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$_{(aq)}$) $H\text{-}X_{(aq)} \longrightarrow H^+_{(aq)} + X^-_{(aq)}$

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**: **H-X** $_{(aq)}$
In general, the **larger** the atom X, the **stronger** the acid.
For larger atoms of X, the e^- cloud is more diffuse, the atomic overlap is weaker.
Therefore, H-$X_{(aq)}$, bond breaks EASILY than in the molecule of $HX_{(aq)}$ where the atom of X is smaller.

Thus, Acid strength increases with Increasing Radius of X.

Ex.	H — Cl	<	H — Br	<	H — I
Covalent Bond Length:	0.128		0.141		0.160

(2) **Electronegativity of X, i.e. the polarity of X**
In general, the strength of an acid **increases** as electronegativity of X **increases.**
The greater the electronegativity of X, the more strongly it attracts e^-'s from the H- atom, thereby permitting the H^+ to ionize off. Thus, the stronger the acid.

$$\mathbf{d^+\ H \text{ —— } X\ d^-}$$

H_2O	Increasing Acid	HF		H_2S	< H_2Se	< H_2Te
H_2S	Strength with	HCl	Atomic Radius	104	117	137
H_2Se	Increasing	HBr	Electronegativity	2.5	2.4	2.1
H_2Te	Atomic Radius	HI				

However, in general, going **down a group**, the **atomic radius of X predominates,** (i.e. atomic radius of X is more significant) than the electronegativity of X.
Therefore, **acid strength increases down a group**.

Going Across a Period

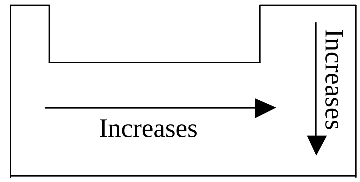
NH_3 H_2O HF ⟶
Acid Strength Increases

	PH_3	< H_2S	< HCl
Atomic Radius	110	104	99
Electronegativity	2.1	2.5	3.0

⟶ Increasing Acid Strength
⟶ Decreasing At. Radius
⟶ Increasing e.negativity

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

Therefore, the **strength of binary acids**, **H-X** $_{(aq)}$, **increases** from **left to right** across a period, and from **top to bottom** in groups.



Strength of OXY-ACIDS

I. <u>For Same Structure, but different central atom</u>

Ex. **H – O – X :** H– O – Cl > H– O – Br > H – O – I

The ability of X to withdraw e⁻ density from O-H bond increases with increasing electronegativity of X. e.g. $HClO_{3\,(aq)}$ > $HBrO_{3\,(aq)}$

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. <u>For Same Central Atom, but with different number of Oxygen-atoms</u>

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

	HClO	<	$HClO_2$	<	$HClO_3$	<	$HClO_4$
Oxidation N^o:	+1		+3		+5		+7
	hypochlorous acid		chlorous acid		chloric acid		perchloric acid
	chloric (I) acid		chloric (III) acid		chloric (V) acid		chloric (VII) acid

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: State which of following in each pair is the stronger acid. Justify your answer.

(a) HCl , HBr (b) HCl, H_2S (c) $HClO_3$, $HBrO_3$ (d) H_3PO_4 , H_3PO_3

(e) HNO_2 , HNO_3 (f) CH_4 , NH_4 (g) HOBr , HOI (h) CH_4 , SiH_4

(i) H_2CO_3 , H_2SiO_3 (j) H_3AsO_4 , H_3AsO_3 (k) H_3AsO_4 , H_3PO_4

(l) H_2Se , AsH_3 (m) H_2Te , H_2Se