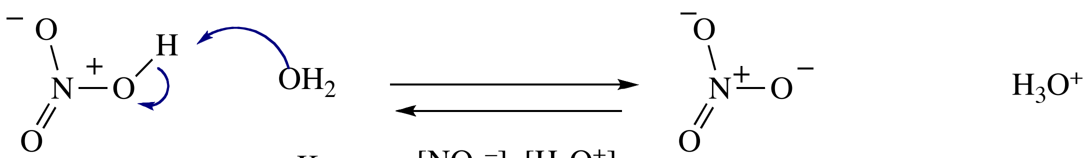
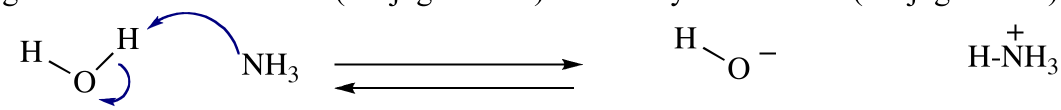
CHAPTER 2



$$K_a = \frac{[NO_3^-]\ [H_3O^+]}{[HNO_3]\ [H_2O]}$$

26. (a)

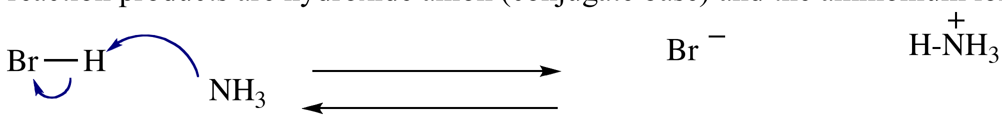
Nitric acid is a stronger acid than water, so water is the base and nitric acid is the acid in this reaction to generate the nitrate anion (conjugate base) and the hydronium ion (conjugate acid).



$$K_a = \frac{[HO^-]\ NH_4^+]}{[H_2O]\ [NH_3]}$$

(b)

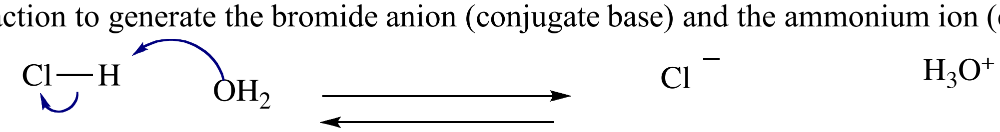
Water is a stronger acid than ammonia, so ammonia is the base and water is the acid in this reaction. The reaction products are hydroxide anion (conjugate base) and the ammonium ion (conjugate acid).



$$K_a = \frac{[Br^-]\ [NH_4^+]}{[HBr]\ [NH_3]}$$

(c)

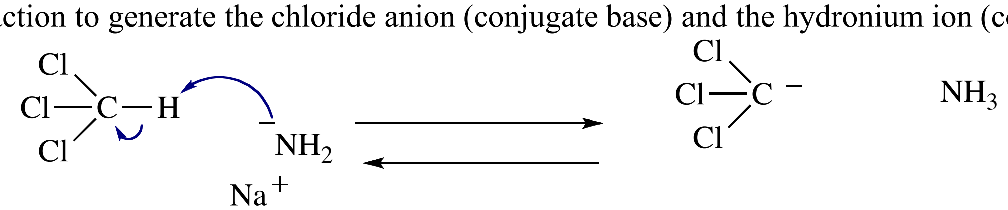
Hydrobromic acid is a stronger acid than ammonia, so ammonia is the base and HBr is the acid in this reaction to generate the bromide anion (conjugate base) and the ammonium ion (conjugate acid).



$$K_a = \frac{Cl^-]\ [H_3O^+]}{[HCl]\ [H_2O]}$$

(d)

Hydrochloric acid is a stronger acid than water, so water is the base and HCl is the acid in this reaction to generate the chloride anion (conjugate base) and the hydronium ion (conjugate acid).



$$K_a = \frac{[CCl_3^-]\ [NH_3]}{[HCCl_3]\ NaNH_2]}$$

(e)

The amide anion is clearly a base, which makes the proton of chloroform a stronger acid, so NH_2^- is the base and chloroform is the acid in this reaction to generate the $^-CCl_3$ anion (conjugate base) and ammonia, NH_3, as the conjugate acid.

27. The main reason is likely the relative size of the bromide ion (182 pm) versus the chloride ion (100 pm). Greater charge dispersal for the bromide ion leads to greater stability of that conjugate base, and a larger K_a.

28. $$\boxed{K_a = \frac{[H_3O^+]\quad[Cl^-]}{[HCl]}} \qquad \boxed{K_a = \frac{[H_3O^+]\quad[Cl^-]}{[HCl]\ \ H_2O}}$$

In this reaction, water is the base that reacts with the HCl. If water is omitted, the base has been excluded from the equilibrium constant expression for an acid-base reaction.

29. (a) NH_3 (b) H_3CO^- (c) $^-NO_3$ (d) Br^- (e) $^-\!:\!NH_2$ (f) $^-CH_3$

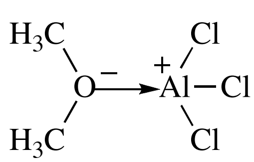
30. $$H_3N\!: \quad BF_3 \longrightarrow \boxed{F_3\overset{-}{B}\!\longrightarrow\!\overset{+}{N}H_3}$$

The ate complex in the "box" is the reaction product, where N of ammonia is the electron donor (the base).

31. Oxygen is more electronegative than nitrogen, so nitrogen is more electron rich, and will be a better electron donor. In addition, the ate complex from ammonia is an ammonium salt whereas water will react to form an oxonium salt. The ammonium salt is more stable, which contributes to the overall increased Lewis basicity of the nitrogen atom in ammonia.

32. In these neutral molecules, phosphorus is larger than nitrogen, with covalent radii of 106 pm and 71 pm, respectively. The charge density of nitrogen is greater. Therefore, ammonia is expected to be the stronger Lewis base.

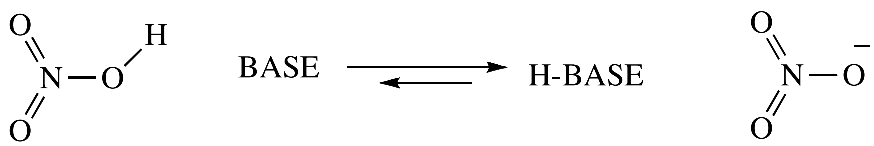
33. An ate complex is the salt generated by reaction of a Lewis acid with a Lewis base. The atom derived from the Lewis base expands its valence and assumes a positive charge, whereas the atom derived from the Lewis base expand its valence and assumes a negative charge.

34. 

35. The C-H bond is much stronger than the N-H bond, so it is more difficult to break. Nitrogen is larger and better able to accommodate charge relative to carbon, so H_3C^- is significantly less stable (more reactive) than H_2N^-. If the $^-NH_2$ conjugate base is more stable, Ka is larger, and ammonia is a stronger acid.

36. (a) CH_3OH is the strongest acid in this series. The O-H bond is more polarized and easier to break, and the methoxide anion, H_3CO^-, is more stable than the anions from CH_4 or CH_3NH_2. NaF does not have an acidic proton, and it is not a Brønsted-Lowry acid.
(b) As explained in section 2.4 of the text, the size of the conjugate base increases from fluoride towards iodide, so the iodide in is more stable. This means that K_a is larger for HI and decreases going towards HF. Since iodide is much larger, the H-I bond is longer, and weaker, s it is easier to break relative to the others.

37. The iodide in is much larger, and the charge is dispersed over a greater area. Therefore, it is more difficult for iodide to donate electrons to an acid relative to fluoride. In other words, iodide is a weaker base.

38. 

As shown, nitric acid generates the resonance stabilized nitrate anion. In the nitrate anion, the charge is dispersed over several atoms, which makes it more difficult for that species to donate electrons to an acid. For hydroxide ion, HO^-, the charge is concentrated on the oxygen atom, and it is much easier to donate electrons. The charge is not dispersed as in the nitrate anion, and hydroxide is more basic.

39. The fluoride is much more stable relative to the methide anion, $H_3C{:}^-$, which means that carbon will donate electron more easily. The methide anion is the stronger base.

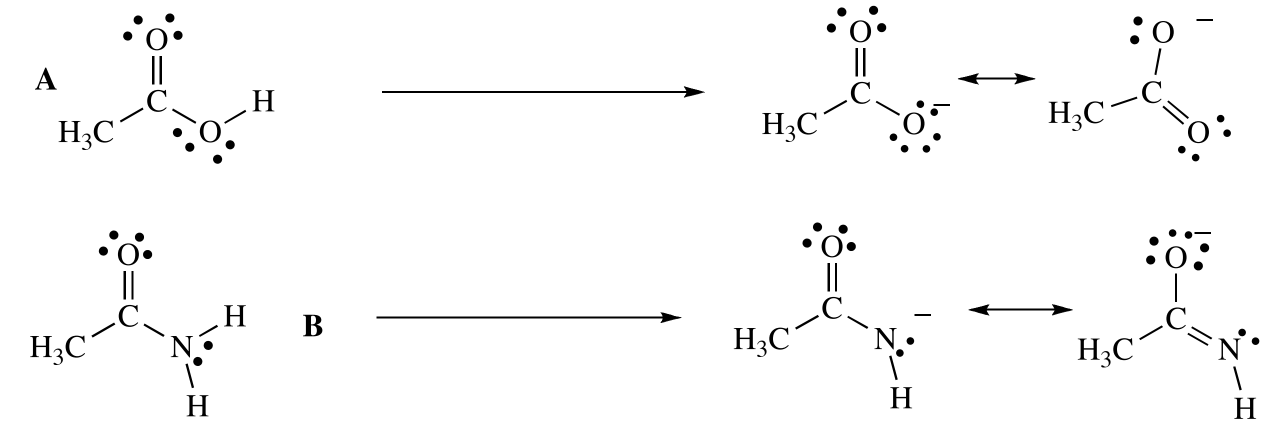
40. Determine the pK_a for each of the following.
(a) $K_a = 1.45\text{x}10^5$ (b) $K_a = 3.6\text{x}10^{-12}$ (c) $K_a = 6.7\text{x}10^{-31}$ (d) $K_a = 18$ (e) $K_a = 3.8\text{x}10^{14}$
$pK_a = -\log_{10} K_a$. (a) 5.16 (b) 11.44 (c) 30.17 (d) –1.26 (e) -14.6

41. The more acidic acid will have the smaller pK_a. Of this series, HCl is the strongest acid (pK_a –7) relative to HF (pK_a 3.17). Water has a pK_a of 15.7 and ammonia has a pK_a of about 25. Clearly, HCl has the smallest pK_a.

42. The least acidic acid will have the largest pK_a. Of this series, HCl is the strongest acid (pK_a –7) relative to HF (pK_a 3.17). Water has a pK_a of 15.7 and ammonia has a pK_a of about 25. Clearly, ammonia is the least acidic and has the largest pK_a.

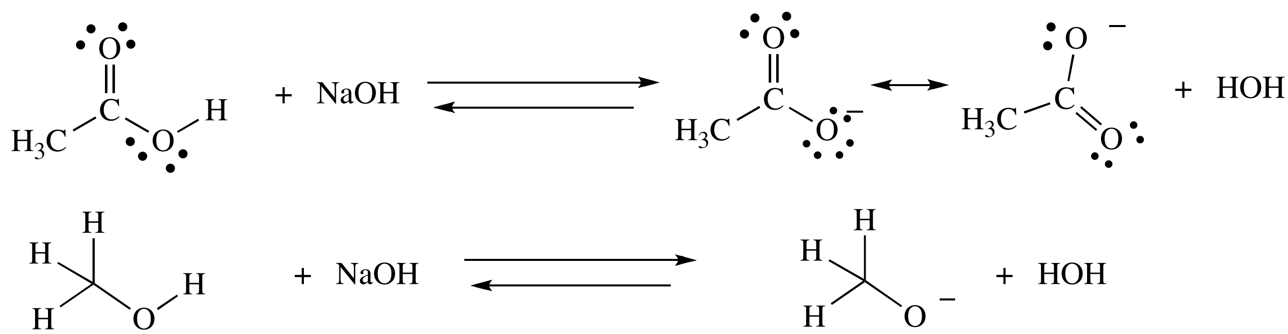
43. NaF is an ionic salt, Na^+ and F^-. The electron rich fluoride ion is the only atom of these two that can donate electrons, so F is the basic atom.

44. As described in section 2.4, HI is a stronger acid, as is evident from the smaller pK_a for HI, because of the weaker HI bond and the larger size of the iodide ion (the conjugate base), which leads to charge dispersal that makes that conjugate base less reactive.



45.

The reaction of A gives the conjugate base shown, and B gives the conjugate base indicated. In both cases, the charge is dispersed over three atoms (resonance). The OH bond is weaker than the NH bond, and that proton is easier to remove. Oxygen holds onto electron better than nitrogen (it is more electronegative), so the conjugate base from A is less likely to donate electrons (it is more stable, which shifts the equilibrium towards the conjugate base). Although it is not obvious from the diagram, the charge dispersal is more efficient in the conjugate base from A. All of these combine to make A much more acidic (pK_a of 4.8 versus 46).



46.

(a) The conjugate base derived from formic acid is resonance stabilized by charge dispersal over several atoms, as shown. The conjugate base from methanol has the charge concentrated on oxygen, and no charge dispersal is possible.

(b) If there is a larger concentration of the conjugate base, the equilibrium is shifted towards the right (towards the conjugate base), and K_a is larger.

(c) If K_a for formic acid is much larger, it will be the stronger acid, and will react better with NaOH.