

The Effect of Structure on Acid-Base Properties



Acid Strength depends on (1) the strength of the bond
(2) The stability of the anion, X^- , formed

For BINARY ACIDS (ex. H-X)

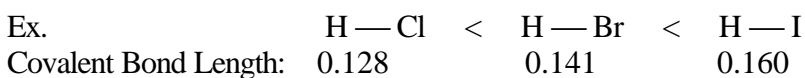
The strength of the acids depends on the strength of the H-X bond. This depends on two most important factors influencing the H-X bond:

(1) Radius of the X:

In general, the **larger** the atom X, the **stronger** the acid.

H-X For larger atoms of X, the e^- cloud is more diffuse. Therefore, H-X bond breaks **EASILY** than in a smaller atom of X.

Thus, Acid strength increases with Increasing Radius of X.



(2) Electronegativity of X, i.e. the polarity of X

In general, the strength of an acid **increases** as electronegativity of X **increases**.

$\delta^+ \text{H} - \text{X} \delta^-$ The greater the electronegativity of X, the more strongly it attracts e^- 's from the H-atom, thereby permitting the H^+ to separate. Thus, the stronger the acid.

H ₂ O	Increasing Acid	HF		H ₂ S	<	H ₂ Se	<	H ₂ Te
H ₂ S	Strength with	HCl	Atomic Radius	104		117		137
H ₂ Se	Increasing	HBr	Electronegativity	2.5		2.4		2.1
H ₂ Te	↓ Atomic Radius	↓ HI						

However, in general, the atomic radius of X **predominates** (is more significant than) the electronegativity of X.

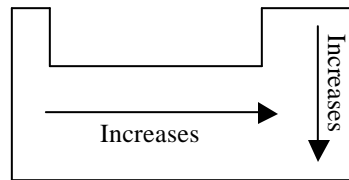
Therefore, Acid strength increases down a group.

Going Across a Period

NH ₃	H ₂ O	HF		PH ₃	<	H ₂ S	<	HCl
			→	110		104		99
			Acid Strength Increases	2.1		2.5		3.0

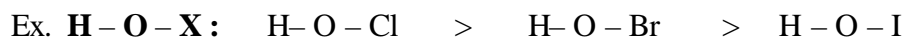
Going across a period, the electronegativity factor **predominates** the smaller decrease in atomic radius, which is insignificant.

Therefore, the strength of binary acids **increases** from left to right across a period, and from top to bottom in groups.



Strength of OXY-ACIDS

I. For Same Structure, but different central atom

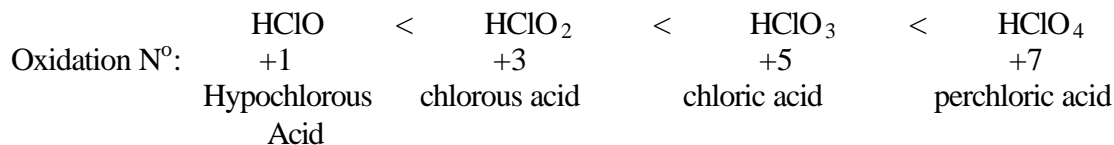


The ability of X to withdraw e^- density from O-H increases with increasing electronegativity of X. e.g. $\text{HClO}_3 > \text{HBrO}_3$

Thus, for acids of the same structure, the strength of an acid increases as the electronegativity of X, the central atom increases, and where the central atom X is small.

II. For Same Central Atom, but with different number of Oxygen-atoms

The acid strength increases with the increase in number of Oxygen-atoms, i.e. with increase in oxidation number of the central atom.



Each O-atom withdraws e^- density from the O–H bond. Thus, lengthening and weakening the O – H bond further. Therefore, the stronger the acid as the number of oxygen atoms increase in the molecule.

Assignment: Which is the stronger acid in each pair?

- (a) HCl , HBr (b) HCl, H₂S (c) HClO₃ , HBrO₃ (d) H₃PO₄ , H₃PO₃
 (e) HNO₂ , HNO₃ (f) CH₄ , NH₄ (g) HOBr , HOI (h) CH₄ , SiH₄
 (i) H₂CO₃ , H₂SiO₃ (j) H₃AsO₄ , H₃AsO₃ (k) H₃AsO₄ , H₃PO₄
 (l) H₂Se , AsH₃ (m) H₂Te , H₂Se