

3.7: Problems

1. Classify each of the substances below as an acid or base, and as strong or weak or as a spectator in the solvent listed. For each case, write out the dissociation reaction.

(a) H_3AsO_4 in water

(b) HCl in glacial acetic acid

(c) CH_3COOH in liquid ammonia

(d) H_2O in molten NaOH

(e) Cl^- in liquid ammonia

2. Write out the dissociation reactions for an acid HA and its conjugate base A^- in water. Use the equilibrium expressions for K_a and K_b to prove that $K_a K_b = K_w$.

3. Calculate the percent ionization of 1 M acetic acid ($K_a = 1.8 \times 10^{-5}$) in water.

4. For each pair of compounds below, indicate which one is a stronger acid and explain your choice:

(a) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ or $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$

(b) H_3BO_3 or H_3PO_3

(c) $[\text{Ga}(\text{H}_2\text{O})_6]^{3+}$ or $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$

(d) HIO_3 or HIO_4

(e) H_3PO_4 or H_2SeO_4

5. The Mg^{2+} and Cu^{2+} cations have similar ionic radii, but the acidities of aqueous nitrate solutions containing the two ions are different. Explain which ion is more acidic and why.

6. Cobalt reacts with excess fluorine to make CoF_3 , but higher oxidation states of cobalt do not exist in binary fluorides. However, Co(IV) is stable in oxides such as CoO_2 and BaCoO_3 . Explain why these oxides can stabilize a higher oxidation state of cobalt than fluorides.

7. (a) When solutions of the hydrosulfide (SH^-) salts of As^{3+} , Sb^{3+} , and Sn^{4+} are reacted with aqueous solutions of ammonium hydrosulfide (NH_4^+SH^-), the sulfide salts As_2S_3 , Sb_2S_3 , and SnS_2 precipitate. When excess aqueous Na_2S is added, however, these sulfides re-dissolve to form soluble anionic complexes. In contrast, solutions of Cu^{2+} , Pb^{2+} , Hg^{2+} , Bi^{3+} and Cd^{2+} precipitate as solid sulfides but do not re-dissolve in solutions that contain excess sulfide. We may consider the first group of ions to be amphoteric for soft acid-base reactions that involve SH^- instead of OH^- . The second group is more basic (less acidic) in the sense that it does not react with excess soft base. Use this information to locate the amphoteric diagonal in the periodic table for sulfides. Compare this with the diagonal that defines the amphoteric oxides, which dissolve in either acidic or basic solutions. Does your analysis agree with the description of S^{2-} as a softer base than O^{2-} ?

(b) Au^+ is also precipitated by SH^- ions, and the sulfide Au_2S redissolves to form a soluble complex in excess SH^- . Does this fit the trend you discovered in part (a)? Does it make sense in terms of the electronegativity of Au ? Explain.

8. Calculate the enthalpy for the adduct $(\text{CH}_3)_3\text{B-N}(\text{CH}_3)_3$ and compare it to the measured value of -73.6 kJ/mol . Parameters can be found at ECW Model.

9. Calculate the enthalpy for the adduct formation for the Lewis acid $(\text{CH}_3)_3\text{SnCl}$ with each of the following Lewis bases $(\text{C}_2\text{H}_5)_2\text{O}$, $(\text{CH}_2)_4\text{O}$, and CH_3CN . Their respective measured enthalpies are -9.2 , -21.3 and -20.1 kJ/mol . Explain the any differences between the calculated and measured enthalpies. Parameters can be found at ECW Model.

10. Refer to the Cramer-Bopp plot found at ECW Model and indicate the order of Lewis base strength for

(a) An acid with $R_a = -0.5$

(b) An acid with $R_a = 0.33$

(c) An acid with $R_a = -0.9$

11. The Lewis acid $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ has a W value of -43.47 kJ/mol

- (a) What does W refer to?
- (b) The E, C, and W parameters found at ECW Model give the enthalpy for forming one mole adduct, that is,
$$B + \frac{1}{2} [Rh(CO)_2Cl]_2 \longrightarrow B-RhCl(CO)_2$$
- (1) What is the heat of dissociation of one mole of $[Rh(CO)_2Cl]_2$?
- (2) What is the enthalpy of $2 B + [Rh(CO)_2Cl]_2 \longrightarrow 2 B-RhCl(CO)_2$
- (3) Calculate the enthalpy per mol of B- $RhCl(CO)_2$ for C_5H_5N , $(CH_3)_2CO$

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