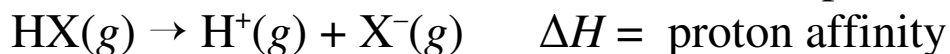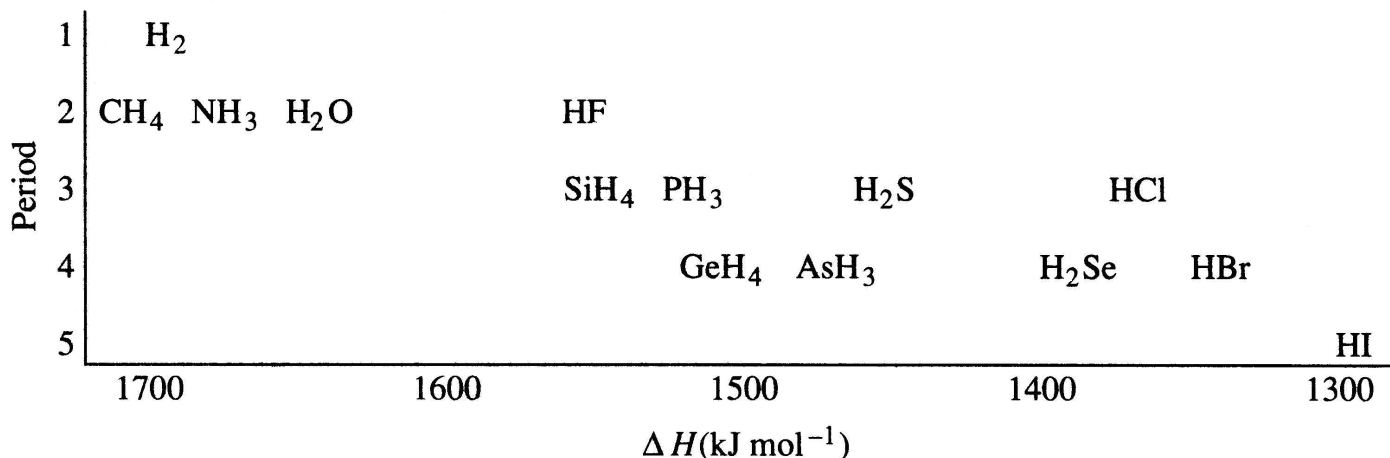# Acidity of H$_n$X Compounds
No Solvent

- In the absence of a solvent, the acidity of HX compounds is related to the ease of dissociation into ions, which defines the proton affinity:
$$HX(g) \rightarrow H^+(g) + X^-(g) \qquad \Delta H = \text{ proton affinity}$$
 - Lower ΔH means greater acidity of HX and lesser basicity of X^-.

- Group trend — Acidity increases with increasing size of X.
  - H–X bond becomes weaker with larger X.

- Period trend — Acidity increases across the period.
  - Positive charge on H increases as electronegativity of X increases, facilitating formation of H$^+$.

Period 2 H$_n$X	q(H)	Period 3 H$_n$X	q(H)
CH$_4$	–0.04	SiH$_4$	–0.72
NH$_3$	+0.35	PH$_3$	–0.57
H$_2$O	+0.63	H$_2$S	–0.14
HF	+0.78	HCl	+0.22

Data from R. J. Gillespie and P. L. A. Popelier, *Chemical Bonding and Molecular Geometry*, Oxford University Press, NY, 2001, pp. 192 & 238.

HX Strength in Water

- Acid strength in water depends on more than proton affinity.

- K_a is related to the Gibbs free energy of the following process:

$$HX(aq) \rightarrow H^+(aq) + X^-(aq) \quad \Delta G^\circ_{diss} = -RT \ln K_a$$
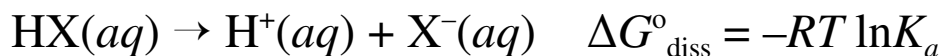
  in which $H^+(aq)$ is H_3O^+.

- Converting to base-10 logarithms and assuming $T = 298.15K$,

$$\Delta G^\circ_{diss} = -(2.303)(8.314 \times 10^{-3} \text{ kJ/mol·K})(298.15K) \log K_a$$

$$pK_a = \Delta G^\circ_{diss}/5.709$$

- If $\Delta G^\circ_{diss} < 0$, the acid is strong; if $\Delta G^\circ_{diss} > 0$, the acid is weak.

Hess's Law Cycle Analysis of ΔG^o_{diss}

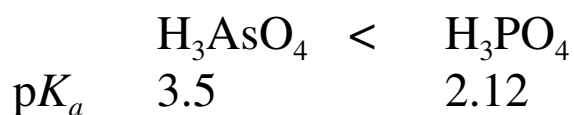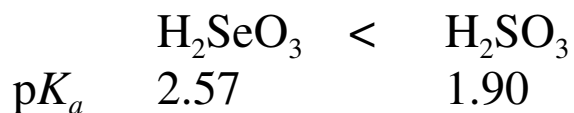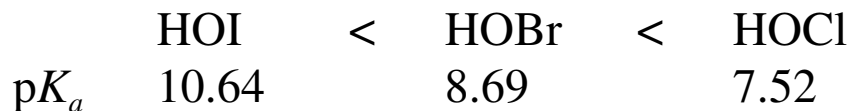- ΔG^o_{diss} can be analyzed in terms of a Hess's Law cycle such as the following:

$$
\begin{array}{ccc}
HX(g) & \xrightarrow{\;\;\Delta G^o_P\;\;} & H^+(g) \;\; + \;\; X^-(g) \\
\Big\uparrow {-\Delta G^o_{aq}(HX)} & & \Big\downarrow \Delta G^o_{aq}(H^+) \quad \Big\downarrow \Delta G^o_{aq}(X^-) \\
HX(aq) & \xrightarrow[\;\;\Delta G^o_{diss}\;\;]{} & H^+(aq) \;\; + \;\; X^-(aq)
\end{array}
$$
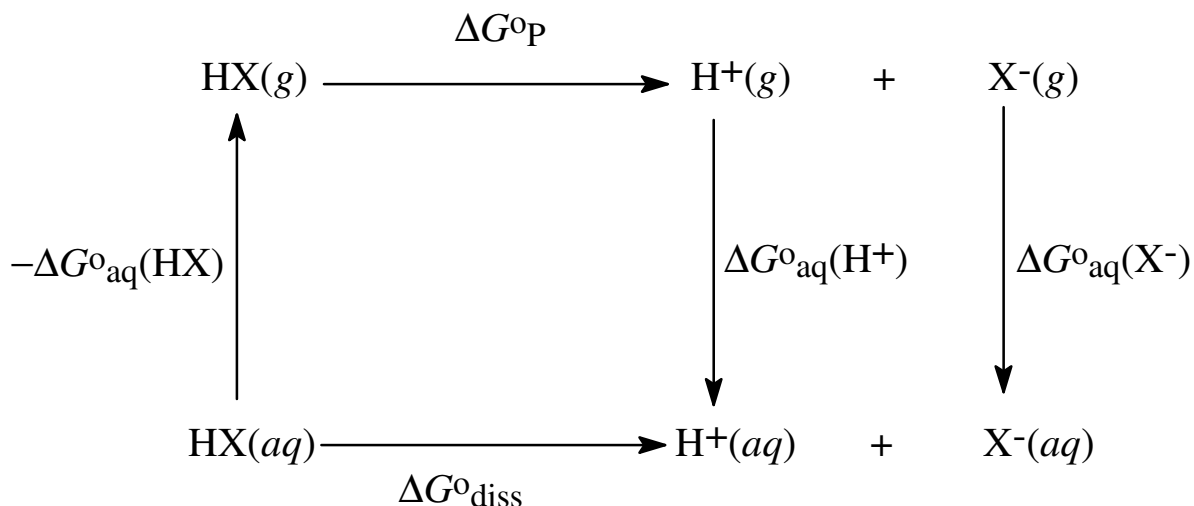
$$
\Delta G^o_{diss} = -\Delta G^o_{aq}(HX) + \Delta G^o_P + \Delta G^o_{aq}(H^+) + \Delta G^o_{aq}(X^-)
$$
$$
\qquad\qquad + \qquad\qquad\quad + \qquad\qquad - \qquad\qquad -
$$

- The balance between the positive and negative contributions of these steps determines whether the acid is strong or weak and the value of pK_a.

- Although precise analysis of acid strengths requires thermodynamic considerations, for some classes of acids empirical relationships based on structure can be remarkably predictive.
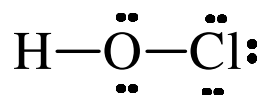
Oxoacids, $HOXO_n$

1. Among acids of the same structure type, acid strength increases with the electronegativity of the central X atom.

$$HOI \quad < \quad HOBr \quad < \quad HOCl$$
$$pK_a \quad 10.64 \qquad 8.69 \qquad 7.52$$

$$H_2SeO_3 \quad < \quad H_2SO_3$$
$$pK_a \quad 2.57 \qquad 1.90$$

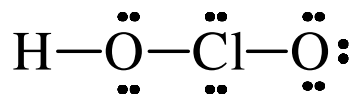$$H_3AsO_4 \quad < \quad H_3PO_4$$
$$pK_a \quad 3.5 \qquad 2.12$$

✓ The acidic H atom is always part of an –OH group.

✓ As electronegativity of X increases, the polarity of the –O–H bond increases, making removal of H^+ by solvent water more favorable.
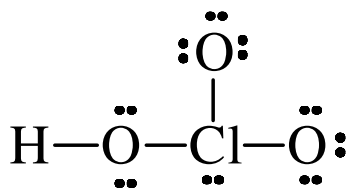
Oxoacids, $HOXO_n$

2. Acidity increases as the number of terminal (or non-hydroxy) oxygen atoms attached to X increases.
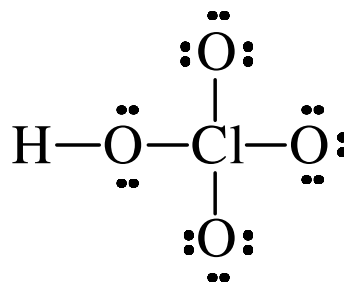
$$HOCl < HOClO < HOClO_2 < HOClO_3$$

H—Ö—Cl:

$K_a = 3.2 \times 10^{-8}$

H—Ö—Cl—Ö:

$K_a = 1.1 \times 10^{-2}$

:Ö:
|
H—Ö—Cl—Ö:

$K_a \gg 1$

:Ö:
|
H—Ö—Cl—Ö:
|
:Ö:

$K_a \gg 1$

✓   The electron withdrawing ability of the terminal –O atoms increases the formal charge on the central X atom, decreasing electron density in the –O–H bond, thereby weakening it. This is an example of an ***inductive effect***.

Oxoacids, HOXO$_n$

☞ The number of terminal (non-hydroxy) oxygen atoms in the oxoacids bears a strong correlation to K_a.

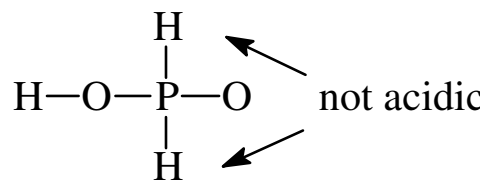| –O atoms	K_a range	pK_a	Strength
0	$10^{-7} - 10^{-10}$	8.5 ± 1.5	very weak
1	$10^{-1} - 10^{-4}$	2.5 ± 1.5	weak
2	$> 10^{-1}$	< 1	strong
3	$\gg 1$	$\ll -1$	very strong

Oxoacids, HOXO$_n$

☞ Some care must be used in predicting acid strengths from formulas, because the actual structure may not be apparent.

✓ For example, H_3PO_4, H_3PO_3, and H_3PO_2 all have only one terminal –O in their structures and therefore have similar strengths.
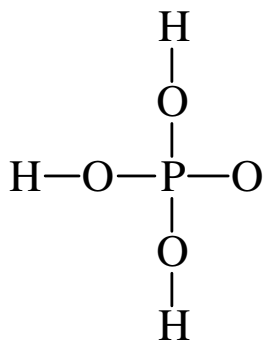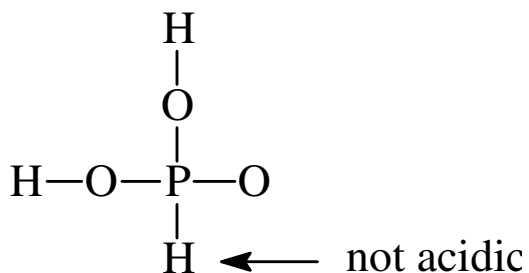
$K_a = 7.6 \times 10^{-3}$ $\qquad$ $K_a = 1.6 \times 10^{-2}$ $\qquad$ $K_a = 1 \times 10^{-2}$
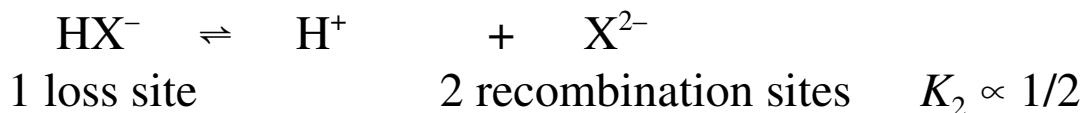
Successive K_a Values of Polyprotic Acids

☞ Virtually all polyprotic acids have decreasing successive K_a values; i.e., $K_1 > K_2 > ... > K_n$

● For typical inorganic and small organic acids this trend can be understood as a result of *statistical* and *Coulombic* factors.
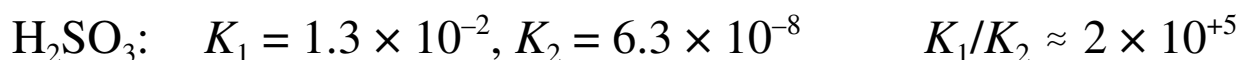
Statistical Argument for $K_1 > K_2$

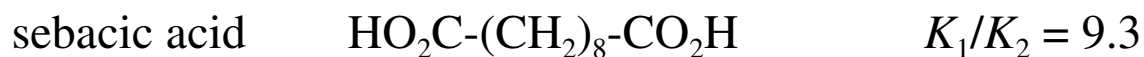☞ Statistics of available sites for H^+ loss versus HX recombination predict $K_1 > K_2$.

$$HXH \rightleftharpoons H^+ \quad + \quad HX^-$$

2 loss sites   1 recombination site $K_1 \propto 2/1$

$$HX^- \rightleftharpoons H^+ \quad + \quad X^{2-}$$

1 loss site   2 recombination sites $K_2 \propto 1/2$

$$K_1/K_2 = 4$$

● K_1/K_2 is always greater than 4, usually being a factor of several orders of magnitude.

H_2SO_3: $K_1 = 1.3 \times 10^{-2}$, $K_2 = 6.3 \times 10^{-8}$ $K_1/K_2 \approx 2 \times 10^{+5}$

● Only with large molecules, where acidic sites are widely separated, does K_1/K_2 approach a value of 4.

malonic acid $HO_2C\text{-}CH_2\text{-}CO_2H$ $K_1/K_2 = 1120$

sebacic acid $HO_2C\text{-}(CH_2)_8\text{-}CO_2H$ $K_1/K_2 = 9.3$
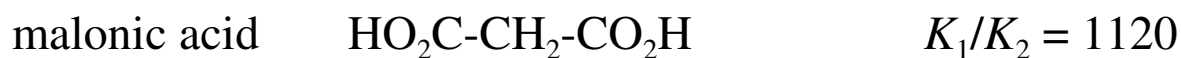
Coulombic Argument for $K_1 > K_2$

☞   Coulombic repulsion is usually responsible for $K_1/K_2 > 4$.

● When one H^+ is removed, the second H^+ must be removed from a negative HX^- ion.

● Most oxoacids have $K_1/K_2 \approx 10^4 - 10^6$.

<p style="text-align:center">Example: H_2SO_3, $K_1/K_2 \approx 2 \times 10^{+5}$</p>

● For acids with both hydrogen atoms bound directly to the same atom, $K_1/K_2 \approx 10^7 - 10^{12}$.

<p style="text-align:center">Example: H_2S, $K_1/K_2 \approx 10^{-7}/10^{-19} = 10^{+12}$</p>

Hydrated Cations

☞   The ***total hydration sphere*** is the total number of water molecules associated with an ion in solution.

✓   The number of water molecules in the total hydration sphere is determined by the ***charge density*** of the ion.

Crystallographic and Approximate Hydrated Radii of Alkali Metal Ions

Ion	r_{ion} (pm)	r_{hyd} (pm)	$n_t(H_2O)$
Li^+	60	340	25.3
Na^+	95	276	16.6
K^+	133	232	10.5
Rb^+	148	228	~10
Cs^+	169	228	9.9

First Hydration Sphere

☞   The *first hydration sphere* is defined as the number of water molecules in *direct contact* with the ion.

✓   The number of water molecules in the first hydration sphere depends only on the size of the ion.

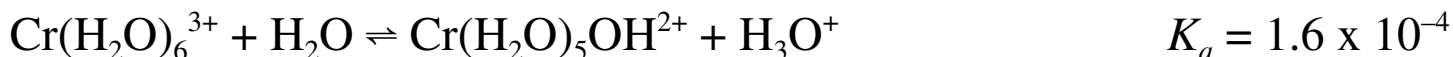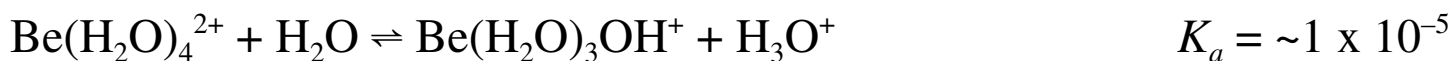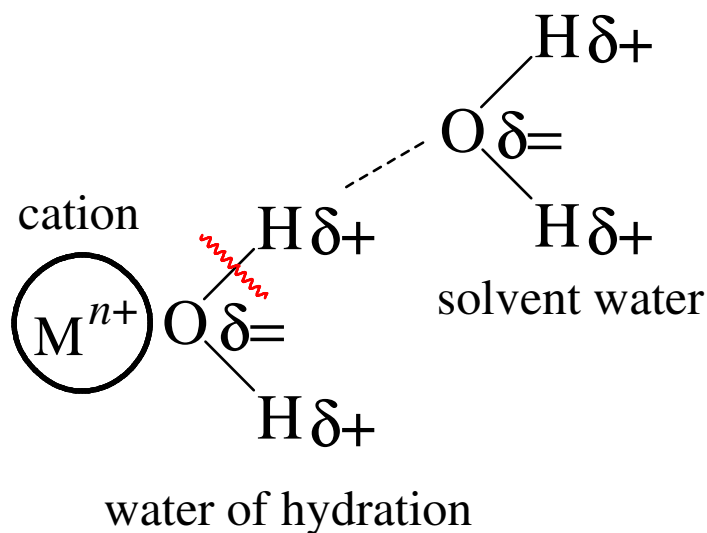✓   Typical cations have first hydration spheres with four to six water molecules; e.g.,

$$Be(H_2O)_4^{2+} \qquad Mg(H_2O)_6^{2+} \qquad Al(H_2O)_6^{3+}$$

$$Hg(H_2O)_6^{2+} \qquad\qquad Cr(H_2O)_6^{3+}$$

● The number of water molecules in the first hydration sphere depends principally on cation size.

r_{ion} (pm)	$n(H_2O)$
<30	3
30 – 50	4
50-110	6
>110	>8

●   Contrary to these criteria, the lighter alkali metal cations appear to be $Li(H_2O)_4^+$, $Na(H_2O)_4^+$, $K(H_2O)_4^+$.

Acidic Hydrated Cations

☞ Ion-dipole attractions have an inductive effect on the O–H bonds of the water molecules in the first hydration sphere, which weakens the bond and may allow H^+ to be lost to solvent water.

water of hydration

$Be(H_2O)_4{}^{2+} + H_2O \rightleftharpoons Be(H_2O)_3OH^+ + H_3O^+$ $\qquad K_a = \sim 1 \times 10^{-5}$

$Cr(H_2O)_6{}^{3+} + H_2O \rightleftharpoons Cr(H_2O)_5OH^{2+} + H_3O^+$ $\qquad K_a = 1.6 \times 10^{-4}$

✓ This means that when we dissolve an ionic compound in water, the cation may affect the acid-base character of the solution.

Acidic and Non-Acidic Hydrated Cations

☞ As the charge density experienced by water molecules in the first hydration sphere increases the acidity increases.

✓ Smaller and more highly charged cations tend to be acidic.

✓ The alkali and alkaline earth cations (with the exceptions of Be^{2+} and Mg^{2+}) are too large and too lowly charged to have any appreciable acidity.

✓ Transition metal cations tend to be more acidic than non-transition metal ions of comparable charge and size, because the poorer shielding d-subshell allows more of the nuclear charge to be experienced by the attached water molecules; i.e., they have higher effective nuclear charges, Z^*.
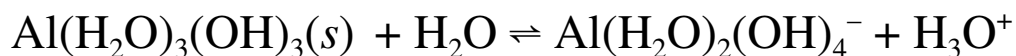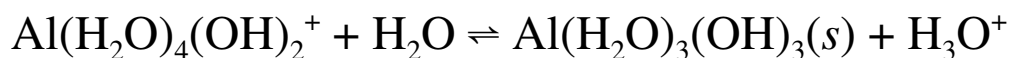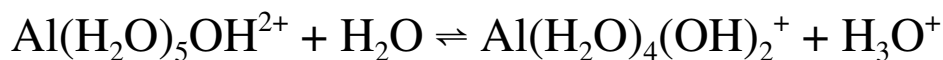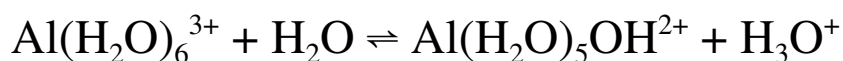
K_a Values of Some Hydrated Cation Species

Species	K_a
$Fe(H_2O)_6^{3+}$	1.84×10^{-3}
$Hg(H_2O)_6^{2+}$	2.6×10^{-4}
$Cr(H_2O)_6^{3+}$	1.6×10^{-4}
$Be(H_2O)_4^{2+}$	$\sim 1 \times 10^{-5}$
$Al(H_2O)_6^{3+}$	7.9×10^{-6}
$Cd(H_2O)_6^{2+}$	8.32×10^{-7}
$Cu(H_2O)_6^{2+}$	1.6×10^{-7}
$Pb(H_2O)_6^{2+}$	1.5×10^{-8}
$Co(H_2O)_6^{2+}$	1.3×10^{-9}
$Zn(H_2O)_6^{2+}$	2.5×10^{-10}
$Ni(H_2O)_6^{2+}$	2.5×10^{-11}
$Fe(H_2O)_6^{2+}$	$\sim 1 \times 10^{-11}$
$Mn(H_2O)_6^{2+}$	$\sim 6 \times 10^{-12}$
$Mg(H_2O)_6^{2+}$	$\sim 4 \times 10^{-12}$
$Ag(H_2O)_2^{+}$	$\sim 7 \times 10^{-13}$
$Al(H_2O)_3(OH)_3(s)$	$\sim 4 \times 10^{-13}$
$Ca(H_2O)_6^{2+}$	3.2×10^{-13}

Hydrated Cations as Polyprotic Acids

☞ Hydrated cations with appreciable acidity often act as polyprotic acids.

✓ Hydrated Al^{3+} can act as a tetraprotic acid:

$$Al(H_2O)_6^{3+} + H_2O \rightleftharpoons Al(H_2O)_5OH^{2+} + H_3O^+$$

$$Al(H_2O)_5OH^{2+} + H_2O \rightleftharpoons Al(H_2O)_4(OH)_2^+ + H_3O^+$$

$$Al(H_2O)_4(OH)_2^+ + H_2O \rightleftharpoons Al(H_2O)_3(OH)_3(s) + H_3O^+$$

$$Al(H_2O)_3(OH)_3(s) + H_2O \rightleftharpoons Al(H_2O)_2(OH)_4^- + H_3O^+$$

✓ The addition of a strong base, such as OH^-, is necessary to drive the equilibria to the right by removal of the H_3O^+ by neutralization.

Oxoanions as Bases
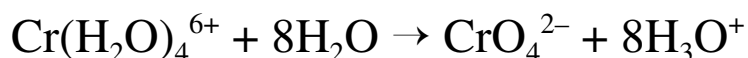
- Most inorganic oxoanions, AO_n^{x-}, have a central atom in a high oxidation state.

Anion	CO_3^{2-}	SO_3^{2-}	SO_4^{2-}	ClO_4^{-}	CrO_4^{2-}	MnO_4^{-}
A ox. state	+4	+4	+6	+7	+6	+7

- If such highly charged cations were real and were added to water, they would immediately lose all hydrogen ions from their waters of hydration to become the oxoanions; e.g.,

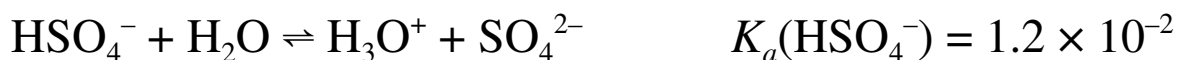$$Cr(H_2O)_4^{6+} + 8H_2O \rightarrow CrO_4^{2-} + 8H_3O^+$$

- Aprotic oxoanions are the conjugate bases of an acid, and as such may be genuine bases in water.

  - If the conjugate acid is strong, the oxoacid has no basic character.

  $$HClO_4 + H_2O \rightarrow H_3O^+ + ClO_4^- \qquad K_a(HClO_4) \gg 1 \quad K_b \ll 10^{-14}$$

  - If the conjugate acid is weak, the oxoanion will be a weak base whose strength is greater as its related acid's strength is weaker.

  $$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-} \qquad K_a(HSO_4^-) = 1.2 \times 10^{-2}$$

  $$K_b(SO_4^{2-}) = K_w/K_a = 1.0 \times 10^{-14}/1.2 \times 10^{-2} = 8.3 \times 10^{-13}$$

 $$HCrO_4^- + H_2O \rightleftharpoons H_3O^+ + CrO_4^{2-} \qquad K_a(HCrO_4^-) = 3.2 \times 10^{-7}$$
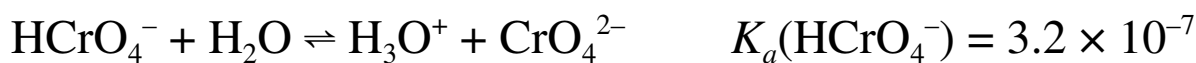
  $$K_b(CrO_4^{2-}) = K_w/K_a = 1.0 \times 10^{-14}/3.2 \times 10^{-7} = 3.1 \times 10^{-8}$$

Inductive Effects

- Electron withdrawing or donating groups can affect acid-base strengths.

- The acidity of a carboxylic acid can be enhanced by adding electronegative atoms to the rest of the molecule.

  - The electron-withdrawing ability of electronegative atoms weakens the $-O-H$ bond (inductive effect), thereby enhancing the ability of solvent water to remove H^+.

Acid	K_a
CH_3CO_2H	1.77×10^{-5}
$BrCH_2CO_2H$	2.05×10^{-3}
$ClCH_2CO_2H$	1.40×10^{-3}
Cl_2CHCO_2H	3.32×10^{-2}
Cl_3CCO_2H	2×10^{-1}
F_3CCO_2H	5×10^{-1}

- Base strengths of pyramidal NX_3 species depend on the donor or acceptor nature of the X ligands.

  - Lewis base strength:
 $$NMe_3 > NHMe_2 > NH_2Me > NH_3 > NHF_2 >> NF_3$$
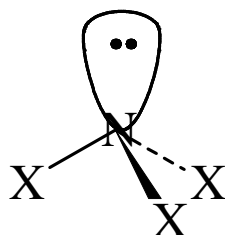
Inductive Effects - Mitigating Factors

- Acid strength of the BX_3 compounds (X = F, Cl, Br) might be expected to increase with increasing electronegativity of X, but the observed order of acid strength is

$$BBr_3 > BCl_3 \gg BF_3$$

- Classic explanation of this is that loss of π-bonding on adduct formation is most important in BF_3 and less important in BCl_3 and BBr_3, where the energies of the central B $2p_z$ orbital does not match as well with the energy of either the $3p$ orbitals of Cl or the $4p$ orbitals of Br.

"filled" p_z

"empty" p_z
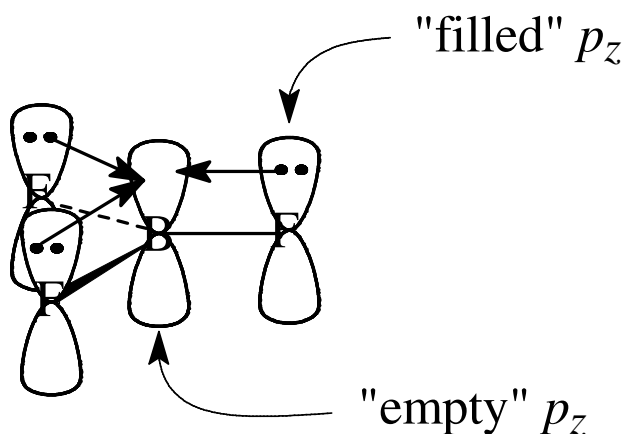
- Some properties of BX_3 adducts suggest that the strength of the boron-to-adduct bonds may be $BBr_3 > BCl_3 > BF_3$, which would also predict that BF_3 would be the weakest Lewis acid.

- Steric factors may be important, with more room available for donor approach in BBr_3.

☞   No one explanation appears to give an entirely satisfactory explanation for the Lewis acid trend of the boron trihalides.