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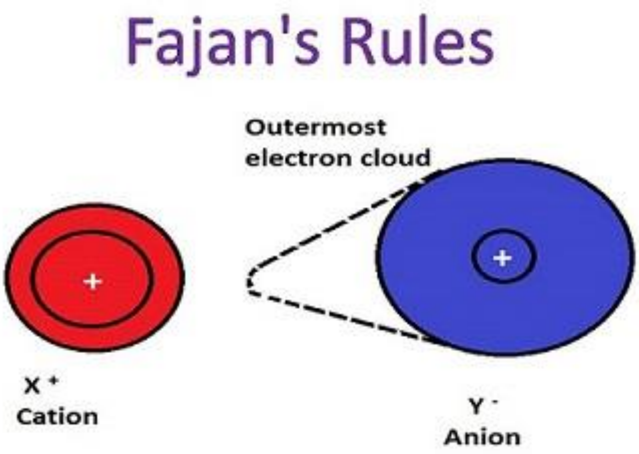
FAJANS RULE

Fajans' rule predicts whether a chemical bond will be covalent or ionic. Few ionic bond have partial covalent characteristics which were first discussed by **Kazimierz Fajans** in **1923**. In the time with the help of X-ray crystallography, he was able to predict ionic or covalent bonding with What is Fajans' rule?

We classify certain compounds as ionic and other compounds as covalent. Now if we were to ask the question, amongst the alkali chlorides, which is the most ionic? To answer these kinds of questions, we employ Fajans' rules as a tool.



Fajans' rule for Ionic and Covalent Compounds

the attributes like ionic and atomic radius

To understand the Fajans' rule, Let us first understand a few terms:

Polarising power

It is the extent to which a cation can polarise an anion. It is proportional to charge density. Charge density is the ratio of charge to volume. Polarising power α Charge density. More the charge density, greater is the polarising power for that cation.

Polarisability

It is the extent to which an ion can be polarised. It can also be called as the ease with which an ion can be polarised. Polarisation is the distortion of a spherically symmetric electron cloud to an unsymmetric cloud.

Postulates of Fajans' Rule

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.

Explanation of Fazans' Rule

Rule 1:

The **first rule** speaks about the polarising power of the cation. If the cation is smaller, then we can say that the volume of the ion is less. If the volume is less, we can conclude that the charge density of the ion would be high.

Since the charge density is high, the polarising power of the ion would be high. This makes the compound to be more covalent.

Rule 2:

The **second rule** speaks about the polarizability of the anion. Larger the anion, less is the effective nuclear charge that holds the valence electron of the ion in place. Since the last electron is loosely bound in large anions, it can easily be polarised by a cation, thereby making the compound more covalent.

Rule 3:

The **third rule** is a special case. Let us use an example to explain this point.

Example: If we want to find the more covalent compound among $HgCl_2$ and Calcium Chloride we cannot use size as a factor to conclude. This is because both Hg^{2+} and Ca^{2+} are of almost equal size. To explain this, we employ the **third rule**.

The electronic configuration of Hg^{2+} is $6s^0 5d^{10}$. This configuration is called pseudo-octet because d-orbital is fully filled, but the element does not have 8 electrons or an octet.

We know that d orbitals are not good at shielding, so we can say that the anion (Cl^-) would be more polarised because the d orbital is poor at shielding making $HgCl_2$ more covalent than $CaCl_2$ because Ca^{2+} ion has a noble gas configuration.

Now to answer the question that we asked first, amongst the alkali chlorides, which one is the most covalent?

Since the anion is the same, we have to compare the cations. According to **Fajans' rules**, smaller the cation, more is the covalency. Therefore, LiCl is the most covalent.

Let us Understand Fajans' Rule Using a Detailed Illustration:

Consider Aluminum Iodide (AlI_3)

This is an ionic bond which was formed by transfer of electrons.

- The iodine being bigger in size 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 electron 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)

This is an ionic bond which was also formed by transfer of electron. But here the fluorine being smaller in size attracts the shared pair of an electron more towards itself and so there is sufficient charge separation to make it ionic.

Examples on Fajans’ rule

Illustration 1: Which compound should theoretically the most ionic and the most covalent amongst the metal halides?

Solution:

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.

Illustration 2: Arrange the following according to the increasing order of covalency:

- NaF, NaCl, NaBr, NaI
- LiF, NaF,KF,RbF,CsF

Solution:

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 < Li