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BS-109 Engineering chemistry-I

Unit-1

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Fajans' rule: Fajans' rule predicts whether a chemical bond will be covalent or ionic. A few ionic bonds have partial covalent characteristics which were first discussed by **Kazimierz Fajans** in **1923**.

The rule can be stated on the basis of 3 factors, which are:

1. **Size of the ion:** Smaller the size of cation, the larger the size of the anion, greater is the covalent character of the ionic bond.
2. **The charge of Cation:** Greater the charge of cation, greater is the covalent character of the ionic bond.
3. **Electronic configuration:** For cations with same charge and size, the one, with $(n-1)d^n\ ns^o$ which is found in transition elements have greater covalent character than the cation with $ns^2\ np^6$ electronic configuration, which is commonly found in alkali or alkaline earth metals.

Fajans' Rule can be summarized as:

Ionic Characteristic	**Covalent Characteristic**
Large Cation	Small Cation
Small Anion	Large Anion
Small-charge	Large Charge

Consider Aluminium Iodide (AlI_3)

The iodine being bigger has a lesser effective nuclear charge. Thus, the bonding electrons are attracted lesser towards the Iodine nucleus.
On the contrary, the aluminium having three positive charges attracts the shared pair of electrons towards itself.
This leads to insufficient charge separation for it to be ionic and so it results in the development of covalent character in AlI_3.

Consider Aluminium Fluoride (AlF_3)

Here the fluorine being smaller attracts the shared pair of an electron more towards itself and so there is sufficient charge separation to make it ionic.

- **Which compound should theoretically the most ionic and the most covalent amongst the metal halides?**

The smallest metal ion and the largest anion should technically be the most covalent. Therefore, LiI is the most covalent.
The largest cation and the smallest anion should be the most ionic. Therefore, CsF should be the most ionic.

- **Arrange the following according to the increasing order of covalency:**

1. **NaF, NaCl, NaBr, NaI**
2. **LiF, NaF,KF,RbF,CsF**

1. Since the cation is the same, compare the anions. Amongst the anions, larger the size more would be the covalency. Therefore the order is: NaF < NaCl < NaBr < NaI

2. Here the anion is the same, so we compare with cations. Smaller the cation more is the covalency. Therefore, the order is: CsF < RbF < KF < NaF < LiF

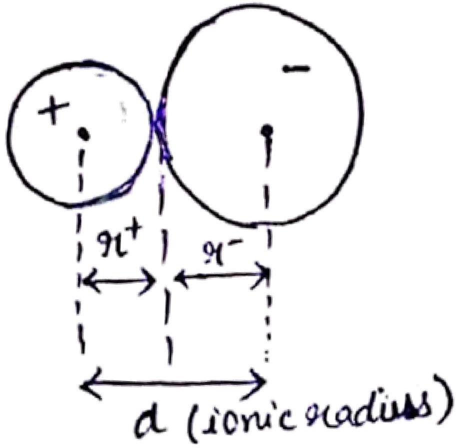
Calculation of ionic radii : Pauling's method

- Pauling has calculated the radii of the ions on the basis of the observed internuclear distances in four crystals namely NaF, KCl, RbBr and CsI.
- In each ionic crystal the cations and anions are isoelectronic with inert gas configuration.

NaF crystal : $Na^+ \rightarrow 2, 8$; $F^- \rightarrow 2, 8$ } Ne type configuration $Z = 10\ (2, 8)$

KCl crystal : $K^+ \rightarrow 2, 8, 8$; $Cl^- \rightarrow 2, 8, 8$ } Ar type configuration $Z = 18\ (2, 8, 8)$

∴) Now, the cations and anions of an ionic crystal are assumed to be in contact with each other and sum of their radii will be equal to the internuclear distance between them.



where, equation is

$$r(C^+) + r(A^-) = d(C^+ - A^-) \quad \text{--- (1)}$$

$r(C^+)$ = radius of cation

$r(A^-)$ = radius of anion

$d(C^+ - A^-)$ = inter nuclear distance between C^+ and A^- in ionic crystal.

(2) Now, for a noble gas configuration,

the radius of an ion is inversely proportional to its effective nuclear charge.

$$r(C^+) \propto \frac{1}{Z_{eff}(C^+)} \quad \text{——— (2)}$$

$$r(A^-) \propto \frac{1}{Z_{eff}(A^-)} \quad \text{——— (3)}$$

On combining eq (2) and (3)

$$\frac{r(C^+)}{r(A^-)} = \frac{Z_{eff}(A^-)}{Z_{eff}(C^+)} \quad \text{——— (4)}$$

So, from eq (1) and (4), we can evaluate the value of $r(C^+)$ and $r(A^-)$ provided the value of $d(C^+-A^-)$, $Z_{eff}(C^+)$ and $Z_{eff}(A^-)$ are known.

$$r(C^+) + r(A^-) = d(C^+ - A^-) \quad \text{—①}$$

$$\frac{r(C^+)}{r(A^-)} = \frac{Z_{eff}(A^-)}{Z_{eff}(C^+)} \quad \text{—(4)}$$

From your Slater Rule, we can calculate Z_{eff}:

$$Z_{eff} = Z - \sigma \qquad (\sigma = \text{screening constant})$$

$$\sigma = \left\{0.35 \times [\text{number of remaining electrons in } n^{th} \text{ shell}]\right\} + \left\{0.85 \times [\text{number of electrons in } (n-1)^{th} \text{ shell}]\right\} + \left\{1.00 \times [\text{number of electrons in inner shells}]\right\}$$

→ let's calculate Z_{eff} for K atom and K^+ ion.

(i) for K atom = At No. 19 ⇒ $E.C = \underbrace{1s^2}_{2}\ \underbrace{2s^2\,2p^6}_{8}\ \underbrace{3s^2\ 3p^6}_{8}\ \underbrace{4s^1}_{1}$

σ (calculated for 4s e^-) $= 0.35 \times (0) + 0.85 \times (8) + 1.00 \times (10) = 16.80$

$Z_{eff} = Z - \sigma = 19 - 16.80 = 2.20$

(ii) for K^+ ion ⇒ (18) ⇒ $E.C ⇒ \underbrace{1s^2}_{2}\ \underbrace{2s^2\ 2p^6}_{8}\ \underbrace{3s^2\ 3p^6}_{8}$

σ (calculated for 3p e^-) $= 0.35 \times (7) + 0.85 \times (8) + 1.00 \times (2)$
$= 11.25$

$Z_{eff} = 19 - 11.25 = 7.75$

Ques → Calculate the ionic radii of K^+ and Cl^- ions in KCl crystal. The internuclear distance between K^+ and Cl^- ions are found to be 3.14 Å

Ans- we can calculate Z_{eff} for K^+ and Cl^-,

on solving we get

$$Z_{eff}(K^+) = 7.75$$

For (Cl^-)

$$1s^2\,2s^2\,2p^6\,3s^2\,3p^6$$

$$Z_{eff} = 17 - [0.35(7) + 0.85(8) + 1.00(2)] = 17 - 11.25$$

$$= 5.75.$$

using eq (4)

$$\frac{r(K^+)}{r(Cl^-)} = \frac{Z_{eff}(Cl^-)}{Z_{eff}(K^+)} = \frac{5.75}{7.75} = 0.74$$

$$r(K^+) = 0.74\, r(Cl^-)$$

using eq (1)

$$r(K^+) + r(Cl^-) = d(K^+ - Cl^-)$$

$$0.74\, r(Cl^-) + r(Cl^-) = 3.14 \text{ Å}$$

$$1.74\, r(Cl^-) = 3.14 \text{ Å}$$

$$r(Cl^-) = 1.81 \text{ Å}$$

so, $r(K^+) = 0.74 \times (1.81 \text{ Å}) = 1.33 \text{ Å}$

For practice

Ques Calculate the ionic radii of Na^+ and F^- ions in NaF crystal. The internuclear distance between Na^+ and F^- ions are found to be 2.31 Å.

[Hint: $r(Na^+) = 0.95$ $r(F^-) = 1.36$]