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When discussing acids and bases, most first-year chemistry textbooks *(1–4)* have a section that compares the strengths of binary acids. An attempt is made to correlate the strengths of the acids with molecular properties of the acids. For example, it is argued that the factor determining the relative strength of the hydrohalic acids decreases in the order HF << HCl < HBr < HI owing to the decreasing bond strength over this series. This argument can be applied to the hydrochalcogenic acids $H_2O < H_2S < H_2Se < H_2Te$. To summarize these arguments, going down a particular group in the periodic table, the binary acid strength increases because the H–X bond strength (where X is a nonmetal) decreases. This explanation seems quite reasonable on the surface. While the trend is correct, the explanation is overly simplistic for reasons to be outlined below. This explanation is also misleading and is a point that is not normally addressed again in the curriculum.

Table 1. Gas-Phase Homolytic H–X Bond Strengths, Pauling Electronegativity Differences, and pK_a Values for the Binary Acids

increasing acid strength →				
H–CH₃ 438ᵃ [0.4]ᵇ {49}ᶜ	H–NH₂ 450 [0.9] {34}	H–OH 498 [1.4] {14.0}	H–F 570 [1.9] {3.2}	increasing acid strength ↓
H–SiH₃ 384 [−0.3]	H–PH₂ 351 [0.0]	H–SH 381 [0.4] {7.05}	H–Cl 432 [0.9] {−3}	
		H–SeH 335 [0.3] {3.89}	H–Br 366 [0.7] {−6}	
		H–TeH 277 [0.0] {2.6}	H–I 298 [0.4] {−7}	

ᵃBond strengths, in kJ mol⁻¹, are from ref *8*. ᵇElectronegativity difference [in square brackets] is the electronegativity of X minus the electronegativity of the hydrogen atom. ᶜpK_a values {in curly brackets}.

Table 2. Heterolytic Bond Dissociation Enthalpies in the Gas Phase

Acid	ΔH_{bond}/(kJ mol⁻¹)
CH₄	1744
NH₃	1688
H₂O	1633
H₂S	1468
HF	1554
HCl	1395
HBr	1353
HI	1314
HClO₄	1200

One minor aspect is that the bond strengths used are gas-phase bond strengths. More importantly, though, the bond energies that the textbooks refer to are for homolytic bond dissociation, yielding radicals:

$$HX(g) \rightarrow H^\bullet(g) + X^\bullet(g) \tag{1}$$
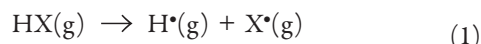
Clearly, when teaching and comparing strengths of acids, the textbooks and instructors are talking about processes in the aqueous phase where the bond strength is for heterolytic cleavage, yielding ions:

$$HX(aq) \rightarrow H^+(aq) + X^-(aq) \tag{2}$$
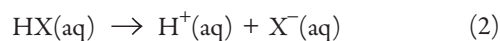
Probably the most confusing aspect of correlating the trend in binary acid strength with the bond dissociation energies corresponding to eq 1 is that the trend does not work when going across a period. For example, the acid strengths increase over the series $CH_4 < NH_3 < H_2O < HF$, yet the H−X bond strengths *also increase* over this series as seen in Table 1. To explain the trend in acid strengths of binary acids when going across the periodic table, bond polarity is the physical property that is used. It is argued, correctly, that the greater the difference in electronegativity, the more polar the bond. Therefore the H−X bond will break with a greater propensity for losing H⁺. The difference in electronegativity, then, is used as a correlative measure of the acid strength when going across the periodic table. In Table 1 it can be seen that this is true when going from left to right across a period. The pK_a decreases and the bond polarity does increase as indicated by the increasing electronegativity difference. The problem, though, is that when going down a group, the bond polarity decreases but the acid strength increases, which should be quite unsatisfactory to an instructor of undergraduate students and at best confusing for students if they really thought about it.

Clearly the two physical properties that are used to explain the observed trends in acid strength appear to be contradictory. It would be an easy task to show that the acid strength is correlated with the gas-phase heterolytic bond dissociation energies (Table 2) that are readily available *(5)*. However, the molecular properties of the acids are hidden in the heterolytic bond dissociation energies and this still ignores solvation energies of the ions.

A slightly more complicated explanation breaks down the heterolytic bond dissociation energies into homolytic bond dissociation energies and the energies associated with electron transfer and also accounts for the hydration energies. It preserves the homolytic bond dissociation explanation, but replaces the bond polarities with an electron affinity rationalization. It is this explanation that I hope will be adopted by general chemistry textbooks such as those cited above using molecular properties to compare acid strengths. This topic typically follows the teaching of concepts such as thermochemistry, Hess's law, Born–Haber cycles, bond dissociation energy (ΔH_{bond}), ionization energy (IE), and electron affinity (EA) that have already been introduced. The EA used here follows the IUPAC definition as the energy released when an electron is added to a neutral atom or molecule. Admittedly, the explanation given here is not complete since entropy effects are necessary to have a more complete

discussion. The trends in acid strengths have been explained using free energies associated with eq 2 but only for the hydrohalic acids (6). It should be pointed out that ΔH_{acid} is not associated with the reaction in eq 2 since enthalpy values for dissolving and not dissociating the acids in water are unknown.

The Born–Haber cycle, which relates the enthalpy associated with dissolving an acid in its standard state (gas for all acids except water) and dissociating them in aqueous solution (ΔH_{acid}) to the bond dissociation energy, the electron affinity of X(g), the ionization energy of a hydrogen atom, and the hydration energies ($\Delta_{hyd}H$) of the gaseous ions, is shown in Figure 1. It is the value of ΔH_{acid} that we want to compare with the trend in acid strength and is given by

$$\Delta H_{acid} = \Delta H_{bond} + IE(H) - EA(X) \qquad (3)$$
$$+ \Delta_{hyd}H(H^+) + \Delta_{hyd}H(X^-)$$

The values to be used in this equation are given in Table 3 along with the values of ΔH_{acid}. The ionization energy of hydrogen and the hydration energy of the proton used here are 1312 and -1103 kJ mol^{-1}, respectively (7). Note also that for water, HX must be vaporized ($\Delta_{vap}H = 41$ kJ mol^{-1}). Also in Table 3 are the values of ΔH_{acid} for the binary acids as well as for some chloro-oxoacids. It can be seen for the binary acids the values of ΔH_{acid} follow the trends observed for acid strength. Also looking at Table 3 it can be seen that the trend for the hydrohalic acids can be "mostly" attributed to bond dissociation energies. These fall considerably as the halogen gets larger so it plays the largest factor in determining the acid strength. Note that for HF, HCl, HBr, and HI, the electron affinities do not change considerably. The hydration energies also change somewhat, but these changes do not increase acidity, they actually counter acid strength. The changes in the hydration energies are more than offset by the decrease in bond dissociation energies though. There is a slight discrepancy in that the ΔH_{acid} values for HBr and HI are reversed compared to the acid strengths. This discrepancy could be taken care of when entropies are taken into account but probably is due to error in one or more of the bond energy, electron affinity, or, most likely, the hydration energy. Nevertheless the ΔH_{acid} values are close as are the observed acid strengths.

For methane, ammonia, water, and hydrofluoric acid the trend in acidity can be seen to be mainly due to the large increase in electron affinities since the bond energies do not change dramatically over this series. There is also not expected to be a large difference in hydration energies. While students may not be versed in electron affinities of polyatomic species, it can be noted that the electron affinity of the hydride follows the same trend as the electron affinity of the central atoms, C, N, and O.

While the discussion has been entirely on binary acids, these arguments can also be applied to the oxoacids. At the bottom of Table 3 are also listed the parameters to calculate ΔH_{acid} for perchloric, chloric, and chlorous acids. The H−O bond energies do not change to any appreciable extent while the electron affinities of ClO_4, ClO_3, and ClO_2 change significantly, which is due to the extra oxygen atom. Note also that similar to the hydrohalic acids, the hydration energy opposes the acid strength but this is offset by the larger change in electron affinities.

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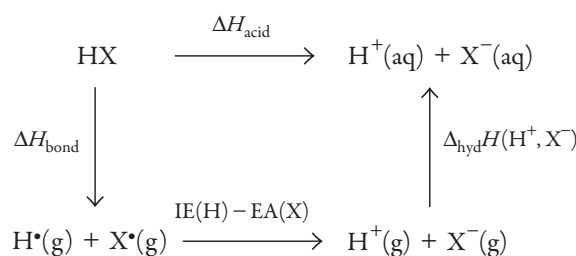
Figure 1. Thermodynamic cycle to determine the enthalpy associated with acid dissociation.

Table 3. Bond Dissociation Energies (ΔH_{bond}), Electron Affinities (EA), Hydration Energies ($\Delta_{hyd}H$), and the Derived Values of ΔH_{acid}

Acid	ΔH_{bond}[a]/ (kJ mol^{-1})	EA(X)[b]/ (kJ mol^{-1})	$\Delta_{hyd}H(X^-)$[c]/ (kJ mol^{-1})	ΔH_{acid}/ (kJ mol^{-1})
CH_4 (X = CH_3)	438	9	−480[e]	158
NH_3 (X = NH_2)	450	71	−500[e]	88
H_2O (X = OH)	498	178	−520	50
H_2S (X = SH)	381	222	−340	−19
HF	570	328	−510	−59
HCl	432	349	−367	−75
HBr	366	325	−336	−86
HI	298	295	−291	−79
$HClO_4$ (X = ClO_4)	430[d]	507	−246	−122
$HClO_3$	415[d]	410	−299	−85
$HClO_2$	390[c]	207	−475	−83

[a]Data from ref 8. [b]Data from ref 5. [c]Data from ref 6. [d]These numbers were estimated using electronic structure calculations (B3LYP/6-311+G*). [e]The hydration enthalpies for −CH_3 and −NH_2 are estimated to be 480 kJ mol^{-1} and 500 kJ mol^{-1}. They are likely to be less than that for −OH owing to size and there is an absence of potential hydrogen bonding in −CH_3.

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