

CHEM-457 PS4 Solutions

1.

MF&T #6.1

| | <u>Acid</u> | <u>Base</u> | <u>Definition</u> |
|----|------------------|-----------------------------------|-----------------------|
| a. | AlBr_3 | Br^- | Lewis |
| b. | HClO_4 | CH_3CN | Lewis, Brønsted-Lowry |
| c. | Ni^{2+} | NH_3 | Lewis |
| d. | ClF | NH_3 | Lewis |
| e. | SO_2 | ClO_3^- | Lewis |
| f. | HF | $\text{C}_3\text{H}_7\text{COOH}$ | Lewis, Brønsted-Lowry |

MF&T #6.2

| | <u>Acid</u> | <u>Base</u> | <u>Definition</u> |
|----|--|---------------------------------|--|
| a. | XeO_3 | OH^- | Lewis This is not a Brønsted-Lowry reaction since the product connectivity is $[\text{XeO}_3(\text{OH})]^-$. |
| b. | Pt | XeF_4 | Lewis |
| c. | H_2SeO_4 | $\text{C}_2\text{H}_5\text{OH}$ | Lewis, Brønsted-Lowry |
| d. | $[\text{CH}_3\text{Hg}(\text{H}_2\text{O})]^+$ | SH^- | Lewis This reaction likely occurs via the following steps: $[\text{CH}_3\text{Hg}(\text{H}_2\text{O})]^+ + \text{SH}^- \rightarrow [\text{CH}_3\text{Hg}(\text{SH})] + \text{H}_2\text{O}$ $[\text{CH}_3\text{Hg}(\text{SH})] + \text{H}_2\text{O} \rightarrow [\text{CH}_3\text{HgS}]^- + \text{H}_3\text{O}^+$ While a Brønsted-Lowry reaction occurs in the second step, the species listed in Problem 6.2d are involved in the initial Lewis acid-base reaction. |
| e. | CH_3COOH | $(\text{benzyl})_3\text{N}$ | Lewis, Brønsted-Lowry |
| f. | HCl | SO_2 | Lewis |

MF&T #6.30

CsI and LiF fit Basalo's principle that ions of similar size and equal (but opposite) charge form the least soluble salts. CsF and LiI have ionic sizes that are very different, and they do not fit as well into an ionic lattice. In addition, CsI and LiF are soft—soft and hard—hard combinations, which combine better than the hard—soft LiI and soft—hard CsF.

MF&T #6.34

- TeH₂ is the strongest acid, because Te is more electronegative than either Sn or Sb. Therefore, the hydrogen is more positive and acidic.
- NH₃ is the strongest base because N is more electronegative than either P or Sb.
- (CH₃)₃N is the strongest base in the gas phase because the methyl groups contribute electron density to the nitrogen. In solution, the order is scrambled, probably due to solvation (Section 6.3.6).
- 4-Methylpyridine > pyridine > 2-methylpyridine. Again, the methyl group adds electron density to the N. However, with methyl in the 2 position, steric hindrance makes bonding to BMe₃ more difficult.

MF&T #6.37

BF₃ > B(CH₃)₃ > B(C₂H₅)₃ > B(C₆H₂(CH₃)₃)₃. Alkyl groups are electron-donating and increase the electron density on B and reduce the attraction for the lone pair of NH₃. The bulky mesityl groups render B(C₆H₂(CH₃)₃)₃ less Lewis acidic on the basis of the steric hindrance introduced when these boron centers adopt the required tetrahedral geometry upon complexation of NH₃.

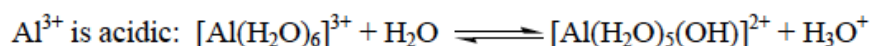
MF&T #6.38

- CH₃NH₂ is a stronger base on the basis of the electron-releasing ability of the methyl group.
- Although 2-methylpyridine is the stronger base with smaller acid molecules, the methyl group interferes with adduct formation with trimethylboron (F-strain) and the pyridine-trimethylboron dative bond is stronger.
- Trimethylboron forms a stronger adduct with ammonia because the three phenyl rings of triphenylboron cannot bend back readily to allow the boron to become tetrahedral (B-strain).

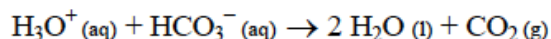
MF&T #6.42

- a. As the Lewis acids BF_3 and BCl_3 interact with NH_3 , the geometry around boron changes from planar to trigonal pyramidal; however, in accord with the LCP model the nonbonded $\text{F}\cdots\text{F}$ and $\text{Cl}\cdots\text{Cl}$ distances are nearly constant, suggesting that these atoms remain in contact with each other. Because these nonbonded distances remain essentially constant, the boron–halogen distance must increase as the distortion from trigonal geometry occurs. Because of the strength of the B–F bond, a consequence of the large electronegativity difference between B and F and the small size of the fluorine atom, more energy is required to distort BF_3 from planarity than to similarly distort BCl_3 . (Calculations in support of this argument are presented in the reference.) The consequence of this energy requirement is that BF_3 is a weaker Lewis base than BCl_3 toward NH_3 . The article does not address the relative Lewis basicity of BBr_3 , but a similar argument could apply for this compound.
- b. This article does not consider the LCP model but focuses on ab initio calculations on the adducts $\text{X}_3\text{B–NH}_3$. These calculations show a higher B–N bond dissociation energy in the BCl_3 adduct than in the BF_3 adduct. Although many factors are involved, an important issue is that BCl_3 has a lower energy LUMO that is able to interact more strongly with the donor orbital of NH_3 , giving a stronger covalent interaction (and stronger B–N bond) in $\text{Cl}_3\text{B–NH}_3$.

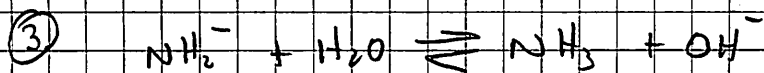
2.



The hydronium ions react with the basic bicarbonate to form CO_2 :



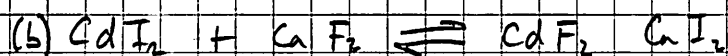
With pK_a values of 5.0 for $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, 6.4 for H_2CO_3 , and 2.0 for HSO_4^- , the pH is about 3, low enough to convert the bicarbonate to CO_2 .



(a) $K > 1$ based on electronegativity of the central atom, NH_2^- is a stronger base than OH^- . \therefore in H_2O , the pK_a of H_2O will be less than the pK_a of NH_3

$pK_a \text{ H}_2\text{O} = 15.7$ $pK_a \text{ NH}_3 = 38$ $\therefore \Delta pK_a$ for this reaction is approx -23

\therefore Rxn is spontaneous ($K > 1$) + complete



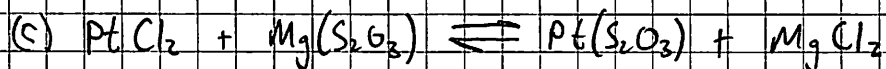
$\text{Cd}^{2+} \Rightarrow \text{acid}$ $\text{Ca}^{2+} \Rightarrow \text{acid}$

$\text{I}^- \Rightarrow \text{base}$ $\text{F}^- \Rightarrow \text{base}$

This reaction will lay to the left ($K < 1$)

on left side, the softer acid + softer base are paired + the harder acid + harder base are paired.

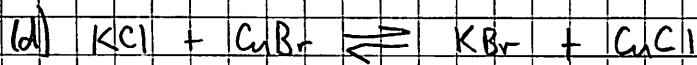
These pairings are mismatched on the left



$\text{Pt}^{2+} \Rightarrow \text{Soft acid}$ $\text{Mg}^{2+} \Rightarrow \text{Hard Acid}$

$\text{Cl}^- \Rightarrow \text{hard base}$ $\text{Si}_2\text{O}_3 \Rightarrow \text{Soft base}$

This reaction will lie to the right ($K > 1$) where hard acid is paired w/ hard base + soft acid is paired w/ soft base



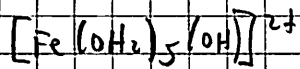
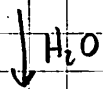
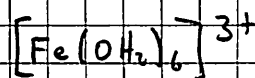
$\text{K}^+ \Rightarrow \text{Hard Acid}$ $\text{Cu}^+ \Rightarrow \text{Soft acid}$

$\text{Cl}^- \Rightarrow \text{Hard Base}$ $\text{Br}^- \Rightarrow \text{Soft base}$

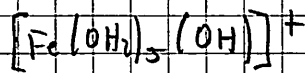
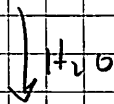
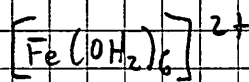
This reaction will lie to the left ($K < 1$) where hard acid is paired w/ hard base + soft acid w/ soft base

4.

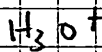
(a)



+



+

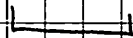
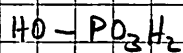


Fe^{3+} complex is more acidic since central Fe^{3+} ion is more electron withdrawing than Fe^{2+} .

Also Fe^{3+} is harder than Fe^{2+} + will \therefore be better stabilized by the hard OH^- ligand generated during the acid/base reaction.

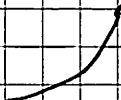
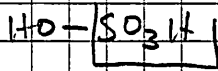
(b) HClO_4 is more acidic than HClO_3 . HClO_4 has more e^- withdrawing oxo groups that increase the electron deficiency of the central chlorine atom. \therefore The Cl of $\text{HO}-\text{ClO}_3$ is more electron deficient than the chlorine atom of $\text{HO}-\text{ClO}_2$.

(c) H_3PO_4 is less acidic than H_2SO_4 because the central phosphorus has a lower electronegativity than S.



less e^-

withdrawing than



(d) HNO_3 is much more acidic than $\text{B}(\text{OH})_3$ due to the much higher electronegativity of N vs. B.

- ⑤
- (a) Zn^{2+} is harder than Hg^{2+} . Both ions have the same charge, but Hg^{2+} is larger + much more diffuse.
- (b) Alkali metals tend to be harder than other metal ions of the same size + charge. $\therefore K^+$ is harder than Ca^{2+} .
- (c) Fe^{3+} is harder than Fe^{2+} because it is more highly charged.
- (d) Me_3N is a harder base than Me_3P because N is smaller + its valence shell is less diffuse than that of P.
- (e) Cl^- is a harder base than I^- . Both ions have the same charge, but Cl is more electronegative + less polarizable.