CHAPTER ONE

INTRODUCTION

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, • Molecules interact with each other with varying degrees of intensity. At one extreme are the very Weak non-specific interactions e.g., interactions amongst gaseous molecules causing them to deviate from ideal behaviour and in condensation. The interaction is explained in terms of Van der Waals forces. Here molecules preserve their identity. At the other extreme are the strong interactions leading to chemical reactions. In the latter case the molecules lose their identity. Molecular complexes lie between these two extreme cases.

Mulliken and Person¹ defined a molecular complex as "A molecular complex between two molecules is an association, somewhat stronger than ordinary Van der Waals associations of definite stoichiometry". The partners have closed shell (saturated valence) electronic structures. In loose complexes the original molecules preserve their identities. The tendency to form complexes occurs when one partner is an electron acceptor (the Lewis acid) and the other is an electron donor (Lewis base). These complexes are thus designated as "Electron-Donor-Acceptor" (EDA) complexes. The term AD is used to designate the molecular complex with stoichiometry 1:1, where A is the electron acceptor and D is the electron donor. These complexes are also called "Charge Transfer Complexes".

The existence of molecular complexes has long been recognized by chemists. Certain aromatic hydrocarbons, amines, phenols etc., when mixed with large class of aromatic

nitro-compounds, quinones, etc., intensely coloured molecular complexes are formed. Pfeiffer² was the first to classify these complexes. Lewis³ explained these complexes on the basis of his acid_base theory. A strong interest was developed in the subject when Benesi and Hildebrand^{4,5} observed a new absorption band in the ultraviolet spectrum of solutions of iodine in benzene. This band was a characteristic of I₂. Benzene complex which was not observed in the spectrum of either component alone. Although the new band found by Benesi and Hildebrand is in the ultraviolet region, an analogous band occurs in the visible region for many other complexes. The interpretation of the new absorption band led to an extension of the Lewis acid_base theory in a quantum theoretical form which provides the basis for the interpretation of a wide variety of phenomena associated with molecular complexes. A satisfactory quantum mechanical explanation was given by Mulliken⁶⁻⁸. The theory was further developed by Mulliken^{9,10}, Orgel and Mulliken¹¹, Mulliken and Person.^{1,12} Mullikens valence bond description is given on page 5 . An alternative approach to the energetics of the intermolecular charge transfer transitions has been made by Dewar and his co-workers¹³⁻¹⁸ using simple molecular orbital description. This is explained in Fig. 1.2. The charge transfer band is due to the transition of an electron from the highest occupied molecular orbital (HOMO) of the donor to the lowest empty molecular orbital (LEMO) of the acceptor.

Electron-donor-acceptor complexes and their spectra have been the subject of several reviews. Andrews¹⁹ emphasized experimental aspects for 1:1 complexes involving an aromatic hydrocarbon as one partner. This review gives early ideas about the stability of complexes, experimental techniques and types of interactions. The spectroscopic aspect was discussed by Orgel²⁰ in a general review of charge transfer spectra with special emphasis on molecular complexes. McGlynn²¹ reviewed the subject in 1958 from the point of view of theorist with special emphasis on spectroscopic aspects and pointed out some difficulties in reconciling theory with experiment. Briegleb and Czekalla²² in 1960 emphasized the spectroscopic studies and the experimental data have been correlated.

The most comprehensive book on the subject is that by Briegleb²³. Another book by Andrews and Keefer²⁴ emphasizes applications to organic chemistry. The third book by Mulliken and Person¹ deals with 1:1 complexes in solutions. After 1969 several books²⁴⁻²⁷ deal with charge transfer or molecular complexes in solutions and in solid states.

Because of the experimental difficulties involved in the vapour phase investigations, most of the studies of complexes have been made in solution, in solvents that are as inert as possible. The London dispersion attractions, which are important between D and A in the vapour state are very approximately cancelled by losses of solute-solvent dispersion force attractions

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when complex is formed from free donor and acceptor in solution. Roughly, one donor-solvent plus one acceptor-solvent contact is replaced by one donor-acceptor and one solvent-solvent contact.

Some Characteristic Features of Charge Transfer Complexes

Any theory of charge transfer complexes should explain satisfactorily the following general features of the absorption spectra and energy changes associated with such complex formation.

- 1) The characteristic absorption of visible or ultraviolet radiation by the complex. λ_{max} is several thousand Angstroms greater than the wavelengths of absorption by the individual components of the complex. This indicates a decrease in energy of the order of 20 K.cal/mole for the most loosely bound electron in the complex.
- 2) Although the electron excitation energy decreases considerably on complex formation, the heats of formation for several complexes are of a much smaller order (~ 1_5 K.cal/mole). This indicates the weak nature of binding in the ground state of the complex.
- 3) The high intensity of the absorption band. The extinction coefficient is often of the order of 10⁴ litre/mole cm. Several of the earlier theories of such complex formation

could not account for the high intensities of charge transfer absorption bands.

4) The absorption band extends over a range of wavelength continuously. The breadth of the band suggests the loose nature of binding in the ground state of the complex.

Theory of Donor-Acceptor Complexes

The theory of donor-acceptor complexes and their spectra as presented below is a vapour state theory, except for the omission of the London-dispersion attraction terms. This theory is essentially valid for solutions in inert solvents with small corrections for solvation energies. This is the resonance structure theory (Valence Bond treatment) developed by Mulliken⁶⁻⁸, Mulliken and Person¹², McGlynn²¹, and Briegleb²³. The ground state structures of 1:1 donor-acceptor complexes between electron donors (D) and electron acceptors (A) can be represented by wave functions ψ_{N1} , where

$$\psi_{N}(AD) = a \psi_{O}(A,D) + b \psi_{1}(A^{-}, D^{-}) \qquad \dots \qquad (1.1)$$

The donor and acceptor, though in many interactions are neutral molecules, can be atoms or ions. For convenience assume that they are neutral molecules. The wave function ψ_0 (AD) is the "no bond" wave function with coefficient a. It reflects all those forces which make up the normal "physical" attraction between two molecules such as dispersion, dipole-dipole, dipole-induced dipole an quadrupolar forces. The wave function ψ_1 with coefficient b corresponds to a dative structure in which one electron has been transferred from the donor to the acceptor molecule whilst maintaining the overall spin multiplicity of the state ψ_0 . ψ_1 is an important additional correction term in the case of donor-acceptor complexes. To convert the approximation represented in equation (1.1) into an exact equality, further terms should be added, but these are relatively small in typical loose complexes.

When two molecules interact, in addition to 'physical' interaction, there will be additional interaction. This additional interaction leads to extra stability, a dipole moment, changes in geometry, a new ultraviolet or visible absorption band, and other noticeable effects. The inclusion of the ψ_1 term explains this additional interaction. It is assumed that in most interactions a \gg b. Simple valence-bond theory demands that there shall be an excited electronic state, ψ_E , which is given by

$$\psi_{\rm E}$$
 (AD) = a* ψ_1 (A⁻ = D⁺) = b* $\psi_{\rm O}$ (AD) ... (1.2)

where $a \sim a^*$ and $b \sim b^*$. Here a^* and b^* are determined by the requirements that ψ_E be normalised and orthogonal to $\psi_N^{'}$. The electronic absorption characteristic of the complex is the transition $\psi_E \leftarrow \psi_N$. This occurs generally with high intensity.

The state described by equation (1.2) is called a charge transfer (CT) state. The donor-acceptor system A.D. is stabilized by resonance between ψ_0 and ψ_1 with maximum stabilization if a \sim b. For a weak electron-donor-complex the dependence of energies of various states on inter-molecular distance A-D is shown in Fig. (1.1). For a series of complexes of different donors with same acceptor species, the charge transfer energy h $\mathcal{V}_{\rm CT}$ is given by

$$h \mathcal{V}_{CT} = E_{CT} = I^{D} - C_{1} + \frac{C_{2}}{I^{D} - C_{1}} \qquad \dots \qquad (1.3)$$

where C_1 and C_2 are constants for a given acceptor. This is also written as

$${}^{\mathrm{h}}\mathcal{V}_{\mathrm{CT}} = \mathrm{I}^{\mathrm{D}} - \mathrm{E}^{\mathrm{A}} - \mathrm{W} \qquad \dots \qquad (1.4)$$

where W is the dissociation energy of the charge transfer excited state. In general

$$h \mathcal{V}_{CT} = a I^{\mathbb{D}} + b$$
 ..., (1.5)

where a and b are some constants. Thus the plots of $h\mathcal{V}_{CT}$ against I^{D} will be linear.

Oscillator Strengths

The molar absorptivity or extinction coefficient ϵ_{v} of any molecular species is defined by Beer's law:

$$I = I_0 10^{-6}$$
 ... (1.6)

- Fig. 1.1: A diagram showing the energetics for a weak charge transfer complex between a donor (D) and an acceptor (A)
- $W_{\rm N}$: energy corresponding to the ground state wave function $\psi_{\rm N}~({\rm AD})$
- $W_{\rm E}$: energy corresponding to excited state wave-function $\psi_{\rm E}\,(AD)$
- W_o and : are the energies if there were no resonance W₁ stabilization
- E^{AD} : energy of optical intermolecular charge transfer transition
- I : ionization potential of the donor.
- E^A : electron affinity of the acceptor





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Fig. 1.2: Electronic excitation

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1	lowest energy CT band
2	excitation from penultimate donor level
3	excitation to higher empty acceptor level
4	higher energy acceptor to donor CT band
5	Intramolecular donor excitation
6	Intramolecular acceptor excitation

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Fig. 1-2 : ELECTRONIC EXCITATION

Here C is the concentration in moles per litre, 1 is the path length in centimetres, and I and I^O are the intensities of the transmitted and incident light of frequency γ .

The oscillator strength f for an electronic transition is defined by

$$f = \frac{2.303 \text{ mc}^2}{\pi \text{ e}^2 \text{ N}_0} \int \mathbf{e}_{\gamma} \cdot d\boldsymbol{\nu} \qquad \dots \qquad (1.7)$$

or, substituting for the values of the fundamental constants

$$f = 4.318 \times 10^{-9} \int e_{\eta} d\nu$$
 ... (1.8)

The integration is made over the entire absorption band or bands that belong to the particular electronic transition (see Fig. 1.3 for the case in which the transition shows no vibrational structure). If \mathbf{e}_{γ} is known empirically equation (1.8) can be used to obtain an empirical value of the oscillator strength. The integral is approximated by taking the product $\mathbf{e}_{\max} \Delta \mathcal{V}_{1/2}$; that is

$$E \sim 4.32 \times 10^{-9} \epsilon_{\rm max} \cdot \Delta \mathcal{V}_{1/2}$$
 (1.9)

where $\Delta \mathcal{V}_{1/2}$ is the width in cm⁻¹ of the band between the two frequencies at which $\mathbf{G} = \frac{1}{2} \mathbf{e}_{\max}$. The theoretically computed oscillator strength is related to the magnitude of the theoretical electronic transition dipole $\mu_{\mathbf{EN}}^{\text{el}}$ in esu. cm

$$f_{EN} = \left(\frac{8\pi^2 mc}{3h}\right) \overline{\nu} (\mu_{EN}^2 / e^2)$$



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or

$$\mu_{\rm EN}$$
 (debyes) $\simeq 0.0958 \left(\frac{\varepsilon_{\rm max} \cdot \Delta \mathcal{V}_{1/2}}{\mathcal{V}_{\rm max}} \right)^{1/2}$ (1.10)

where \mathcal{V}_{\max} is the wave number of maximum absorption.

Methods for the Determination of Association Constants of EDA Complexes

The following are some of the several methods for the determination of association constants of 1:1 electron-donoracceptor complexes:

- i) Ultraviolet and Visible Spectroscopy
- ii) Infrared and Raman Spectroscopy 25,28-32
- iii) Nuclear Magnetic Resonance Measurements 25,33
- iv) Paramagnetic Resonance Study³⁴
- v) Solubility Method³⁵
- vi) Calorimetry³⁶⁻⁴¹ and so on.

Out of these methods, the ultraviolet and visible spectroscopic method is widely used. The equations used for evaluation the elevation of the association constants and the molar extension coefficients for 1:1 and 2:1 (donor_acceptor) EDA complexes are given below:

(a) <u>Consider 1:1 (donor-acceptor) complexes</u>:

The equilibrium between the donor, acceptor and the

complex is given by

 $A + D \longrightarrow AD$

The equilibrium constant is given by

$$K_{C}^{AD} = \frac{C_{AD}}{C_{A} \cdot C_{D}}$$

where C_A and C_D are the equilibrium concentrations of the acceptor and the donor respectively. Here it is assumed that the quotient of activity coefficients $\gamma_{AD} / \gamma_A \cdot \gamma_D$, is unity.

The above equation is often written as

$$K_{C}^{AD} = \frac{C_{AD}}{(C_{A}^{\circ} - C_{AD})(C_{D}^{\circ} - C_{AD})} \qquad (1.11)$$

where C_A^O and C_D^O are the initial molar concentrations of the acceptor and the donor respectively. Rearrangement of equation (1.11) gives

$$C_{AD} = \frac{\frac{C_{A}^{\circ} + C_{D}^{\circ} + \frac{1}{K_{C}^{AD}}}{2} - (C_{A}^{\circ} + C_{D}^{\circ} + \frac{1}{K_{C}^{AD}})^{2} - C_{A}^{\circ} \cdot C_{D}^{\circ}$$
(1.12)

Many spectroscopic methods sought generally to reduce the form of equation to a linear function of two experimentally measurable quantities. Assume that only the complex absorbs at the wavelength of absorption. Assume d is the molar absorbance (optical density) for a one cm. path length of solution and $\varepsilon_{\lambda}^{AD}$ is the molar absorption coefficient of the complex at the wavelength of absorption. Then equation (1.11) can be written as

$$\frac{C_{A}^{O}}{d} = \frac{1}{\substack{K^{AD}, e^{AD} \\ C}, \frac{1}{\lambda}} \cdot \frac{1}{\substack{C^{O} \\ D}, \frac{1}{\lambda}} + \frac{1}{\substack{C^{AD} \\ C^{O}, \frac{1}{\lambda}}} + \frac{C_{A}^{O}}{\substack{C^{O} \\ D}, \frac{1}{\lambda}} - \frac{d}{\substack{C^{O} \\ \lambda}} \cdot \frac{1}{\substack{C^{O} \\ D}} \cdot \frac{1}{\substack{C^{O} \\ \lambda}} \cdot \frac{1}{\substack{C^{O} \\ D}, \frac{1}{\lambda}} \cdot \frac{1}{\substack{C^{O} \\ \lambda}} + \frac{1}{\substack{C^{O} \\ D}, \frac{1}{\lambda}} + \frac{C_{A}^{O}}{\substack{C^{O} \\ D}, \frac{1}{\lambda}} \cdot \frac{1}{\substack{C^{O} \\ \lambda}} \cdot \frac{1}{\substack{C^{O} \\ D}, \frac{1}{\lambda}} \cdot \frac{1}{\substack{C^{O} \\ \lambda}} \cdot \frac{1}{\substack{C^{O}$$

when $C_A^o \ll C_D^o$, equation (1.13) becomes

$$\frac{c_{A}}{d} = \frac{1}{\kappa_{C}^{AD} \cdot e_{\lambda}^{AD}} \cdot \frac{1}{c_{D}^{o}} + \frac{1}{e_{\lambda}^{AD}} \qquad \dots \qquad (1.14)$$

This is the Benesi-Hildebrand equation. According to this equation the plot of C_A^O/d against $1/C_D^O$ should be linear with a slope of $(K_C^{AD}, \epsilon_A^{DD})^{-1}$ and an intercept of $(\epsilon_A^{AD})^{-1}$ from which the value of K_C^{AD} may be evaluated. Rearrangement of equation (1.14) also gives

$$\frac{C_{A}^{o} \cdot C_{D}^{o}}{d} = \frac{1}{\kappa_{C}^{AD} \cdot e_{\lambda}^{AD}} + \frac{C_{D}^{o}}{e_{\lambda}^{AD}} \qquad \dots \qquad (1.15)$$

which is the Scott⁴² equation.

A linear plot results when $C_{A}^{o} \cdot C_{D}^{o}/d$ is plotted against C_{D}^{o} whose slope gives the value of $(\epsilon_{\lambda}^{AD})^{-1}$ while the intercept gives $(K_{C}^{AD}, \epsilon_{\lambda}^{AD})^{-1}$. Another modification of the equation (1.14) gives

$$\frac{d}{c_{A}^{o},c_{C}^{o}} = - K_{C}^{AD}, \quad \frac{d}{c_{A}^{o}} + K_{C}^{AD}, \quad \frac{d}{\lambda_{A}^{i}} \qquad \dots \qquad (1.16)$$

which is the Scatchard (Foster, Hamick and Wardley) 43 equation. Several modifications of these methods have been described $^{44-46}$. In view of the inadequacy of Benesi-Hildebrand treatment⁵, where the linearity of the plots is not a sufficient evidence of 1:1 stoichiometry the optical data were subjected to the Rose-Drago treatment^{40,41}. The equation derived by these authors is

$$\frac{c_{A}^{\circ} \cdot c_{D}^{\circ}}{d'} = \frac{1}{K_{C}^{AD} \cdot \varepsilon_{\lambda}'} + \frac{c_{A}^{\circ} + c_{D}^{\circ}}{\varepsilon_{\lambda}'} \qquad (1.17)$$

where $\epsilon'_{\lambda} = \epsilon_{C} - \epsilon_{D} - \epsilon_{A}$ and ϵ_{C} , ϵ_{D} and ϵ_{A} correspond to the molar absorptivities of the complex, donor and acceptor respectively. If the complex is the only absorber, equation (1.17) gives:

$$\frac{C_{A}^{o} C_{D}^{o}}{d} = \frac{1}{\kappa_{c}^{AD} \varepsilon_{\lambda}^{AD}} \frac{C_{A}^{o} + C_{D}^{o}}{\varepsilon_{\lambda}^{AD}}$$
(1.18)

The plot of $\frac{C_A^{O,C_D^{O}}}{d}$ against $C_A^{O} + C_D^{O}$ should be linear with slope of $(\varepsilon_{\lambda}^{AD})^{-1}$ and intercept of $(K_C^{AD} \cdot \varepsilon_{\lambda}^{AD})^{-1}$ from which K_C^{AD} can be evaluated.

LaBudde and Tamres⁴⁷ have pointed out that these approximations of equation (1.14) are unsatisfactory if K_C^{AD} is large, e.g., greater than about 100 1.mol⁻¹.

(b) Complexes of 2:1 Stoichiometry (Donor-Acceptor)

Jayadevappa and Nagendrappa⁴⁸ obtained equations giving linear plots for systems of 2:1 (donor_acceptor) stoichiometry when only AD, complex is the absorbing species.

For an equilibrium

$$A + 2D = AD_2$$

 $K_C^{AD_2} = \frac{C_{AD_2}}{C_{A} \cdot C_D^2} \qquad (1.19)$

The equation derived by them has the form

$$\frac{c_{A}^{\circ} \cdot c_{D}^{\circ}}{d} = \frac{1}{\frac{AD}{K_{C}}^{\circ} \cdot e_{\lambda}^{\circ}} + \frac{(c_{D}^{\circ} + 4c_{A}^{\circ}) \cdot c_{D}^{\circ}}{\frac{AD}{2}}$$
(1.20)

According to this equation the plot of $\frac{1}{d}$ against $C_D^O(C_D^O + 4C_A^O)$ should give a straight line with a slope $\begin{pmatrix} AD_2 \\ C \end{pmatrix}^{-1}$ and an intercept $\begin{pmatrix} AD_2 \\ C \end{pmatrix}^{-1} \begin{pmatrix} AD_2 \\ C \end{pmatrix}^{-1}$, from which the $AD_2 \qquad AD_2$ values of K $\begin{pmatrix} AD_2 \\ C \end{pmatrix}^{-1} \begin{pmatrix} AD_2 \\ C \end{pmatrix}^{-1}$, from which the plots were obtained by Jayadevappa and Nagendrappa⁴⁸ and Jayadevappa and Budni⁴⁹ for some systems.

(c) <u>Simultaneous existence of Higher Order Complexes</u> <u>With 1:1 Complex</u>

Assume that both the species AD and AD₂ are present in significant amounts. The equilibria and the corresponding equilibrium constants may be written as

$$A + D \xrightarrow{} AD ; K_1 = \frac{C_{AD}}{C_A \cdot C_D} ... (1.21)$$

$$AD + D \longrightarrow AD_2; K_2 = \frac{C_{AD_2}}{C_{AD} \cdot C_D} \dots (1.22)$$

Assume $C_D^{O} \gg C_A^{O}$ and a cell of 1 cm path length is used, then the absorbance

$$\mathbf{d'} = \mathbf{e}_{\mathbf{i}} \mathbf{C}_{\mathbf{A}\mathbf{D}} + \mathbf{e}_{\mathbf{2}} \mathbf{C}_{\mathbf{A}\mathbf{D}} \qquad \dots \qquad (1.23)$$

where \mathbf{e}_1 and \mathbf{e}_2 are the molar absorptivities of AD and AD₂ respectively at the wavelength of measurement. From (1.21) and (1.22)

$$C_{AD} = \frac{K_{1}C_{A}^{0}C_{D}^{0}}{1 + K_{1}C_{D}^{0} + K_{1}K_{2}C_{D}^{0}} \qquad \dots \qquad (1.24)$$

$$C_{AD_{2}} = \frac{K_{1}K_{2}C_{A}^{0}C_{D}^{0}}{1 + K_{1}C_{D}^{0} + K_{1}K_{2}C_{D}^{0}} \qquad \dots \qquad (1.25)$$

By substituting (1.24) and (1.25) in (1.23) we get

$$\mathbf{d}' = \frac{\mathbf{e}_{1} \mathbf{K}_{1} \mathbf{e}_{A}^{\circ} \cdot \mathbf{e}_{D}^{\circ} + \mathbf{e}_{2} \mathbf{K}_{1} \mathbf{K}_{2} \mathbf{e}_{A}^{\circ} \cdot \mathbf{e}_{D}^{\circ}}{1 + \mathbf{K}_{1} \mathbf{e}_{D}^{\circ} + \mathbf{K}_{1} \mathbf{K}_{2} \mathbf{e}_{D}^{\circ}} \qquad \dots \qquad (1.26)$$

Equation (1.26) can be rearranged into the following three equations:

$$\frac{\underline{C}_{A}^{O}}{d'} = \frac{1 + K_{1}C_{D}^{O} + K_{1}K_{2}C_{D}^{O}}{\varepsilon_{1}K_{1}C_{D}^{O} + \varepsilon_{2}K_{1}K_{2}C_{D}^{O}} \dots (1.27)$$

$$\frac{\underline{C}_{A}^{O}.C_{D}^{O}}{d'} = \frac{1 + K_{1}C_{D}^{O} + K_{2}C_{D}^{O}}{\varepsilon_{1}K_{1} + \varepsilon_{2}K_{1}K_{2}C_{D}^{O}} \dots (1.28)$$

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$$\frac{d'}{c^{\circ}.c^{\circ}} = -\frac{d'K_{i}}{c^{\circ}} (1 + K_{2} c^{\circ}_{D}) + \epsilon_{1}K_{1} + \epsilon_{2}K_{1}K_{2}c^{\circ}_{D}$$
(1.29)

Equations (1.27), (1.28) and (1.29) can be compared with the (i) Beness-Hildebrand equation (1.14), Scott equation (1.15) and Scatchard equation (1.16) respectively.

From equations (1.27 to 1.29) it is immediately apparent that the appropriate plots will not, in general, give linear plots when $K_2 = \neq 0$, although over small concentration ranges experimental data may yield plot in which the deviation from linearity is not detectable. Thus the linearity of the plots in these cases does not supply an adequate test for the absence of complexes with stoichiometry other than 1:1.

Thermodynamics of Charge Transfer Complexes

An evaluation of the thermodynamic properties of charge transfer complexes, such as the changes in ethalpy, ΔH° , entropy, ΔS° , and the standard free energy ΔG° , occurring on complex

formation, provides useful evidence regarding the nature and strength of the binding in the complex. These thermodynamic quantities can be determined from a knowledge of the equilibrium AD_{C}^{AD} of K_{C}^{AD} for complex formation from ideal solutions of the components A and D, and by experimentally determining the variation of the equilibrium constant with temperature. The thermodynamic relationships

$$\Delta G^{O} = -RT \ln K_{C}^{AD} \qquad \dots \qquad (1.30)$$

$$\frac{d\ln K_{C}^{AD}}{dT} = \frac{\Delta H}{RT^{2}} \qquad \dots \qquad (1.31)$$

and $\Delta G^{O} = \Delta H^{O} - T\Delta S^{O}$... (1.32)

are employed to evaluate the changes in these thermodynamic properties. Instead of van't Hoff plot the plot of ln (K^{AD}_{C}, G^{AD}) against T^{-1} is used to get the value of ΔH^{2} .

The methods and the experimental and theoretical results of the numerous physicochemical investigations carried out on electron-donor-acceptor complexes are significant in understanding chemical catalytic processes and in numerous investigations on electron exchange between adsorbed molecules and a solid surface, especially in the case of semiconductors; also in connection with the interpretation of catalytic processes and likewise for biochemical processes; and for consideration of redox processes and of energy transfer and energy conduction mechanisms.

We have in this work, investigated four equilibria (two acceptors and two donors) at different temperatures in one solvent only. We have determined the nature of the complex formed, their stoichiometry, their spectral characteristics and the thermodynamics of their formation. In addition, the oscillator strengths and the transition dipoles have been determined.