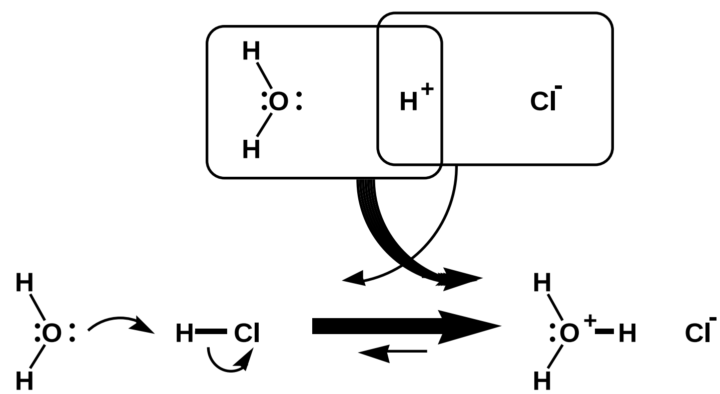
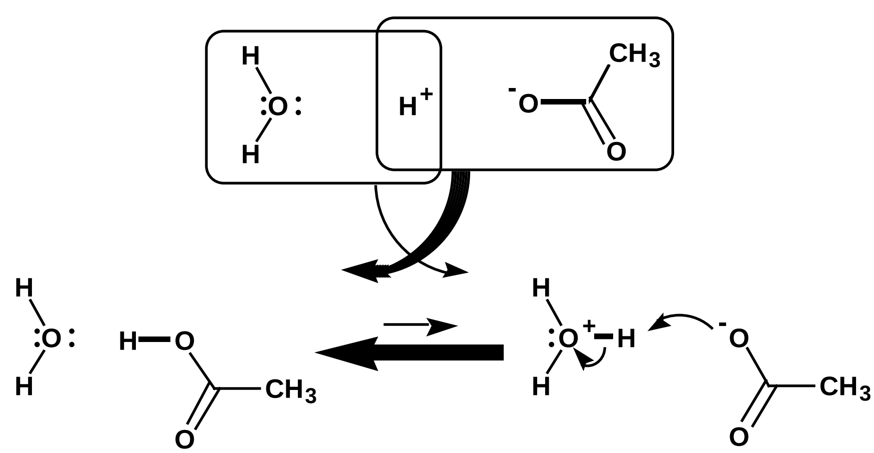
Text Related to Segment 11.03 ©2002 Claude E. Wintner

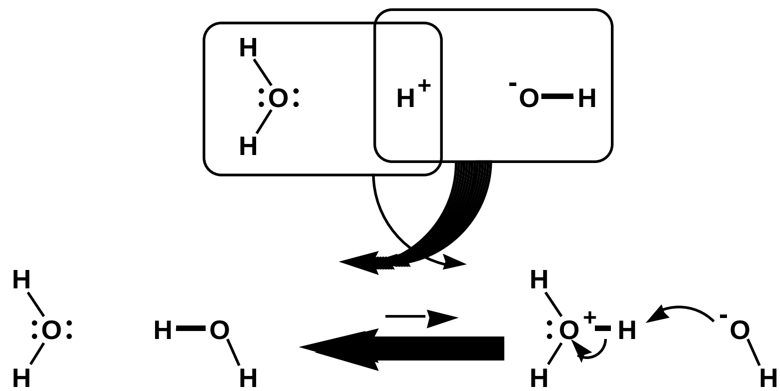
The examples already mentioned not only are readily discussed, but also can be elaborated substantially, when the Lewis definitions are employed. The case of aqueous HCl is interpreted as a competition of two bases, the solvent water and chloride ion, for the proton. Water is the stronger base, forming a bond with the proton to form hydronium ion, H_3O^+, essentially to the exclusion of any bonding of chloride ion with the proton:



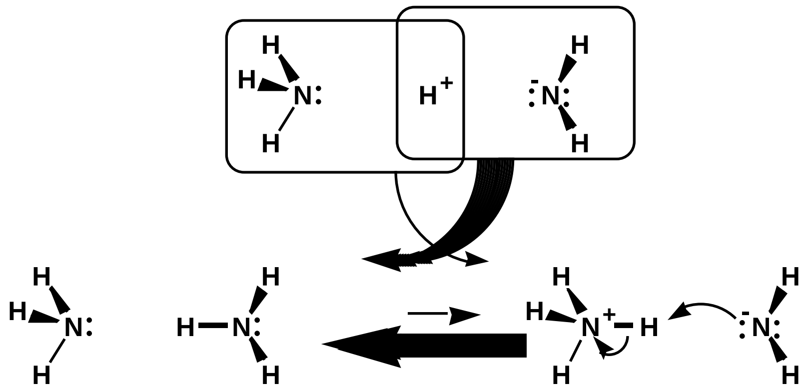
On the other hand, for acetic acid the two competing bases are the solvent water and acetate anion, with the latter being the stronger base, so that acetic acid remains largely undissociated in water solution:



Finally, in the case of water itself hydroxide ion is a far stronger base than is water. In consequence — and as we already have emphasized in Segment 11.01 — protons (or, equivalently, hydronium ions) cannot exist in any significant concentration in the presence of an excess of hydroxide ions:



Of course, water need not always be the solvent, but the Lewis definitions permit an equivalent analysis when it is not. Amide anion, NH_2^-, is a much stronger base than is ammonia, and ammonia is an extremely weak acid, not losing a proton except in the presence of very strong bases, that is, bases stronger than amide anion; the pK_A of ammonia is 32:

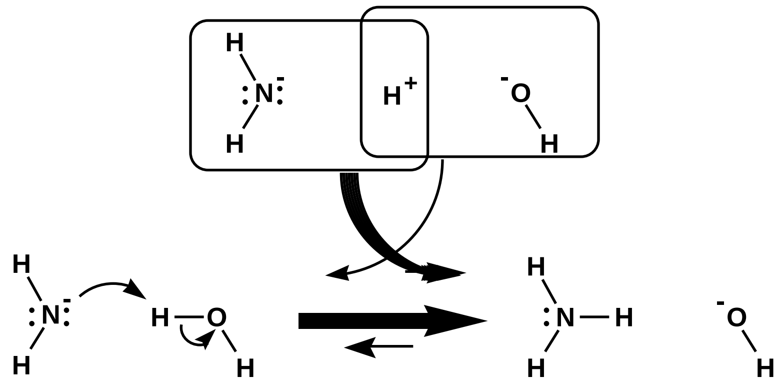


$$NH_3 \rightleftharpoons H^+ \quad {}^-NH_2$$

$$K_A = \frac{[H^+][{}^-NH_2]}{[NH_3]} = 10^{-32}$$

$$pK_A = 32$$

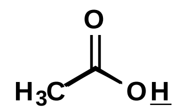
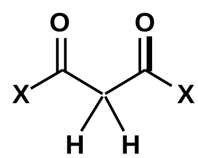
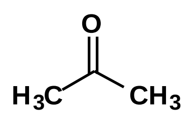
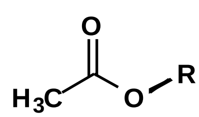
Thus, amide anion is a far stronger base than is hydroxide ion. From this we can know both that hydroxide ion cannot be used effectively to remove a proton from ammonia and that amide anion will — essentially quantitatively — remove a proton from water, to form hydroxide ion; that is, amide anion is neutralized by the relatively strong acid water, and so cannot exist in the presence of water. Again, then, there is an important general point to be remembered — in this case particularly when one is writing reaction mechanisms involving both water and ammonia: *do not invoke a base to pull off the proton from an acid whose corresponding base ("conjugate base") is stronger than the base that is being invoked!*



$$K_{eq} = \frac{[NH_3]\,[^{-}OH]}{[^{-}NH_2]\,[H_2O]} = \frac{[NH_3]\,[^{-}OH]\,[H^+]}{[^{-}NH_2]\,[H_2O]\,[H^+]} = \frac{[NH_3]}{[^{-}NH_2]\,[H^+]} \times \frac{[^{-}OH]\,[H^+]}{[H_2O]}$$

$$K_{eq} = 10^{32} \times 10^{-15.8} = 10^{16.2}$$

This is perhaps a good moment to attach a listing of just a few useful pK_A values, among them those that already have been mentioned:

	pK_A
HBr	< 0
H_3O^+	[0]
	4.8
H_2S	7
RSH	8 - 12
$^+NH_4$	9.3
	9 - 13
H_2O	15.8
ROH	16 - 18
	19
	22
$H-C\equiv C-H$	25
NH_3	32
CH_4	> 50

some useful pK_A values

In the sequel we shall be using such data routinely. For example, in substitution reactions we shall see that hydroxide ion can replace bromide ion. Such reactions are initiated by bases, and it makes thermodynamic sense that strong bases should replace weak ones. As another illustration, hydroxide ion is a base sufficiently strong to remove a proton from hydrogen sulfide or a thiol, or from an ammonium cation. However, a base stronger than hydroxide ion must be used to remove a proton in significant concentration from most alcohols or from any other species having a pK_A value higher than that of water:

$$\mathbf{ROH} \qquad {}^{-}\mathbf{OH} \quad \rightleftharpoons \quad {}^{-}\mathbf{OR} \qquad \mathbf{H_2O}$$

$$K_{eq} = \frac{[{}^{-}OR]\,[H_2O]}{[ROH]\,[{}^{-}OH]} = \frac{[{}^{-}OR]\,[H_2O]\,[H^+]}{[ROH]\,[{}^{-}OH]\,[H^+]} = \frac{[{}^{-}OR]\,[H^+]}{[ROH]} \times \frac{[H_2O]}{[{}^{-}OH]\,[H^+]}$$

$$K_{eq} \approx 10^{-18} \times 10^{15.8} \approx 10^{-2}$$

hydroxide ion is not a strong enough base to remove a proton in significant concentration from most alcohols

It will be noted that in moving from right to left in the periodic table from the hydride of oxygen (water) to the hydride of nitrogen (ammonia) the acidity has decreased (and thus the pK_A has increased, as has the base strength of the corresponding base). Going left one column further brings us to the hydride of carbon, that is, to methane, which might then be expected to be an acid even weaker than ammonia. Indeed, there is no practical way to remove a proton from methane to form methide anion directly. On the other hand, methide anion can be formed indirectly by what is known as a Grignard reaction. Bromomethane reacts with magnesium metal in *dry* diethyl ether to form methylmagnesium bromide. This species, although it is, in fact, more covalent than ionic, nevertheless effectively behaves as though it were methide anion accompanied by the bromomagnesium complex cation:

$$CH_3Br \quad Mg \xrightarrow[\text{diethyl ether}]{\text{dry}} CH_3MgBr \longleftrightarrow H_3C^{-} \; {}^{+}MgBr$$

The pK_A of methane must be estimated indirectly, but it is at least 50. Methylmagnesium bromide therefore is a base strong enough (by at least 18 powers of 10) to remove a proton from ammonia, to form methane and amide anion:

$$K_{eq} = \frac{[CH_4]\,[^{-}NH_2]}{[^{-}CH_3]\,[NH_3]} = \frac{[CH_4]\,[^{-}NH_2]\,[H^+]}{[^{-}CH_3]\,[NH_3]\,[H^+]} = \frac{[CH_4]}{[^{-}CH_3]\,[H^+]} \times \frac{[^{-}NH_2]\,[H^+]}{[NH_3]}$$

$$K_{eq} \approx 10^{50} \times 10^{-32} \approx 10^{18}$$

Furthermore, methylmagnesium bromide is a base strong enough (by at least 34 powers of 10) to remove a proton from water, to form methane and hydroxide ion. This is why the ether in a Grignard reaction must be absolutely free of water, or else the reaction will fail because, in effect, it never can start.

$$K_{eq} = \frac{[CH_4]\,[^{-}OH]}{[^{-}CH_3]\,[H_2O]} = \frac{[CH_4]\,[^{-}OH]\,[H^+]}{[^{-}CH_3]\,[H_2O]\,[H^+]} = \frac{[CH_4]}{[^{-}CH_3]\,[H^+]} \times \frac{[^{-}OH]\,[H^+]}{[H_2O]}$$

$$K_{eq} \approx 10^{50} \times 10^{-15.8} \approx 10^{34}$$