



Ionic Solids

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Abstract:

The paper illustrates the structure and general properties of ionic compounds.

Keywords: Ionic bond, lattice energy, radius ratio rule.

I. INTRODUCTION

Matter exists in three physical states solid, liquid & gas. The three states of matter differ from each other in the strength of force of attraction. Solids have maximum strength of force of attraction, while gases have least. Solids maintain their shape and volume. These are rigid. In solids, atoms or molecules don't have enough energy to move. Solids may be crystalline and amorphous. Crystalline solids are well ordered at the atomic level, with each atom or molecule inhabiting a specific point on a lattice. Amorphous solids are disordered at an atomic level, with the atom or molecules held together in a completely random formation. Crystalline solids are of mainly four types depending upon the type of constituents present,

- | | |
|----------------------|--|
| (1) Molecular solids | (2) Ionic solids |
| (3) Metallic solids | (4) Three dimensional covalent network solids. |
- Here area of interest is ionic solid.

II. BONDING AND STABILITY

Ionic solids are composed of cations and anions held together by electrostatic force of attraction. Due to the presence of ions and ionic bond, these are known as ionic solids. In an ionic compound, the cations and anions are arranged in space to form an extended three dimensional array that maximizes the number of attractive electrostatic interactions and minimizes the number of repulsive electrostatic interactions. The electrostatic energy of the interaction between two charged particles is proportional to the product of the charges on the particles and inversely proportional to the distance between them.

$$\text{Electrostatic energy} \propto - \frac{Q_1 Q_2}{r}$$

Where Q_1 and Q_2 are the electrical charges on particles 1 and 2, and r is the distance between them. The electrostatic energy is negative only when the charges have opposite sign; that is, positively charged species are attracted to negatively charged species and vice-versa.

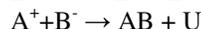
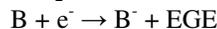
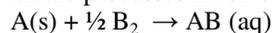
III. HOW TO FORM IONIC COMPOUND?

For the formation of Ionic compound, anion and cation is required. The main conditions for the formation are:

1. An element with small ionization energy.

2. An element with large electron gain enthalpy.
3. Large lattice energy.

When an element has small ionization energy, it will easily lose an electron to form cation. Element having high electron gain enthalpy will gain electron to form an anion. When one mole of ionic compound is formed from its ions, the energy released is lattice energy. Higher the lattice energy, stable will be the compound. Heat of formation of ionic compound can be also calculated with the help of Born-Haber's cycle. This cycle involves all the processes involved in a cyclic manner e.g.



$$\Delta H_f = S + IE + D/2 - EGE - U$$

Here S = Sublimation energy

IE = ionization energy

D = Dissociation energy

EGE = Electron Gain Enthalpy

U = Lattice Energy

ΔH_f = Heat of formation of ionic compounds

IV. LATTICE ENERGY

When Ionic solid is formed from its constituent, the energy released is lattice energy.

- More the lattice energy released, more will be the stability of compounds.
- Higher the lattice energy of an ionic compound, the higher is the melting point.
- Higher the lattice energy, lesser will be its solubility in any quantity of solvent.

Structure, Radius Ratio and Coordination Number

- Each ion in an ionic solid is surrounded by ions of the opposite charge in a three – dimensional crystal lattice. In Sodium Chloride, for example, each Sodium ion (Na^+) is surrounded by six Chloride (Cl^-) ions. Similarly, each Chloride ion is surrounded by six Sodium ions. In another ionic solid, Calcium Fluoride, each Ca^{2+} is surrounded by eight F-ions, while each fluoride ion is surrounded by four

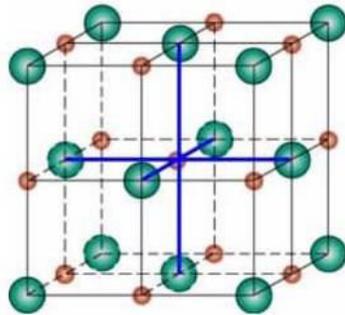
Calcium ions. The number of oppositely charged ions surrounding an ion in an ionic solid is called its co-

ordination number. Thus, in Sodium Chloride, the coordination number of both Sodium and Chloride is six

Rock Salt Structure

Same concepts can be applied to ionic solids in general.

Example: NaCl (rock salt) structure



● Na⁺ $r_{Na} = 0.102 \text{ nm}$

● Cl⁻ $r_{Cl} = 0.181 \text{ nm}$

$r_{Na}/r_{Cl} = 0.564$

∴ cations prefer O_H sites

V. RADIUS RATIO RULE:-

In co-ordination compounds the negatively charged anion is surrounded by positively charged cations and vice-versa. This number of ions surrounding each other is known as co-ordination number.

The co-ordination number depends on the size of ions present. To calculate co-ordination number, the radius ratio of the compound is calculated. Radius Ratio is the ratio of radius of positive and negative ions.

$$\text{Radius Ratio} = \frac{\text{Radius of Positive ion } r_+}{\text{Radius of negative ion } r_-}$$

Cation is kept in centre and anions are placed around it, then different combination are possible, but the most stable arrangement is that where all the anions are touching each other and cation as well. The radius ratio can be increased or decreased either by changing the size of cation or by changing the size of anion. Experimentally it has already been found that the structure can be determined by radius ratio and its co-ordination number.

Table. 1.

$\frac{r_+}{r_-}$	Co-ordination number	Structural arrangement	Example
0.155 – 0.225	3	Planar triangle	Boron oxide
0.225 – 0.414	4	Tetrahedral	ZnS
0.414 – 0.732	6	Octahedral	NaCl
0.732 – 0.999	8	Cubic	CsCl

But this rule is not universally acceptable. In some crystals like ZnO, HgS, radius ratio is greater than 0.5 indicating coordination number 6, but these crystals have tetrahedral structure. It also fails to explain why some compounds crystallize in more than one modification with different co-ordination number.

VI. GENERAL CHARACTERISTICS

- Physical properties of the various ionic compounds like melting point and boiling point, depends on the strength of the ionic bonds holding them together. This will depend chiefly on the things :

- The charges on each ion.
- The size of the ion.

Magnesium oxide has much higher melting point and boiling point (2825°C and 3600°C respectively) than for Sodium Chloride (801°C and 1413°C)

- Ionic solids, in their solid form are insulating material. In crystalline structure, there are no free electrons. But in solution, these became good conductors of electricity. When ionic compound is dissolved in water, the positively charged

sodium is attracted by negatively charged oxygen atom, while the negatively charged chloride ions are attracted to the positively charged hydrogen. These attractions cause the dissociation of Sodium Chloride and ions are generated and hence now, it is a good conductor.

- Ionic solids are brittle. An ionic solid may be hard, but when force is applied to an ionic crystal, the ionic layers shift with respect to one another. When these move, ions of same charges move close to each other. Due to repulsive forces, compound breaks.

VII. DEFECTS IN CRYSTAL STRUCTURE:-

There is regular arrangement of ions in an ionic crystal. But this arrangement is ideal only at the absolute zero of temperature i.e., at 0K. Above this temperature, there are many thermal vibrations which cause disorder or defects in the crystal. These defects are present in both stoichiometric crystals as well as in non-stoichiometric crystals. Schottky defects, Frenkel defects etc are studied in this and these defects are responsible for the flow of

small amount of current through the crystal. Semiconductor belong to this category of crystals.

VIII. CONCLUSION

Ionic compounds are an interesting class of compounds. These are very useful in our day to day life. Various chemical phenomenon and process can be studies on these compound.

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