PERIODIC VARIATIONS OF ACIDIC AND BASIC PROPERTIES

(a) Hydracids of the elements of the same periods:

Consider the hydracids of the elements of II period, Viz., CH_4, NH_3, H_20 and HF. These hydrides become increasingly **acidic** as we move from CH_4 to HF. CH_4 has negligible **acidic properties** while HF is a fairly stronger acid. The increase in **acidicproperties** is due to the fact that the stability of their conjugate bases increases in the order

$CH^-_3 < NH^-_2 < OH^- < F^-$

The increase in **acidic properties** is supported by the successive increase in the dissociation constant.

$CH_4(=10^{-58}) < NH_3\ (=10^{-35}) < H_20(=10^{-14}) < HF(=10^{-4})$

(b) Hydracids of the elements of same group:

(i) Hydrides of V group elements (NH_3, PH_3, AsH_3, SbH_3, BiH_3) show basic character which decreases due to increase in size and decrease in electronegativity from N to Bi. There is a decrease in electron density in, sp^3-hybrid orbital and thus electron donor capacity decreases.

(ii) Hydracids of VI group elements (H_20, H_2S, H_2Se, H_2Te) act as weak acids. The strength increases in the order $H_20 < H_2S < H_2Se < H_2Te$.

The increasing **acidic properties** reflects decreasing trend in the electron donor capacity of OH^-, HS^-, HSe^- or HTe^- ions.

(iii) Hydracids of VII group elements (HF, HCI, HBr, HI) show **acidic properties**which increase from HF to HI. This is explained by the fact that bond energies decrease. (H-F = 135 kcal/mol, HCI = 103, HBr = 88 and HI = 71 kcal/mol).

(c) Oxyacids:

(i) The **acidic properties** of **oxyacids** of the same element which is in different oxidation states increases with increase in oxidation number.

+ 1 +3 +5 +7

$HCIO < HC1O_2 < HC1O_3 < HCIO_4$

+4 +6 +3 +5

$H_2SO_3 < H_2SO_4$; $HNO_2 < HNO_3$

But this rule fails in **oxyacids** of phosphorus.

$H_3PO_2 > H_3PO_3 > H_3PO_4$

(ii) The **acidic properties** of the **oxyacids** of different elements which are in the same oxidation state decreases as the atomic number increases. This is due to increase in size and decrease in electronegativity.

$HC1O_4 > HBrO_4 > HIO_4$

$H_2SO_3 > H_2SeO_3$

Limitations:

There are a number of acid-base reactions in which no proton transfer takes place, e.g.,

$SO_2 + SO_2 \leftrightarrow SO^{2+} + S$

$Acid_1$ $Base_2$ $Acid_2$ $Base_1$

Thus, the protonic definition cannot be used to explain the reactions occurring in non-protonic solvents such as $COCl_2$, $S0_2$, N_20_4, etc.

Relative Strength of Acids and Bases:

According to Arrhenius concept, an acid is a substance which furnishes H^+ ions when dissolved in water. All the acid properties on an acid are due to H^+ ions present in the solution.

The extent to which an acid property is given by an acid is a measure of its **acid strength**. The **acid strength** of a solution does not depend on its concentration but on the number of H^+ ions present. The concentration of H^+ ions depends on the ionisation of an acid in solution. On dilution, the ionisation increases and more of H^+ions come to solution with the result that the **acid strength** increases. Thus, **acid strength** increases on dilution while its concentration decreases.

At infinite dilution the dissociation of an acid is nearly complete and all acids are equally strong at infinite dilution.

The concentration of H^+ ions at all other dilutions of equimolar solutions of the acids may not be equal and depends on their degree of dissociation. Thus, to measure the relative **acid strength** of the two acids, the measurements of hydrogen ion concentration, i.e., degree of dissociation is made of equinormal solutions of the two acids. Various methods are used for this purpose. Some are described below.

(i) The conductivity method: The degree of dissociation of a weak acid is equal to conductivity ratio Λ_1/Λ_∞. Thus, the degrees of dissociation a, and a_2 for two equinormal acids are given by:

For acid I, $\alpha_1 = \Lambda_1/\Lambda_\infty$

For acid II, $\alpha_2 = \Lambda_2/\Lambda_{\infty 2}$

At infinite dilution, all weak electrolytes have almost the same value of Λ_∞; hence,

$\Lambda_{\infty 1} = \Lambda_{\infty 2}$

(Strength of acid I)/(Strength of acid II)=α_1/α_2 = Λ_1/Λ_2 = ((1000×sp.cond.acid I)/C)/((1000×sp.cond.acid II)/C)

= (Sp.cond.acid I)/(Sp.cond.acid II)

The relative strength of two acids is, thus, equal to the ratio of their equivalent conductance or specific conductance of equinormal solutions which can be determined experimentally.

(ii) Comparing dissociation constants: Let K_1 and K_2 be the dissociation constants of two acids and let and a_2 be their degree of dissociation in equinormal solutions.

Applying Ostwald's dilution law, $\alpha_1 = \sqrt{K_1/c}$ and $\alpha_2 = \sqrt{K_2/c}$

Thus, (Strength of acid I)/(Strength of acid II) = $\alpha_1/\alpha_2 = \sqrt{(K_1/K_2)}$

Dissociation constants of some weak acids are given in the table:

Acid-ionisation Constants at 25°C

Substance	**Formula**	**K_a**
Acetic acid	$HC_3H_3O_2$	1.7×10^{-5}
Benzoic acid	$HC_7H_5O_2$	6.3×10^{-5}
Boric acid	H_3BO_3	5.9×10^{-10}
Carbonic acid	H_2CO_3	4.3×10^{-7}
	HCO^-_3	4.8×10^{-11}
Cyanic acid	HOCN	3.5×10^{-4}

Substance	**Formula**	K_a
Formic acid	$HCHO_2$	1.7×10^{-4}
Hydrocyanic acid	HCN	4.9×10^{-10}
Hydroflourine acid	HF	6.8×10^{-4}
Hydrogen Sulfate ion	HSO^-_4	1.1×10^{-2}
Hydrogen Sulfide	H_2S	8.9×10^{-8}
	HS-	1.2×10^{-13}
Hypochlorous acid	HClO	3.5×10^{-8}
Nitrous acid	HNO_2	4.5×10^{-4}
Oxalic acid	$H_2C_2O_4$	5.6×10^{-2}
	$HC_2O^-_4$	5.1×10^{-5}
Phosphoric acid	H_3PO_4	6.9×10^{-3}
	$H_2PO^-_4$	6.2×10^{-8}
	$H_2PO^{2-}_4$	4.8×10^{-13}
	H_2PHO_3	1.6×10^{-2}
Phosphorous acid	$HPHO^-_3$	7.0×10^{-7}
	$HC_3H_5O_2$	1.3×10^{-5}
Propionic acid	$HC_3H_3O_3$	1.4×10^{-4}
Pyruvic acid	H_2SO_3	1.3×10^{-2}
Sulfurous acid	HSO^-_3	6.3×10^{-8}

(iii) Thomson thermal method: In this method, heat of neutralisation of two acids is first determined separately with NaOH. Let it be 'x' and 'y' calorie. The one gram equivalent of each of the two acids is mixed and one gram equivalent of NaOH is added. Let the heat evolved in this case be 'z' calorie. The two acids will neutralise a fraction of the base proportional to their relative strength. Suppose n gram equivalent of NaOH is neutralised by acid I and the rest (1 - n) by acid II.

Total Heat solved, $z = nx + (1-n)y$

$= nx + y - ny$

or $z-y = n(x-y)$

or $n = (z-y)/(x-y)$

So (Strength of acid I)/(Strength of acid II) = $n/((1-n)) = (((z-y))/((x-y)))/(1-((z-y))/((x-y))) = ((z-y))/((x-z))$

Relative strength of bases: A base is a substance which gives OH" ions when dissolved in water. The base strength depends on OH^- ion concentration. The above methods can be used for measuring relative base strengths also. In the Thomson thermal method, the two bases and their mixtures will be neutralised by strong acid, say HC1.

The relative strengths of some of the acids are as follows:

(i) $HClO_4 > HBr > HC_1 > HNO_3 > H_2SO_4 > H_3O^+ > H_2SO_3 > H_2CO_3 > CH_3COOH$

(ii) $HClO_4 > HCl0_3 > HClO_2 > HClO$

(iii) $HI > HBr > HCl > HF$

(iv) $HClO_3 > HBrO_3 > HIO_3$

(v) $CCI_3COOH > CHCl_2COOH > CH_2C1COOH > CH3COOH$

(vi) $HCOOH > CH_3COOH > C_2H_5COOH$

The relative strengths of some of the bases are as follows:

(i) $KOH > NaOH > Ca(OH)_2 > NH_4OH$

(ii) $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

(iii) $(C_2H_5)_2NH > C_2H_5NH_2 > NH_3 > (C_2H_5)_3N$

(iv) $NaOH > NH_3 > H_20$

(v) $NH_3 > NH_2NH_2 > NH_2OH$

(vi) $NH_3 > C5H5N > C_6H_5NH_2$

Source : http://ciseche10.files.wordpress.com/2013/12/ionic-equilibrium.pdf