the frontier orbitals of AsBr_3 and C_6Et_6 can interact to form chemical bonds that stabilize this structure.

6.18 When AlCl_3 and OPCl_3 are mixed, the product, Cl_3Al—O—PCl_3 has a nearly linear Al—O—P arrangement (bond angle 176°).
of $-71.1$ and $-64$ kJ/mol for pyridine—B(CH$_3$)$_3$ and $-105$ kJ/mol for pyridine—BF$_3$.

b. Explain the differences found in part a in terms of the structures of BF$_3$ and B(CH$_3$)$_3$.

c. Explain the differences in terms of HSAB theory.

6.28 Repeat the calculations of the preceding problem using NH$_3$ as the base, and put the four reactions in order of the magnitudes of their $\Delta H$ values.

6.29 Compare the results of Problems 6.20 and 6.21 with the absolute hardness parameters of Appendix B-5 for BF$_3$, NH$_3$, and pyridine (C$_6$H$_5$N). What value of $\eta$ would you predict for B(CH$_3$)$_3$? Compare NH$_3$ and N(CH$_3$)$_3$ as a guide.

6.30 CsI is much less soluble in water than CsF, and LiF is much less soluble than LiI. Why?

6.31 Rationalize the following data in HSAB terms:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H$(kcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$CH$_3$ + H$_2$ $\rightarrow$ CH$_3$OH + CH$_4$</td>
<td>12</td>
</tr>
<tr>
<td>CH$_3$COCH$_3$ + H$_2$O $\rightarrow$ CH$_3$COOH + CH$_4$</td>
<td>-13</td>
</tr>
</tbody>
</table>

6.32 Predict the order of solubility in water of each of the following series, and explain the factors involved.

a. MgSO$_4$, CaSO$_4$, SrSO$_4$, BaSO$_4$

b. PbCl$_2$, PbBr$_2$, PbI$_2$, PbS

6.33 In some cases CO can act as a bridging ligand between main-group and transition-metal atoms. When it forms a bridge between Al and W in the compound having the formula (C$_6$H$_3$)Al—[bridging CO]—W(CO)$_2$(C$_2$H$_2$), is the order of atoms in the bridge Al—CO—W or Al—OC—W? Briefly explain your choice.

6.34 Choose and explain:

a. Strongest Brønsted acid: SnH$_4$, SbH$_3$, TeH$_2$

b. Strongest Brønsted base: NH$_3$, PH$_3$, SbH$_3$

c. Strongest base to H$^+$ (gas phase):

   NH$_3$, CH$_3$NH$_2$, (CH$_3$)$_2$NH, (CH$_3$)$_3$N

d. Strongest base to BMe$_3$: pyridine 2-methylpyridine 4-methylpyridine

6.35 B$_2$O$_3$ is acidic, Al$_2$O$_3$ is amphoteric, and Sc$_2$O$_3$ is basic. Why?

6.36 Predict the reactions of the following hydrogen compounds with water, and explain your reasoning.

a. CaH$_2$

b. HBr

c. H$_2$S

d. CH$_4$

6.37 List the following acids in order of their acid strength when reacting with NH$_3$.

BF$_3$, B(CH$_3$)$_3$, B(C$_2$H$_5$)$_3$, B[C$_6$H$_2$(CH$_3$)$_3$]

$\{C$_6$H$_2$(CH$_3$)$_3\} = 2.4,6$-trimethylphenyl

6.38 Choose the stronger acid or base in the following pairs, and explain your choice.

a. CH$_3$NH$_2$ or NH$_3$ in reaction with H$^+$

b. Pyridine or 2-methylpyridine in reaction with trimethylboron

c. Triphenylboron or trimethylboron in reaction with ammonia

6.39 List the following acids in order of acid strength in aqueous solution:

a. HMnO$_4$, H$_3$AsO$_4$, H$_2$SO$_3$, H$_2$SO$_4$

b. HClO, HClO$_4$, HClO$_2$, HClO$_3$

6.40 Solvents can change the acid–base behavior of solutes. Compare the acid–base properties of dimethylamine in water, acetic acid, and 2-butanone.

6.41 HF has $H_0 = -11.0$. Addition of 4% SbF$_5$ lowers $H_0$ to $-21.0$. Explain why SbF$_5$ should have such a strong effect and why the resulting solution is so strongly acidic that it can protonate alkenes.

$\text{(CH}_3\text{)}_2\text{C} \equiv \text{CH}_2 + \text{H}^+ \rightarrow \text{(CH}_3\text{)}_3\text{C}^+$

6.42 The reasons behind the relative Lewis acidities of the boron halides BF$_3$, BCl$_3$, and BBr$_3$ with respect to NH$_3$ have been controversial. Although BF$_3$ might be expected to be the strongest Lewis acid on the basis of electronegativity, the Lewis acidity order is BBr$_3$ > BCl$_3$ > BF$_3$. Consult the references listed below to address the following questions. (See also J. A. Plumley, J. D. Evanseck, *J. Phys. Chem. A*, 2009, 113, 5985.)


b. What explanation has been offered on the basis of the calculations presented in F. Bessac, G. Frenking, *Inorg. Chem.*, 2003, 42, 7990?

The following problems use molecular modeling software.

6.43 a. Calculate and display the molecular orbitals of NO$^-$. Show how the reaction of NO$^-$ and H$^+$ can be described as a HOMO–LUMO interaction.

b. Calculate and display the molecular orbitals of HNO and HON. On the basis of your calculations, and your answer to part a, which structure is favored?

6.44 Calculate and display the frontier orbitals of Br$_2$, methanol, and the Br$_2$—methanol adduct to show how the orbitals of the reactants interact.


b. Examine the bonding and antibonding orbitals involved in the B—N bond in F$_3$B—NH$_3$. Is the bonding orbital polarized toward the B or the N? The antibonding orbital? Explain briefly.

6.46 Section 6.4.5 includes a diagram of a halogen bond between Br$_2$ and acetylene.

a. Use sketches to show how a $\pi$ orbital of acetylene interacts with the LUMO of Br$_2$ to form the adduct.

b. Calculate and display the molecular orbitals of the acetylene–Br$_2$ adduct. Describe the interactions that you observe between the $\pi$ orbitals of acetylene and orbitals of Br$_2$. 