aqueous solution, can nonetheless be prepared using other solvents.

Finally, in relation to the *Macrocyclic Effect,* I want to show you how careful we chemists need to be. One of the first, and very popular hypotheses, which was formulated about the origin of the stability of macrocyclic complexes was based on a ΔH° value obtained from the temperature dependence of the appropriate stability constant. It was concluded that the origin of this enhanced stability derived from the smaller solvent-interaction of macrocyclic as opposed to non-cyclic ligands. To-day, this attractive hypothesis is recognized as only one of the possible contributions to this extra stability and this change has essentially been brought about by the direct calorimetric determination of the enthalpies of formation of macrocyclic metal complexes, revealing gross discrepancies from the ΔH° values obtained by indirect route, of which a criticism has already been levelled.

Thermodynamics of Complex Formation with Multidentate Ligands

G. ANDEREGG

Laboratorium für Anorganische Chemie, E.T.H.Z, Universitätstrasse 6, CH-8091 Zurich, Switzerland

Complex formation in solution is generally described by a reaction of type I. This formulation does not correspond to what actually takes place, namely

$$M^{z+} + L^{n-} \rightarrow ML^{(z-n)+} \qquad \text{I}$$

process II, because of the omission of the solvent as

$$M(H_2O)_q^{z+} + L(H_2O)_m^{n-} \rightarrow ML(H_2O)_p^{(z-n)+} + (q + m - p)\,H_2O \qquad \text{II}$$

reacting partner. Indeed the entropy of complex formation is generally positive and large, depending strongly on the dentateness of the ligand, and not negative as it would be expected for reaction I, because of the decrease of the number of species in solution. The influence of the solvent seems also to be reflected in the value of the enthalpy of complex formation: for complexes with multidentate charged O-ligands it is generally not very different from zero. This is because the endothermic effect for the dehydration of the reacting species is almost compensated by the exothermic effect of the ligand coordination. On the contrary, for neutral ligands, the enthalpy is remarkably negative as result of (*1*) the lower hydration of the ligand, (*2*) the covalency of the bonding, and (*3*) no charge neutralisation occurs.

In multidentate ligands the donor atoms connected together by chains which, on complex formation, give rise to chelate rings. These are considered responsible for the higher stability of complexes with multidentate ligands with respect those of monodentate ligands, if in the complexes the same number of donor atoms are involved. The interpretation of this effect, the *Chelate Effect,* has been the subject of active discussion over the last thirty years and it is still a matter of opinion. In this connection, one should consider not only for five-, six- and seven-membered chelate rings a positive *Chelate Effect* is observed. If there are more than six atoms between the donor atoms or chelating units, their neutral influence decreases and eventually reduces to that of a statistical effect.

The values of the enthalpy and of the entropy for complex formation with the same ligand and a series of related metal ions, such as the alkaline earth, the 3d divalent metal or the 4f trivalent lanthanide ions can be correlated with stereochemical and electronic effects at the central ion such as the dentateness of the ligand, the coordination number of the metal ion and ligand field effects.

The formation of mixed (ternary) complexes will be also considered in some detail. These have recently received more attention, especially because of their increased stability with respect to that expected by statistical consideration and in relation of their importance in biological systems.

The Macrocyclic Effect in Tetraaza-Macrocyclic Ligands

ROBERT D. HANCOCK* and GLORIA J. McDOUGALL

National Institute for Metallurgy, Randburg, South Africa

The origin of the Macrocyclic Effect [1] in complexes of *cyclam* as compared with those of its open-chain analogue *2,3,2-tet* is discussed. It is not readily apparent that the presence of four secondary (2°) nitrogens in *cyclam,* as opposed to two primary (1°) and two 2° in *2,3,2-tet* should make much difference, since the pK_a's of 2° amines are not much different from those of 1°. Proton basicity in water is a misleading guide to base-strength. For example, $\log K_n$-(RNH_2) with Ag(I) increases strongly as R changes