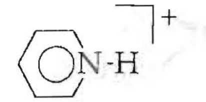
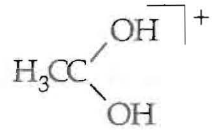


$C_5H_6N^+$



$CH_3C(OH)_2^+$

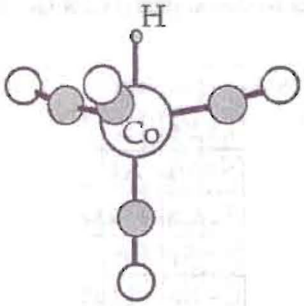
(b) HPO_4^{2-}? The conjugate acid is $H_2PO_4^{2-}$.

(c) O^{2-}? The conjugate acid is OH^-.

(d) CH_3COOH? The conjugate acid is $CH_3C(OH)_2^+$, shown above.

(e) $[Co(CO)_4]^-$? The conjugate acid is $HCo(CO)_4$, shown below.

A drawing of the $HCo(CO)_4$ molecule, the conjugate acid of the tetrahedral $Co(CO)_4^-$ anion. The C atoms of the CO ligands are bound to the Co atom. The O atoms are unshaded.

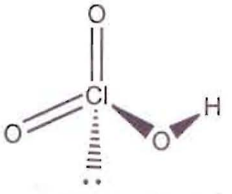


(f) CN^-? The conjugate acid is HCN.

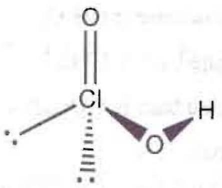
4.4 **What is the K_b of ethanoic acid?** To find the K_b, use Equation 4.1:

$$K_a \times K_b = K_w$$
$$K_b = K_w/K_a = 1.0 \times 10^{-14}/1.8 \times 10^{-5} = 5.6 \times 10^{-10}$$

4.5 **What are the structures and the pK_a values of chloric ($HClO_3$) and chlorous ($HClO_2$) acid?** The structures for chloric acid and chlorous acid are shown below. Chloric acid is π bond to two oxygen atoms and σ bond to another oxygen atom, and has one lone pair, giving it a geometry of trigonal pyramidal. Chlorous acid is π bond to one oxygen atom and σ bond to one oxygen atom, and has two sets of lone pairs, thus the geometry is bent.



chloric acid



chlorous acid

Pauling's first rule for predicting the pK_a of a mononuclear oxoacid is p$K_a \approx 8 - 5p$ (where p is the number of oxo groups attached to the central element). Since $p = 2$ for chloric acid, the predicted pK_a for $HClO_3$ is $8 - (5 \times 2) = -2$. The actual value, given in Table 4.2, is –1. For chlorous acid, $p = 1$, therefore the pK_a for $HClO_2$ is $8 - (5 \times 1) = 3$. The actual value, given in Table 4.2, is 2.

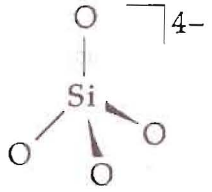
pK_a for $H_2SO_4 = 8 - (5 \times 2) = -2$

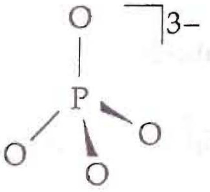
pK_a for $HBrO_3 = 8 - (5 \times 2) = -2$

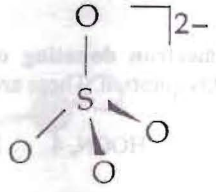
pK_a for $HClO_4 = 8 - (5 \times 3) = -7$

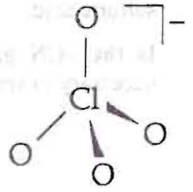
The lowest pK_a is for $HClO_4$, so this is the strongest acid. Next we have H_2SO_4 and $HBrO_3$, which have the same pK_a of −2 according to Pauling's rules for predicting the pK_a of mononuclear oxoacids. Bromine is more electronegative than sulfur; inductively, $HBrO_3$ is a stronger acid than H_2SO_4. HNO_2 has the highest pK_a and is the weakest acid. Therefore the order is $HClO_4 > HBrO_3 > H_2SO_4 > HNO_2$.

4.10 **Account for the trends in the pK_a values of the conjugate acids of SiO_4^{4-}, PO_4^{3-}, SO_4^{2-}, and ClO_4^-?** The structures of these four anions, which can be determined to be tetrahedral using VSEPR, are shown below. As can be seen, the charge on the anions decreases from −4 for the silicon-containing species to −1 for the chlorine-containing species. The charge differences alone would make SiO_4^{4-} the most basic species. Hence $HSiO_4^{3-}$ is the least acidic conjugate acid. The acidity of the four conjugate acids increases in the order $HSiO_4^{3-} < HPO_4^{2-} < HSO_4^- < HClO_4$.







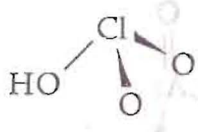


4.11 **Which of the following is the stronger acid? (a) $[Fe(OH_2)_6]^{3+}$ or $[Fe(OH_2)_6]^{2+}$?** The Fe(III) complex, $[Fe(OH_2)_6]^{3+}$, is the stronger acid by virtue of the higher charge. The electrostatic parameter, $\xi = z^2/(r + d)$, will be considerably higher for $z = 3$ than for $z = 2$. The minor decrease in $r + d$ on going from the Fe(II) to the Fe(III) species will enhance the differences in ξ for the two species.

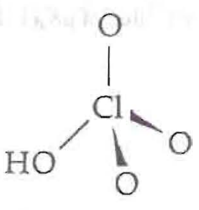
(b) $[Al(OH_2)_6]^{3+}$ or $[Ga(OH_2)_6]^{3+}$? In this case, z is the same but $r + d$ is different. Since the ionic radius, r, is smaller for period 3 Al^{3+} than for period 4 Ga^{3+}, $r + d$ for $[Al(OH_2)_6]^{3+}$ is smaller than $r + d$ for $[Ga(OH_2)_6]^{3+}$ and the aluminum-containing species is more acidic.

(c) $Si(OH)_4$ or $Ge(OH)_4$? As in part (b) above, z is the same but the $r + d$ parameter is different for these two compounds. The comparison here is also between species containing period 3 and period 4 central atoms in the same group, and the species containing the smaller central atom, $Si(OH)_4$, is more acidic.

(d) $HClO_3$ or $HClO_4$? These two acids are shown below. According to Pauling's rule 1 for mononuclear oxoacids, the species with more oxo groups has the lower pK_a and is the stronger acid. Thus, $HClO_4$ is a stronger acid than $HClO_3$. Note that the oxidation state of the central chlorine atom in the stronger acid (+7) is higher than in the weaker acid (+5).



$HClO_3$



$HClO_4$

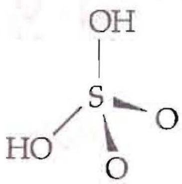
(e) H_2CrO_4 or $HMnO_4$? As in part (d) above, the oxidation states of these two acids are different, VI for the chromium atom in H_2CrO_4 and VII for the manganese atom in $HMnO_4$. The species with the higher central-atom oxidation state, $HMnO_4$, is the stronger acid. Note that this acid has more oxo groups, three, than H_2CrO_4, which has two.

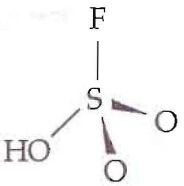
(f) H_3PO_4 or H_2SO_4? The oxidation state of sulfur in H_2SO_4 is VI, while the oxidation state of phosphorus in H_3PO_4 is only V. Furthermore, sulfuric acid has two oxo groups attached to the central sulfur atom, while phosphoric acid has only one oxo group attached to the central phosphorus atom. Therefore, on both counts (which by now you can see are really manifestations of the same thing) H_2SO_4 is a stronger acid than H_3PO_4.

4.12 **Arrange the following oxides in order of increasing basicity? Al_2O_3, B_2O_3, BaO, CO_2, Cl_2O_7, and SO_3?** First you pick out the intrinsically acidic oxides, since these will be the *least* basic. The compounds B_2O_3, CO_2, Cl_2O_7, and SO_3 are acidic, since the central element for each of them is found in the acidic region of the periodic table (see the *s* and *p* block diagram in the answer to Exercise 4.1). The most acidic compound, Cl_2O_7, has the highest central-atom oxidation state, +7, while the least acidic, B_2O_3, has the lowest, +3. Of the remaining compounds, Al_2O_3 is amphoteric, which puts it on the borderline between acidic and basic oxides, and BaO is basic. Therefore, a list of these compounds in order of increasing basicity is $Cl_2O_7 < SO_3 < CO_2 < B_2O_3 < Al_2O_3 <$ BaO.

4.13 **Arrange the following in order of increasing acidity? HSO_4^-, H_3O^+, H_4SiO_4, CH_3GeH_3, NH_3, and HSO_3F?** The weakest acids, CH_3GeH_3 and NH_3, are easy to pick out of this group since they do not contain any –OH bonds. Ammonia is the weaker acid of the two, since it has a lower central-atom oxidation state, III, than that for the germanium atom in CH_3GeH_3, which is IV. Of the remaining species, note that HSO_3F is very similar to H_2SO_4 as far as structure and sulfur oxidation state (VI) are concerned, so it is reasonable to suppose that HSO_3F is a very strong acid, which it is. The anion HSO_4^- is a considerably weaker acid than HSO_3F, for the same reason that it is a considerably weaker acid than H_2SO_4, namely, Pauling's rule 2 for mononuclear oxoacids. Since HSO_4^- is not completely deprotonated in water, it is a weaker acid than H_3O^+, which is the strongest possible acidic species in water. Finally, it is difficult to place exactly $Si(OH)_4$ in this group. It is certainly more acidic than NH_3 and CH_3GeH_3, and it turns out to be *less* acidic than HSO_4^-, despite the negative charge of the latter species. Therefore, a list of these species in order of increasing acidity is $NH_3 < CH_3GeH_3 < H_4SiO_4 < HSO_4^- < H_3O^+ < HSO_3F$.

The structures of H_2SO_4 and HSO_3F:





4.14 **Which aqua ion is the stronger acid, Na^+ or Ag^+?** Even though these two ions have about the same ionic radius, Ag^+–OH_2 bonds are much more covalent than Na^+–OH_2 bonds, a common feature of the chemistry of *d*-block vs. *s*-block metal ions. The greater covalence of the Ag^+–OH_2 bonds has the effect of delocalizing the positive charge of the cation over the whole aqua complex. As a consequence, the departing proton is repelled more by the positive charge of $Ag^+(aq)$ than by the positive charge of $Na^+(aq)$, and the former ion is the stronger.

4.15 **Which of the following elements form oxide polyanions or polycations? Al, As, Cu, Mo, Si, B, Ti?** As discussed in Sections 4.7 and 4.8, the aqua ions of metals that have amphoteric oxides generally undergo polymerization to polycations. The elements Al, Cu, and Ti fall into this category. On the other hand, polyoxoanions (oxide polyanions) are important for some of the early *d*-block metals, especially for V, Mo, and W in high oxidation states. Furthermore, many of the *p*-block elements form polyoxoanions, including As, B, and Si.

4.16 **The change in charge upon aqua ion polymerization?** One example of aqua ion polymerization is

$$2[Al(OH_2)_6]^{3+} + H_2O \rightarrow [(H_2O)_5Al\text{–}O\text{–}Al(OH_2)_5]^{4+} + 2H_3O^+$$

The charge per aluminum atom is +3 for the mononuclear species on the left-hand side of the equation but only +2 for the dinuclear species on the right-hand side. Thus, poly*cation* formation reduces the average positive charge per central M atom by +1 per M.

and Te; the trifluorides and pentafluorides of Cl, Br, and I are Lewis acids, as is the heptafluoride IF_7; the tetrafluoride and hexafluoride of xenon, XeF_4 and XeF_6, are also Lewis acids.

4.20 **Identifying acids and bases: (a) $SO_3 + H_2O \rightarrow HSO_4^- + H^+$?** The acids in this reaction are the Lewis acids SO_3 and H^+ and the base is the Lewis base OH^-. The complex (or adduct) HSO_4^- is formed by the displacement of the proton from the hydroxide ion by the stronger acid SO_3. In this way, the water molecule is thought of as an adduct of H^+ and OH^-. Since the proton must be bound to a solvent molecule, even though this fact is not explicitly shown in the reaction, the water molecule exhibits Brønsted acidity. Note that it is easy to tell that this is a displacement reaction instead of just a complex formation reaction because, while there is only one base in the reaction, there are *two* acids. A complex formation reaction only occurs with a single acid and a single base. A double displacement, or metathesis, reaction only occurs with two acids and two bases.

(b) $Me[B_{12}]^- + Hg^{2+} \rightarrow [B_{12}] + MeHg^+$? (Note: $[B_{12}]$ designates the Co center of the macrocyclic complex called coenzyme B_{12}.) This is a displacement reaction. The Lewis acid Hg^{2+} displaces the Lewis acid $[B_{12}]$ from the Lewis base CH_3^-.

(c) $KCl + SnCl_2 \rightarrow K^+ + [SnCl_3]^-$? This is also a displacement reaction. The Lewis acid $SnCl_2$ displaces the Lewis acid K^+ from the Lewis base Cl^-.

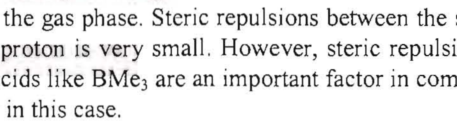
(d) $AsF_3(g) + SbF_5(g) \rightarrow [AsF_2][SbF_6]$? Even though this reaction is the formation of an ionic substance, it is *not* simply a complex formation reaction. It is a displacement reaction. The very strong Lewis acid SbF_5 (one of the strongest known) displaces the Lewis acid $[AsF_2]^+$ from the Lewis base F^-.

(e) EtOH readily dissolves in pyridine? A Lewis acid–base complex formation reaction between EtOH (the acid) and py (the base) produces the adduct EtOH–py, which is held together by the kind of dative bond that you refer to as a hydrogen bond.

4.21 **Select the compound with the named characteristic? (a) Strongest Lewis acid: BF_3, BCl_3, or BBr_3?** The simple argument that more electronegative substituents lead to a stronger Lewis acid does not work in this case. Boron tribromide is observed to be the strongest Lewis acid of these three compounds. The shorter boron–halogen bond distances in BF_3 and BCl_3 than in BBr_3 are believed to lead to stronger halogen-to-boron p–p π bonding (see Section 4.8). According to this explanation, the acceptor orbital (empty p orbital) on boron is involved to a greater extent in π bonding in BF_3 and BCl_3 than in BBr_3; the acidities of BF_3 and BCl_3 are diminished relative to BBr_3.

$BeCl_2$ or BCl_3? Boron trichloride is expected to be the stronger Lewis acid of the two for two reasons. The first reason, which is more obvious, is that the oxidation number of boron in BCl_3 is +3, while for the beryllium atom in $BeCl_2$ it is only +2. The second reason has to do with structure. The boron atom in BCl_3 is only three-coordinate, leaving a vacant site to which a Lewis base can coordinate. Since $BeCl_2$ is polymeric, each beryllium atom is four-coordinate, and some Be–Cl bonds must be broken before adduct formation can take place.

A piece of the infinite linear chain structure of $BeCl_2$. Each Be atom is four-coordinate, and each Cl atom is two-coordinate. The polymeric chains are formed by extending this piece to the right and to the left:



$B(n\text{-}Bu)_3$ or $B(t\text{-}Bu)_3$? The Lewis acid with the unbranched substituents, $B(n\text{-}Bu)_3$, is the stronger of the two because, once the complex is formed, steric repulsions between the substituents and the Lewis base will be less than with the bulky, branched substituents in $B(t\text{-}Bu)_3$.

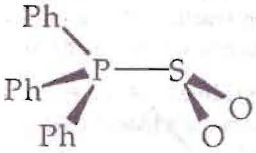
(b) More basic toward BMe_3: NMe_3 or NEt_3? These two bases have nearly equal basicities toward the proton in aqueous solution or in the gas phase. Steric repulsions between the substituents on the bases and the proton are negligible, since the proton is very small. However, steric repulsions between the substituents on the bases and *molecular* Lewis acids like BMe_3 are an important factor in complex stability, and so the smaller Lewis base NMe_3 is the stronger in this case.

2-Me-py or 4-Me-py? As above, steric factors favor complex formation with the smaller of two bases that have nearly equal Brønsted basicities. Therefore, 4-Me-py is the stronger base toward BMe_3, since the methyl substituent in this base cannot affect the strength of the B–N bond by steric repulsions with the methyl substituents on the Lewis acid.

4.22 **Which of the following reactions have $K_{eq} > 1$? (a) $R_3P\text{–}BBr_3 + R_3N\text{–}BF_3 \rightarrow R_3P\text{–}BF_3 + R_3N\text{–}BBr_3$?** From the discussion in Section 4.10, you know that phosphines are softer bases than amines. So, to determine the position of this equilibrium, you must decide which Lewis acid is softer, since the softer acid will preferentially form a complex with a soft base than with a hard base of equal strength. Boron tribromide is a softer Lewis acid than BF_3, a consequence of the relative hardness and softness of the respective halogen substituents. Therefore, the equilibrium position for this reaction will lie to the left, the side with the soft–soft and hard–hard complexes, so the equilibrium constant is less than 1. In general, it is found that soft substituents (or ligands) lead to a softer Lewis acid than for the same central element with harder substituents.

(b) $SO_2 + Ph_3P\text{–}HOCMe_3 \rightarrow Ph_3P\text{–}SO_2 + HOCMe_3$? In this reaction, the soft Lewis acid sulfur dioxide displaces the hard acid *t*-butyl alcohol from the soft base triphenylphosphine. The soft–soft complex is favored, so the equilibrium constant is greater than 1.

The adduct formed between triphenylphosphine and sulfur dioxide:



(c) $CH_3HgI + HCl \rightarrow CH_3HgCl + HI$? Iodide is a softer base than chloride, an example of the general trend that elements later in a group are softer than their progenors. The soft acid CH_3Hg^+ will form a stronger complex with iodide than with chloride, while the hard acid H^+ will prefer chloride, the harder base. Thus, the equilibrium constant is less than 1.

(d) $[AgCl_2]^-(aq) + 2\,CN^-(aq) \rightarrow [Ag\,(CN)_2]^-(aq) + 2Cl^-(aq)$? Cyanide is a softer and generally stronger base than chloride (see Table 4.3). Therefore, cyanide will displace the relatively harder base from the soft Lewis acid Ag^+. The equilibrium constant is greater than 1.

4.23 **Choose between the two basic sites in Me_2NPF_2?** The phosphorus atom in Me_2NPF_2 is the softer of the two basic sites, so it will bond more strongly with the softer Lewis acid BH_3 (see Table 4.3). The hard nitrogen atom will bond more strongly to the hard Lewis acid BF_3.

4.24 **Why does Me_3N form a relatively weak complex with BMe_3?** Since trimethylamine is the strongest Brønsted base in the gas phase, the reason that it does not form the most stable complex with trimethylboron can only be steric repulsions between the methyl substituents on the acid and those on the base.

4.25 **Discuss relative basicities? (a) Acetone and DMSO?** Since both E_B and C_B are larger for DMSO than for acetone, DMSO is the stronger base regardless of how hard or how soft the Lewis acid is. The ambiguity for DMSO is that both the oxygen atom and sulfur atom are potential basic sites.

(b) Me_2S and DMSO? Dimethylsulfide has a C_B value that is two and a half times larger than that for DMSO, while its E_B value is only one quarter that for DMSO. Thus, depending on the E_A and C_A values for the Lewis acid, either base could be stronger. For example, DMSO is the stronger base toward BF_3, while SMe_2 is the stronger base toward I_2. This can be predicted by calculating the ΔH of complex formation for all four combinations:

$$\text{DMSO–BF}_3\text{: } \Delta H = -[(20.21)(2.76) + (3.31)(5.83)] = -75.1 \text{ kJ/mol}$$

$$\text{SMe}_2\text{–BF}_3\text{: } \Delta H = -[(20.21)(0.702) + (3.31)(15.26)] = -64.7 \text{ kJ/mol}$$

$$\text{DMSO–I}_2\text{: } \Delta H = -[(2.05)(2.76) + (2.05)(5.83)] = -17.6 \text{ kJ/mol}$$

$$\text{SMe}_2\text{–I}_2\text{: } \Delta H = -[(2.05)(0.702) + (2.05)(15.26)] = -32.7 \text{ kJ/mol}$$