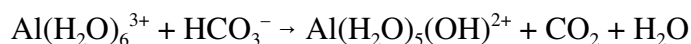


Chem 370 - Spring, 2019
Assignment 7 - Solutions

6.1

Acid	Base	Theories
AlBr_3	Br^-	Lewis
HClO_4	CH_3CN	Brønsted-Lowry, Lewis
Ni^{2+}	NH_3	Lewis
ClF	NH_3	Lewis
SO_2	ClO_3^-	Lewis
HF	$\text{C}_3\text{H}_7\text{CO}_2\text{H}$	Brønsted-Lowry, Lewis

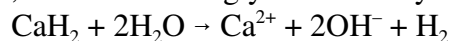
6.3 In the moist batter the aluminum sulfate would be present as $\text{Al}(\text{H}_2\text{O})_6^{3+}(\text{aq})$ ions and $\text{SO}_4^{2-}(\text{aq})$ ions, and the sodium hydrogen carbonate would be present as $\text{Na}^+(\text{aq})$ ions and $\text{HCO}_3^-(\text{aq})$ ions. The $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ions are acidic and the HCO_3^- ions are basic, so they react to form $\text{CO}_2(\text{g})$:



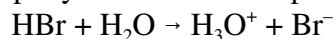
6.4 This suggests the formation of ions by the reaction $\text{KF} + \text{BrF}_3 \rightleftharpoons \text{K}^+ + \text{BrF}_4^-$. On the basis of the solvent system concept, the solution would be considered to be basic. The solvent BrF_3 has a dissociation equilibrium $2 \text{BrF}_3 \rightleftharpoons \text{BrF}_2^+ + \text{BrF}_4^-$, from which BrF_2^+ is identified as the acid and BrF_4^- is identified as the base in this solvent system.

- 6.22 a. This is similar to the solvent effects on the uv-vis spectrum of I_2 , described in section 6.4.2 (6.2.7 in the 4th edition) and in class. Br_2 forms charge transfer complexes with donor solvents such as methanol.
- b. As with the I_2 case, the 500 nm band in hexane is due to a $\pi^* \rightarrow \sigma^*$ transition. This shifts to higher energy (shorter wavelength) with adduct formation, such as $\text{Br}_2 \cdot \text{CH}_3\text{OH}$. As shown in Figure 6.9, the interaction of the donor CH_3OH HOMO with the Br_2 σ^* LUMO results in a new bonding and antibonding pair of MOs with the extra electron pair in the system occupying the new bonding MO. The new antibonding MO is essentially the Br_2 σ^* MO, raised in energy, which accounts for the blue shift in the $\pi^* \rightarrow \sigma^*$ transition on adduct formation. Note that a new charge-transfer band can also be expected, arising from the transition from the new bonding MO to the new antibonding (σ^*) MO, as shown in Figure 6.9.

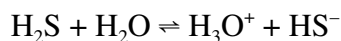
6.36 a. CaH_2 contains H^- ions, which are strongly basic and hydrolyze to give H_2 .



- b. HBr is a strong acid, principally due to its lower proton affinity.



- c. H_2S is a weak acid, principally due to the strength of the H–S bond. It is only partially dissociated in water.



- d. CH_4 has virtually nonpolar bonds and a resulting high proton affinity. Therefore it has no acid hydrolysis.

6.37 The acid character of these trigonal boron species depends on their ability to accept electron density into a LUMO that is essentially an empty $2p_z$ orbital on B. Moreover, in forming the adduct, the three original ligands about the boron must fold back to assume an approximately tetrahedral geometry. Electron donating groups and bulky ligands will inhibit the ability to accept electron density from the HOMO of the base. Therefore, the expected order is $\text{BF}_3 > \text{B}(\text{CH}_3)_3 > \text{B}(\text{C}_2\text{H}_5)_3 > \text{B}(\text{C}_6\text{H}_5)_3$.

6.39 The order of acid strength can be judged on the basis of the number of terminal oxygen atoms about central atom (more terminal oxygen atoms make the acid stronger), and for cases with equal numbers of such oxygen atoms on the basis of electronegativity (higher electronegativity of the central atom makes the acid stronger).

- a. $\text{H}_3\text{AsO}_4 < \text{H}_2\text{SO}_3 < \text{H}_2\text{SO}_4 < \text{HMnO}_4$
b. $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$

7.3 The edge of the cube in terms of the radius of the corner atoms (which are touching) is $2r$. The cube diagonal is $\sqrt{3}$ times the cube edge, or $(\sqrt{3})(2r) = 3.464r$. Each corner atom contributes r to this length, so the diameter of the central hole is $d = (3.464 - 2)r = 1.464r$. The radius of the hole, then, is $r_h = 0.734r$. Thus, a sphere with any radius less than this will fit.

7.5 NaCl lattice

Ions	Corners	Edges	Face centers	Body centers	Internal	Total	Formula
Na ⁺	8 x 1/8		6 x 1/2			4	
Cl ⁻		12 x 1/4			1 x 1	4	NaCl

CsCl lattice

Ions	Corners	Edges	Face centers	Body centers	Internal	Total	Formula
Cs ⁺				1 x 1		1	
Cl ⁻	8 x 1/8					1	CsCl

CaF₂

Ions	Corners	Edges	Face centers	Body centers	Internal	Total	Formula
Ca ²⁺					4 x 1	4	
F ⁻	8 x 1/8	12 x 1/4	6 x 1/2	1 x 1		8	CaF ₂

7.11 Although an individual Hg⁺ ion would have the valence configuration $5d^{10}6s^1$, making it paramagnetic, mercury(I) is always a diatomic ion; i.e., Hg₂²⁺. A simple MO scheme for this ion would form bonding and antibonding sigma MOs through interactions of the 6s orbitals on each Hg⁺. The two electrons (one from each Hg⁺) would pair in the σ_{6s} bonding MO, giving a bond order of 1 and a diamagnetic state.

7.16 CaO is harder and has a higher melting point than KF, because it has a much higher lattice energy. CaO has ionic charges of +2 and -2 charges and radii of 114 and 126 pm (total distance 240 pm). KF has ionic charges of +1 and -1 and radii of 152 and 119 (total distance 271 pm). The much higher charges and shorter distances give CaO the higher lattice energy.

MgO is harder and has a higher melting point than CaF₂, because it has a much higher lattice energy. MgO has ionic charges of +2 and -2 and radii of 86 and 126 pm (total distance 212 pm) and a Madelung constant of 1.75. CaF₂ has ionic charges of +2 and -1 and radii of 126 and 119 (total distance 245 pm), with a Madelung constant of 2.52.

7.19 Using the Born-Mayer equation with a presumed NaCl-type lattice ($M = 1.748$) and $r_0 = 212$ pm (see answer to 7.16, above), we can calculate U_o as follows:

$$U_o = \frac{NMZ^+Z^-e^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{\rho}{r_0} \right)$$

$$U_o = \frac{(6.011 \times 10^{23} \text{ mol}^{-1})(1.748)(+2)(-2)(2.307 \times 10^{-28} \text{ J}\cdot\text{m})}{212 \times 10^{-12} \text{ m}} \left(1 - \frac{30}{212} \right) = -3934 \text{ kJ}\cdot\text{mol}^{-1}$$

The value calculated from the Born-Mayer equation is negative and corresponds to the negative of the lattice energy as customarily defined thermodynamically; viz.,



Use this thermochemical equation in the reverse (with a negative sign on the value) in the Born-Haber cycle to calculate ΔH_f° for MgO.

