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Trends in solubilities of sulfates of group II

The sulfate is a large anion compared to hydroxide and the group II cations. As the anion is large, increase in the size of the cation will not show a significant change in the sum of the ionic radii. Therefore, the lattice energies of the sulfates of group II will be very similar.

But the hydration energy of group II sulfates decreases down the group as the size of the cation increase. (Unlike lattice energy hydration energy does not depend on the sum of the ionic radii but the ionic radii of the variable ion.)

The relative solubility of sulfate which is the net effect of lattice energy & the hydration energy will therefore be largely depended on the hydration energy of the cation. Being on the same group the charges of ions are identical. Therefore, hydration energy of group II sulfates depends on size of the cation.
The hydration energies decrease in the order: $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$

Both lattice energy & hydration energy therefore decreases down the group but the decrease in hydration is greater than the decrease in lattice.

Therefore, solubility of sulfates of group II decreases in the order:

$$MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$$

The enthalpy of solution become more endothermic/ less exothermic down the group.

Trends in solubilities of hydroxides of group II

As the size of the cation increases down the group the standard enthalpy of solution become more negative down the group. The enthalpy and entropy of hydroxide is left out here as the ion is common to all metal hydroxide. The decrease in lattice energy will be significant down the group as hydroxide is a smaller anion compared to sulfate.

$$H^{\theta}_{sol} = -L.E + H_{hyd(cat)}$$

The positive value of L.E decreases as the sum of the ionic radius increase also the negative value of H_{hyd} decreases down the group. But the decrease in H_{hyd} is less than decrease in lattice. This results in increase negative value of enthalpy of solution. These favours increase solubility down the group II hydroxides.

$$Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$$

Thermal Stability

1. Explain the term 'Thermal stability'

If a compound can be heated to very high temperature without causing it to undergo any change, then the compound is said to be thermally stable. Higher the temperature required for the decomposition greater thermal stability & vice versa. Therefore, the thermal stability depends on the decomposition temperature of compounds.

2. Explain the concept of thermal stability of group 1 & 2 nitrates & carbonates based on polarizing power of the cation.

Thermal stability depends on the polarizing power of the cation, which depends on the charge/size ratio (charge density) the larger the charge smaller the size, higher the charge density which results in high polarizer power. Such cation polarizes the anion strongly result co-valent character. Such molecules are easily decomposed than those with less polarizing power as they favor ionic characters. (Ionic compounds are thermally stable compound to co-valent compounds).

'Li' & group 2 cations have a relatively high polarizing power than rest of group 1 elements due to their smaller size & higher charge. 'Li' though with +1 charge, being very small also Possess a relatively high charge density. This means 'Li' & group 2 cations will polarize better the anion resulting covalent character hence less thermally stable.

Both group 1 & 2, the ease of decomposition decreases down the group due to low polarizing power. This is due to increase ionic radii down the group, which results in low charge density. Therefore, the thermal stability increases down the group due to less polarizing power of the cation, which results in ionic character.

3. **Thermal stability of group 1 nitrates:-**

All groups I nitrates decompose when strongly heated. Producing Colourless gas of O_2 & white residue of the metal nitrite. Expect for $LiNO_3$, which produce Li_2O, brown gas of NO_2 & O_2.

The anomalous behaviour of $LiNO_3$ is due to the larger charge density of 'Li' which polarize the O-N bond in the NO_3^- ion. The other group 1 cations are large. Therefore, on heating their nitrates does not decompose. But very strong heating causes them to melt resulting the molten nitrite & O_2 gas.

4. Thermal stability of group 2 nitrates: -

Group 2 nitrates thermally decompose same as $LiNO_3$ due to its higher polarizing power than group I.
All these nitrates when heated results brown gas of & NO_2, O_2 gas & the white residue of the metal oxide.

All group 2 nitrates are thermally unstable.

- $Mg(NO_3)_2$ decomposes at very low heating, while $Ba(NO_3)_2$ requires high temperature.
- The thermal stability of group 2 nitrates increases down the group with increase atomic number due to polarizing power of the cation decreases resulting ionic character.

5. Thermal stability of group 1 carbonates: -

All group I carbonates are thermally stable even at very high temperature except for Li_2CO_3

Li_2CO_3 decomposes on heating result CO_2 gas white residue of Li_2O.

This is because Li^+ is small hence possess high polarizing power & polarizes the O-C bond in the CO_3^{2-} ion.

6. **Thermal stability of group 2 carbonates: -**

All carbonates of group 2 decompose at very little heat except for $BaCO_3$, which needs high temperature to produce white residue of metal oxide & CO_2.

$BeCO_3$ is unstable & does not exist at room temperature.

Therefore, all group 2 carbonates are thermally unstable, but thermal stability increases down the group as the atomic radius increase.

7. Describe an experiment to study the thermal decomposition of group 1 & 2 nitrates & carbonates

Place same amount (same moles) of each carbonate/each nitrate in a series of combustion tubes.
Fix a delivery tube to the hard glass tube & set up the following apparatus.

- Mark the test tube on the apparatus used to collect the gas as shown.
- As the carbonate/nitrate decompose gases will be evolved which will be collected by the down ward displacement of H_2O.
- Note the time taken for the gas evolved to reach the mark on the test tube in the water bath.
- Take the same amount of moles of remaining carbonate/nitrate the repeat the experiment & record the time taken for the gas to reach the mark.

Observations:

Carbonates & nitrates which are easily decomposed fills the mark at lesser time, than the one which are difficult to decompose.

Accuracy:

To ensure highest accuracy same conditions should be given for all experiments. The Bunsen flame should be the same for all reactions. Also, the distance between the burner & the hard glass tube should be kept constant. Also, the thickness of the hard glass tube should be the same ensure equal heat absorption.

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