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C. Laurence and J.-F. Gal, *Lewis Basicity and Affinity Scales Data and Measurement*, John Wiley & Sons, New York, 2010, is an outstanding reference with respect to both tabulated data and discussion of methodology. G. Gilli and P. Gilli, *The Nature of the Hydrogen Bond*, Oxford University Press, New York, 2009, provides an in-depth discussion of this topic. For an excellent review of superbases: *Superbases for Organic Synthesis: Guanidines, Amidines, and Phosphazenes and Related Organocatalysts*, Ishikawa, T., eds., Wiley, New York, 2009.

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. $AlBr_3 + Br^- \rightarrow AlBr_4^-$
 b. $HClO_4 + CH_3CN \rightarrow CH_3CNH^+ + ClO_4^-$
 c. $Ni^{2+} + 6\,NH_3 \rightarrow [Ni(NH_3)_6]^{2+}$
 d. $NH_3 + ClF \rightarrow H_3N\cdots ClF$

 e. $2\,ClO_3^- + SO_2 \rightarrow 2\,ClO_2 + SO_4^{2-}$
 f. $C_3H_7COOH + 2\,HF \rightarrow [C_3H_7C(OH)_2]^+ + HF_2^-$

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. $XeO_3 + OH^- \rightarrow [HXeO_4]^-$
 b. $Pt + XeF_4 \rightarrow PtF_4 + Xe$
 c. $C_2H_5OH + H_2SeO_4 \rightarrow C_2H_5OH_2^+ + HSeO_4^-$

    d. $[CH_3Hg(H_2O)]^+ + SH^- \rightleftharpoons [CH_3HgS]^- + H_3O^+$

    e. $(benzyl)_3N + CH_3COOH \rightarrow (benzyl)_3NH^+ + CH_3COO^-$

    f. $SO_2 + HCl \rightarrow OSO \cdots HCl$

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:

$$2\,Cs[\ \ ]^- + [\ \ ]^+ [Sb_2F_{11}]^- \rightarrow 3\,BrF_5 + 2\,CsSbF_6$$

    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_2SO_4 and anhydrous H_3PO_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 acetone, 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.

	pK_a of Conjugate Acid	Gas-Phase Basicity (kJ/mol)
Methanol	−2.05	724.5
Ethanol	−1.94	746.0
Water	−1.74	660.0
Dimethylether	−2.48	764.5
Diethylether	−2.39	801.0

    a. Qualitatively, how well do these gas phase and solution data correlate? Explain.

    b. Rationalize the positions of the ethers on your graph relative to the alcohols and water.

    c. 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.

6.11 Consider these BF_3 affinities for various sulfoxides from C. Laurence and J.-F. Gal, *Lewis Basicity and Affinity Scales Data and Measurement*, John Wiley and Sons, United Kingdom, 2010, p. 99. Rationalize this BF_3 affinity trend with inductive and resonance arguments.

Lewis base	Formula	BF_3 Affinity (kJ/mol)
Diphenylsulfoxide	Ph_2SO	90.34
Methyl phenyl sulfoxide	$PhSOMe$	97.37
Dimethyl sulfoxide	Me_2SO	105.34
Di-n-butyl sulfoxide	$(n\text{-}Bu)_2SO$	107.60
Tetramethylene sulfoxide	$cyclo\text{-}(CH_2)_4SO$	108.10

6.12 The development of new Lewis basicity scales is of ongoing interest. Maccarrone and Di Bella recently reported a scale of Lewis basicity that employs a zinc(II) complex as a reference Lewis acid (I. P. Oliveri, G. Maccarrone, S. Di Bella, *J. Org. Chem.*, **2011**, *76*, 8879).

    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 $P(t\text{-}C_4H_9)_3$ and $B(C_6F_5)_3$ is mixed with 1 bar of the gas N_2O 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_2O in this reaction.

    b. Propose a structure of the product. (See E. Otten, R. C. Neu, D. W. Stephan, *J. Am. Chem. Soc.*, **2009**, *131*, 9918.)

6.14 FLP chemistry continues to afford remarkable reactions that proceed without transition metals. Metal-free aromatic hydrogenation of N-bound phenyl rings can be achieved in the presence of H_2 and $B(C_6F_5)_3$ to form N-cyclohexylammonium hydridoborate salts (T. Mahdi, Z. M. Heiden, S. Grimme, D. W. Stephan, *J. Am. Chem. Soc.*, **2012**, *134*, 4088).

**a.** Sketch the reaction coordinate diagram in Figure 2 of this report, including the structures of intermediates and transition states.

b. Discuss the hypothesized steps for initial addition of H^+ to the aromatic ring of *t*-BuNHPh.

c. How does this diagram support the outcome of the reaction of *t*-BuNHPh, $B(C_6F_5)_3$, and H_2 in pentane (at 298 K) versus in refluxing toluene (383 K)?

d. What happens if the utilized amine becomes *too* basic?

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. Grimme, 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?).

a. Use the arrow-pushing formalism to propose mechanisms for the reaction of **2b** with 1,4-cyclohexadiene, and of **2b** with toluene.

b. Explain why C—O bond formation in the toluene reaction occurs exclusively at the primary carbon and not at a carbon atom within the aromatic ring.
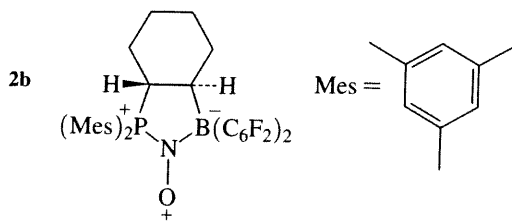
6.16 Use the pK_a *Slide Rule* in P. Gilli, L. Pretto, V. Bertolasi, G. Gilli, *Acc. Chem. Res.*, **2009**, *42*, 33 to answer these questions:

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 $A \cdots H_2O$ 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 $Br_3As \cdot C_6Et_6 \cdot AsBr_3$ (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°).

a. Suggest an explanation for this unusually large angle.

b. The O—P distance in $Cl_3Al—O—PCl_3$ is only slightly longer than the comparable distance in $OPCl_3$ even though the latter has a formal double bond. Suggest why there is so little difference in these bond distances. (See N. Burford, A. D. Phillips, R. W. Schurko, R. E. Wasylishen, J. F. Richardson, *Chem. Commun.*, **1997**, 2363.)

6.19 Of the donor–acceptor complexes $(CH_3)_3N—SO_3$ and $H_3N—SO_3$ in the gas phase,

a. Which has the longer N—S bond?

b. Which has the larger N—S—O angle?

Explain your answers briefly. (See D. L. Fiacco, A. Toro, K. R. Leopold, *Inorg. Chem.*, **2000**, *39*, 37.)

6.20 Xenon difluoride, XeF_2, can act as a Lewis base toward metal cations such as Ag^+ and Cd^{2+}.

a. In these cases, do you expect the XeF_2 to exert its basicity through the lone pairs on Xe or those on F?

b. $[Ag(XeF_2)_2]AsF_6$ and $[Cd(XeF_2)_2](BF_4)_2$ have both been synthesized. In which case, AsF_6^- or BF_4^-, do you expect the fluorines to act as stronger Lewis bases? Explain briefly. (See G. Tavcar, B. Zemva, *Inorg. Chem.*, **2005**, *44*, 1525.)

6.21 The ion NO^- can react with H^+ to form a chemical bond. Which structure is more likely, HON or HNO? Explain your reasoning.

6.22 The absorption spectra of solutions containing Br_2 are solvent dependent. When elemental bromine is dissolved in nonpolar solvents such as hexane, a single absorption band in the visible spectrum is observed near 500 nm. When Br_2 is dissolved in methanol, however, this absorption band shifts and a new band is formed.

a. Account for the appearance of the new band.

b. Is the 500 nm band likely to shift to a longer or shorter wavelength in methanol? Why?

In your answers, you should show clearly how appropriate orbitals of Br_2 and methanol interact.

6.23 AlF_3 is insoluble in liquid HF but dissolves if NaF is present. When BF_3 is added to the solution, AlF_3 precipitates. Explain.

6.24 Why were most of the metals used in antiquity class (b) (*soft*, in HSAB terminology) metals?

6.25 The most common source of mercury is cinnabar (HgS), whereas Zn and Cd in the same group occur as sulfide, carbonate, silicate, and oxide. Why?

6.26 The difference between melting point and boiling point (in °C) is given below for each of the Group IIB halides.

	F⁻	Cl⁻	Br⁻	I⁻
Zn^{2+}	630	405	355	285
Cd^{2+}	640	390	300	405
Hg^{2+}	5	25	80	100

What deductions can you draw?

6.27 a. Use Drago's E and C parameters to calculate ΔH for the reactions of pyridine and BF_3 and of pyridine and $B(CH_3)_3$. Compare your results with the reported experimental values

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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 ΔH 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$_5$H$_5$N). What value of η 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:

	ΔH(kcal)
CH$_3$CH$_3$ + H$_2$O $\rightarrow$ CH$_3$OH + CH$_4$	12
CH$_3$COCH$_3$ + H$_2$O $\rightarrow$ CH$_3$COOH + CH$_4$	-13

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$_5$)$_3$ Al $-$ [bridging CO] $-$ W(CO)$_2$(C$_5$H$_5$), 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$_3$)$_3$]$_3$

[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$_3$
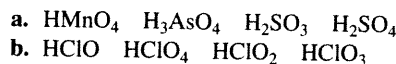
6.40 Solvents can change the acid–base behavior of solutes. Compare the acid–base properties of dimethylamine in water, acetic acid, and 2-butanone.

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.
$$(CH_3)_2C{=}CH_2 + H^+ \rightarrow (CH_3)_3C^+$$
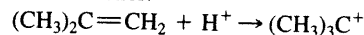
6.42 The reasons behind the relative Lewis acidities of the boron halides BF$_3$, BCl$_3$, and BBr$_3$ with respect to NH$_3$ have been controversial. Although BF$_3$ might be expected to be the strongest Lewis acid on the basis of electronegativity, the Lewis acidity order is BBr$_3$ > BCl$_3$ > BF$_3$. 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.)
a. How does the LCP approach account for a Lewis acidity order of BBr$_3$ > BCl$_3$ > BF$_3$? (See B. D. Rowsell, R. J. Gillespie, G. L. Heard, *Inorg. Chem.*, **1999**, *38*, 4659.)
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.

6.45 a. Calculate and display the molecular orbitals of BF$_3$, NH$_3$, and the F$_3$B $-$ NH$_3$ Lewis acid–base adduct.
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 π 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 π orbitals of acetylene and orbitals of Br$_2$.