STUDY MATERIAL

VIVEKANANDA COLLEGE
THAKURPUKUR

NAAC ACCREDITED GRADE—’A’

Subject: Inorganic Chemistry

Topic: Periodic Properties

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PERIODIC PROPERTIES AND IT'S FACTORS

1. ***Atomic Radii***-[Expressed in the unit of Angstrom or pm, 1 Angstrom=100 pm]

Factors:-

a) Multiplicity of bond- Atomic radius of carbon in $H_3C\text{-}CH_3$, $H_2C{=}CH_2$, C_2H_2 are not equal, from exponential results C-C > C=C > carbon-carbon triple bond.

b) Percentage of ionic character or electronegativity difference- the radius of H atom in H-F, H-Cl, H-Br, H-I are different, size of H atom in H-F has the lowest value and it gradually increases to a maximum value of H-I. This is due to decrease in electronegativity difference. Radius of H: H-F < H-Cl < H-Br < H-I. This can also be explained by partial ionic character as calculated from Hannoy and Smith equation,

Percentage of ionic character=$16(X_A\text{-}X_B)+3.5(X_A\text{-}X_B)$.

It gives $X_A\text{-}X_B$ in A-B bond that 50% ionic character is found for difference in electronegativity 2.1.

c*) Effective nuclear charge- Inversely proportional to atomic radii:* Effective nuclear charge (Z)=(Z-S), Z=actual no. of proton, S=screening constant, screening effect of electron s>p>d>f. For this incoming d-electrons gradually decrease atomic radii. For isoelectric system,atomic radii is inversely proportional to Z_{eff}. Na^+(10), Ne(10), O^{2-}(10), F^-(10)- isoelectric, the respective Z/e values: Na^+=11/10=1.1, e=10/10=1, O^{2-}=8/10=0.8, F^-=9/10=0.9 r is inversely proportional Z/e → Atomic radius order: $Na^+<Ne<F^-<O^{2-}$.

d) Formal charge on the atom:- Negative formal charge increases atomic radii whereas positive formal charge decreases the atomic radii.

Ex- For O_3, all the O atoms are not equal in size because of the presence of formal charge.

e)Types of atomic radii- Generally 3 types of atomic radii are considered in the following order, Vander- waal radii> Metallic radii > Covalent radii.

Pauling's univalent method for the calculation of atomic radii: On the basis of following assumptions Pauling was able to calculate the radii of univalent ions like Na^+, K^+, Rb^+, F^-, Cl^-, Br^-, I^-.
i)Radii of isoelectronic univalent ions should vary inversely with their their effective nuclear charge i.e. $r=C/Z_{eff}$, C= Proportionality constant

ii) Ions are hard solid spheres and do not undergo any deformation in crystal lattice.

Iii) The interionic distance in its lattice is equal to the sum of their atomic radii.

Calculation: Let AB be an ionic solid where the radius of cation, A^+, and that of anion, B^-, are respectively x and y.

Therefore, x=C/Z_{eff} of A^+ or, x=C/(Z_A-S_A), where Z_A=Atomic no. of A , S_A=Screening constant for A^+

Similarly, y=C/Z_{eff} of B^- or,y=C/(Z_B-S_B), where Z_B=Atomic no. of B & S_B=Screening constant for B^-

So, x/y ratio is easily calculated as actual atomic number and screening constants, both are known(obtained from Slater's rule).

Assume x/y=a……… (1)

The interionic distance between A^+ and B^- is accurately measured by X-ray crystallography(Bragg's equation). Therefore, x+y=d (Lattice distance)…………(2)

Solving (1) and (2) x and y can be calculated as x=(a.d)/(1+a) and y=d/(a+1)

Limitations: i) The method is apparently correct for univalent ions only for multivalent ions it is not true.

ii) The rule is valid only when AB is 100% ionic, which is practically impossible.

iii) The ions are assumed perfectly spherical in shape, is not always true (Due to John Taller effect). Hence, in such cases the above method is not valid.

2***. Ionisation Enthalpy-*** [Expressed in eV, 1eV=23.053 Kcal mol^{-1}=96.7 KJ mol^{-1}]

Factors:-

a)Size of the atom- For this, along a period from left to right I.E increases, but downwards the group decreases.

b)Nuclear charge(Z_{eff})- For this, 4s electrons are ionized first than 3d. $Cu^0(4s^1 3d^{10}) \rightarrow Cu^+(4s^0 3d^{10})$

c)Penetration effect of electrons- Greater the penetration greater is the I.E.

d)Screening effect- The effective nuclear charge, Z_{eff}, is given by the relation Z_{eff}=Z-S, where Z is actual nuclear charge and S is screening constant. So, greater the screening effect lesser will be the Z_{eff}. Hence, if other factors remain the same, the I.E decreases with an increase in screening effect.

e)Electronic configuration: Half filled and completely filled shells are found to possess extra stability. Such atoms possess less tendency to lose valence electron and consequently have higher values of I.E.

Distinction between Electron Affinity and Electronegativity-

Electronegativity	Electron affinity
It is related to the atom present in a covalent bond of any compound. $H^{\delta+} \rightarrow Cl^{\delta-}$	It is related to isolated atom in gaseous state. $Cl(g) + e^- \rightarrow Cl^-(g)$ + E(Energy)

Electronegativity is the power of attraction on bond pair of electrons.	It is the power of attraction of free electron in the outermost shell.
It leads to polarity or nonpolarity of the molecule.	It leads to formation of anion.
It is a vector quantity (having particular direction).	It is a scalar quantity (amount of energy released due to formation of anion).

Radius ratio rule and its basis: If the ionic radius of constituting cation and anion are known for an ionic solid, the radius ratio can be calculated. Hence, the coordination number and shape i.e. geometrical arrangement of ions can be predicted. This prediction of shape and coordination number on the basis of limiting radius ratio, r^+/r^-, is called radius ratio rule, which is given below:

Limiting radius ratio, r^+/r^-	Coordination number	Shape
<0.155	2	Linear
0.155-0.225	3	Planer triangle
0.225-0.414	4	Tetrahedral
0.414-0.732	4	Square planer
0.414-0.732	6	Octahedral
0.732-0.999	8	Body centered cubic

It is obvious that cations are smaller in size than anions. So, considering the relative sizes of cation and anion, a limiting case arises when the anions are in contact with one another and the cation is just filled into the hole of them. This is the lower limit radius ratio for a fixed coordination number(i.e. number of around a cation). If the radius ratio is lower than this, the cation is not in contact with negative ions and it rattles in the hole and the structure is unstable. Again, as the difference in the size of the two ions increases, radius ratio also increases i.e., the hole increases. At some point it becomes possible to fit an extra ion round the cation. This is the higher limit of radius ratio. Coordination number 3, 4, 6 and 8 are common and the appropriate limiting radius ratio can be worked out by simple geometry, with the

following assumptions:

a)that exact values of ionic radii are known.

b)that the ions behave as hard inelastic spheres.

c)that stable arrangements are only possible if the positive and negative ions touch.

d)that the spherical shape is retained in clusters of +ve and –ve ions.

e)that ions always adopt the highest possible coordination number.

f)that bonding is 100% ionic.

Limitations- i)The radius of an ion is not constant but changes depending on its environment, i.e. radius changes when its coordination number changes. The radii usually mentioned for a coordination number for a coordination number 6, but radius effectively increases 3% when coordination number changes from 6 to 8, and decreases 6% for the change from 6 to 4.

ii) Ions are not hard inelastic spheres. They are sometimes fitted into holes that are slightly too small, i.e. the ions are compressed and the lattice may be distorted.

iii)There are a number of exceptions of radius ratio rule where the ions have an inert pair, e.g. Ga^+, In^+, Sn^{2+}, Pb^{2+},I^+, I^{3+} which do not have a centre of symmetry.

iv) Radius ratio rule is effective with 100% ionic character of the compound which is most unlikely.

Born – Lande equation and its application: The source of lattice is the attractive force between two opposite ions. Thus, lattice energy may be theoretically calculated as the Electrostatic energy(E) between cation and anion given by, $E=-\frac{Z^{+}.Z^{-}.e^{2}}{r}$

Where, Z^+= charge of cations, Z^-=charge of anions, e=charge on an electron, r = interionic distances.

The above equation is valid only when the ions are considered as point charges.

For more than two ions, the electrostatic energy depends on the number of ions and on A, their arrangement in space. For one mole, the energy is: $E=-\frac{N_o.A.Z^{+}.Z^{-}.e^{2}}{r}$ Where, N_o=Avogadro constant, A=Madelung constant.

The equation for attractive forces between the ions gives a negative value for energy i.e., energy is released when a crystal is formed. Thus, smaller the value of r, the greater is the amount of energy evolved and hence the more stable the crystal will be. Mathematically, the equation suggests that an infinite amount of energy should be evolved if the distance r is 0. But it is not the fact. When the interionic distance becomes small enough for the ions to touch, they begin to repel each other. This repulsion originates from the mutual repulsion of the electron clouds on the two ions. The repulsive forces increase rapidly as r decreases. The magnitude of repulsive force is given by $\frac{B}{r^n}$, where *B* is a constant that depends on the structure and *n* is also a constant called the Born exponent. For one gm-formula weight of crystal, total repulsive force is $\frac{N_o.B}{r^n}$ [generally n=9].

Therefore, total energy holding the crystal together i.e. lattice energy(U) is given by:

$$U=-\frac{N_o.A.Z^+.Z^-.e^2}{r}+\frac{N_o.B}{r^n}$$

The equilibrium distance between ions is determined by the balance between the attractive and repulsive forces. At equilibrium, $\frac{dU}{dr}$=0 and the equilibrium distance $r=r_o$,

i.e. $$\frac{dU}{dr}=\frac{N_o.A.Z^+.Z^-.e^2}{r_o^2}-\frac{n.N_o.B}{r_o^{n+1}}=0$$

Rearranging, $B=\frac{A.Z^+.Z^-.e^2.r_o^{n-1}}{n}$

Therefore, $U=-\frac{N_o.A.Z^+.Z^-.e^2}{r_o}+\frac{N_o.A.Z^+.Z^-.e^2.r_o^{n-1}}{n.r_o^n}$

or, $U=\frac{N_o.A.Z^+.Z^-.e^2}{r_o}(1-\frac{1}{n})$

This equation is called the Born–Lande equation. When using SI units, $U=-\frac{N_o.A.Z^+.Z^-.e^2}{4\pi\epsilon_o r_o}(1-\frac{1}{n})$

Where $\epsilon_o$is the permittivity of free space=8.854x10^{-12}

This equation gives a calculated value of U=-778 KJ mol^{-1}. For the lattice energy of NaCl, which is close to experimental value of 775 KJ mol^{-1} at 25°C(obtained from Born-Haber cycle).

Application of Born-Lande equation-

a) Lattice energy becomes more as the interionic distance decreases i.e., U is inversely proportional to *r* when Z^+, Z^- remain constant. The greater lattice energy for LiF(*r*=2.01 Angstrom, U=-1004 KJ mol^{-1}) can be explained in comparison with CsI(*r*=3.95 Angstrom, U=-527 KJ mol^{-1}).

b) Lattice energy depends on product of ionic changes i.e., U is directly proportional to ($Z^+.Z^-$), if *r* remains nearly same for different crystals,

Compound	*r*(Angstrom)	$Z^+.Z^-$	U(KJ mol^{-1})

LiF	2.01	1	-1004
MgO	2.10	4	-3933

c)There are two opposite factors in Born-Lande equation. Increasing *r* reduces the lattice energy. It is almost impossible to change *r* without changing structure, and therefore changing Madelung constant, *A*. Increasing *A* increases the lattice energy, hence the effects of changing *r* and *A* may cancel each other.

This may be illustrated by choosing a constant value for *n* in the above equation. Taking a constant value of *n*=9, we may compare the interionic distances as follows:

Coordination number →	12	8	6	9
Ratio of interionic distance ($\frac{r_x}{r_b}$) →	1.091	1.037	1.000	0.951

For a change of coordination number from 6 to 8, i.e. NaCl structure to CsCl structure, The interionic distance increases by 3.7% and the Madelung constants('*A*' for NaCl=1.74756 and for CsCl=1.76267) change by 0.9% only. Thus, a change in coordination number from 6 to 8 would result in a reduction in lattice energy. So, 6-coordinated NaCl is more stable than 8-coordinated structure. In a similar way reducing the coordination number from 6 to 4 decreases *r* by 4.9% whereas the corresponding decrease in *A* is 6.1% or 6.3%(depending on Zincblende type or Wurtzite type structure). In either case it compensates more than requirement for the change in *r.* So, U decreases as coordination number changes from 6 to 4. Thus suggests that neither 4 nor 8 coordinate structure should exist. But existence of ZnS(coordination number 4) and CsCl, CsBr, CsI(coordination number 8) contradicts this suggestion. We therefore look for a mistake in theoretical assumptions made. First the value of *n* is assumed to be 9, when it may vary from 5 to 12. Second, the calculation of electrostatic attraction assumes that the ions are point charges which is not true. Third, The assumption is made that there is no reduction in charge because of interaction i.e. the bond is 100% ionic- is incorrect. Fourth, it has been seen that a number of salts which might be expected from radius ratio rule to have a CsCl structure, in fact adopt a NaCl structure. The reason is that the Madelung constant fro CsCl is larger that NaCl and could give a larger lattice energy. However, the interionic distance will be larger in CsCl type of structure than NaCl type of structure and this would decrease the lattice energy. These two factors, *A* and *r* work in opposite directions and party cancel each other. This makes the lattice energy more favorable for NaCl type of structure.