PG- I Semester

Inorganic Chemistry

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TOPIC:- Thermodynamic Importance of Stability Constants

2.1 Thermodynamic Importance of Stability Constants

In order to reach accurate conclusions regarding the nature of the forces acting within complex species during their formation in solution, the energy changes accompanying the reaction in question i.e. a complete thermodynamic characterisation of the reactions is necessary at the very least, determination of enthalpy (ΔH), entropy (ΔS) and free energy (ΔG)changes accompanying complexation.

In the language of thermodynamics, the equilibrium constant of the reaction is a measure of the change in free energy, heat content and entropy. A more useful manner of stating equilibrium constant is in terms of the standard free energy change ΔG, i.e. the difference of free energy between the products and the reactants in a standard state, which is related to equilibrium constants by the thermodynamic expression:

$$- RT \log K = \Delta G = \Delta H - T\Delta S \quad \text{.....................................(8.2)}$$

The reactions tends to go in the direction written, when ΔG is negative.

Enthalpy change (ΔH) gives the amount of heat either consumed or liberated per mole of products and is related to the strength of the ligand to metal bonds, compared to that of the metal to solvent bonds.

Entropy change (ΔS) is related to the change in randomness (the disorder) of a system. As is quite evident from the relation given above (8.2), complex formation is most favoured by the negative enthalpy and positive entropy changes (either of the two or both) as may be expressed by the equation:

$$\log K = \frac{\Delta S - \Delta H / T}{2.303\, R} \quad \text{..(8.3)}$$

In many reactions both the heat and entropy changes favour complex formation but their relative importance changes markedly with minor variations from ML to M'L or ML'.

FACTORS AFFECTING STABILITY

Factors related with Metal

The nature of the metal ions and the effect of the different physical properties of the metal ions on the stability of the complex are:

1. Stability (or stability constant) increases with decreasing size of metal ion. K generally varies are 1/r.
2. Stability constants for a complex increase with the charge of the central ion. The K for the Fe(II) complexes will be less then the K for the corresponding Fe(III) complexes.
3. The ions with high polarizability give complexes with higher stability constants. Thus Cu(I) complexes have higher K values than the similar sized Na^+ complexes, similarly of Ca^{2+} and Cd(II) or Al (III) and Ga(III) the former have low K values for the complex formation.
4. Electronegativity increases the polarizing power and the ions with higher electronegativity give stable complexes.
5. **Ionization Energies:** The electronegativity, covalent nature and ionic radii can be related to the ionization energies of the atoms. It is found that the stability constants for the metal complexes with a ligand increases with the ionization energies of the metallic species.

Observations of Bjerrum Niecilson and others show that although most of the metals of the periodic table form complexes, this tendency is the most with transition metals. The reason being that the chelate effect is almost an entropy effect for the metal ions of nontransitional group, while for the transitions metals it is partly an enthalpy effect which increases the crystal field strength. The increase in crystal field strength increases the points of attachment of the ligand to the metal ion imparting greater chelating tendency to the latter (cf. CFS). Fig 8.1

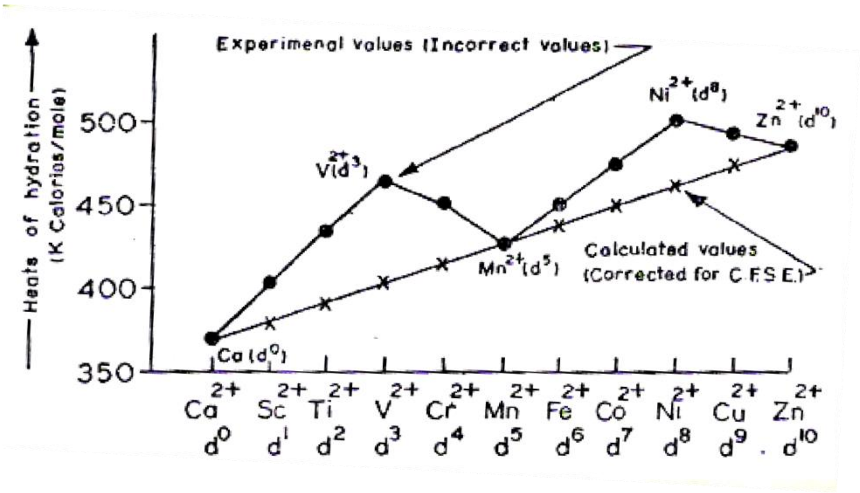

Fig. 8.1: CFSE affecting stability of aquo-complexes

Chatt Ahrland classified the metals into a and b classes while a class metals form stable complexes with ligands having the coordinating atoms, N, O, F (second period elements), b class metals form stable complexes with ligands in which donor atom is P, S, Cl (third or latter period elements).

The a class metals include H, alkali and alkaline earth metals; the elements from Sc to Cr, Al to Cl, Zn to Br and lanthanides and actinides. While amongst b class Rh, Pd, Ag, Ir, Pt, Au and Hg are included.

Elements from Mn to Cu, Tl to Po, Mo, Te, Ru, W, Re, Os, Cd are border line metals.

It can be said with some approximation that increase in the ionic charge of the metal ion and donor, will bring an increase in the chelating tendency while the increase in ionic radius will decreases it. Thus small cation size, comparatively large ionic charge and appropriate electronic arrangements are responsible for the maximum ability of complex formation by transition elements.

Mellor and Maley have shown that the stabilities of the complexes of bivalent metal ions follow the order: Pd > Cu > Ni > Pb > Co > Zn > Cd > Fe > Mn > Mg irrespective of the nature of the ligand. Irving and Williams from the analysis of the data on stability constants of transition metal ions, found that the order

Mn(II) < Fe(II) < Co(II) < Ni(II) < Cu(II) > Zn(II),

holds good. This order according to them follows logically from a consideration of the reciprocal of ionic radius and second ionization potential of the metal, and is known as 'Natural Order of Stability'.

Univalent ions have not been extensively studied but data on the complexes of the univalent ions with dibenzol methanate ion shows the order of the stability as:

Ag > Tl > Li > K > Rb > Cs

For tetravalent metals much less information is available, the greater ease of hydrolysis of these ions making potentiometric titrations more difficult. Irving and Williams suggest from a considerable limited number of investigations that a rough order of stabilities be:

Ti > Fe > Ga > In > Al > Cr > Sc

Factors Related With Ligands

The properties of the ligands which affect the stability of the metal complexes are as under:

1. **Basicity of the ligands:** The greater is the Lewis base strength, higher is expected to be the stability constant of the complex. Thus K values for the complexes are expected to change in a manner similar to the changes in the proton association constant (BH) for the ligands.

2. **Dipole moment and polarizability of the ligands:** Due to the greater electrostatic interactions between the metal ion and the ligands, polarity and ploarizability of ligand results in higher K for the complexes.

3. **(M→L) π-bonding** always increases the stability of the complex.

4. **Steric factor:** It play an important rule in determining the stability constants for the complexes. Thus the 2 methyl derivative of 3 hydroxyquinoline gives much less stable complexes then the parent compound because of the steric hindrance caused by the methyl group adjacent to the site of co-ordination.

In complex formation hydrogen behaves just like a metal ion. Therefore, a ligand with a larger affinity for proton will show the same behaviour towards the metal ions. According to Riley any factor which can increases the localization of negative charge in the co-ordinating ligands makes the electron more readily available and thus increasing the co-ordinating ability of a base. The correlation between the basic strength of the ligand and the stability constant of the complexes was pointed our first by Calvin and Wilson.

Ring Formation and Size of the Ring

Ring complexes or chelates are very stable due to reduced strain. The number of ring formed, the size of the rings and stabilizing or interfering resonance interactions are determined by the structure of the chelating agent. The work of Ley on the chelates of amino-acids showed that five and six membered rings are the most stable. Much evidence has accumulated since then to prove that all chelates have either five or six membered rings. Pfeiffer observed that in general the five membered rings is the more stable when the ring is entirely saturated but when one or more double bonds are present, the six membered rings is favoured. Schwarzenbach and Co-workers have observed that there is a decrease in clate stability with the increase in ring size. The stability of a five membered ring is not chiefly due to entropy but rather to the enthalpy of formation; the example being 1, 2, 3 triamine- propane tetra chloroplatinum. Further the stability increases with the increase in the number of rings in the molecule:

M(en) < M(trien) < M(EDTA).
(one ring) (two rings) (five rings)

Steric Effect:

Steric hindrance can influence stability in many ways, e.g.

(i) Metal-ligand bonds are weakened due to the presence of bulky group near the coordinating site.

(ii) The substituting group prevents the ligand from assuming the planar configuration and hence introduce strain in the metal-donor bond.

(iii) Steric hinderacne is also due to strained structure of the chelated ring, since it breaks the usual linear configuration of the complexes.

From the study of the copper complexes of substituted malonic acids Riley concluded that ethyl and propyl groups had a larger effect then methyl in reducing the stability.

Resonance Effects

The stability of a chelated ring will depend on the possibilities of resonance in the ring and on how these will fit in with resonance in the organic ligand itself. That resonance may affect the formation of a chelate was first shown by Calvin and Wilson. The double bond resonance has been attributed as a reason to be unusual stability of histamine cobalt chelate.

Orbital hybridisation

There are certain factors which serves to make a specific bonding arrangement stable. As an example, the shape of β, β', β" triaminotriethylamine is such that the bonding atoms must be grouped tetrahedral round a metal atom. The ligand will therefore tend to form a stable complex with a metal such a zinc, which favours sp^3 hybridisation in its 4-co-ordinate compounds, rather than with one such as copper which is limited to dsp^2 (planar) hybridisation. Similarly, triethylene tetra amine gives stable complex with metal ions having dsp^2 hybridisation, rather then sp^3 hybridisation.

Chelate Effect And Its Thermodynamic Origin

The chief factor responsible for the stability of the chelate ring is the entropy change which can be viewed statistically or as probability factor. Considering the electronic effect of the donor atom to be the same in the monodentate and the bidentatc ligands, it can be seen that the dissociation of a monodentate from a complex will be higher than that in the chelating bidentate. The dissociation of the M-L bond in monodentate will release the ligand completely from the coordination sphere of the metal, so that it can be easily swept off by the solvent. But the dissociation of one M-L bond for the bidenate ligand does not release the ligand completely (for which simultaneous dissociation at both ends is required). Hence the stability constant for metal chelate must be higher. Consider the equilibrium reactions (Fig. 8.4):

$$[Co(NH_3)_6]^{3+} + 3en \leftrightarrows [Co(en)_3]^{3+} + 6NH_3 \text{....................} (8.4)$$

Assuming that (i) Co-N bond strength in the two complexes is same (the f value of ammonia and ethylendiamine are within 3%), and (ii) the entropy changes due to structure making and structure breaking are negligible due to the similar size of the complexes, it can be seen that the ΔS^o will increase for the reaction as the number of moles of the products are more than those for the reactants. This will help the reaction to go to the right

Import Question For Revision

(i) Stability of metal complexes is primarily related with the thermodynamic stability. Which deals with.......................... and...................

(ii) Overall stability constant, β_n for ML_n complex is related with the stepwise constants as- β_n = ...

(iii) The thermodynamic expression relating equilibrium constant is- ....

The reaction goes in the direction written when...................

(iv) CFSE results in the maximum increase in the stability of aquo-complexes of divalent metal ions in the first transition series at d^n configuration......................and........................

(v) The Irving Williams order of stability is..

(vi) Chelate effect is primarily due to............................ factor.