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A STUDY OF
SOME MOLECULAR COMPLEXES OF TETRACYANOETHYLENE
WITH NAPHTHALENE AND METHYLATED NAPHTHALENES

by

Edward Stanislaus Gregorek Jr.

A Dissertation
Presented to the Graduate Faculty
of Lehigh University
in Candidacy for the Degree of
Doctor of Philosophy

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CERTIFICATE OF APPROVAL

Approved and recommended for acceptance as a dissertation in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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DEDICATION

To my parents.

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ABSTRACT

The thermodynamic and spectral properties of the molecular complexes of tetracyanoethylene (TCNE) with naphthalene (N) and several methylated naphthalenes were studied in CH_2Cl_2 solution. These complexes are characterized by three charge-transfer (CT) bands in the visible and near UV region, the high energy one of which is sometimes obscured by the absorption characteristic of the donor. These complexes were determined to have a 1:1 stoichiometry by the method of Job.

A new and rigorous expression for evaluation of the mole fraction equilibrium constant ^xK is presented. A comparison of this expression with the comparable expression for the molar concentration equilibrium constant ^cK helps to clarify several problems of long standing concerning the relationship between the ^cK and ^xK values determined by the Benesi-Hildebrand or similar methods. It makes clear the fact that no simple relationship exists between ^cK and ^xK , except at infinite dilution, and explains the fact that two different values for the extinction coefficient ϵ_c of the complex are obtained, depending on whether ^cK or ^xK is evaluated. These effects, which have long been attributed to a departure from ideal behavior, are shown to be due solely to the fact that mole fraction and molar concentration units are not linearly related, except at infinite dilution. It is also pointed out that ^xK is of greater fundamental signif-

icance than ^cK , and that the value of ϵ_c evaluated in conjunction with ^xK best represents its "true" value.

The fit of the experimental data to the expressions used to evaluate ^cK and ^xK indicates that the systems studied deviate from ideal behavior when the donor is present in high concentration. An analysis of the possible factors contributing to this behavior, both in the thermodynamic sense of deviations from Raoult's law, and in terms of possible competing equilibria, is presented, in greater detail than has heretofore been attempted. It is concluded that the observed behavior (increase in ^cK and ^xK with increasing concentration of donor) is probably due principally to the formation of solvent-donor complexes and, to a less certain extent, to the presence of D_2A complexes.

The possibility that the deviations from ideal behavior exhibited by these systems may arise from a variation of ϵ_c with increasing concentration of donor is also examined. Although slight variations in ϵ_c , and in ^xK as well, can be expected to occur with changing dielectric constant of the solution, these should have an effect opposite to that observed; hence they can be regarded as unimportant in the systems studied.

An analysis of the wavelength shifts and changes in relative intensities of the first two C-T bands of TCNE-N complex with changes in temperature, pressure and solvent composition is made in terms of several factors which would

theoretically be expected to influence these quantities. On the basis of this analysis it is tentatively concluded that the first two absorption maxima observed in TCNE-naphthalene complexes represent two different C-T transitions, each due to a different 1:1 complex. The assignment of these two C-T bands to different configurational isomers of the complex is supported by theoretical considerations involving the symmetries of the donation and acceptation orbitals involved in complex formation.

It was shown recently by Lepley that the two lowest-energy C-T bands of TCNE-N correspond to electronic promotions from each of the two highest energy occupied π -MO's (Ψ_5^N and Ψ_4^N) of N to the lowest energy unoccupied π -MO of TCNE (Ψ_6^{TCNE}). It is suggested that the third C-T band may correspond either to the promotion $\Psi_3^N \rightarrow \Psi_6^{TCNE}$ or to the promotion $\Psi_5^N \rightarrow \Psi_7^{TCNE}$.

Section I. Introduction

Although the existence of solid molecular complexes has long been recognized, interest in the formation and spectral properties of molecular complexes in solution was not aroused until Benesi and Hildebrand [1], in 1949, discovered a new absorption band, characteristic of a 1:1 complex, in benzene solutions of iodine. Shortly thereafter, Mulliken [2,3], through a quantum mechanical extension of Lewis acid-base theory, provided a theoretical basis for understanding both the stability and spectral properties of such complexes. Since that time a great many studies, over 1000 in number, have been made on a large variety of molecular complexes and their physical properties.

The book by G. Briegleb [4] thoroughly discusses all aspects of the field of molecular complexes, making a special effort to explain experimental results in terms of Mulliken's charge-transfer theory. In addition, several reviews published since 1950 are valuable because of their differences in emphasis and general approach. The earliest review, by Andrews [5], emphasized experimental methods for studying 1:1 complexes, and is particularly valuable for its coverage of early ideas on the stability of molecular complexes and its survey of types of donor-acceptor interactions. (Classification of complexes in terms of donor and acceptor type is considered in detail by Mulliken [6,7].) McGlynn [8] and Murrell [9] have reviewed the subject from a theoretical

standpoint, with particular emphasis on spectral properties. Spectroscopic aspects have also been emphasized in reviews by Orgel [10], Mason [11] and Briegleb and Czekalla [12]. Szent-Györgyi [13] and McGlynn [14] have pointed out the importance of the charge-transfer complex concept in regard to biological problems, and Booth [15] has emphasized the role of molecular complexes in chemical reactions. Andrews and Keefer [16] have reviewed the molecular complexes of the halogens, and Hassel and Rømming [17] have reviewed the work on the structures of molecular complexes in the solid state. Mulliken and Person [18] have briefly reviewed several topics, especially the observed relationship between charge-transfer band energy and the ionization potential of the donor. Finally, in a review on the electron affinities of organic molecules, Briegleb [19] has discussed the relationships between charge-transfer band energy and several quantities related to the orbital energies of the components; namely the ionization potential, the half-wave oxidation potential and the energy of the ^1La band of the donor; and the electron affinity and half-wave reduction potential of the acceptor. A brief sketch of Mulliken's charge-transfer theory, to the extent that it relates to the discussion developed later in this dissertation, is given at the end of this introductory section.

The molecular complexes of tetracyanoethylene (TCNE) were first studied by Merrifield and Phillips [20]. Their

study revealed that TCNE was the strongest π -type acceptor molecule then known. As a consequence of its acceptor strength, the π,π -complexes formed between aromatic donors and TCNE have well defined charge-transfer bands with their absorption maxima in the visible region, well separated from the characteristic absorption of either component. This fact makes these complexes particularly well suited to spectrophotometric study. Among the donors studied by Merrifield and Phillips were several of the methylated benzenes. It was found that the ionization potentials of these donors could be linearly correlated with both the free energies of formation of the corresponding complexes and the energies of their charge-transfer transitions. Particularly interesting was the fact that the small differences in ionization potential among the xylene isomers were reflected in the values of their free energies of formation. Another point of interest was that the charge-transfer band of the p-xylene complex showed a doublet structure, while for several of the remaining methyl benzene complexes, particularly for the durene complex, the half-band widths were considerably greater than that for TCNE-benzene. This behavior was explained, following Orgel [21], on the basis of the hypothesis that ring substitution splits the double degeneracy of the two highest energy occupied π -orbitals in benzene, thereby allowing transitions from the ground state of the complex to two different excited states, formed by transfer of an electron to the acceptor from each of the split

degenerate levels of the donor.

In view of the interesting spectral and equilibrium properties exhibited by TCNE complexes of the methyl benzenes, it seemed desirable that Merrifield and Phillips' studies be extended to other polysubstituted aromatic systems. The present work was originally intended as a study of both the spectral and equilibrium properties of the methyl naphthalenes, especially the di-substituted derivatives. Early in the course of the present investigation, however, it became apparent that serious difficulties existed in the methods commonly employed for evaluating the equilibrium constants and extinction coefficients of weak molecular complexes. Consequently, emphasis was placed on the development of exact methods for evaluating these constants in the case of 1:1 complexes.

A new and rigorous method for evaluation of the mole fraction equilibrium constant is presented in Section V. The analysis given therein helps to clarify several problems of long standing (see, for example, the reviews by McGlynn [8] and Andrews and Keefer [16]) concerning the relationship between the molar concentration and mole fraction equilibrium constants ^cK and ^xK . It makes clear the fact that no simple relationship exists between ^cK and ^xK , and explains the fact that different values of the extinction coefficient are obtained, depending on whether ^cK or ^xK is evaluated. It is pointed out that these effects, which have long been attributed to a departure from ideal

behavior, are due solely to the fact that mole fraction and molar concentration units are not linearly related, except at infinite dilution. It is also pointed out that ϵ_K is of greater fundamental significance than ϵ_K , and that the value of the extinction coefficient evaluated in conjunction with ϵ_K comes closest to the true or infinite dilution value.

In regard to spectral properties, Lepley [22,23] has recently investigated the charge-transfer spectra of a wider variety of TCNE-methyl naphthalene complexes than was studied here. These are all characterized by two (or, in one case, three) distinct charge-transfer maxima in the visible region. Lepley has adequately explained the wavelength shifts exhibited by these complexes, compared to TCNE-naphthalene, in terms of the changes upon methylation in the orbital energies of the two highest-lying occupied π -MO's of naphthalene. On the basis of considerations involving the symmetries of these donor MO's, Lepley [23] has suggested that each of the two charge-transfer bands is due to a different complex conformational isomer. This suggestion is supported by the analysis presented in the present dissertation, where a similar conclusion is reached, chiefly on the basis of various solvent effects on the charge-transfer bands of TCNE-naphthalene (see Section V). A discussion of the origin of the observed multiple charge-transfer bands, and of the structures of the absorbing species, is presented in Section VII.

In order to define several quantities encountered below and to facilitate later discussion, a sketch of Mulliken's charge-transfer theory, in its simplest form, will now be given. According to Mulliken, the ground state of a molecular complex can be best represented as a resonance hybrid between a no-bond form (DA) of the complex, and a dative form (D^+A^-), in which an electron has been transferred from the donor to the acceptor. In wave mechanical terms,

$$\Psi_N = a \Psi_0 (DA) + b \Psi_1 (D^+A^-). \quad (I-1)$$

For the relatively weak, π, π -complexes encountered here the no-bond form will make the largest contribution to Ψ_N ; i.e. $a \gg b$. Corresponding to this ground state, there exists an excited state whose wave function is given by

$$\Psi_E = a^* \Psi_1 (D^+A^-) - b^* \Psi_0 (DA), \quad (I-2)$$

with $a^* \approx a$, $b^* \approx b$. (Equations (I-1) and (I-2), as they are written here, are only first approximations. For more general expressions, see, for example, Mulliken [7].) The electronic transition between these two states is strongly allowed, and gives rise to the intense charge-transfer band characteristic of the molecular complex.

The energy of state N is given by

$$\begin{aligned} W_N &\equiv \int \Psi_N H \Psi_N dv \approx W_0 - \frac{(H_{01} - S W_0)^2}{(W_1 - W_0)} \\ &= W_0 - \frac{\beta_0^2}{(W_1 - W_0)} = W_0 + R_N \end{aligned} \quad (I-3)$$

where H is the exact Hamiltonian operator for the entire set of nuclei and electrons, and

$$\begin{aligned} H_{01} &= \int \Psi_0 H \Psi_1 dv \\ S &= \int \Psi_0 \Psi_1 dv \\ W_0 &= \int \Psi_0 H \Psi_0 dv \\ W_1 &= \int \Psi_1 H \Psi_1 dv \end{aligned}$$

The quantity β_0 and the ground state resonance stabilization energy R_N are defined by equation (I-3); R_N in general has a negative numerical value.

Similarly, for the energy of the excited state,

$$\begin{aligned} W_E &= \int \Psi_E H \Psi_E dv \approx W_1 + \frac{(H_{01} - SW_1)^2}{(W_1 - W_0)} \\ &= W_1 + \frac{\beta_1^2}{(W_1 - W_0)} = W_1 + R_E \end{aligned} \quad (\text{I-4})$$

where β_1 and the excited state resonance energy R_E are defined by equation (I-4)

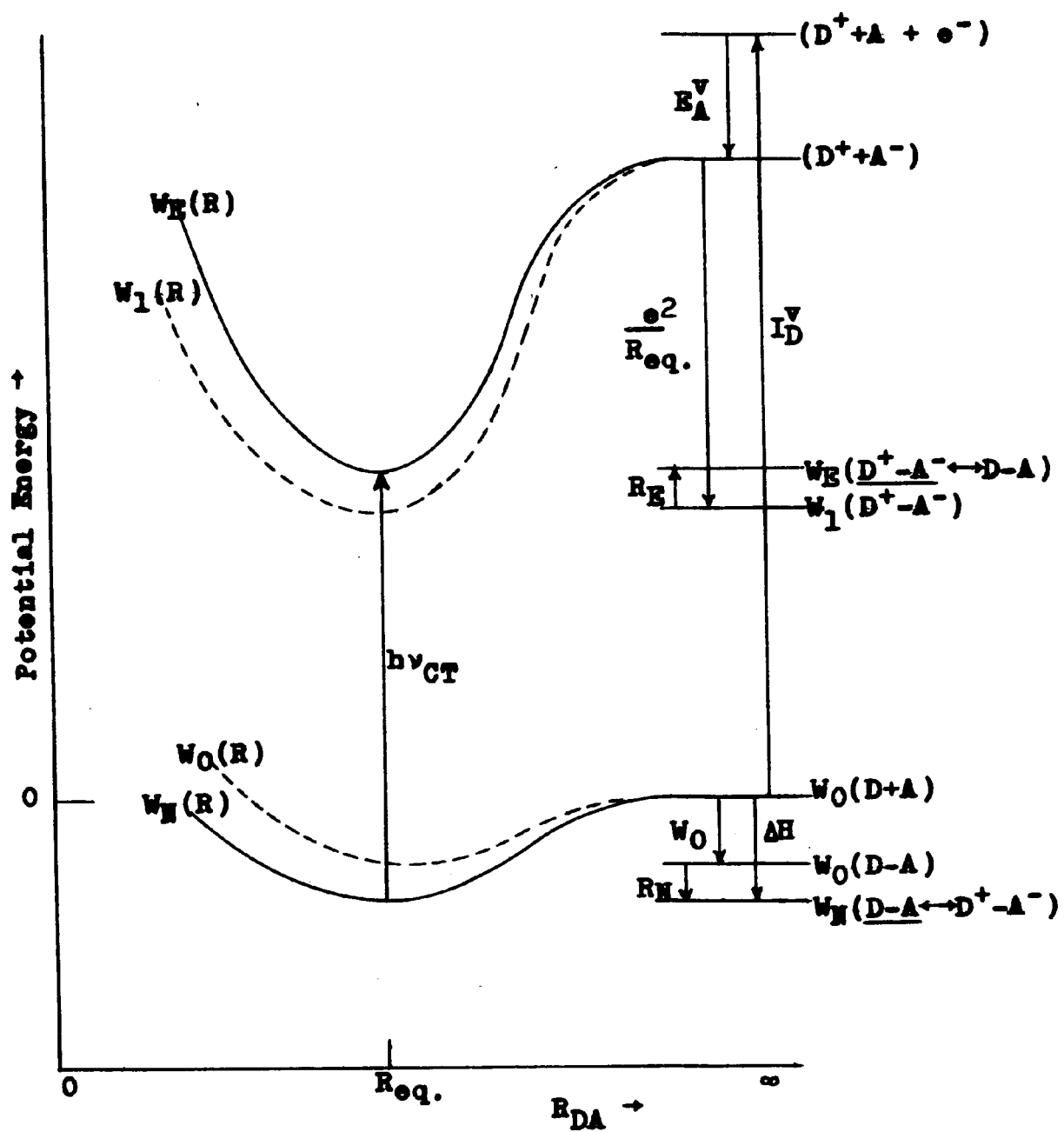
The relationship between the various energy terms involved in describing the charge-transfer interaction are best visualized from a potential energy diagram (see Figure 1).

The energy of the ground state can be expressed as

$$W_N = W_\infty + \Delta H = W_\infty + W_0 + R_N = W_0 + R_N \quad (\text{I-5})$$

Here W_∞ is the energy of the two separated molecules and ΔH is the enthalpy of formation of the complex. W_0 is the energy of interaction between the two molecules exclusive of the charge-transfer resonance stabilization energy; it

FIGURE 1

Potential Energy Diagram for Complex Formation

Comments on Figure 1. Conventions regarding the signs attached to the energy terms in Figure 1 vary from author to author. The conventions adopted in Figure 1, and in equations (I-5) and (I-6), are those used by Briegleb [4]. Mulliken and Person [18] (see also Mulliken [3]) have defined ΔH and R_N in the sense opposite to that shown here. In addition, E_A^V and $e^2/R_{eq.}$ as indicated in Figure 1 are positive quantities, rather than negative, as might have been assumed from the directions of the arrows. In order to avoid confusion, the signs of the energy terms in Figure 1, as indicated by the arrows, are tabulated below (Table 1).

Table 1

Signs of the Energy Terms of Figure 1,

as Indicated by Arrows

I_D^V	E_A^V	$e^2/R_{eq.}$	R_E	ΔH	W_O	R_N
+	+	+	+	-	-	-

is the sum of several terms including electrostatic energy (dipole-dipole etc.) and van der Waals energy, and can be either positive or negative, depending on the nature of the donor and acceptor and the magnitude of their separation.

Similarly, for the energy of the excited state

$$W_E = W_\infty + I_D^V - E_A^V - e^2/R_{eq.} + R_E = W_1 + R_E. \quad (I-6)$$

Here I_D^V is the vertical ionization potential of the isolated donor, E_A^V is the vertical electron affinity of the isolated acceptor, and $e^2/R_{eq.}$ is the rather large coulombic energy of the ion-pair D^+A^- . To be exact, equation (I-6) should include a term representing the valence energy of the dative D^+A^- bond, plus other small corrections (see Mulliken and Person [18]); because of their small magnitude, these terms will be neglected in the present treatment.

The energy of the charge-transfer transition can now be expressed as

$$h\nu_{CT} = (W_E - W_N) = I_D^V - E_A^V - e^2/R_{eq.} - W_0 + R_E - R_N. \quad (I-7)$$

It has long been recognized [24] that, for the complexes of a series of donors with a common acceptor, a linear relationship exists between $h\nu_{CT}$ and I_D . It has been stressed by Mulliken and Person [18], among others, that the validity of such a correlation requires that the last five terms in equation (I-7) remain constant throughout the series of complexes being compared, a condition which in general will not be satisfied. Nevertheless, the success of this simple relationship, particularly in the case of aromatic hydrocarbon donors, has given it widespread acceptance and led to the development

of correlations between $h\nu_{CT}$ and other energy quantities related to I_D . The basis for these correlations is that, in the case of aromatic hydrocarbons, the orbital energies of the highest-lying occupied and lowest-lying unoccupied π -MO's can be readily correlated (see, for example, Streitwieser [25]) with several experimentally measured quantities; namely, the polarographic half-wave oxidation and reduction potentials, the ionization potential, the electron affinity, and the energy of the ^1L_a transition (Clar's p band). Correlations between each of these quantities and $h\nu_{CT}$ have been proposed by various workers; a review of these correlations is given by Briegleb [19].

In addition to the equations set forth above, several other expressions taken from Mulliken's charge-transfer theory will be encountered in the discussion presented below; these are introduced as required.

Section II. Experimental

Part A. Materials

1. Solvents. Methylene chloride was used as solvent in all equilibrium studies. Since TCNE is known to be sensitive to hydrolysis [26,27], special precautions were taken in drying this solvent. (Methylene chloride and water form an azeotrope boiling at 38.1°C and containing 1.5% H₂O by weight [28]. Water is soluble in CH₂Cl₂ to the extent of 0.17 g. H₂O/100 g. CH₂Cl₂ at 20°C and 0.21 g. H₂O/100 g. CH₂Cl₂ at 30°C [29].) The material used was Matheson, Coleman and Bell spectroquality grade methylene chloride, with a water content normally 0.01% or less [30], as determined by the Karl Fischer method in anhydrous methanol. This was further dried by three or more repetitive distillations from P₂O₅ and passage through a column (51 x 2.2 cm) of activated silica gel (28-200 mesh, Davison Chemical Corporation). The final drying operations were carried out under an atmosphere of dry nitrogen.

The optical clarity of the solvent in the visible and near ultraviolet regions was not measurably changed by the above drying procedure. Since saturated solutions (ca. 0.1 M) of pure TCNE in this solvent remained water-white for periods longer than several days, CH₂Cl₂ dried in the above manner was judged to be sufficiently dry for the purpose of these experiments. (Solutions of TCNE in undried CH₂Cl₂ rapidly acquire a yellow coloration due to the hydrolysis products of TCNE.)

Several other solvents were used in locating the singlet-triplet absorption band of 1-methylnaphthalene by the external heavy atom spin-orbit perturbation technique [8,31]. Normal hexane, "Baker Analyzed" reagent grade, was used without further purification. Bromoform (Eastman Kodak Co. practical grade) and 1-iodobutane (Eastman Kodak Co. white label grade) were purified by several passes through columns (20 x 0.6 cm) of alumina (80-200 mesh, Fisher Scientific Co.).

2. Tetracyanoethylene. The TCNE used was the generous gift of Dr. B. C. McKusick of E. I. du Pont de Nemours and Company. This material was purified by repeated vacuum sublimation. (TCNE sublimes readily under reduced pressure at temperatures above 100°C to form clear, colorless crystals.) The observed melting point of the purified material was 197.2-198.2°C (uncorrected, sealed tube); the literature value [32] is 198-200°C.

3. Donors. Naphthalene (N)⁽¹⁾ was J. T. Baker Analyzed Reagent grade, and 2-methylnaphthalene (2-MN)⁽¹⁾ of 98% minimum purity was purchased from Rütgerswerke-Aktiengesellschaft. All other donors (1-MN and 1,2-; 1,5-; 1,6-; 1,7-; 2,3-; 2,6-; and 2,7-DMN⁽¹⁾) were purchased from Aldrich Chemical Company, Inc., and were of a minimum purity of 98% [33]. Analysis of the dimethylnaphthalenes via temperature programmed vapor phase chromatography revealed only trace

⁽¹⁾Naphthalene, methylnaphthalene and dimethylnaphthalene will be abbreviated as N, MN and DMN, respectively.

quantities of impurities other than isomeric dimethylnaphthalenes.

The solid donors (N, 2-MN and 1,5-; 2,3-; 2,6-; and 2,7-DMN) were further purified by recrystallization from 95% ethanol and repeated vacuum sublimation at temperatures slightly below the melting points of the solids. The liquid donors (1-MN and 1,2-; 1,6-; and 1,7-DMN) were used without further purification. Several attempts at fractional distillation showed negligible improvement in the purity of the distillate as evidenced by measurement of refractive index and absorption spectrum. Tables 2 and 3 list the observed melting points, boiling points and refractive indices of the donors, together with the best literature values.

Table 2

Melting Points of Solid Donors

<u>Compound</u>	<u>M.P. (experimental)</u>	<u>M.P. (literature)</u>
N	79.8-81.2°C	80.29 [34], 80.55 [35]
2-MN	33.8-34.7	34.58 [34]
1,5-DMN	80.9-81.8	82.0 [34]
2,3-DMN	104.7-105.3	105.0 [34]
2,6-DMN	110.3-111.7	112.0 [34]
2,7-DMN	95.7-96.3	98.0 [34]

Table 3

Boiling Points and Refractive Indices of Liquid Donors

Compound	B.P. (exp.)	B.P. (760 mm.) lit. [34]	n_D (23°C) (exp.)	n_D (23°C) lit. (1)
1-MN	241.5-242.3 (uncorr.)	244.642°C	1.6139	1.6159
1,2-DMN		266	1.6095	1.6151
1,6-DMN		263	1.6054	1.6060
1,7-DMN		263	1.6050	1.606

(1) Interpolated from values given at 20°C and 25°C [34].

Part B. Apparatus

All spectral data were obtained on a Beckman DK2-A ratio-recording spectrophotometer. The wavelength scale of this instrument was calibrated [36] by use of the Hg lines from a low pressure mercury arc (Beckman 2260). The absorbance scale was checked before and after each series of measurements by use of a solution of cobalt sulfate of known concentration [37]. This compound has an absorption maximum at 510 mμ, about in the center of the spectral region under investigation. Care was taken that the spectral bandpass was always sufficiently small compared to the bandwidth of the bands being measured.

The reproducibility of absorbance readings obtained on the DK2-A can be judged from the constancy of the results of the standard CoSO_4 solution. A statistical analysis of 35 measurements on the standard over a period of 12 months yields the following results: average absorbance $\overline{\text{Abs}} = 0.993$,

standard deviation $s = 0.0057$, and coefficient of variation, defined by $V (\%) \equiv 100 s/\overline{\text{Abs}} = 0.57$. This value of V compares favorably with the values found ($V = 0.5 - 1.0\%$) in several collaborative studies [38-41] wherein the same absorbance standard was measured on several different instruments produced by the same manufacturer (these studies covered the Cary models 11 and 14, the Beckman DU and the Perkin-Elmer 4000 A). The short term reproducibility (on successive scans) was considerably better, the peak absorbance seldom differing by more than 0.001 or 0.002 absorbance units. A linearity check, using successive dilutions of the CoSO_4 standard, of the absorbance scale between 0.5 and 1.75 absorbance units gave a V value of 0.59% for the extinction coefficient of CoSO_4 . Again, this compares favorably with comparable results ($V = 0.3 - 0.8\%$) [38] obtained for glass filters of varying thickness. It can be concluded from the above that measured absorbances lying close to 1.0 are probably accurate to within 0.006 absorbance units.

It was observed early in this work that the measured absorbances, and therefore the extinction coefficients and equilibrium constants of the molecular complexes, were very sensitive to changes in temperature. A repeat spectral scan of a solution containing a complex generally gave a curve differing significantly in absorption intensity from the curve obtained on the first scan. This behavior was found to be caused by heating of the sample cell in the cell

compartment of the spectrophotometer. In order to maintain the sample at constant temperature, a demountable, totally-jacketed 1-cm. cell was constructed, through which distilled water from a constant temperature bath could be circulated. By means of this cell, the sample could be readily maintained at any desired temperature (between 0° and 40°C) $\pm 0.02^{\circ}\text{C}$, as determined by a sensitive thermometer placed in the thermostating liquid at the outlet of the cell compartment. The optical path of this cell could be kept clear when care was taken to prevent microbubbles in the circulating fluid (a centrifugal pump could not be used because of cavitation, but a peristaltic pump served adequately) and when the interior surfaces of the jacket windows and exterior surfaces of the sample compartment windows were cleaned as indicated by an increase in the blank absorbance of the cell.

Part C. Methodology

Because of the volatility of the solvent (CH_2Cl_2 boils at 40°C) great care was exercised to keep sample containers, volumetric flasks, cells, etc. tightly sealed at all times and to work as expeditiously as possible in transferring solutions and in recording spectra after solutions were prepared. Since TCNE is sensitive to hydrolysis, care was also taken to avoid traces of moisture being picked up by the solvent. Only clean, dry pipets were used in transferring solvent and solutions since pipets, once used, tend to pick up moisture, which condenses on the cool surfaces left by the rapidly vaporizing solvent.

In recording charge-transfer spectra the lowest sensitivity of the photomultiplier detector was used, thus minimizing noise in the recorded spectrum. Although under these conditions the slit is at its widest, the spectral bandpass was still negligible compared with the bandwidths of the charge-transfer bands under investigation. A short time constant, 0.1 sec., was used, together with a slow scanning speed, the scanning time over the visible range, 700 to 345 m μ , being about 5 min. Absorbances measured under static conditions, wavelength fixed and time constants between 0.1 and 2 sec., agreed with the scan-recorded absorbances within 0.001 or 0.002 absorbance units.

In using the thermostatted cell, spectra were recorded vs. air in the reference beam of the spectrophotometer, the absorbance of the solvent blank being subtracted from the measured absorbance to give the true absorbance of the solution in question.

1. Determination of Stoichiometry of Complexes by the Method of Job [42,43]. Solutions having a mole ratio of donor to TCNE between 9:1 and 1:9 were prepared by pipetting appropriate volumes of stock solutions into clean, dry 60 ml. screw-cap bottles equipped with tight-fitting polyethylene lined caps. The concentrations of the stock solutions were chosen such that the sample solution having the greatest absorbance (the one with a 1:1 mole ratio) would have an absorbance near 2.0 absorbance units, the highest readable on

the DK2-A. The sample solutions were allowed to stand one to four hours before their spectra were recorded. This work was carried out at room temperature with ordinary 1.00 cm. cells, no attempt being made to control the sample temperature. It was at this point that the above described temperature sensitivity of the complexes was noted. All further work was carried out with the thermostatted cell.

In the case of the TCNE-1-methylnaphthalene complex, whose charge-transfer spectrum changes with time, Job's method was carried through using the thermostatted cell, the sample being placed in the cell immediately upon mixing, and five minutes being allowed for chemical and thermal equilibrium to be established before the spectrum was recorded.

2. Determination of Formation Constants and Extinction Coefficients.

Several different procedures were used in the course of this work. These are separately described below.

Procedure A. This procedure was essentially the same as that employed by Merrifield and Phillips [20] in their work on TCNE complexes. Appropriate amounts of donor were weighed directly into calibrated, glass-stoppered 10 ml. volumetric flasks. A fixed volume of TCNE in CH_2Cl_2 , from a freshly prepared stock solution, was then pipetted into each flask, this volume being chosen such that the absorbance of the most strongly colored solution was close to 1.0. The flasks were immediately reweighed, so that the weights of TCNE and CH_2Cl_2 added could be calculated from a knowledge of the

concentration (w./w.) of the stock solution. Methylene chloride was then added to near the mark and the flasks swirled to dissolve any solid donor still remaining. The flasks were then placed in a thermostat at the temperature at which spectra were to be determined. After 10-15 min. the flasks were individually removed, made up exactly to the mark, and quickly reweighed (this final weighing allowed the concentration of all components in the sample to be calculated on both a molar concentration and mole-fraction basis). Samples were then transferred to the thermostatted cell, and after allowing ten minutes for thermal and chemical equilibrium to be established, spectra over the range 700-345 μ were scanned as previously described.

Procedure B. In procedure A, the concentration of TCNE remains essentially constant while the concentration of donor changes, thus the measured absorbances vary in accord with the concentration of donor. Since the relative error in the measured absorbance is a minimum near 1.0 [44] and increases as the absorbance decreases, an effort was made to prepare samples whose concentrations of TCNE and donor were such that the absorbance due to the complex remained nearly constant at a value close to 1.0. These concentrations could be calculated from equation (V-18) provided that estimates of ^cK and ϵ_c at $\lambda_{\max}$ were available. Sample solutions were prepared and run in the manner described under procedure A, except that several (usually three) solutions of TCNE were prepared by dilution of one fresh stock solution, and

appropriate volumes of these pipetted into the sample flasks.

Procedure C. It was noted that even with stable complexes (e.g. TCNE-naphthalene) the absorbance changed upon standing 1-2 days by an amount (1-3% of the original absorbance) greater than could be accounted for by the increase in concentration due to solvent evaporation over this period of time. In order to eliminate any effects due to samples standing for varying periods of time before their spectra were recorded (the time required to complete a run of eight samples was 4-6 hours), samples were prepared and run individually, so that the elapsed time between mixing of components and recording of the spectrum remained constant. Five minutes after the components were mixed (allowing time for weighing and swirling the flask to dissolve components) the flask was placed in the thermostat for 10 min. Five more minutes were allowed for diluting to the mark, reweighing, and transferring to the thermostatted cell. The sample was allowed to stand 10 min. in the cell to permit equilibration and the spectrum recorded exactly 30 min. after the components had been mixed.

Section III. Survey of Spectral Properties of TCNE-Methyl Naphthalene Complexes and their Components

Molecular complexes of TCNE are in general characterized by well defined charge-transfer bands whose maxima occur at wavelengths to the red of the absorption due to the pure donor [20, 45-48]. In most instances this places the charge-transfer band well into the visible region of the spectrum. For the complexes under consideration here, all of whose components are colorless, formation of the complex is accompanied by a striking coloration which appears immediately and at full intensity upon mixing of CH_2Cl_2 solutions of the components. Colors of the complexes vary markedly throughout the series of donors (see Table 4 below).

Table 4

Colors of TCNE Complexes

<u>Complex</u>	<u>Color</u>	<u>Complex</u>	<u>Color</u>
TCNE-N	ruby red	TCNE-1,6-DMN	green-blue
TCNE-1-MN	maroon-gray	TCNE-1,7-DMN	green-gray
TCNE-2-MN	blue-gray	TCNE-2,3-DMN	blue-violet
TCNE-1,2-DMN	green-blue	TCNE-2,6-DMN	blue-gray
TCNE-1,5-DMN	emerald green	TCNE-2,7-DMN	blue-violet

Part A. Spectra of Pure Components and Complexes

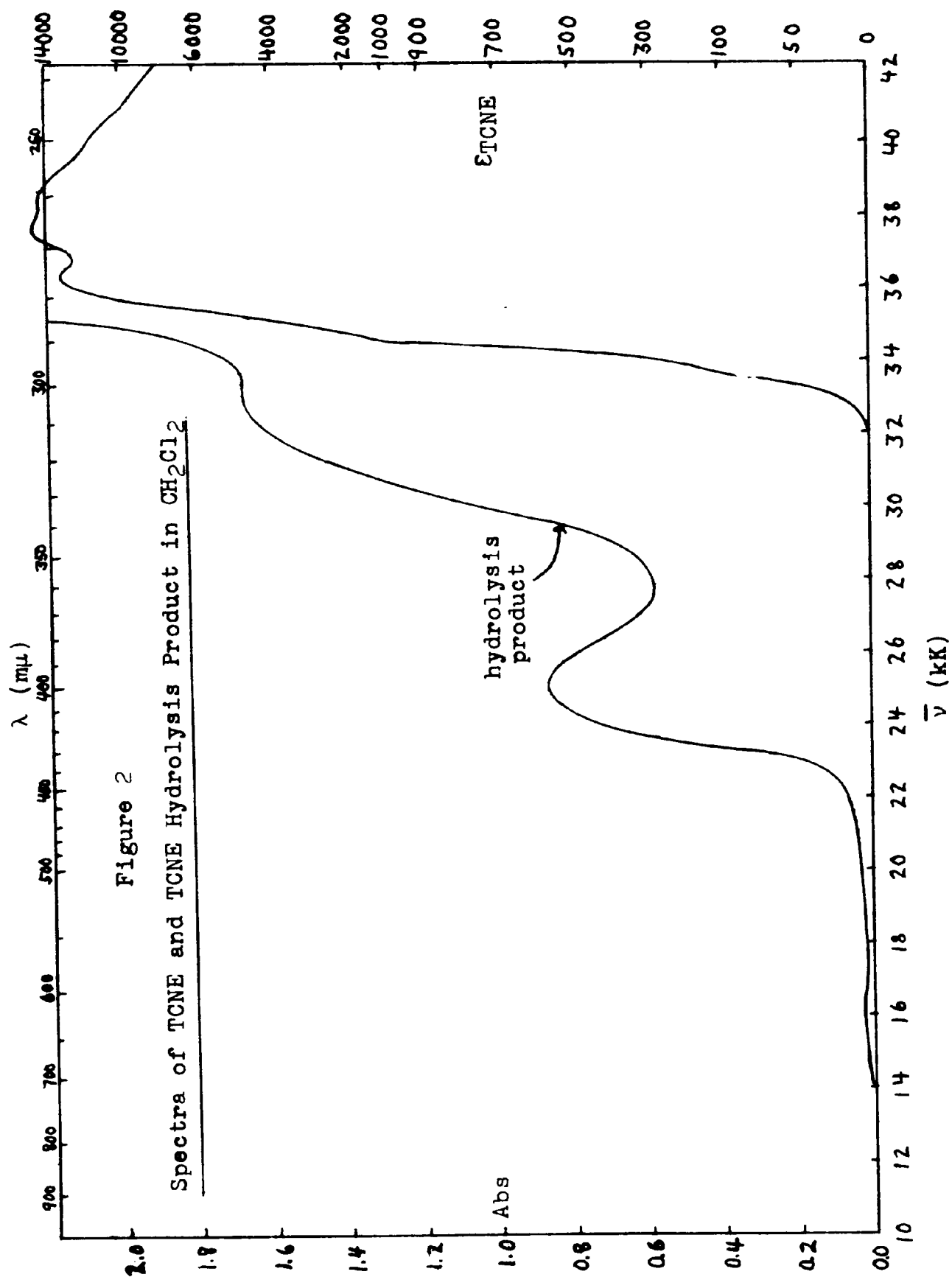
The solvent used in these studies, CH_2Cl_2 , is clear (absorbance of a 1.0 cm layer < 0.1) between 246 and 1150 μ , its UV cutoff (absorbance of a 1.0 cm layer = 1.0) occurring

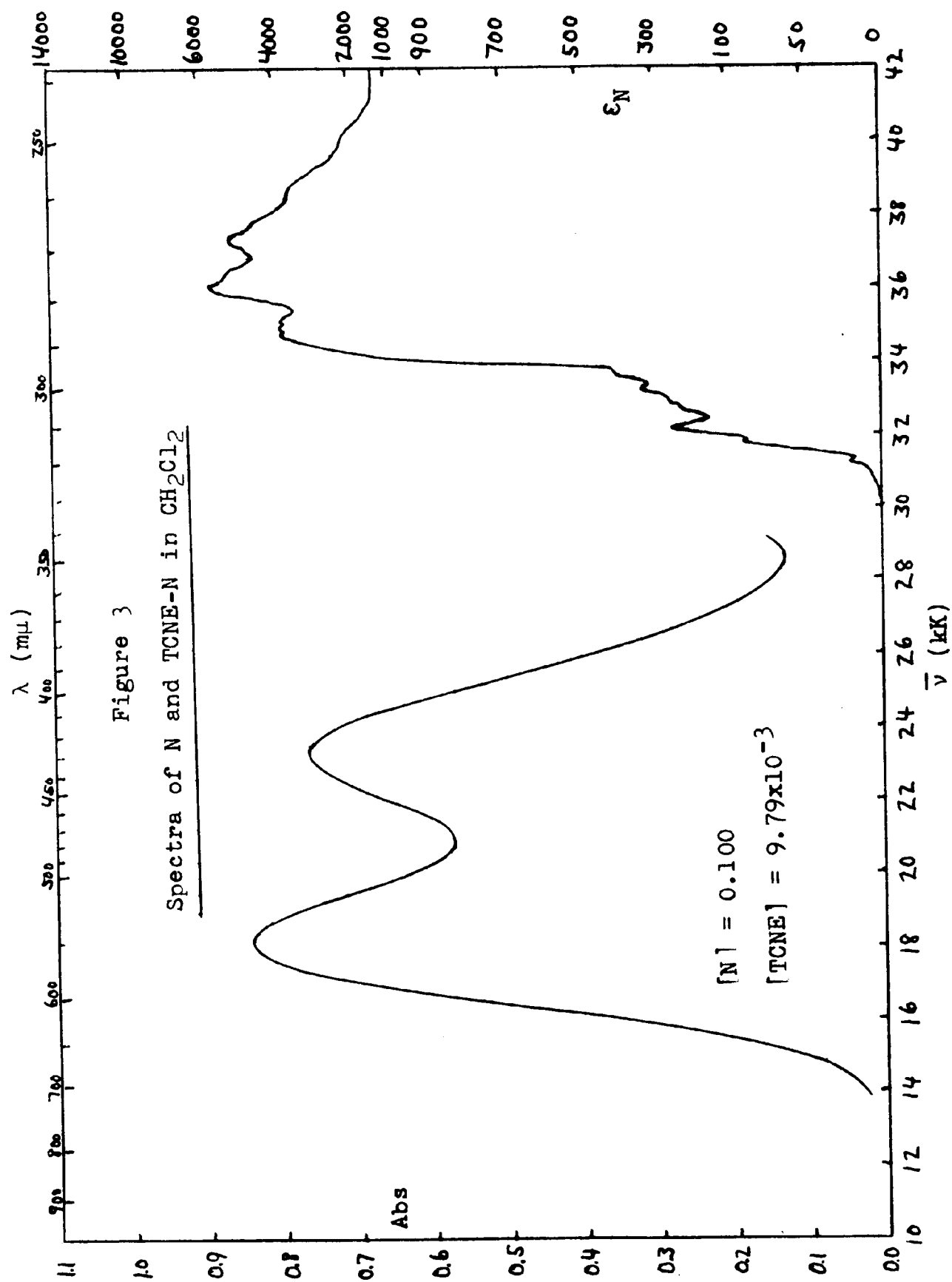
at 232 m μ . Thus, the visible and much of the ultraviolet is available for study.

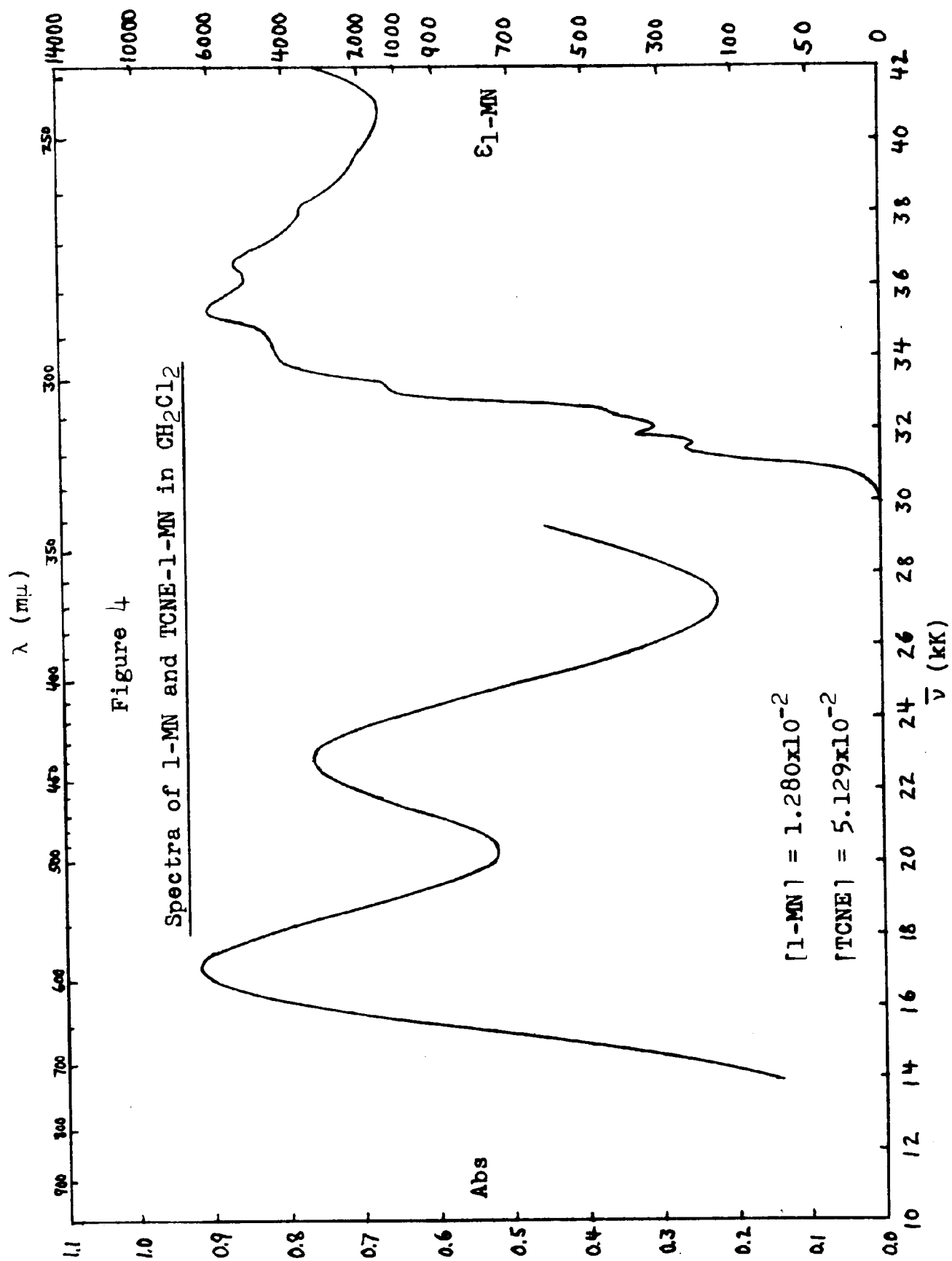
The absorption spectrum of TCNE in CH₂Cl₂, together with that of an approximately saturated solution of the hydrolysis products of TCNE (the latter will be commented upon in Part B) is shown in Figure 2. The right-hand ordinate scale gives the decadic molar extinction coefficient ϵ of TCNE, while the left-hand scale, in units of absorbance, gives the relative absorption intensity of the hydrolysis products.

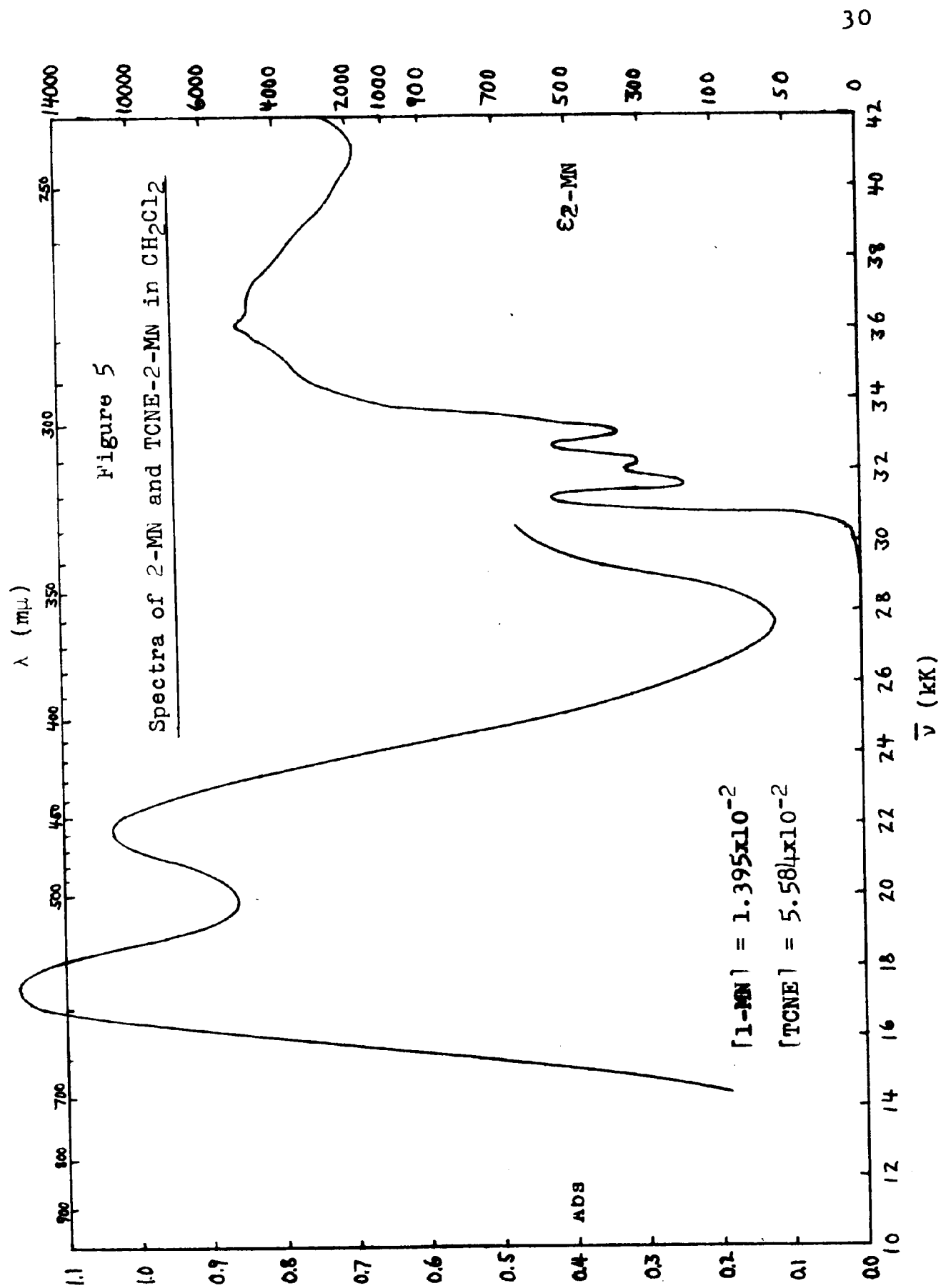
The spectra of the donors, together with the spectra of the corresponding TCNE complexes, are shown in Figures 3-12. Again, the right-hand ordinate scale gives the molar extinction coefficient of the donor, while the left-hand scale, in units of absorbance, gives the relative absorption intensity of the complex. For each of the complexes, the initial concentrations of TCNE and donor are indicated in the appropriate figure.

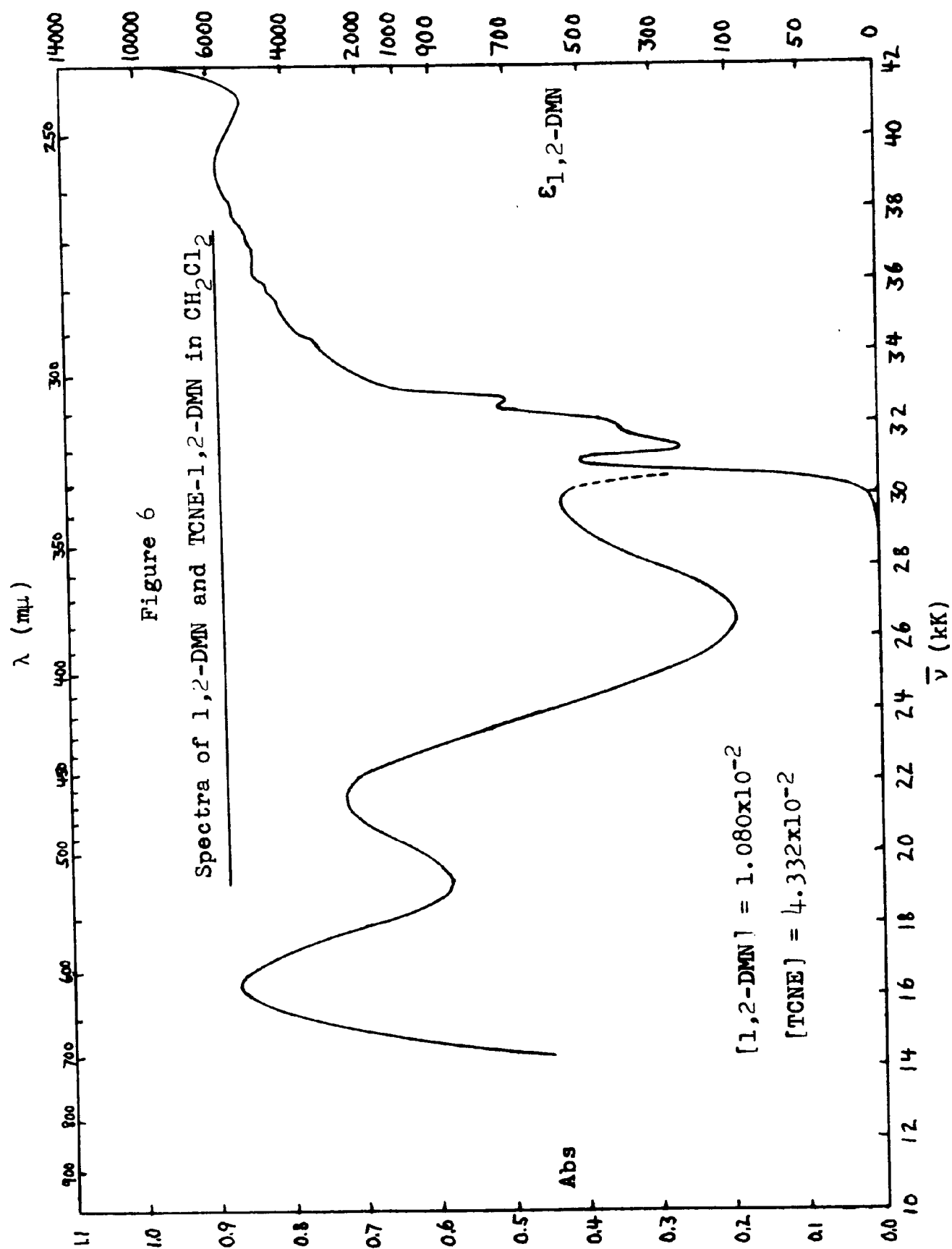
The complexes are characterized by two, or in some cases three, distinct charge-transfer bands in the visible region. A summary of the observed charge-transfer maxima is presented in Table 5, together with the values reported by Lepley [22,23] for many of the same complexes in CHCl₃. In general, λ_{max} in CH₂Cl₂ is somewhat blue shifted (i.e. shifted to shorter wavelengths) compared to λ_{max} in CHCl₃, while the absorbance ratio $\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)$ is less in CH₂Cl₂ than in CHCl₃. These solvent effects are discussed below in

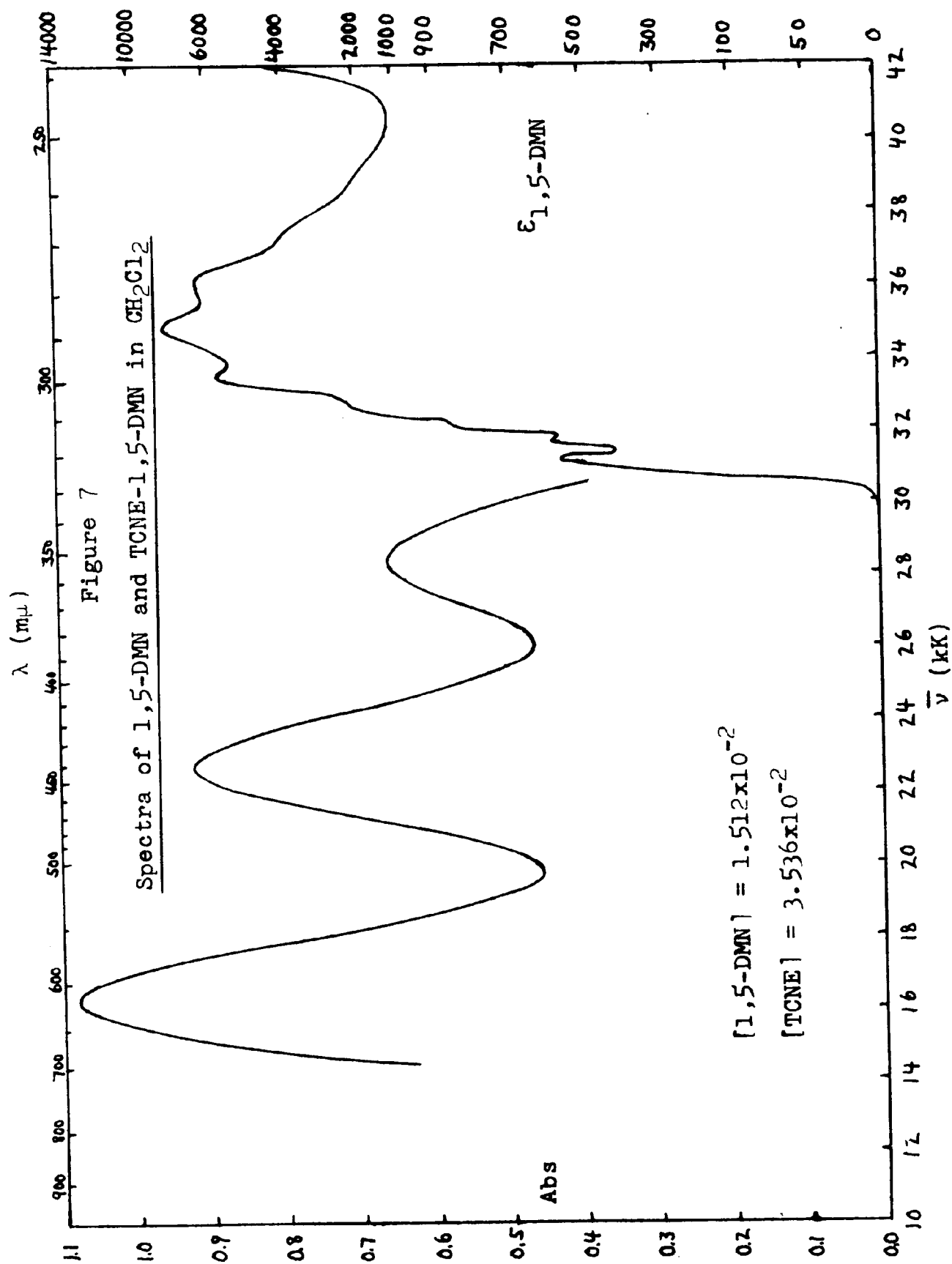


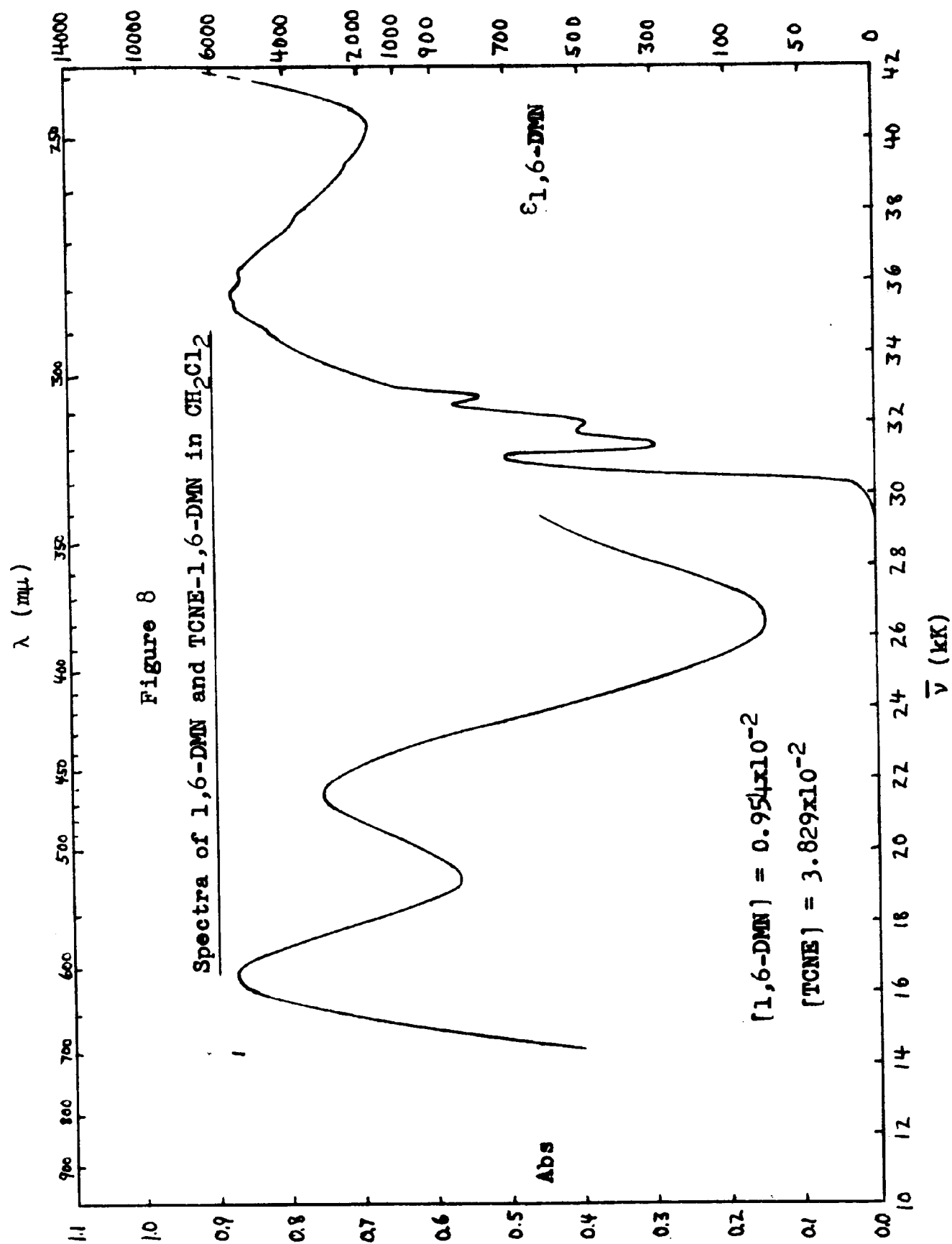


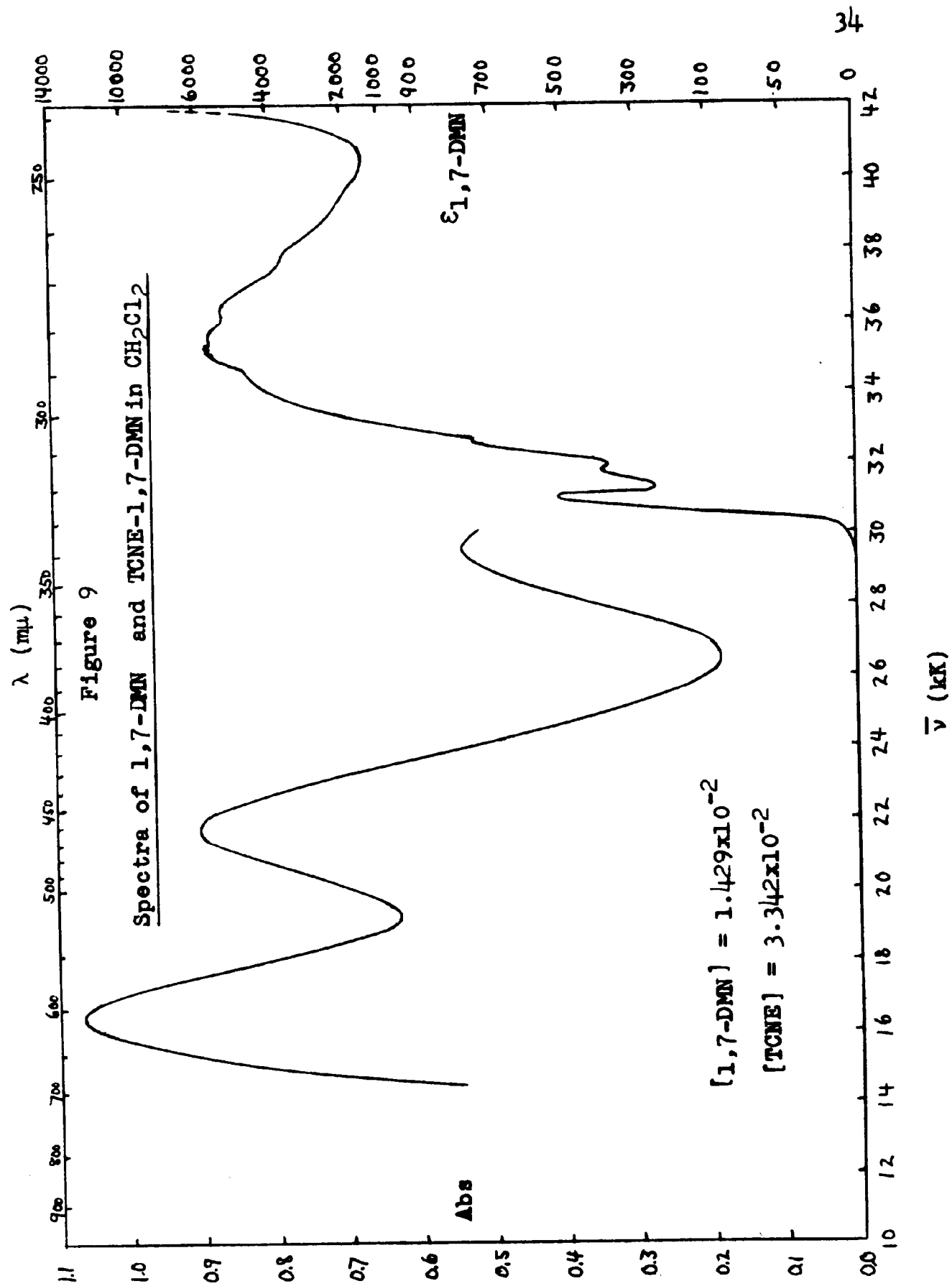


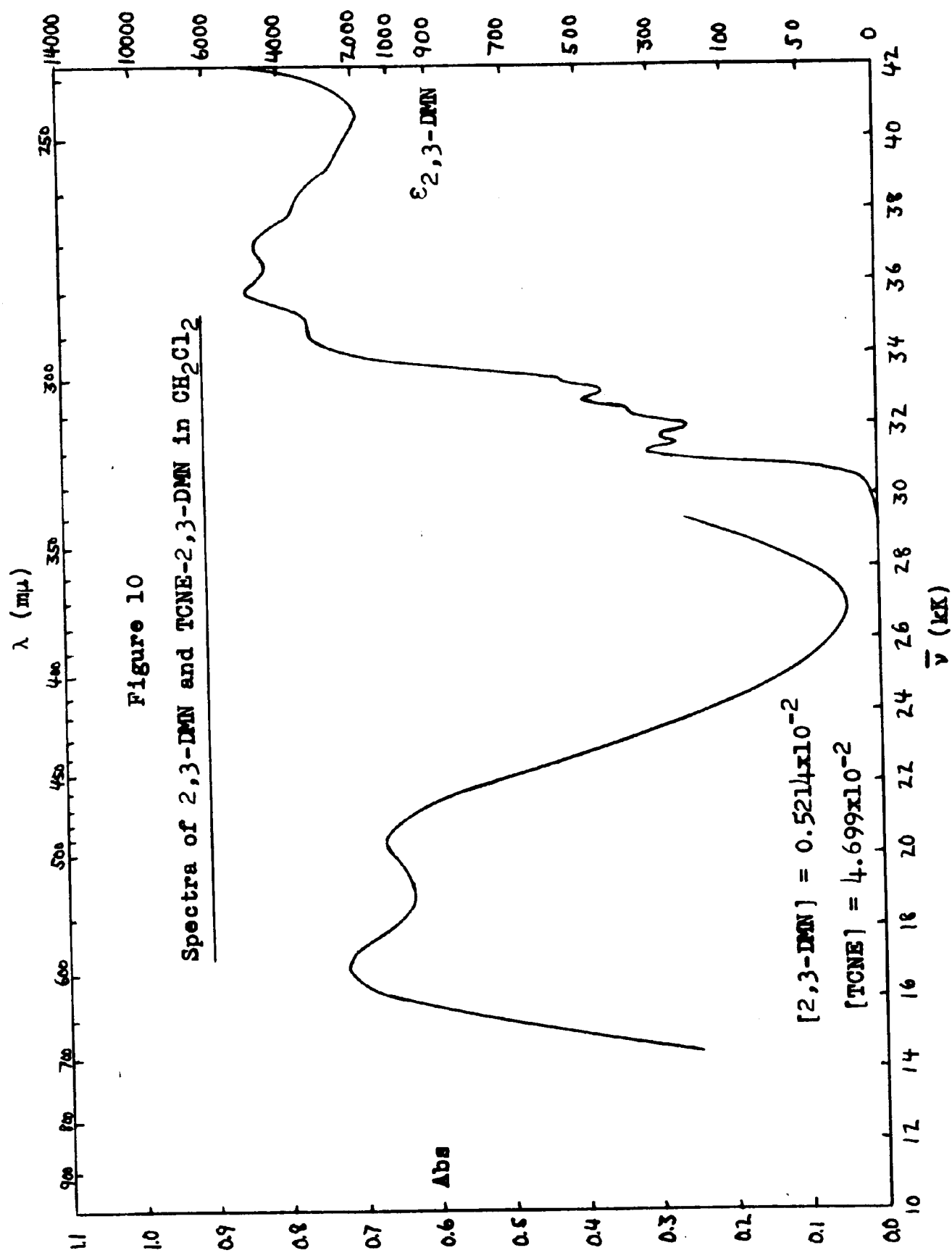


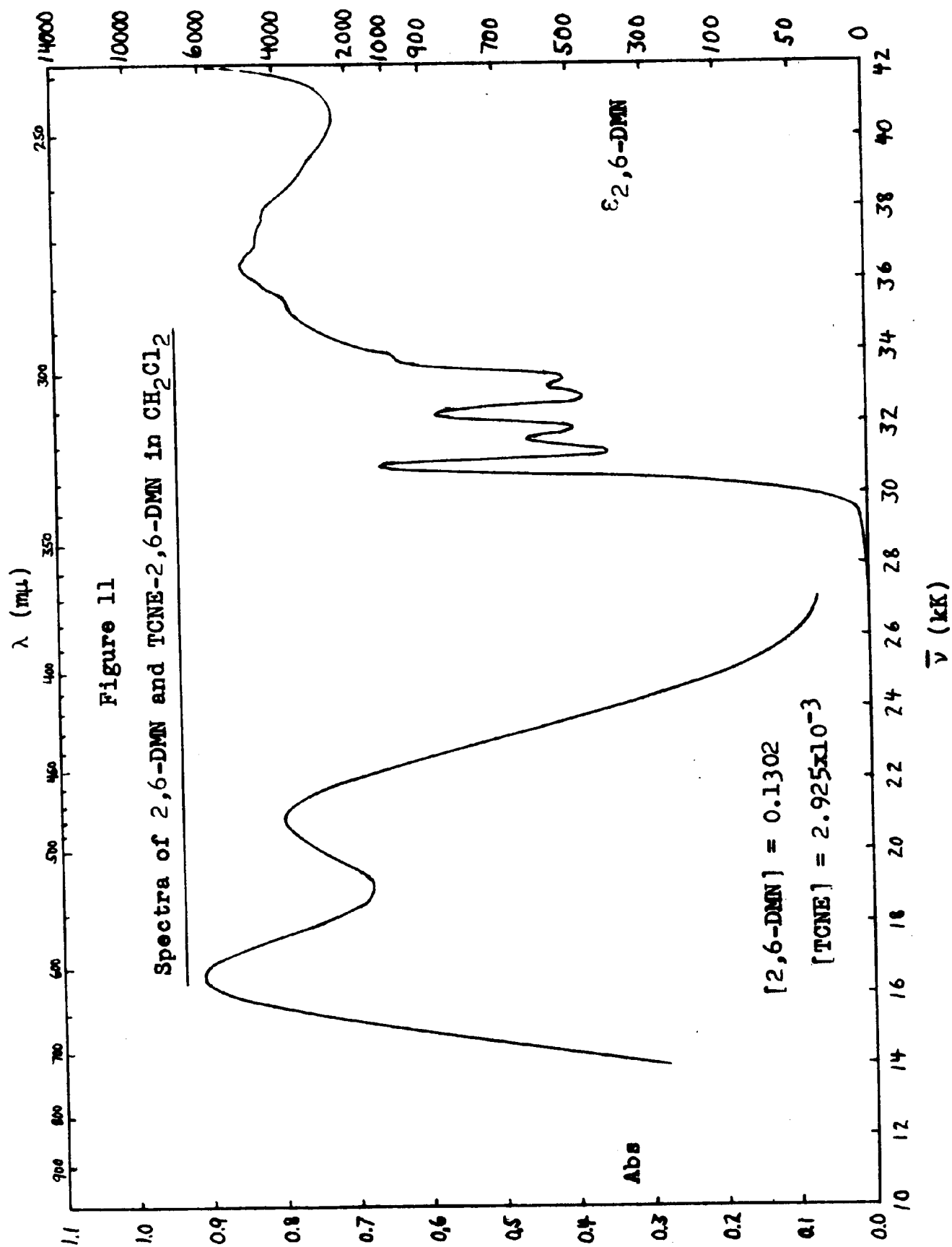












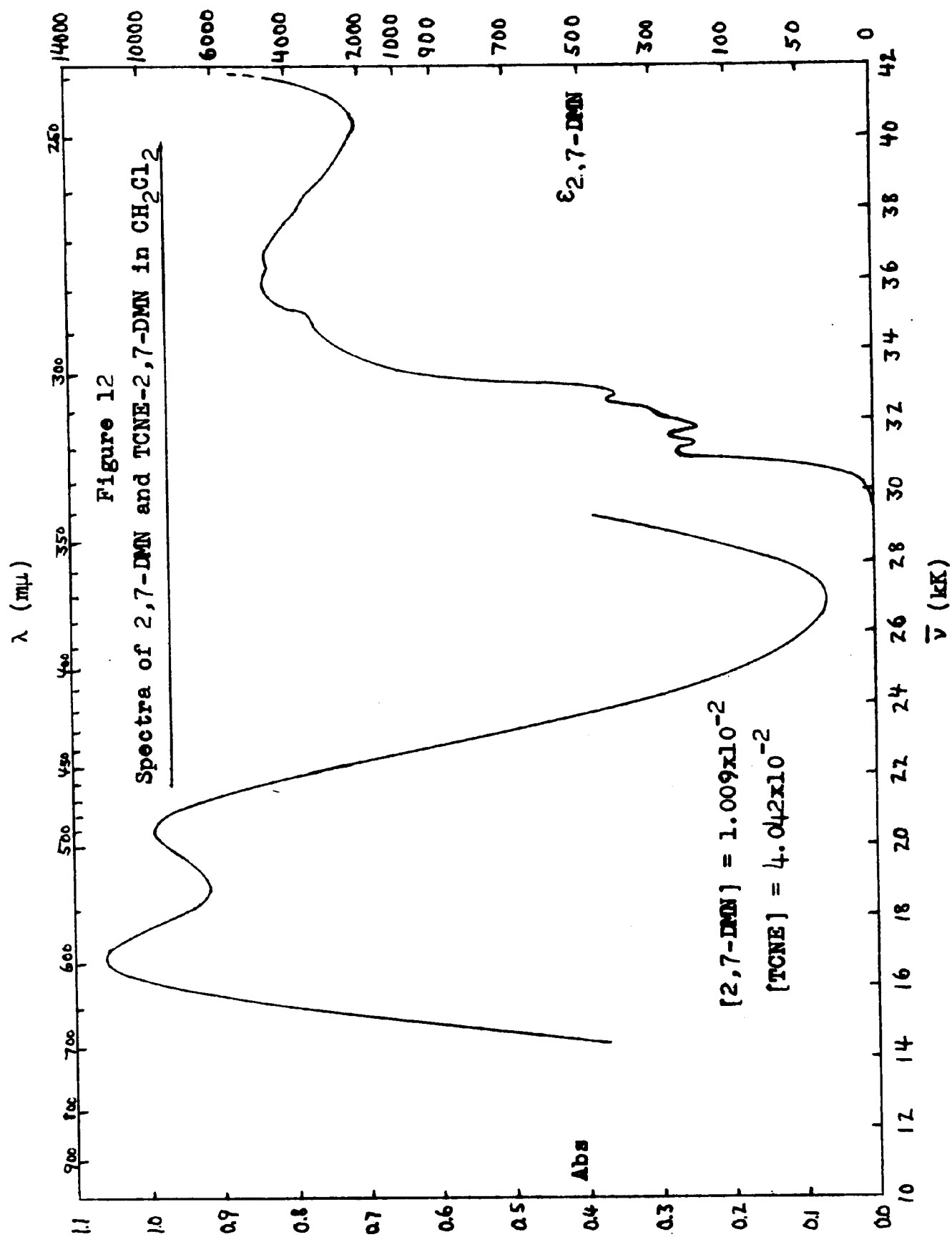


Table 5

Wavelengths⁽¹⁾ of the Charge-Transfer Bands of TCNE-Methyl Naphthalene Complexes

Substituent Position	in CH ₂ Cl ₂ (this work)			in CHCl ₃ (Lepley [22,23])		
	λ_1	λ_2	λ_3	λ_1	λ_2	λ_3
						$\frac{\text{Abs}(\lambda_2)}{\text{Abs}(\lambda_1)}$
0	551	429		555	431	0.97
1	586	436		592	440	0.94
2	578	457		579	458	0.95
1,2	612	464	~336?	613	463	0.88
1,3				607	465	0.92
1,4				624	445	0.77
1,5	619	442		622	444	0.94
1,6	609	465	353	610	466	0.89
1,7	613	462	~331? ~339			
1,8						
2,3	594	493		635	438	0.85
2,6	606	478		598	490	0.99
				606	479	0.94
2,7	596	491		598	491	0.99
2,3,5				632	495	1.02
2,3,6				625	526	0.98

⁽¹⁾ All wavelengths are in m μ . Estimated error limits are ± 2 m μ .

Section V, Part E-3. The theoretical basis for the observed multiple charge-transfer bands and the structures of the species responsible for them are discussed in Section VII.

Part B. Impurities

1. TCNE Hydrolysis Products. It was pointed out in Section II that TCNE is sensitive to hydrolysis, its solutions in undried solvents rapidly acquiring a yellow coloration due to the presence of hydrolysis products. In order to assess the seriousness of this possible source of interference, an approximately saturated solution of hydrolysis products was prepared by adding 1 ml. of H_2O to 25 ml. of a saturated solution of TCNE in CH_2Cl_2 (ca. 0.1 M) and shaking occasionally over the course of several days. The absorption spectrum of this material is shown in Fig. 2; its yellow coloration is due principally to the band centered at 400 m μ . According to Middleton et al. [26], acid or neutral hydrolysis of TCNE yields tricyanoethanol (tricyanovinyl alcohol), while alkaline hydrolysis yields salts of 1,1,2,3,3-pentacyanopropene. Salts of 1,1,2,3,3-pentacyanopropene, as well as the free acid, are yellow in color, while salts of tricyanoethanol have a yellow coloration which disappears upon purification [26]. Since the product obtained here has only one relatively weak band at 400 m μ while the 1,1,2,3,3-pentacyanopropene anion has two strong bands in this region ($\lambda_{max} = 412$, $\epsilon = 22,100$; $\lambda_{max} = 393$, $\epsilon = 22,600$ [26]), it can be concluded that the yellow coloration is due to small

amounts of impurities formed in combination with the principal product, tricyanoethanol. It is apparent from Figure 2 that absorption due to the hydrolysis products will not interfere seriously with measurement of the first (long wavelength, $\lambda_{\text{max.}} > 550 \text{ m}\mu$) charge-transfer band of the TCNE complexes. The possibility of interference with the second or third charge-transfer bands was minimized, in practice, by use of thoroughly dried CH_2Cl_2 (see Experimental, Section II) and by the precaution of measuring the spectra of stock solutions of TCNE used in preparing the complexes.

2. Reaction Between TCNE and Donor Impurities. It was found that for several complexes, especially those of 1-MN, 2-MN and 1,6-DMN, a rapid change in the original spectrum with time occurred when the donor was present in large excess. In the case of TCNE-1-MN the original charge-transfer spectrum disappeared after about 1 day and was replaced by a single intense band, centered at $453 \text{ m}\mu$, which gave the solution a yellow color. In the case of TCNE-2-MN the original charge-transfer spectrum diminished in intensity but did not completely disappear; a strong band appeared at $448 \text{ m}\mu$. A similar effect was noted, in the case of TCNE-1-MN in CHCl_3 , by Lepley [23], who attributed it to a reaction between 1-MN and TCNE. It is believed by this writer, however, that the observed effect, at least in the case of TCNE-1-MN, is caused by a reaction between TCNE and an impurity present in small amounts in the donor. This hypothesis is based on the following:

- (a) The reaction proceeds appreciably only when the donor is present in large excess; this implies that the reaction is limited by the amount of impurity available.
- (b) A small amount of crystalline material having an adsorption spectrum identical with that of the impurity band was isolated from a solution, originally containing TCNE and 1-MN, after the charge-transfer spectrum due to TCNE-1-MN had disappeared. Elemental analysis of the material showed a N content of 15.9%. A 1:1 adduct of TCNE and 1-MN would contain 20.7% N, while the product of a substitution reaction $\text{TCNE} + 1\text{-MN} \rightarrow \text{X} + \text{HCN}$ would contain 17.3% N.
- (c) The presence of a small amount of impurity in the donor is evident from the appearance of several weak absorption bands ($\lambda_{\text{max.}} = 407 \text{ m}\mu$; $\epsilon_{\text{max.}} = 0.124$, based on 1-MN concentration) on the long wavelength tail in the spectrum of 1-MN. Since these bands have an intensity of the order of magnitude of a singlet $\rightarrow$ triplet transition, an attempt to identify them as the first S $\rightarrow$ T absorption band of 1-MN was made by the external heavy atom spin-orbit perturbation technique (see, for example, McGlynn [8,31]). A comparison of the absorption spectrum of 1-MN in bromoform and in 1-iodobutane with its spectrum in n-hexane revealed no apparent intensification in the suspect bands, whereas two new bands appeared with very weak intensity at 448 and 478 m μ . Since the 0,0 band

of the 1-MN $T \rightarrow S$ emission in EPA occurs at 472 m μ [49] the latter two weak bands can be assigned as the true $S \rightarrow T$ absorption; the suspect bands at 407 m μ must therefore be due to an impurity. The weakness and spectral location of these impurity bands suggest that they may represent an $n \rightarrow \pi^*$ transition due to an oxidation product of 1-MN.

Attempts to remove the impurity bands by fractional distillation and chromatography on alumina were unsuccessful. Because of the uncertainty in absorbance measurements introduced by a changing absorption spectrum, the complexes of 1-MN, 2-MN and 1,6-DMN were not studied in detail.

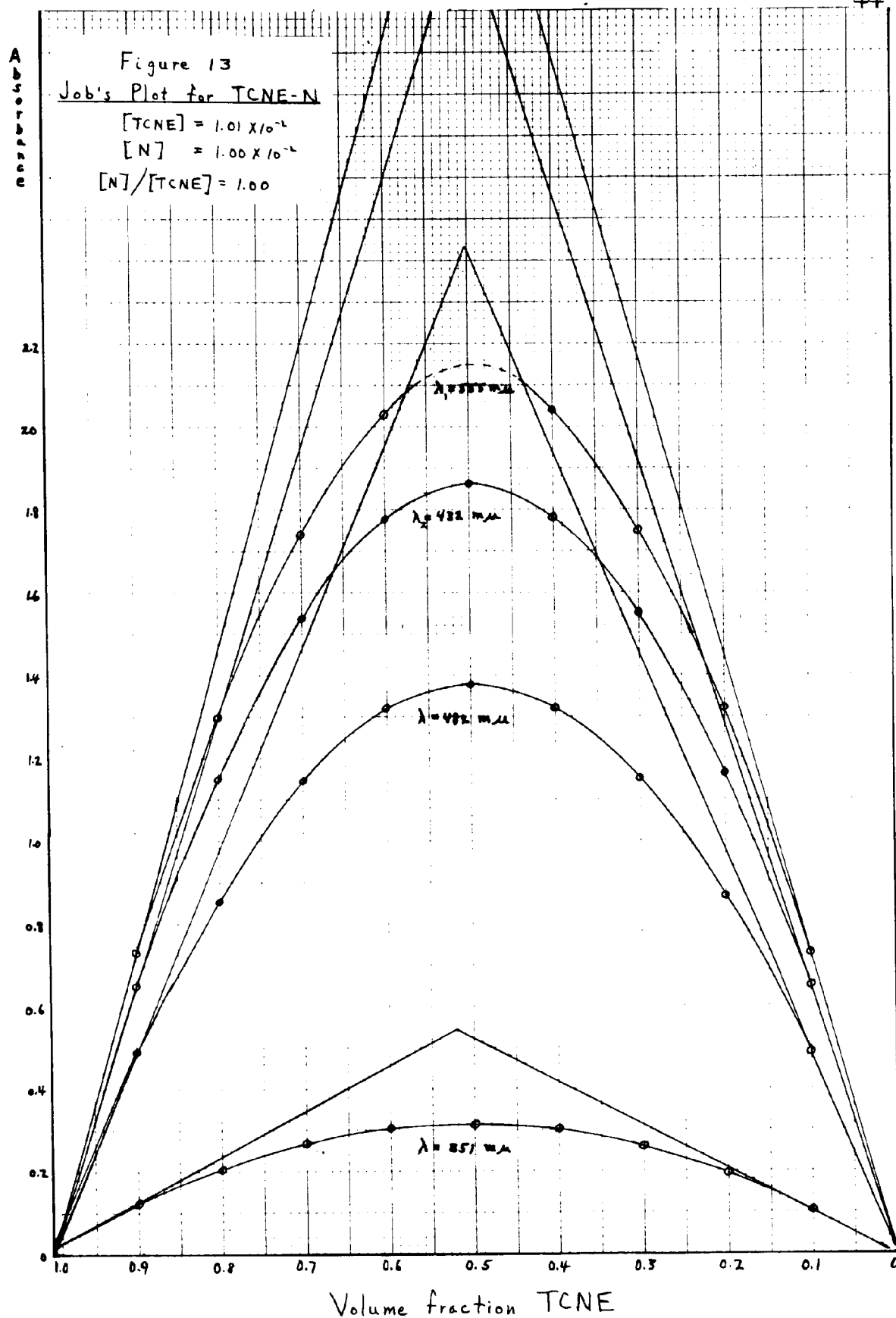
Section IV. Stoichiometry of the Molecular Complexes in Solution

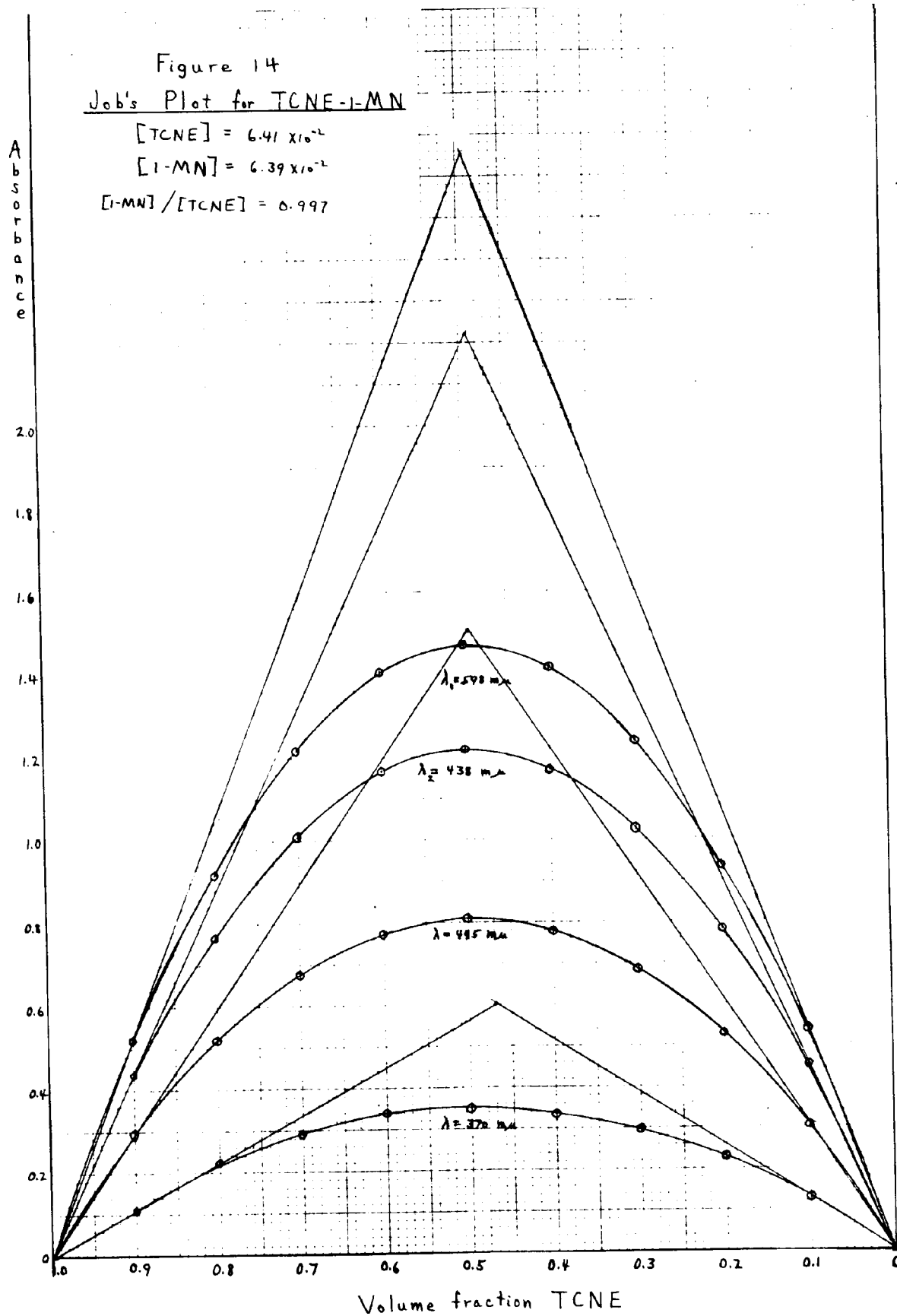
The method of continuous variations (Job's plot) [42,43] was used to determine the stoichiometry of the molecular complexes in solution. This method involves a graphical plot of some property characteristic of the supposed complex and which is a measure of its concentration in solution--in this case the intensity of the charge-transfer band. This property is plotted versus composition, in terms of the fraction of one of the two components present, for a series of test solutions in which the total concentration of the two components is held constant. The composition of the complex corresponds to that point on the composition axis where the property characteristic of the complex attains a maximum or minimum value, provided that only one complex is present.

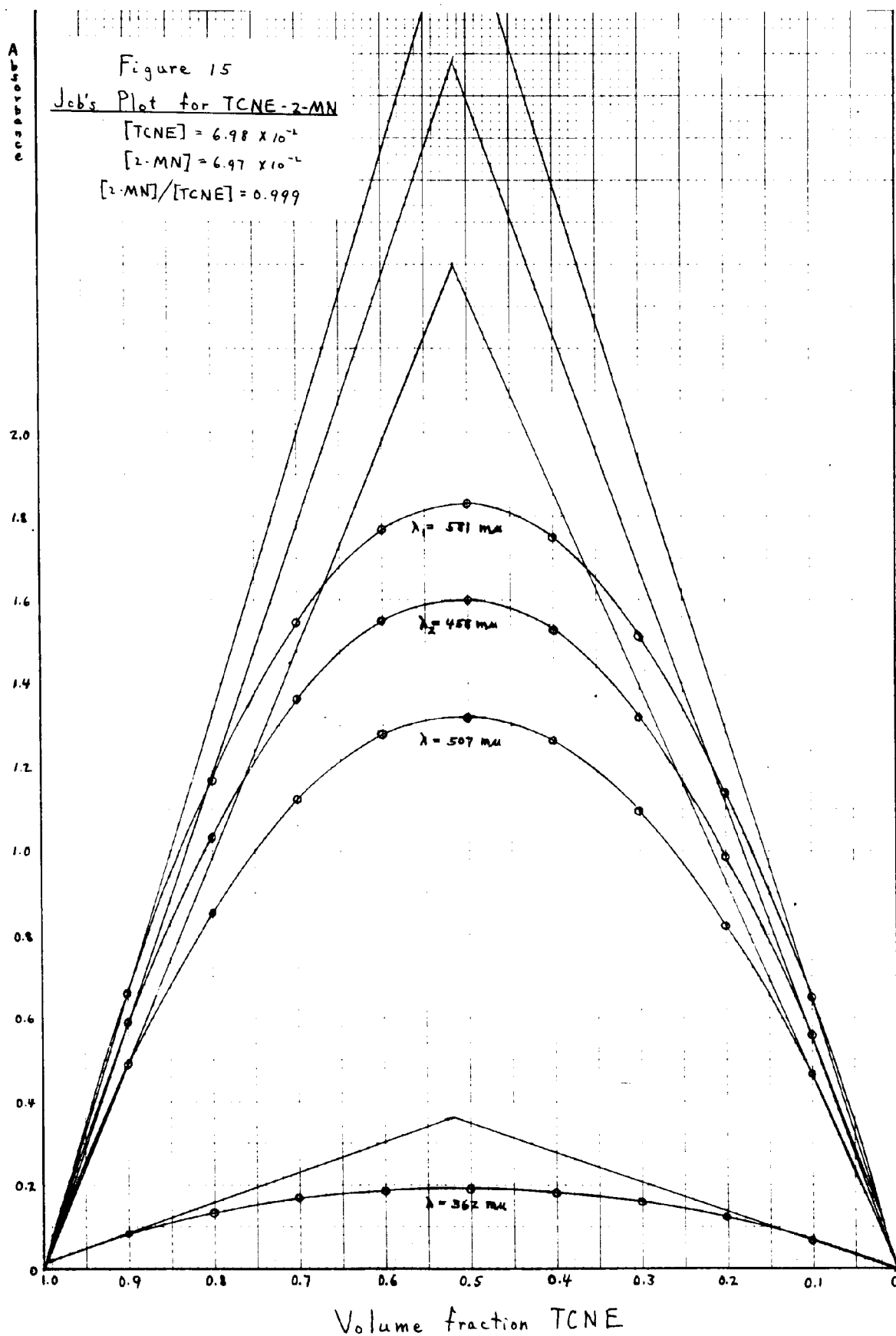
Job's plots for TCNE complexes of naphthalene, the methylnaphthalenes and dimethylnaphthalenes are presented in Figures 13-22. The absorbances of the charge-transfer bands are plotted for all well defined band maxima and minima. The absorbances used in making these plots have been corrected for any slight absorbance (<0.020 absorbance units) due to uncomplexed donor or acceptor, which occurs at wavelengths shorter than 425 m μ .

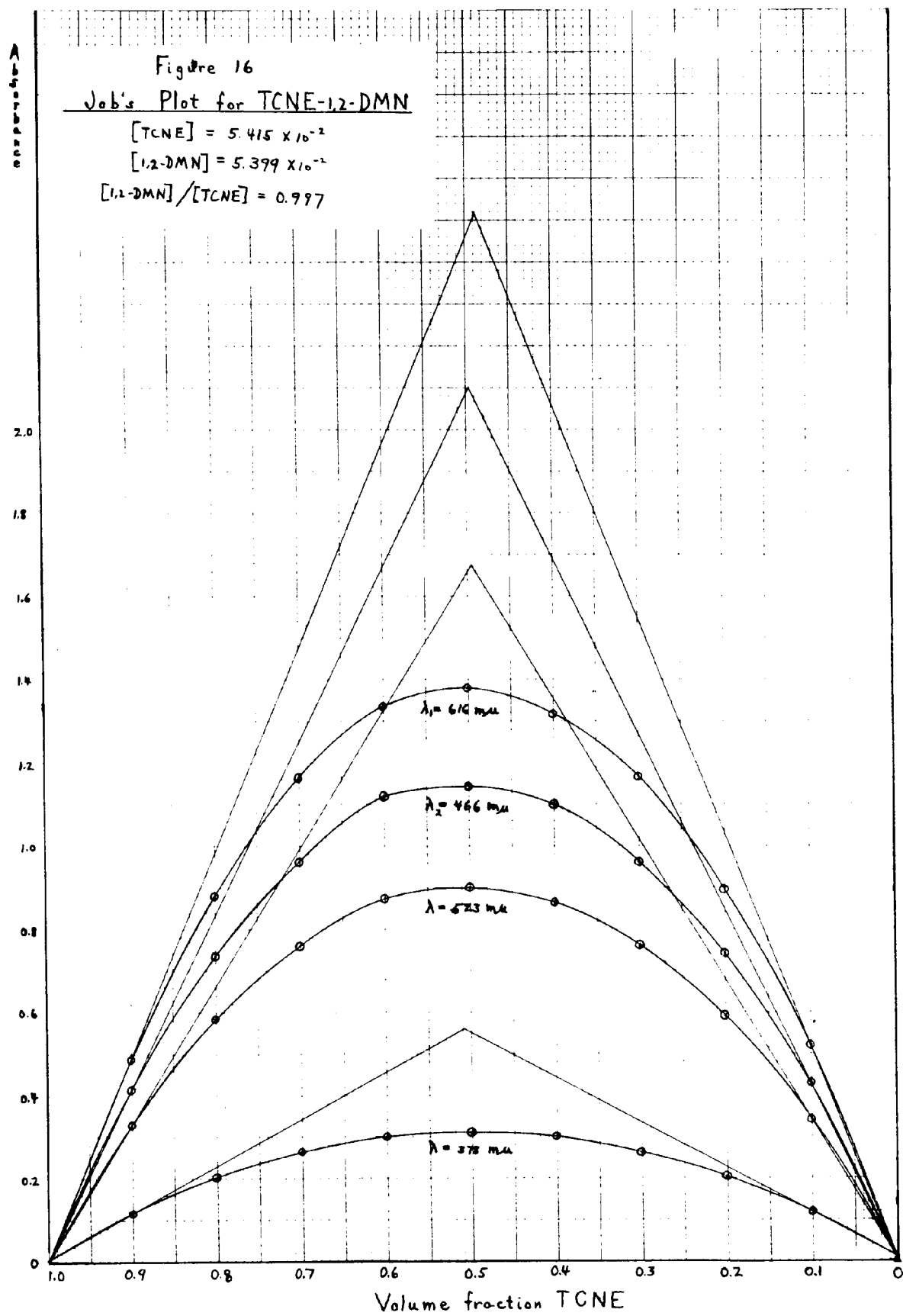
Discussion

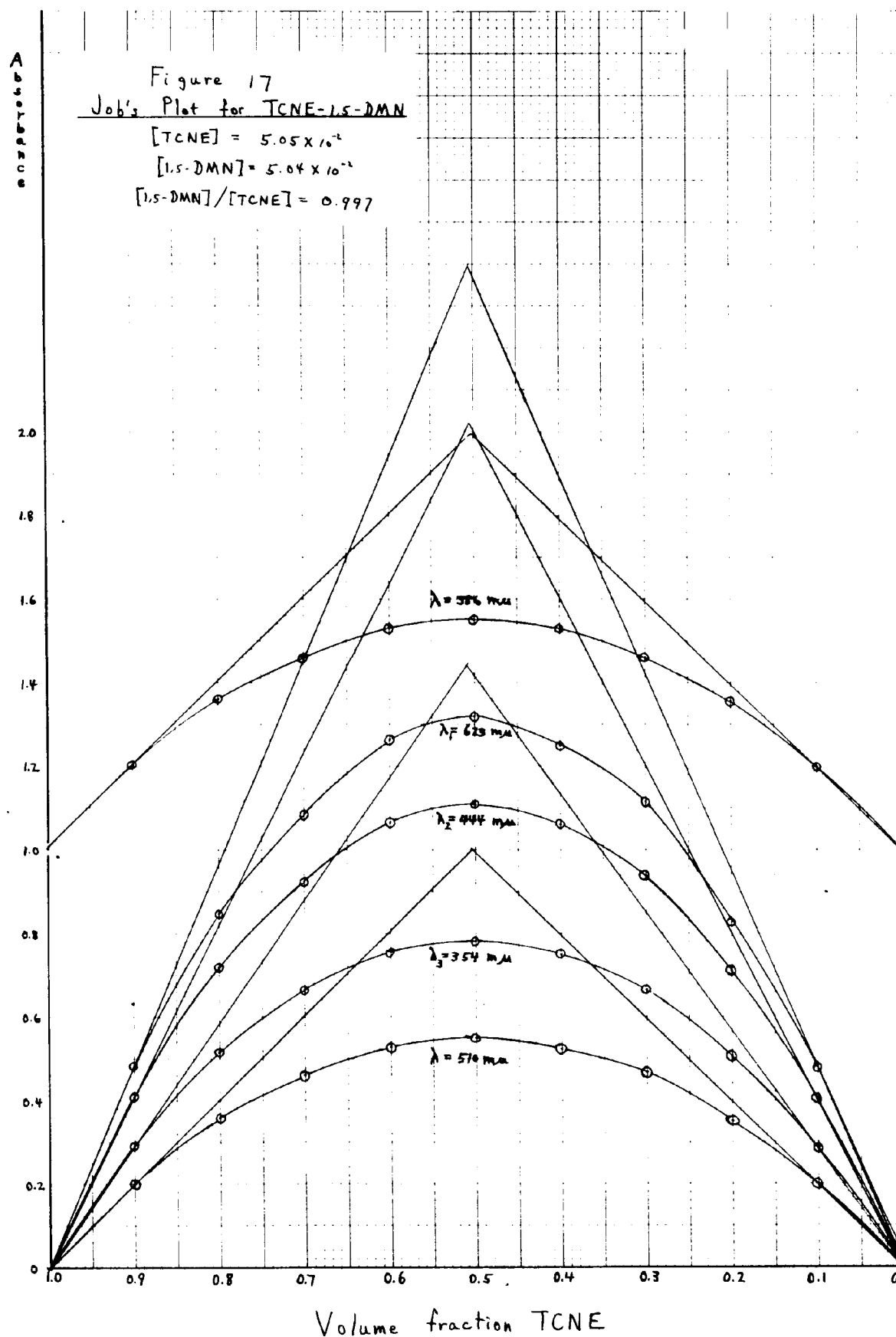
In general, the Job's plots are symmetric, broadly rounded curves of parabola-like shape having their maxima at a volume fraction of TCNE equal to 0.5. This corresponds to

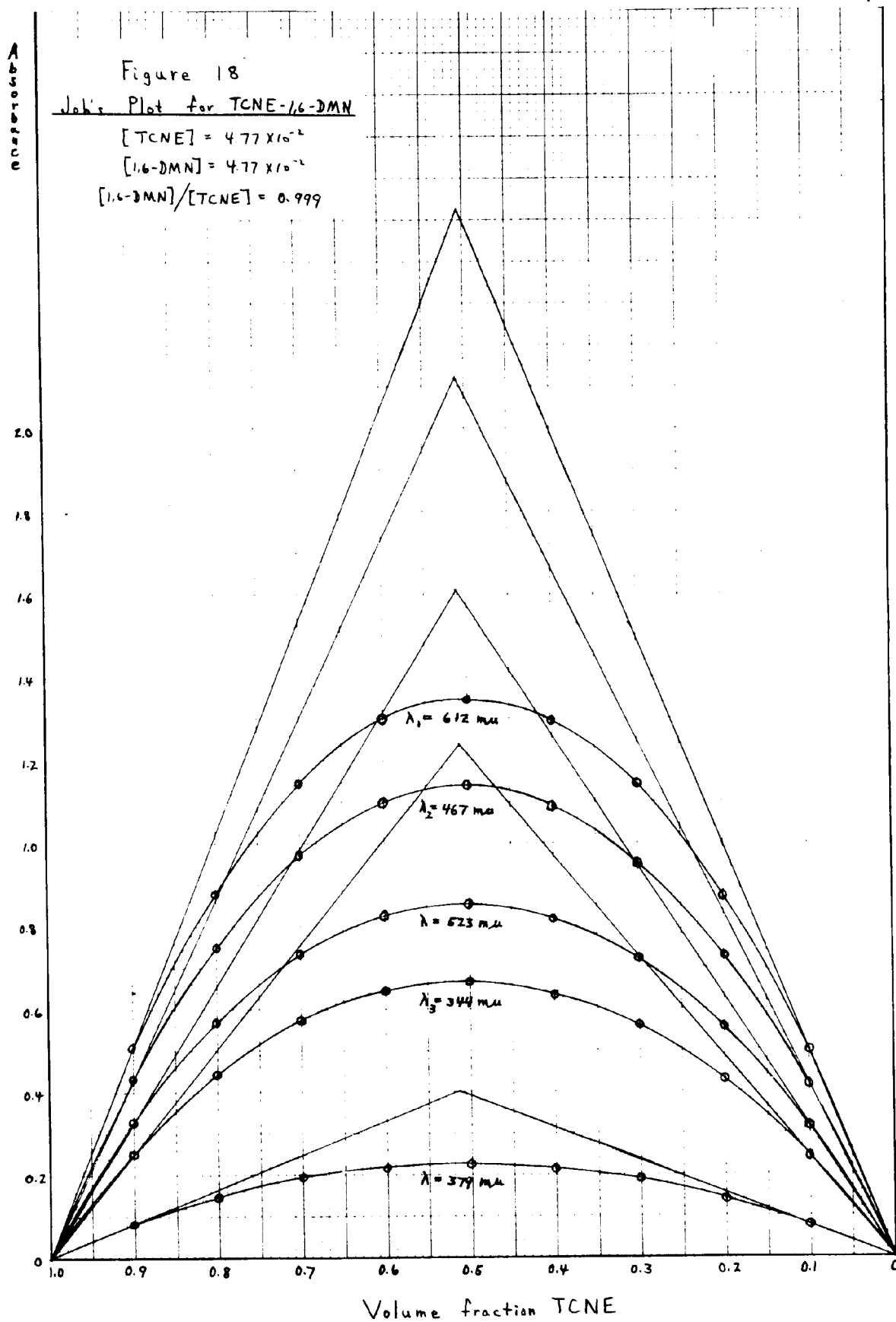


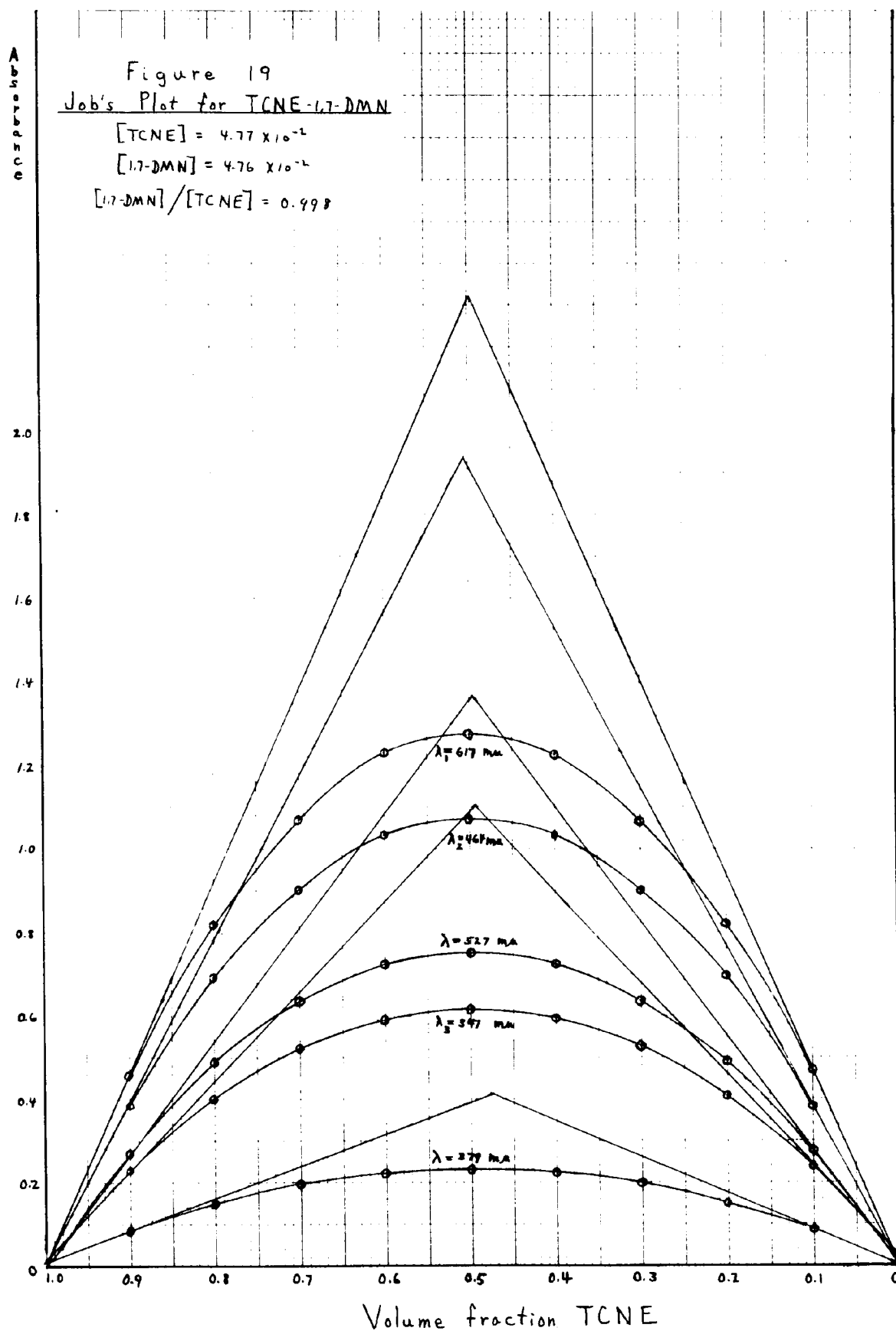


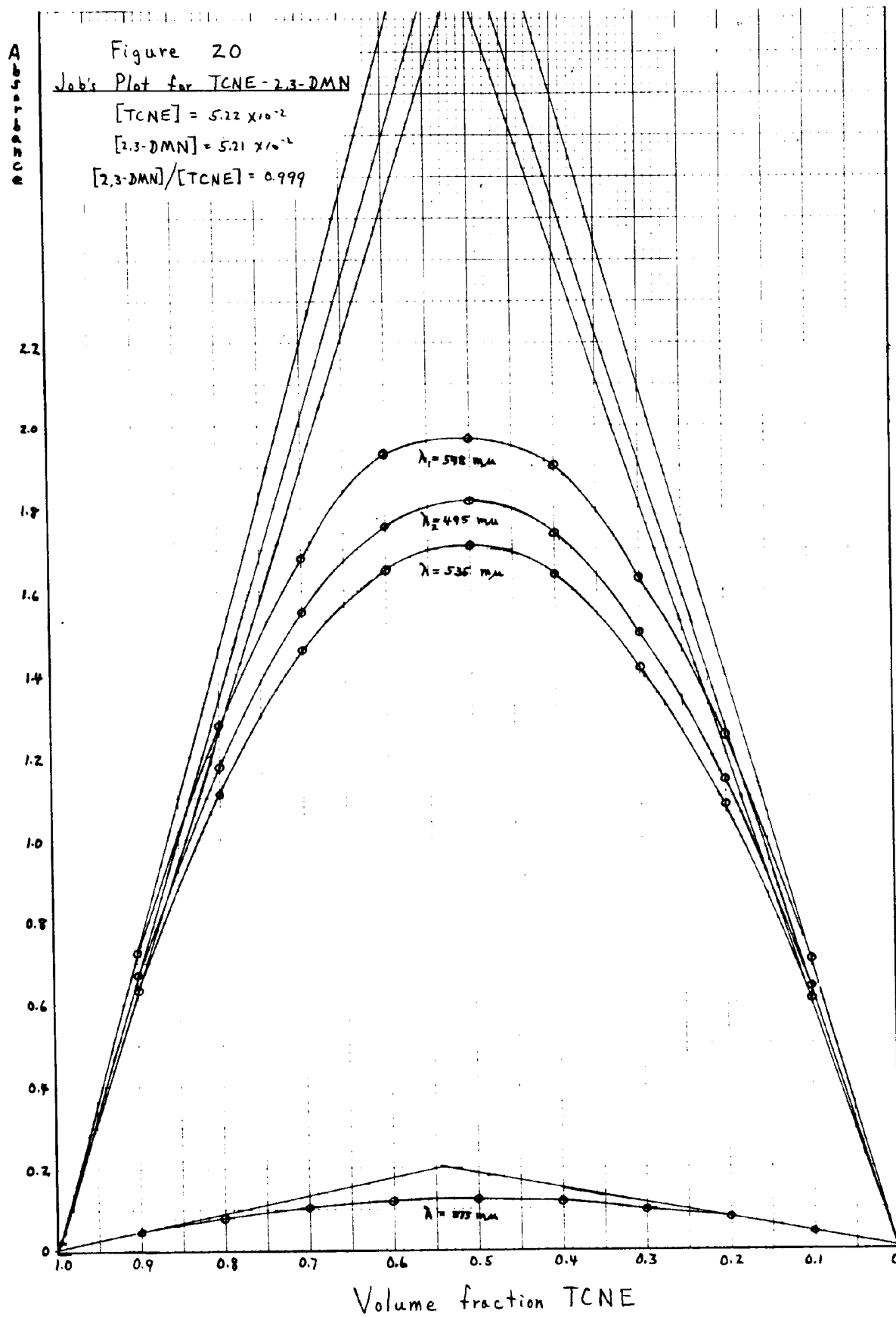


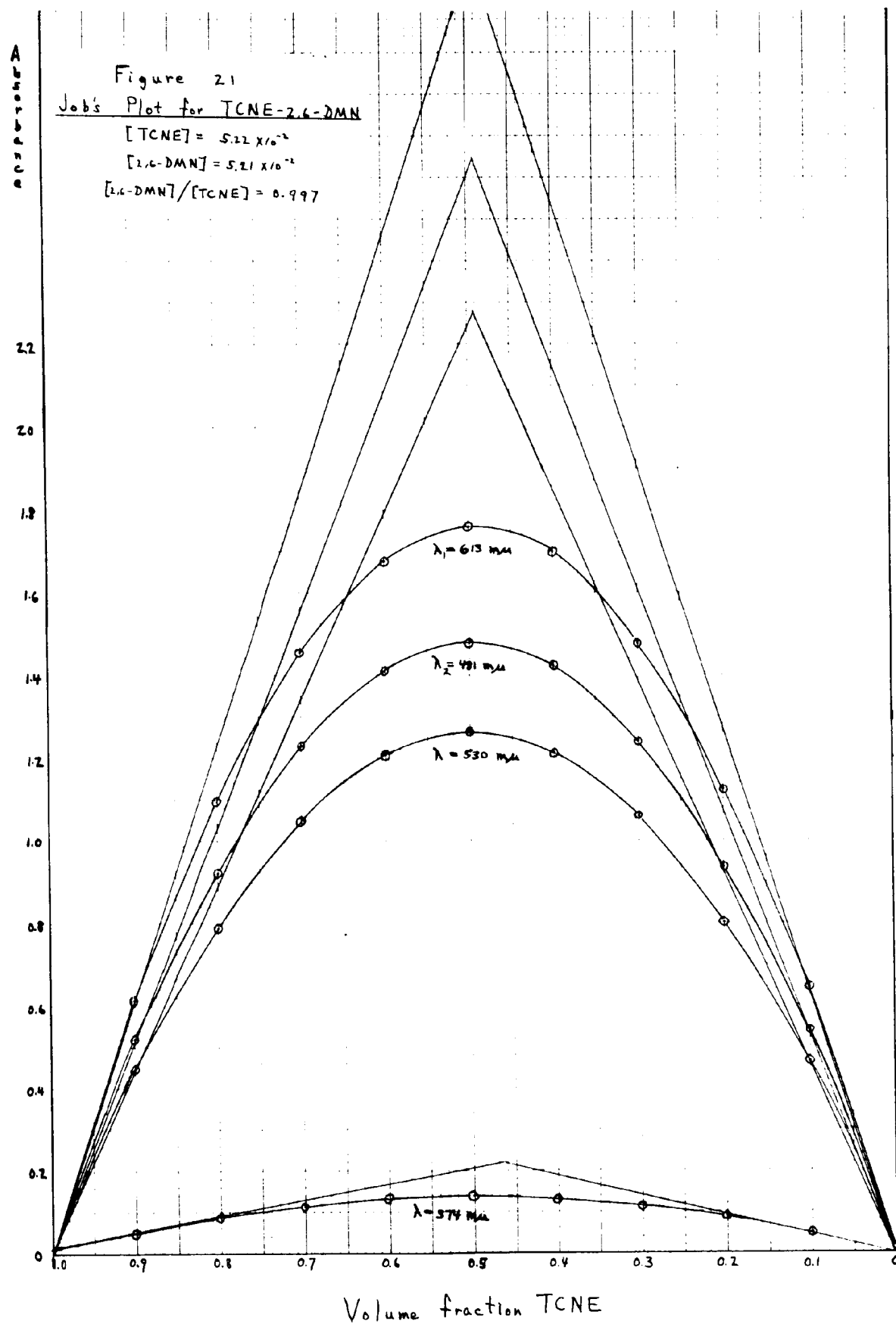


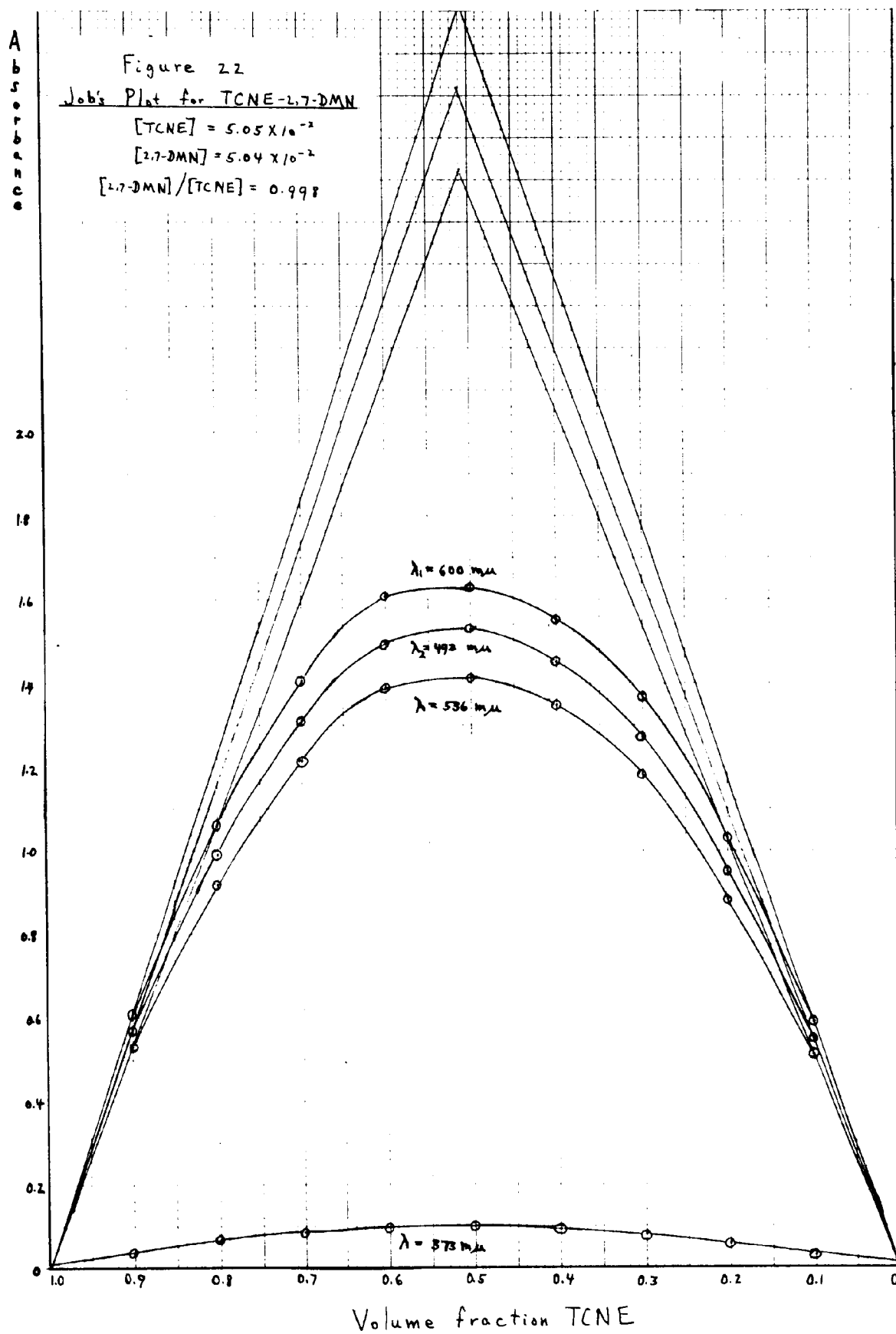












a complex whose composition with respect to donor and acceptor is 1:1. The broad rounding of these curves is a reflection of the small magnitude of the equilibrium constant for complex formation (of the order of magnitude of unity in terms of the molar concentration equilibrium constant--see Section V). For strong complexes, where the complex formation reaction essentially reaches completion, the Job's plot would assume the form of two straight lines whose point of intersection indicates the composition of the complex.

Ideally, for a single 1:1 complex, a Job's plot should show perfect symmetry about the maximum. For most of the complexes investigated, particularly those of 2-MN, 2,3-DMN, and 2,7-DMN, a departure from perfect symmetry was observed. This is probably due, in part, to the fact that these data (except for the case of TCNE-1MN) were obtained without temperature control of the sample cell. Under these conditions, absorbances were observed to change as much as 5% in a period of 5 min., because of heating of the sample cell in the cell compartment of the spectrophotometer. Another factor which may contribute to the lack of symmetry is the fact that for several complexes (especially those of 1-MN, 2-MN, and 1,6-DMN) a rapid change in the original spectrum occurs with time when the donor is present in large excess. This phenomenon has been attributed (see Section III), in the case of the 1-MN complex, to a reaction between TCNE and an impurity present in small amounts in the donor. Because of these complications, the apparent slight asymmetry observed cannot

unequivocally be considered a real property of the complex (or complexes) under investigation.

In the case of TCNE-IMN complex, data for a Job's plot were obtained using the thermostatted cell, and spectra were recorded as soon after mixing of the components as was practicable (see Experimental), thus effectively minimizing any error which might be caused by the two factors cited above. The resulting plot again shows a slight asymmetry, somewhat larger than can be accounted for on the basis of the accuracy of the spectrophotometer (0.005-0.006 absorbance units). In this instance the observed asymmetry probably is real.

Let us consider what kinds of situations might lead to non-symmetric plots. Consider first formation of a single 1:1 complex



where D, A, and C represent donor, acceptor, and complex, respectively. Then

$$^cK \equiv \frac{[C]}{[D][A]} = \frac{\text{Abs}/\epsilon_c}{(C_D - [C])(C_A - [C])} \quad (\text{IV-1})$$

where ^cK is the equilibrium constant in molar concentration units, brackets denote equilibrium molar concentrations, and C_A and C_D represent formal molar concentrations of A and D respectively. It is assumed that the absorbance Abs at the wavelength of measurement is due solely to the complex, with molar extinction coefficient ϵ_c . In applying Job's method the total concentration of A and D is held constant, so that

$$\frac{C_A}{C_A+C_D} + \frac{C_D}{C_A+C_D} = 1 \quad (\text{IV-2})$$

Elimination of C_A between (IV-1) and (IV-2) gives

$$\frac{\text{Abs}}{c_K \epsilon_c} = \frac{[C]}{c_K} = (C_A+C_D)C_D - C_D^2 - (C_A+C_D)[C] + [C]^2$$

Dividing both sides of this equation by $(C_A+C_D)^2$ and making the following identifications

$$x \equiv \frac{C_D}{C_A+C_D} ; y' \equiv \frac{[C]}{c_K(C_A+C_D)^2} = \frac{[C]}{\gamma(C_A+C_D)} ; \gamma \equiv c_K(C_A+C_D)$$

$$\text{yields } \gamma^2(y')^2 - (1+\gamma)y' = x^2 - x \quad (\text{IV-3})$$

Here x , which represents the abscissa of our Job's plot, can vary between 0 and 1 (i.e. $0 < x < 1$) and the ordinate Abs is linearly related to y' by $y = \text{Abs.} = \epsilon_c \gamma (C_A+C_D) y'$. Equation (IV-3) represents two parabola-shaped curves, both symmetric about $x = 0.5$. The parabola obtained upon taking the minus combination in the expression for the roots of (IV-3)

$$y' = \frac{(1+\gamma) \pm \sqrt{(1+\gamma)^2 - 4\gamma^2(x-x^2)}}{2\gamma^2} \quad (\text{IV-4})$$

is the desired solution since it satisfies the boundary conditions that $\text{Abs.} = 0$ at $x = 0$ and $x = 1$. Thus, in the case of a single 1:1 complex a perfectly symmetric Job's plot should be obtained.

Consider next the possibility that the optical absorption is due not to discrete complex species but is related to the presence of "contact pairs" of A and D brought about by random thermal motion in the liquid. The concept of

contact charge-transfer spectra is due to Orgel and Mulliken [50]. In this case the concentration of 1:1 contact pairs obeys the statistical relation

$$c_a \equiv \frac{DA}{[D][A]} = \frac{\text{Abs}/\bar{\epsilon}_{DA}}{C_D C_A} \quad (\text{IV-5})$$

where DA represents the contact pair and c_a can be regarded simply as a proportionality constant. Here $\bar{\epsilon}_{DA}$ represents a suitable average of ϵ_{DA} , since this latter quantity should vary strongly with the relative orientation of D and A, as well as with the mean distance between them. Eliminating C_A between (IV-2) and (IV-5) and dividing by $(C_A + C_D)^2$ gives

$$\frac{\text{Abs}}{c_a \bar{\epsilon}_{DA} (C_A + C_D)^2} = \frac{C_D}{C_A + C_D} - \frac{C_D^2}{(C_A + C_D)^2} = x - x^2 \quad (\text{IC-6})$$

Again, this is the equation of a parabola symmetric about $x = 0.5$ and a symmetric Job's plot is obtained.

The results obtained above can be generalized to the case where a multiplicity of 1:1 complexes are present, each having its own characteristic equilibrium constant and absorption spectrum, both without and with a contribution being made by contact charge-transfer absorption. It can be shown (Appendix II) that the following relations hold:

For several 1:1 complexes

$$c_{K'} = \frac{[C]'}{[D][A]} = \frac{\text{Abs}/\epsilon'}{(C_D - [C]')(C_A - [C]')} \quad (\text{IV-7})$$

where $c_{K'} = \sum c_{K_i}$; $[C]' = \sum [C_i]$; $\epsilon' = \frac{\sum \epsilon_{C_i} c_{K_i}}{c_{K'}}$

and the index i refers to the i -th complex.

For several 1:1 complexes plus 1:1 contact pairs

$$c_{K'} = \frac{[C]'}{[D][A]} = \frac{\text{Abs}/\epsilon''}{(C_D - [C]')(C_A - [C]')} \quad (\text{IV-8})$$

where

$$\epsilon'' = \frac{\bar{\epsilon}_{DA} c_a}{c_{K'}} + \frac{\sum \epsilon_{Ci} c_{Ki}}{c_{K'}}$$

Both (IV-7) and (IV-8) are formally identical with (IV-1). Consequently the earlier analysis holds and symmetric Job's plots are to be expected.

It can be concluded that Job's method cannot distinguish between the presence of a single 1:1 complex, 1:1 contact pairs, or a multiplicity of such species. Provided that the concentrations of light-absorbing species obey a mass action law of the form of (IV-1), perfectly symmetric plots will be obtained. This conclusion is an extension of that reached by Orgel and Mulliken, that any combination of 1:1 complexes, including contact charge-transfer complexes, will yield a straight-line Benesi-Hildebrand plot.

In light of the foregoing analysis, asymmetry can be generated only if a mass action law of the form of (IV-1) is not obeyed. This can be brought about by the existence of complexes of a different stoichiometry (e.g. 1:2 or 2:1), or the existence of other equilibria involving complexing between solvent and donor or solvent and acceptor. The presence of solvent complexes is a strong possibility since the existence of weak complexes between TCNE and CH_2Cl_2 [20],

and between aromatics (benzene, mesitylene) and CCl_4 [51] have been claimed. In addition, the possibility of self complexing by the donor exists, but this should be negligible in the relatively dilute solutions under consideration here. Finally, since ideal behavior has been assumed, deviations from ideality must be considered. The most likely specific contributions to non-ideality have been mentioned above. If these are explicitly taken into account the remaining contributions to non-ideality will be largely due to differences in van der Waals forces (dipole-dipole forces, London dispersion forces) between the various species present in solution. Since the solutions under consideration are relatively dilute and the total concentration of solute is essentially constant (for weak complexes) this contribution to non-ideality should be small and relatively constant for all solutions, and the symmetry of a Job's plot should not be significantly affected.

In any event, it can be concluded that the Job's plots confirm, to a satisfactory first approximation, the existence of one (or more) complexes of 1:1 stoichiometry. To the extent to which the apparent slight asymmetry of some of these plots may be significant, this evidence points to the simultaneous presence of complexes of different stoichiometry or the presence of other equilibria involving the solvent.

Further evidence in support of a 1:1 stoichiometry for these complexes lies in the adherence to a straight line fit of equations (V-18) and (V-26) by data used to determine

equilibrium constants and extinction coefficients (see Section V). These equations are obeyed by any combination of 1:1 complex species and the data used to fit them cover a much wider range of concentrations and mole ratios than were used in the Job's plots. The fits obtained are excellent except for a slight deviation at very high concentrations of donor. This deviation may be due to the same causes as cited above in the case of the Job's plots. In addition, self-complexing by the donor and non-ideality effects of a non-specific nature are expected to become more important due to the high concentrations of donor present in several of the test solutions. For further discussion see Section V, Part E.

It appears possible to prepare the molecular complexes under discussion here in solid form. Upon slow evaporation of a CH_2Cl_2 solution containing equimolar concentrations of TCNE and naphthalene, crystals the same color as the molecular complex in solution were obtained. Elemental analysis of such crystals would fix the stoichiometry of the solid complex and yield indirect evidence as to the stoichiometry of the complex in solution. Such evidence has been obtained in the case of TCNE-N [52].

Section V. Equilibrium Constants and Extinction Coefficients

Evaluation of the equilibrium constants and extinction coefficients of molecular complexes has most commonly been carried out by the classical Benesi-Hildebrand method, either in its original form, or in various modified or extended forms. A review of these methods, along with several other more or less rigorous methods is given in Part A. It is shown in Part B that these methods give unsatisfactory results in the case of weak complexes, if it is attempted to minimize non-ideality effects by working with dilute solutions in which the mole ratios of the components are held close to unity. A method of evaluation is proposed in Part C wherein measurements are made over as wide a range of mole ratios as solubilities will permit. The degree of departure from ideality can be judged by the extent of any systematic deviation of the data from a least squares fit to a linear plot. Since no rigorous equation for the evaluation of the mole fraction equilibrium constant x_K could be found in the literature, the deviation of such an equation is presented in Part C. The derivation of this equation makes clear the fact that no simple relationship exists between the molar concentration and mole fraction equilibrium constants c_K and x_K , and explains the fact that different values of the extinction coefficient ϵ_c are obtained, depending on whether c_K or x_K is evaluated. Although these effects have long been attributed to a departure from ideal behavior, it is

pointed out in Part E-2 that they arise solely from the lack of a linear relationship between molar concentration and mole fraction units.

The experimentally determined values of K and ϵ_c are presented in Part D, together with estimates of their uncertainties (a discussion of methods for graphical and numerical evaluation of these constants is given in Part C). Plots of the experimental data from which these constants were determined are very nearly perfect straight lines; however, a small but definite degree of curvature can be discerned from the residuals to the least squares fit. A discussion, in some detail, of the possible causes of this apparent non-ideal behavior is given in Part E-2, both in terms of deviations from Henry's law, and in terms of neglected competing equilibria. The possibility of a change in ϵ_c with changing solvent properties is discussed in Part E-3. An analysis of the wavelength shifts and changes in relative intensities of the charge-transfer bands with changes in temperature, pressure and solvent composition is made in terms of several factors which would theoretically be expected to influence these quantities. On the basis of this analysis it can be tentatively concluded that the first two absorption maxima observed in TCNE-naphthalene complexes represent two different charge-transfer bands, each due to a different 1:1 complex. It can also be concluded from the discussion in Part E that the major contributing factors to the observed non-

ideality are the formation of complexes between donor and solvent, and, in concentrated solutions of donor, the presence of D_2A complexes.

Part A. Survey of Methods Used to Determine K and ϵ_c

The method most commonly employed for determining the formation constant and molar extinction coefficient of a molecular complex is that due to Benesi and Hildebrand [1], or a modification thereof. These authors derived an expression for ^xK , the formation constant in mole fraction units, which is valid only under the following conditions:

- (1) One component of the complex is present in considerable excess compared to the other. In the case of π, π -molecular complexes where donors are aromatic hydrocarbons, solubility considerations usually require that the donor be present in excess.
- (2) The components do not absorb at the wavelength of interest.

For the equilibrium



^xK is defined by

$$^xK \equiv \frac{[C]}{[A](X_D)_{eq.}} = \frac{[C]}{(C_A - [C])(X_D)_{eq.}} \quad (V-1)$$

where brackets denote equilibrium concentrations in molarity units, C_A is the formal (or initial) concentration of A in molarity units, and $(X_D)_{eq.}$ represents the equilibrium concentration of D in mole fraction units. In view of condi-

tion (1), $(X_D)_{eq.}$ can be replaced by X_D , the initial mole fraction of D. Also, the absorbance per unit path length Abs is given by

$$\text{Abs} = \epsilon_c [C]$$

where ϵ_c is the decadic molar extinction coefficient of the complex. Upon making these substitutions, equation (V-1) rearranges to the familiar Benesi-Hildebrand equation (V-2).

$$\frac{C_A}{\text{Abs}} = \frac{1}{x_K \epsilon_c} \cdot \frac{1}{X_D} + \frac{1}{\epsilon_c} \quad (V-2)$$

x_K and ϵ_c are usually evaluated from the slope and intercept of the straight line obtained upon plotting C_A/Abs vs. $1/X_D$ for a series of solutions containing varying concentrations of A and D. Most authors, however, prefer to evaluate ^cK , the formation constant in molarity units, defined by

$$^cK \equiv \frac{[C]}{[D][A]} = \frac{[C]}{(C_D - [C])(C_A - [C])} \quad (V-3)$$

In this case equation (V-2) becomes

$$\frac{C_A}{\text{Abs}} = \frac{1}{^cK \epsilon_c} \cdot \frac{1}{C_D} + \frac{1}{\epsilon_c} \quad (V-4)$$

The great drawback to the Benesi-Hildebrand method is the fact that it is inapplicable to dilute solutions in which mole ratios of D to A are of the order of magnitude of unity. The latter conditions are preferred since then any non-ideality effects are minimized, whereas with a large excess of donor formation of species such as D_2 , AD_2 and DAD is favored and non-ideality effects can become appreciable.

Although equations (V-2) and (V-4) were derived on the assumption of only one 1:1 complex being present, Orgel and Mulliken [50] have shown that equations of the same form are obeyed when a multiplicity of 1:1 complexes of A and D are present, each having its own characteristic absorption spectrum and formation constant. The K's and ϵ 's evaluated by the Benesi-Hildebrand procedure now have the following significance:

$$x_{K'} = \sum x_{K_i} ; c_{K'} = \sum c_{K_i} ; \epsilon_c' = \frac{\sum c_{K_i} \epsilon_{c_i}}{x_{K'}} = \frac{\sum c_{K_i} \epsilon_{c_i}}{c_{K'}}$$

where the index i refers to the i-th 1:1 complex and primes are used to distinguish these constants from the ones obtained for a single 1:1 complex. Furthermore, if a contribution to the absorbance is made by 1:1 contact charge-transfer complexes, equations formally identical to (V-2) and (V-4) are again obtained, and

$$x_{K'} = \sum x_{K_i} ; c_{K'} = \sum c_{K_i}$$

$$\epsilon_c'' = \frac{1}{x_{K'}} (x_a \bar{\epsilon}_{DA} + \sum x_{K_i} \epsilon_{c_i}) = \frac{1}{c_{K'}} (c_a \bar{\epsilon}_{DA} + \sum c_{K_i} \epsilon_{c_i})$$

where $x_{K'}$ and $c_{K'}$ are the same as above. $\bar{\epsilon}_{DA}$ is a suitable average of ϵ_{DA} , the molar extinction coefficient for the contact pair DA, and x_a and c_a are proportionality constants defined by

$$x_a \equiv \frac{[DA]}{[A](X_D)_{eq.}} ; c_a \equiv \frac{[DA]}{[A][D]} .$$

It should be noted that $x_{K'}$ and $c_{K'}$ are total equilibrium constants and as such are valid thermodynamic measures of the amount of 1:1 complexing taking place; that is

$$c_{K'} = \sum c_{K_i} = \frac{\sum [C_i]}{[A][D]} ; x_{K'} = \sum x_{K_i} = \frac{\sum [C_i]}{[A](X_D)_{eq}} .$$

On the other hand ϵ_c' and ϵ_c'' are weighted average extinction coefficients and give erroneous results for ϵ_c of the supposed single complex. In particular, if there is no contribution from contact absorption and the spectra of the 1:1 complexes are not identical, ϵ_c' will be low; while if contact absorption does contribute, ϵ_c'' will increasingly overestimate ϵ_c until, in the case of pure contact absorption, the Benesi-Hildebrand plot passes through the origin of coordinates and x_K or c_K will equal zero and ϵ_c will be infinite.

Scott [53] has commented on the form in which the Benesi-Hildebrand equation is expressed for the purposes of plotting. He prefers to interchange the role of slope and intercept and write equations (V-2) and (V-4) in the forms

$$\frac{C_A X_D}{Abs} = \frac{1}{x_K \epsilon_c} + \frac{X_D}{\epsilon_c} \quad (V-5)$$

$$\text{and } \frac{C_A C_D}{Abs} = \frac{1}{c_K \epsilon_c} + \frac{C_D}{\epsilon_c} . \quad (V-6)$$

In equations (V-5) and (V-6) the y intercept corresponds to an extrapolation to infinite dilution of donor, whereas in the Benesi-Hildebrand form the y intercept represents an infinitely concentrated donor. Although both forms should

give identical results for ideal solutions, the Scott form has the advantage in the case of non-ideal behavior since ϵ_c and x_K or c_K at infinite dilution can be deduced from the initial slope and intercept of this plot. (The asymptote drawn to the Benesi-Hildebrand plot at high dilutions should lead to the same results, but this would be far more difficult to determine.)

Scott also notes that the same data plotted according to both (V-5) and (V-6) generally yield two different values for ϵ_c , and values for c_K and x_K which do not obey the thermodynamic equation $c_K = V_s x_K$ (where V_s is the molar volume of the solvent) which must be valid at infinite dilution. He ascribes this difficulty to a concentration dependence of the equilibrium constants due to the effects of non-ideality. This is an interesting point, and it will be shown below (Part C) that such disagreement is to be expected even for ideal solutions solely on the basis of the non-linear relationship between mole fraction and molar concentration units.

Ketelaar and coworkers [54] modified the Benesi-Hildebrand equation to cover the case where both complex and one component absorb at the wavelength of interest. If the acceptor absorbs, equations (V-2) and (V-4) become

$$\frac{1}{\epsilon_a - \epsilon_A} = \frac{1}{\epsilon_c - \epsilon_A} \cdot \frac{1}{x_K x_D} + \frac{1}{\epsilon_c - \epsilon_A} \quad (V-7)$$

$$\text{and } \frac{1}{\epsilon_a - \epsilon_A} = \frac{1}{\epsilon_c - \epsilon_A} \cdot \frac{1}{c_K c_D} + \frac{1}{\epsilon_c - \epsilon_A} \quad (V-8)$$

where ϵ_A is the molar extinction coefficient of A and ϵ_a is the apparent extinction coefficient of A, defined by

$$\epsilon_a \equiv \frac{\text{Abs}}{C_A}.$$

A plot of $1/(\epsilon_a - \epsilon_A)$ vs. $1/X_D$ or $1/C_D$ permits evaluation of ϵ_c and ^xK or ^cK . Buckles and Mills [55] have rearranged (V-8) to

$$\epsilon_a = \epsilon_c + \frac{\epsilon_A - \epsilon_a}{^cK C_D} \quad (\text{V-9})$$

whence ^cK can be obtained directly from the slope of a plot of ϵ_a vs. $(\epsilon_A - \epsilon_a)/C_D$.

Foster, Hammick, and Wardley [56] have rearranged the Benesi-Hildebrand equation (V-4) to

$$\frac{\text{Abs}}{C_D} = ^cK \epsilon_c C_A - ^cK \text{Abs}. \quad (\text{V-10})$$

Then, if C_A is held constant, ^cK can be obtained directly from the slope of a plot of Abs/C_D vs. Abs .

Kortüm and Weber [57], under the assumptions employed by Benesi and Hildebrand, derived the following relation

$$\frac{\text{Abs}}{X_D C_A} = ^xK \epsilon_c - ^xK^2 \epsilon_c (X_D + X_A). \quad (\text{V-11})$$

A plot of $\text{Abs}/X_D C_A$ vs. $(X_D + X_A)$ gives $-^xK^2 \epsilon_c$ and $^xK \epsilon_c$ as slope and y intercept, respectively.

Nagakura [58], for the case where both complex and acceptor absorb and where $C_D \gg C_A$, derived the following expression for ^cK

$$c_k = \frac{C_D(k_0 - k') + C_D'(k - k_0)}{C_D C_D'(k' - k)} \quad (V-12)$$

where k_0 , k , and k' are absorbances determined at a fixed concentration of acceptor and concentrations of donor of 0, C_D and C_D' respectively.

If the definition of ^cK , equation (V-3), is written in the following expanded form

$$\frac{1}{^cK} = \frac{C_A C_D}{[C]} - C_D - C_A + [C] \quad (V-13)$$

it can be seen that the Benesi-Hildebrand equation (V-4) and its various rearranged forms, equations (V-6), (V-9) and (V-10), result when the last two terms in (V-13) are neglected. Foster [59] has derived an equation, for use in the case when $C_A = C_D$, which neglects only the last term in (V-13)

$$\frac{C_A}{\text{Abs}} = \frac{1}{^cK \epsilon_c} \cdot \frac{1}{C_A} + \frac{2}{\epsilon_c} \quad (V-14)$$

A plot of C_A/Abs vs. $1/C_A$ gives $1/^cK \epsilon_c$ and $2/\epsilon_c$ as slope and y intercept, respectively.

It has been pointed out by Rose and Drago [60,61] and by Tamres [62] that neglect of the last term, or last two terms (Benesi-Hildebrand equation), in equation (V-13) can lead to large errors in ^cK . Tamres has calculated families of curves of $1/^cK C_A$ as a function of C_c/C_A for various values of C_D/C_A where $1/^cK$ is given by equation (V-13) for the cases where no terms, the last term, and the last two terms, respectively, are neglected. These curves show that for small values of $1/^cK C_A$ and small values of C_D/C_A , relatively large discrep-

ancies for ^cK can occur if the last term or last two terms in (V-13) are neglected. In general ^cK calculated with neglect of the last term will be high, while, if the last two terms are neglected, ^cK will be low.

Several procedures for evaluating ^cK and ϵ_c without neglect of any terms in equation (V-13) have been described. Rose and Drago [60] showed that if both complex and acceptor absorb, equation (V-13) can be written

$$\frac{1}{^cK} = \frac{\text{Abs} - \epsilon_A C_A}{\epsilon_c - \epsilon_A} - C_A - C_D + \frac{C_D \epsilon_A (\epsilon_c - \epsilon_A)}{\text{Abs} - \epsilon_A C_A} \quad (\text{V-15})$$

If only the complex absorbs (V-15) becomes

$$\frac{1}{^cK} = \frac{\text{Abs}}{\epsilon_c} - C_A - C_D + \frac{C_A C_D}{\text{Abs}} \cdot \epsilon_c \quad (\text{V-16})$$

Solutions for ^cK and ϵ_c for each possible pair of data points are obtained by solution of simultaneous equations or by a graphical procedure. In the latter procedure one plots a curve of $1/^cK$ as a function of ϵ_c for each data point.

Intersections of these curves then represent solutions for ^cK and ϵ_c for the pair of data points whose curves intersect.

Keefer and Andrews [63] rearranged equation (V-15) into a form analogous to the Benesi-Hildebrand equation

$$\frac{A}{(\text{Abs})_c} = \frac{B}{^cK \epsilon_c} + \frac{1}{\epsilon_c} \quad (\text{V-17})$$

where

$$A \equiv \frac{C_A C_D}{C_A + C_D - [C]} ; B \equiv \frac{1}{C_A + C_D - [C]} ,$$

and $(\text{Abs})_c \equiv [C] \epsilon_c = \text{Abs} - [A] \epsilon_A$.

These authors use an iterative procedure to obtain ^cK and ϵ_c . First approximations for A, B and $(Abs)_c$ are obtained by assuming that [C] can be neglected in the expressions for A and B and that [A] can be replaced by C_A in the expression for $(Abs)_c$. A plot of $A/(Abs)_c$ vs. B allows first approximations for ^cK and ϵ_c to be evaluated. These values are then used in obtaining new approximations for A, B and $(Abs)_c$. This process is repeated until consistent values of ^cK and ϵ_c are arrived at. Ross and coworkers [64] extended this method to include absorption by both components plus complex. In this case $(Abs)_c$ becomes

$$(Abs)_c \equiv [C]\epsilon_c = Abs - [A]\epsilon_A - [D]\epsilon_D$$

and a first approximation to $(Abs)_c$ is obtained by letting $[A] = C_A$ and $[D] = C_D$. Application of the iteration procedure then proceeds as above. Ross and Labes [65] also applied this method in the special case where $C_A = C_D$.

Lang [66] rearranged equation (V-13) into a form analogous to Scott's form of the Benesi-Hildebrand equation. For the case where only the complex absorbs,

$$\frac{C_A C_D}{Abs} = \frac{1}{\epsilon_c} (C_A + C_D - \frac{Abs}{\epsilon_c}) + \frac{1}{^cK \epsilon_c}. \quad (V-18)$$

A first approximation for ϵ_c is obtained by using data for two experimental points and solving equation (V-18) simultaneously for ϵ_c and ^cK . A plot of $C_A C_D / Abs$ vs. $(C_A + C_D - Abs/\epsilon_c)$ then yields a second approximation for ϵ_c . This iterative process is repeated until consistent values for ϵ_c and ^cK are obtained.

All of the methods described above, except those due to Nagakura and Rose and Drago, employ a graphical method for evaluation of ϵ_c and ^cK or ^xK and are susceptible to subjective error in drawing a straight line to fit a set of experimental points. Estimation of the y intercept is particularly sensitive to small errors since for all plots, except those of Buckles and Mills, and Foster, Hammick and Wardley, the y intercept lies close to the origin. It would appear that these difficulties should be especially troublesome in the case of those methods employing an iterative procedure, since consistent values of ϵ_c and ^cK would be virtually impossible to obtain. Use of a least squares treatment to fit the various equations given above would remove any subjective errors and allow the iterative procedures to converge to consistent values of ϵ_c and ^cK . Tamres [62,67] has advocated the use of least squares treatments and has pointed out that, in general, different forms of an equation used to fit the same experimental points will give different results unless all points happen to lie exactly on the line determined by the calculated values of K and ϵ_c . He has advanced this last point as an explanation of the discrepancy, noted by Scott [53], between values of ϵ_c obtained from plots of equations (V-5) and (V-6). One of the chief advantages of a least squares treatment is that it allows an estimate of the precision of K and ϵ_c to be made by standard statistical methods. The importance of a complete error analysis has been pointed out by Mulliken and Person [18].

The most comprehensive method for the calculation of ϵ_c and ^cK or ^xK is that due to Liptay [68,69]. This author gives details of a weighted least squares treatment for calculation of ϵ_c , ^xK and ^cK as well as expressions for the average relative errors of these quantities. Liptay writes the following equations for ^cK and ^xK respectively:

$$\frac{C_A C_D}{\text{Abs}} + \frac{\text{Abs}}{\epsilon_c^2} = \frac{1}{^cK \epsilon_c} + \frac{1}{\epsilon_c} (C_A + C_D) \quad (\text{V-19})$$

$$\frac{X_A X_D}{\text{Abs} \cdot \bar{V}} + \frac{\text{Abs} \cdot \bar{V}}{\epsilon_c^2} = \frac{1}{^xK \epsilon_c} + \frac{1}{\epsilon_c} (X_A + X_D) \quad (\text{V-20})$$

where $\bar{V}$ is the molar volume of the solution, defined by

$$\bar{V} \equiv \frac{V}{\sum n_i}.$$

V is the volume of the solution and n_i is the number of moles of component i . Unfortunately, equation (V-20) is incorrect since in its derivation Liptay wrongly assumed that mole fractions are additive (e.g. that $X_A = (X_A)_{\text{eq.}} + (X_c)_{\text{eq.}}$). This assumption is wrong since the total number of moles $\sum n_i$ changes upon establishment of equilibrium. A correct expression for ^xK is derived below in Part C.

In addition to the spectrophotometric methods cited above, ^cK or ^xK can be determined by solubility methods, partition methods, and reaction rate methods. These are discussed in several places [16,69,70].

Part B. Preliminary Results for K and ϵ_c

As pointed out in Part A, measurements made on dilute solutions where the mole ratio of D to A is near unity are to be preferred for determination of K and ϵ_c since under these conditions formation of species such as D_2 , AD_2 and DAD , as well as other non-ideality effects, is minimized. Accordingly, the method of Foster [59] in which $C_A = C_D$, equation (V-14), was chosen for evaluation of ^cK and ϵ_c for the TCNE complexes of naphthalene, 2,3-DMN, and 2,6-DMN. The absorbance at λ_{max} . for each of the two charge-transfer bands was measured for successive dilutions of stock solutions of the complexes using path lengths of 1.00, 5.00 and 10.00 cm., as appropriate. The resulting data were plotted both according to equation (V-14), analogous to a Benesi-Hildebrand plot, and in the form preferred by Scott [53], that is

$$\frac{C_A^2}{Abs} = \frac{1}{^cK\epsilon_c} + \frac{2C_A}{\epsilon_c} . \quad (V-14a)$$

In general, the data do not fall on a single straight line but can be reasonably well represented by two straight line segments drawn to fit points representing concentrated or dilute solutions, respectively. Deviations from linearity appear especially pronounced when the Scott form is used. Values of ^cK and ϵ_c derived from these plots are listed below in Table 6. From these it is apparent that:

1. ^cK and ϵ_c depend markedly on whether a straight line is

TABLE 6

Results for c_K and ϵ_c by the Method of Foster [59]

<u>TCNE-N Complex</u>						
<u>Equation</u>	<u>λ_1</u>			<u>λ_2</u>		
	<u>No. of Points</u>	<u>c_K</u>	<u>ϵ_c</u>	<u>No. of Points</u>	<u>c_K</u>	<u>ϵ_c</u>
V-14 all concns.	25	6.22	194	25	8.43	143
V-14a conc. solns.	6	3.51	308	6	5.03	213
V-14a dil. solns. (1 cm. cell)	6	13.7	105	6	21.5	74.6
V-14a dil. solns. (5 cm. cell)	9	12.6	103	9	18.4	75.0

<u>TCNE-2,3-DMN Complex</u>						
<u>Equation</u>	<u>λ_1</u>			<u>λ_2</u>		
	<u>No. of Points</u>	<u>c_K</u>	<u>ϵ_c</u>	<u>No. of Points</u>	<u>c_K</u>	<u>ϵ_c</u>
V-14 conc. solns.	20	6.44	541	19	5.32	606
V-14 dil. solns.	19	29.9	146	17	18.1	204
V-14a conc. solns.	14	7.08	488	15	6.06	530
V-14a dil. solns.	13	30.4	130	12	19.0	184

<u>TCNE-2,6-DMN Complex</u>						
<u>Equation</u>	<u>λ_1</u>			<u>λ_2</u>		
	<u>No. of Points</u>	<u>c_K</u>	<u>ϵ_c</u>	<u>No. of Points</u>	<u>c_K</u>	<u>ϵ_c</u>
V-14 conc. solns.	15	6.04	526	15	6.53	444
V-14 dil. solns.	7	37.1	105	9	52.8	87

fitted to points representing dilute solutions or concentrated solutions.

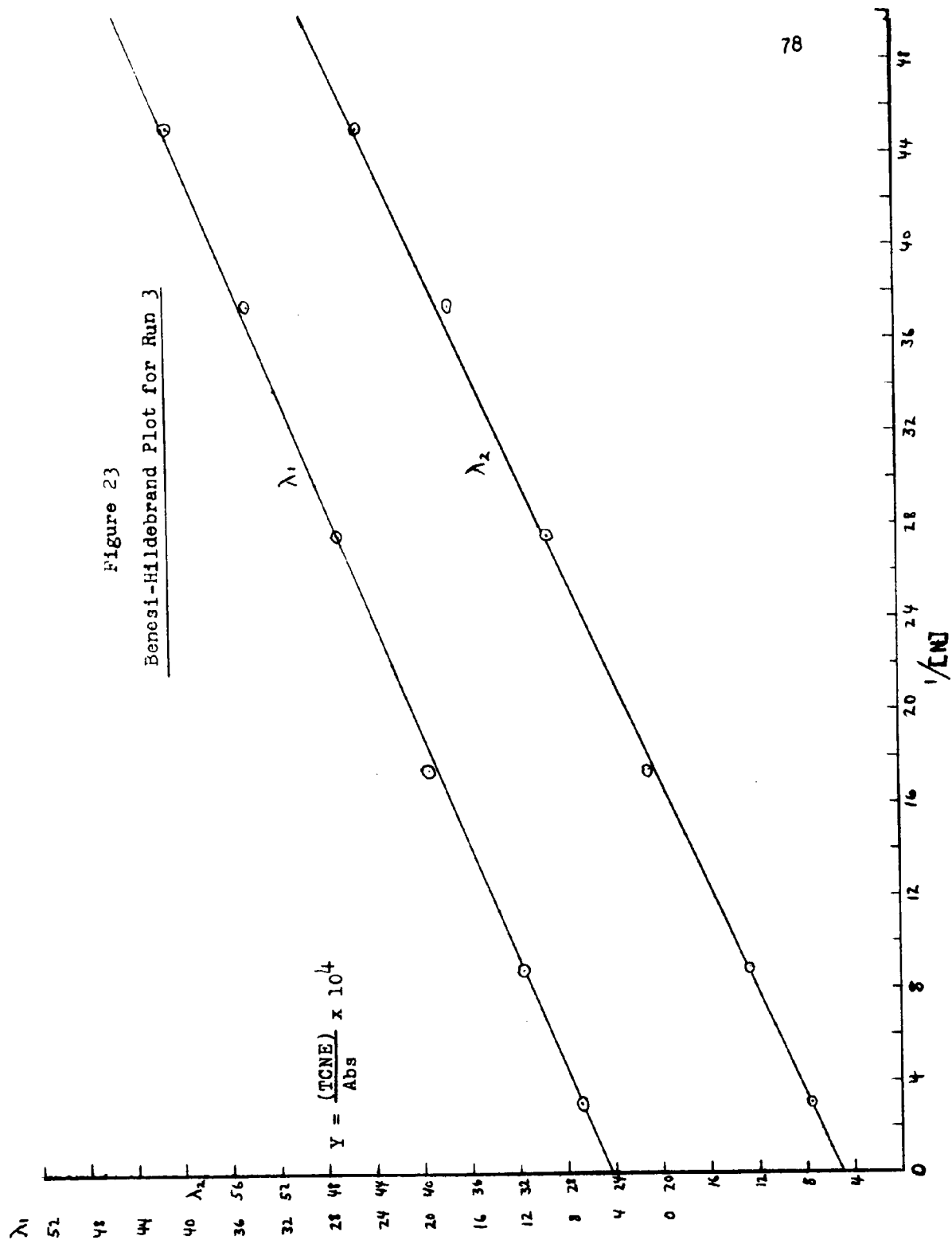
2. There is poor agreement between ^cK determined at λ_1 and at λ_2 .
3. In the case of TCNE-2,3-DMN complex, agreement between the ^cK and ϵ_c values determined from plots according to equations (V-14) and (V-14a) is fair, but relative differences are as great as 10 per cent.
4. Values of ϵ_c for TCNE-N complex are low by an order of magnitude compared with those reported by Merrifield and Phillips [20]. These authors determined ^xK and ϵ_c by the Benesi-Hildebrand method and found $\epsilon_c(\lambda_1) = 1240$ and $\epsilon_c(\lambda_2) = 1120$.

Consideration of the sources of error involved in the experiment described above reveals the following to be important:

1. Neglect of the last term in equation (V-13) in deriving equation (V-14). If $^cK \sim 10$, then at the concentrations employed ($C_A \sim 0.01$), $[C] \sim 0.1 C_A$ and neglect of $[C]$ is unjustified. As pointed out in Part A this approximation tends to make ^cK too high. However, conversion of the ^xK value reported for TCNE-N by Merrifield and Phillips by the relation $^cK = V_s ^xK$ gives $^cK = 0.75$. In this case $[C] \sim 0.007 C_A$ and neglect of the $[C]$ term in equation (V-13) is less serious.
2. Lack of temperature control. As pointed out under Experimental, a change of up to 5 per cent in the measured absorbance could be caused by warming of the sample

- cell in the cell compartment of the spectrophotometer.
3. Measured absorbances covered a wide range, from 0.1 to 2.0. It is felt that since the relative errors of absorbance measurements are greatest at low absorbances (i.e. for the most dilute solutions) ^cK and ϵ_c determined from the data for dilute solutions are most uncertain and that therefore ^cK and ϵ_c for the concentrated solutions represent the better values.

In view of the wide discrepancy between the values of ^cK and ϵ_c for TCNE-N obtained above and those reported by Merrifield and Phillips, an attempt was made to duplicate Merrifield and Phillips' results by application of the Benesi-Hildebrand method. Since optimum precision and accuracy of absorbance measurements are attained near an absorbance of 1.0, an effort was made to choose C_A and C_D such that the absorbances of all solutions remained nearly constant at a value close to 1.0 (see Procedure B under Experimental). Two runs, Nos. 3 and 4, were made without temperature control. These were duplicate runs, except that in Run 3 the maximum mole fraction of N was 0.33 and the ratio $[N]/[TCNE]$ varied between 140 and 6500, while in Run 4 the max. mole fraction of N was 0.25 and $[N]/[TCNE]$ varied between 68 and 3270. The results of Run 3 are plotted according to equation (V-2) in Fig. 23, from which it can be seen that the points fall reasonably well on a straight line. ^xK and ^cK for the data of Run 3 were also calculated by a straightforward application of



the method of least squares (see for example Scarborough [71]) to the Benesi-Hildebrand equations (V-2) and (V-4) and to the Scott equations (V-5) and (V-6). A summary of these results is given below in Table 7. It can be seen that:

1. For the results from Run 3, values of ϵ_c differ depending on whether ^cK or ^xK is being computed, as noted by Scott [53].
2. Differing results are obtained depending on whether the Benesi-Hildebrand form (equations (V-2), (V-4)) or the Scott form (equations (V-5), (V-6)) of the Benesi-Hildebrand equation is used, as pointed out by Tamres [62,67].
3. Values of ^cK and ^xK computed at λ_1 and λ_2 agree reasonably well.
4. The method has fair reproducibility, comparing results between Runs 3 and 4.
5. A large discrepancy again exists between these results and those of Merrifield and Phillips, whose values of ^xK and ϵ_c are approximately twice and one-half, respectively, of those obtained above.

Two more Benesi-Hildebrand runs were made (Runs 7 and 8) using the thermostatted absorption cell at a temperature of $21.80 \pm 0.02^\circ\text{C}$, close to the temperature ($22 \pm 0.5^\circ\text{C}$) employed by Merrifield and Phillips. In these and all subsequent runs care was taken to correct for the small but measurable absorbance due to the long wavelength tail of the naphthalene spectrum. These corrections were necessary only

TABLE 7K and ϵ_c for TCNE-N, Runs 3 and 4

<u>Run No.</u>	<u>Equation</u>	<u>$c_K(\lambda_1)$</u>	<u>$c_K(\lambda_2)$</u>	<u>$\epsilon_c(\lambda_1)$</u>	<u>$\epsilon_c(\lambda_2)$</u>
3	V-4 least squares	.337	.334	2483	2276
3	V-6 least squares	.299	.308	2733	2431
		<u>$x_K(\lambda_1)$</u>	<u>$x_K(\lambda_2)$</u>	<u>$\epsilon_c(\lambda_1)$</u>	<u>$\epsilon_c(\lambda_2)$</u>
3	V-2 B-H plot	5.38	5.44	2299	2083
3	V-2 least squares	5.96	5.92	2122	1941
3	V-5 least squares	5.34	5.47	2308	2060
4	V-2 least squares	5.77	5.88	2178	1939

TABLE 8K and ϵ_c for TCNE-N, Runs 7 and 8

<u>Run No.</u>	<u>Equation</u>	<u>$x_K(\lambda_1)$</u>	<u>$x_K(\lambda_2)$</u>	<u>$\epsilon_c(\lambda_1)$</u>	<u>$\epsilon_c(\lambda_2)$</u>
8	V-2 least squares	6.22	6.33	2198	1961
7&8	V-2 least squares	6.27	6.37	2181	1944
		<u>$c_K(\lambda_1)$</u>	<u>$c_K(\lambda_2)$</u>	<u>$\epsilon_c(\lambda_1)$</u>	<u>$\epsilon_c(\lambda_2)$</u>
7&8	V-4 least squares	.337	.344	2598	2308

because of the high concentrations of naphthalene in some solutions and were less than 0.01 absorbance units (i.e. less than 1 per cent of the measured absorbance) at λ_2 (430 m μ). The concentrations used in these runs were similar to those of Run 3 (max. mole fraction of N = 0.25, ratio [N]/[TCNE] varying between 26 and 4200) but ten experimental points were employed rather than six, as before. Results for Run 8 and combined results for Runs 7 and 8 are listed in Table 8. The significant points are:

1. The values agree reasonably well with the comparable values listed in Table 7, except that x_K tends to be somewhat higher. This may be due solely to the fact that the temperature in Runs 3 and 4 was probably somewhat higher due to lack of temperature control (x_K decreases with temperature).
2. Again, ϵ_c depends on whether x_K or c_K is evaluated.
3. These results disagree with Merrifield and Phillips.

Personal communication with Dr. R. E. Merrifield revealed that his reported value of x_K is based on a Benesi-Hildebrand plot of the data for four solutions with max. mole fraction of N = 0.056. Measured absorbances ranged from 0.2 to 0.77. (It is interesting to note that for the TCNE complexes of substituted benzenes Merrifield and Phillips used a max. mole fraction of donor of essentially unity, so that their results for these complexes are perhaps not strictly comparable with their results for TCNE-N.)

An attempt was made to exactly duplicate the results of Merrifield and Phillips by using the same concentrations of donor and acceptor employed by them. The results of this run (Run 6) are listed below in Table 9. The values of x_K and ϵ_c reported by Merrifield and Phillips [20], as well as values obtained upon application of the method of least squares to their original data, are also shown.

TABLE 9

Duplication of Merrifield and Phillips

<u>Run No.</u>	<u>Equation</u>	<u>$x_K(\lambda_1)$</u>	<u>$x_K(\lambda_2)$</u>	<u>$\epsilon_c(\lambda_1)$</u>	<u>$\epsilon_c(\lambda_2)$</u>
M&P [20]	V-2 B-H plot	11.7		1240	1120
Data of M&P [72]	V-2 least squares	10.7		1340	
6	V-2 least squares	8.28	8.29	1775	1599

It should be noted that:

1. The least squares values of x_K and ϵ_c calculated from the original data of Merrifield and Phillips differ significantly from those reported by these authors. This indicates that large errors can arise from graphical evaluations of K and ϵ_c and that least squares calculations are to be preferred.
2. The results of Run 6 disagree significantly with those of Merrifield and Phillips. The former are felt to be more accurate, however, since the average deviation of the data from the calculated least squares line is only

half as large as that shown by Merrifield and Phillips' data.

3. The results of Run 6 disagree significantly with those of Runs 3, 4, 7 and 8 (Tables 7 and 8). This is thought to be due to the limited number of data points (four) used in Run 6 together with a variation in accuracy of the measured absorbance over the range of absorbances covered (0.2 to 0.9).

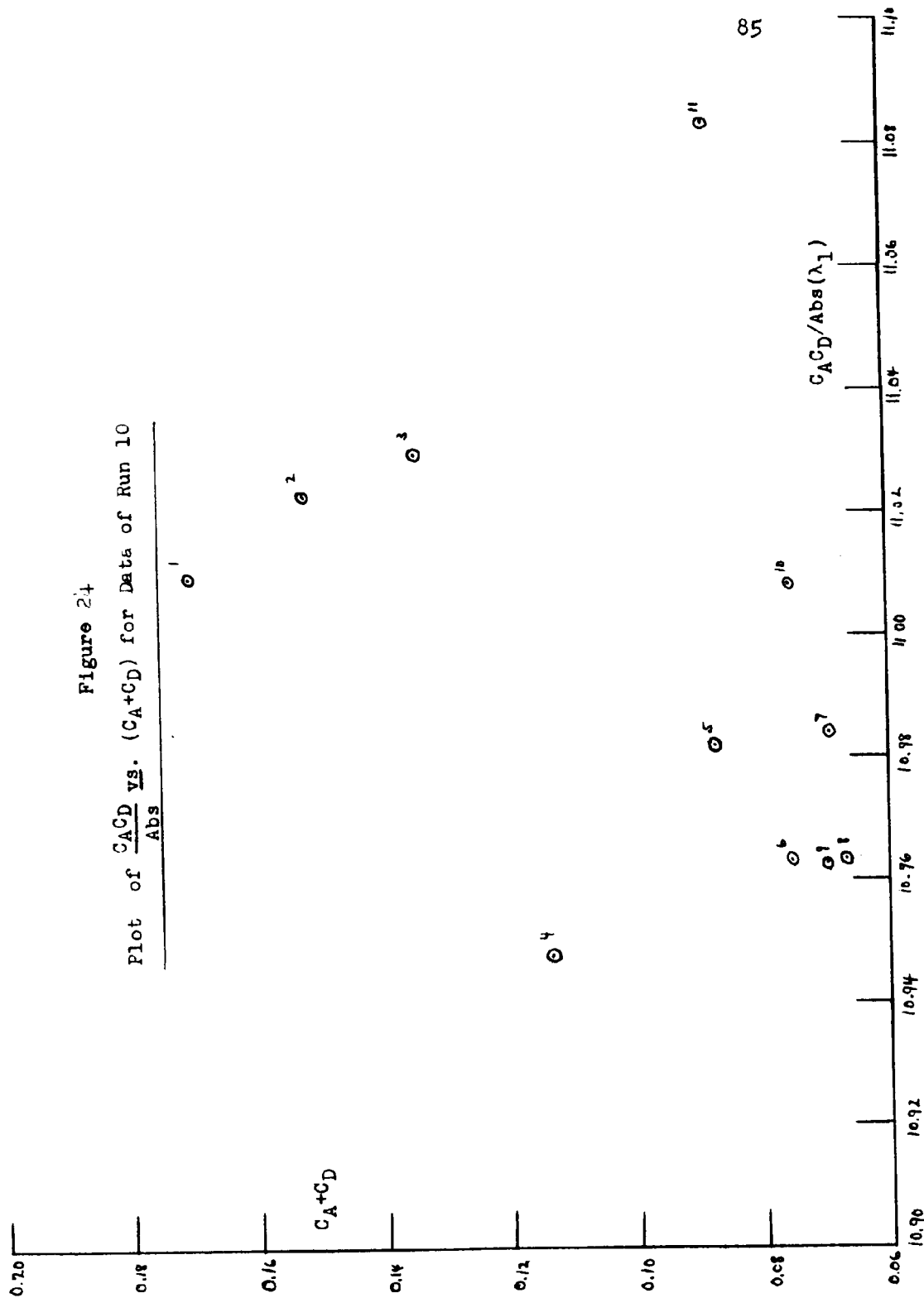
It can be concluded from the results presented in Tables 7, 8 and 9 that Merrifield and Phillips' values are high and that the correct value of x_K lies between 6 and 8, probably closer to 6.

If the results of Run 6 are considered to be of comparable accuracy with those of Runs 3, 4, 7 and 8 it would appear that x_K depends to a large degree on the concentrations of donor used in making the experimental measurements. In view of this uncertainty, a second attempt (Run 10) was made to obtain x_K and ϵ_c using data for relatively dilute solutions and over a range of mole ratios of N/TCNE from 25 to 0.1 (the latter limit dictated by the solubility of TCNE). Concentrations of donor and acceptor were chosen such that the measured absorbance remained essentially constant at about 1 and the data were analyzed by the method of Rose and Drago. Equation (V-16), which retains all terms in equation (V-13), was solved analytically for x_K and ϵ_c for various pairs of experimental points. Results were disastrous--no consistent set of values for x_K and ϵ_c could be

obtained. An insight into what occurred can be gained from a plot of $\frac{C_A C_D}{\text{Abs}}$ vs. $(C_A + C_D)$ (see Figure 24). This differs from the rigorously correct Lang plot (see Part A) only in that $(C_A + C_D - \text{Abs}/\epsilon_c)$ is replaced by $(C_A + C_D)$. This approximation is admissible in this case since the term Abs/ϵ_c is essentially constant and small ($<.001$ for $\epsilon_c \geq 1000$) compared to $(C_A + C_D)$ (0.06 to 0.17). It can be seen from Figure 24 that it is impossible to fit a straight line to the data and that calculations of ^xK and ϵ_c from pairs of points can give almost any value. The reason for this state of affairs is that the term $C_A C_D / \text{Abs}$ does not cover wide enough a range compared to the experimental uncertainty to which it is subject. In this case variation of $C_A C_D / \text{Abs}$ is only about 5% while its probable error is of the order of 1%. It thus becomes apparent that in order to minimize uncertainty in ^xK and ϵ_c the term $C_A C_D / \text{Abs}$ should vary over as wide a range as possible. This in turn implies that C_D (because D generally is more soluble than A) should cover as wide a range as possible. We are thus faced with a dilemma--if measurements are made on solutions which can be expected to approximate ideal behavior the results are too uncertain to be meaningful, whereas if the uncertainty is minimized by use of concentrated solutions of donor, doubt is cast on the significance of the results because of the almost certain presence of various non-ideality effects.

The most important conclusions which can be drawn from these preliminary experiments are summarized below. These

Figure 24
 Plot of $\frac{C_A C_D}{\text{Abs}}$ vs. $(C_A + C_D)$ for Data of Run 10



are quite general and should apply in cases other than those specifically under consideration here.

1. Methods for evaluation of K and ϵ_c based on various approximate equations can give vastly different results and should be applied with caution.
2. Graphical methods are susceptible to subjective error; therefore least squares procedures are preferred, together with an estimate of experimental uncertainty.
3. Least squares evaluation of the same data can give different results, depending on the form of the equation used, unless all data points lie exactly on the calculated straight line.
4. The same data yield different values of ϵ_c , depending on whether ^xK or ^cK is being evaluated.
5. The experimental error resides largely in the term $C_A C_D / \text{Abs}$; therefore in order to minimize uncertainty in K and ϵ_c , $C_A C_D / \text{Abs}$ (or, in effect, C_D) should cover as wide a range as possible.
6. In order to approximate ideal behavior, measurements are best made on dilute solutions and at mole ratios of $D:A$ of close to unity. However, in view of conclusion 5, uncertainty considerations require measurements to be made with a large excess of D (Benesi-Hildebrand conditions), in which case non-ideality effects are probably considerable.

7. Regarding experimental conditions:

- a. Temperature control is essential.
- b. Experimental error can be minimized by making absorbance measurements in the optimum range for the spectrophotometer employed; in this case at $\text{Abs} \approx 1.0$.
Appropriate concentrations of D and A can be chosen if estimates of K and ϵ_c are available.

Part C. General Method for Evaluation of K and ϵ_c . Derivation of a Rigorous Equation for ^xK .

As pointed out in Part B (conclusion 6) a dilemma exists with regard to experimental uncertainty and non-ideality effects: if measurements are made on dilute solutions the results are too uncertain to be meaningful, whereas if the uncertainty is minimized by use of concentrated solutions of donor, non-ideality effects may become significant. In order to effect a working compromise between these two extremes it was decided to make measurements over as wide a range of concentrations and mole ratios as solubilities would permit, and to judge the degree of departure from ideality by the extent of any systematic deviation of the data from a least squares fit to a linear plot. In the event of significant deviations at high concentrations of donor it should be possible, depending on the accuracy of the data, to deduce the limiting slope and intercept at high dilution.

Since no restrictions are placed on the concentrations and mole ratios of A and D to be employed, the various approximate equations given in Part A are inapplicable and a more general equation must be used. Several exact expressions for ^cK have been employed by various workers (see Part A) and the form given by Lang, equation (V-18), will be utilized here. No exact expression for ^xK was found in the literature. The expression given by Liptay, equation (V-20), is incorrect, as has been noted by Hayman [70]. Derivation of a rigorous

equation for x_K is given below.

For the equilibrium



the mole fraction equilibrium constant x_K is defined by

$$x_K \equiv \frac{(X_C)_{eq.}}{(X_A)_{eq.} (X_D)_{eq.}}$$

Now, in general

$$(X_j)_{eq.} = [j] \bar{V} \quad (V-21)$$

where $\bar{V}$ is the molar volume of the solution, defined by

$$\bar{V} \equiv \frac{V}{\sum n_j} = \frac{1}{\sum [j]} \quad (V-22)$$

and where V is the volume of the solution and n_j and $[j]$ are, respectively, the number of moles and molar concentration of component j . In view of (V-21), x_K becomes

$$x_K = \frac{[C]}{[A][D]\bar{V}} = c_K 1/\bar{V}. \quad (V-23)$$

The equilibrium concentrations $[A]$ and $[D]$ are given by

$$[A] = C_A - [C]$$

$$[D] = C_D - [C]$$

and, if C is the only species absorbing at the wavelength of measurement,

$$\text{Abs} = x \epsilon_c [C] .$$

Upon making these substitutions, (V-23) rearranges to

$$\frac{C_A C_D}{\text{Abs}} \cdot \bar{V} = \frac{\bar{V}}{x \epsilon_c} (C_A + C_D - \text{Abs}/x \epsilon_c) + \frac{1}{x_K x \epsilon_c} . \quad (V-24)$$

Since, for the equilibrium under consideration,

$$\bar{V} = \frac{1}{\Sigma[j]} = \frac{1}{[S]+[D]+[A]+[C]} = \frac{1}{C_S+C_D+C_A-Abs/x_{\epsilon_c}} \quad (V-25)$$

equation (V-24) becomes

$$\frac{C_A C_D}{Abs} \cdot \frac{1}{(C_S+C_D+C_A-Abs/x_{\epsilon_c})} = \frac{1}{\epsilon_c} \cdot \frac{(C_A+C_D-Abs/x_{\epsilon_c})}{(C_S+C_A+C_D-Abs/x_{\epsilon_c})} + \frac{1}{x_K x_{\epsilon_c}} \quad (V-26)$$

Equation (V-26) is in a form analogous to that of Lang, equation (V-18), for ^cK , and permits evaluation of x_K and x_{ϵ_c} from a knowledge of the initial molar concentrations of donor, acceptor, and solvent.

It should be mentioned that a rigorous expression in terms of mole fraction units, similar in form to Liptay's incorrect expression, equation (V-20), can be derived. This is given in equation (V-20a)

$$\frac{X_A X_D}{Abs \cdot \bar{V}} + \frac{Abs \cdot \bar{V}}{x_{\epsilon_c}^2} (X_A - 1)(X_D - 1) = \frac{1}{x_K x_{\epsilon_c}} - \frac{(2X_A X_D - X_A - X_D)}{x_{\epsilon_c}} \quad (V-20a)$$

where X_A and X_D are initial mole fractions and $\bar{V}$ is given by equation (V-25). This expression should be compared with equation (V-24), which gives x_K in terms of molar concentration units. Because of its greater simplicity, this writer prefers to use equation (V-24).

Equation (V-23) deserves further comment. It indicates that x_K and ^cK are not related by a constant factor, but that their ratio will vary with concentration since, in general, $\bar{V}$ is a function of concentration. Thus, in the case of a typical run on TCNE-N in CH_2Cl_2 , $1/\bar{V}$ varied between 15.57 at

infinite dilution and 13.34 at a 0.18 mole fraction of N. It is therefore apparent that unless the molar volumes of solvent and donor (i.e. the component present in large excess) are nearly equal, so that $\bar{V}$ remains constant for a series of solutions, a simple relationship between x_K and c_K does not exist under conditions where most experiments are performed (i.e. a large excess of donor compared to acceptor--or vice versa--the conditions employed by Benesi and Hildebrand and most workers since that time).

This is a point of considerable interest and sheds some light on a difficulty first noted by Scott [53], and which has received the attention of several writers since then [8,16,69]. Scott observed that if the same data are used to evaluate both x_K and c_K via equations (V-5) and (V-6) two different values of ϵ_c are obtained and x_K and c_K do not obey the relation

$$c_K = V_S x_K, \quad (V-27)$$

which must hold at infinite dilution. He ascribed this difficulty to a concentration dependence of the equilibrium constant due to a departure from ideal behavior. It can be seen, however, that this behavior is to be expected, even for ideal solutions, as a consequence of equation (V-23). It is apparent that at infinite dilution equation (V-13) reduces to (V-27), so that if x_K and c_K are both evaluated from limiting slopes and intercepts at high dilution equation (V-27) will be obeyed. If, however, x_K and c_K are evaluated from data on concentrated solutions (Benesi-

Hildebrand conditions), x_K and c_K will be related by

$$c_K = \bar{V}_{av} x_K, \quad (V-28)$$

provided that $c\epsilon_c = x\epsilon_c$. Here $\bar{V}_{av}$ is an appropriately weighted average value of $\bar{V}$ for the range of concentrations covered by the measurements.

Andrews and Keefer [16,72] have commented on the discrepancies noted by Scott and have proposed the use of the following relations in converting x_K values to c_K values and $x\epsilon_c$ to $c\epsilon_c$:

$$c_K = x_K V_S + (V_S - V_D) \quad (V-29)$$

$$\frac{x\epsilon_c}{c\epsilon_c} = 1 + \frac{V_S - V_D}{x_K V_S} \quad (V-30)$$

Here V_D is the molar volume of the donor (or acceptor, whichever is present in excess) and $x\epsilon_c$ and $c\epsilon_c$ refer to values of ϵ_c obtained in conjunction with x_K and c_K , respectively. Although these equations reduce to the expected relations when $V_S = V_D$ (i.e. when $\bar{V}$ remains constant), they are not of general utility since they give no indication that the ratios c_K/x_K and $x\epsilon_c/c\epsilon_c$ are functions of the concentration of donor.

A second point of confusion exists in the literature in regard to the significance of x_K and c_K . Apparently because of the discrepancies noted by Scott between c_K and $x_K V_S$, Andrews and Keefer [16] state that there is no clear theoretical basis for deciding whether x_K or c_K values should be reported. It should be pointed out in relation to equation (V-23) that x_K is the true thermodynamic equilibrium constant,

provided that the system under consideration shows ideal behavior, and as such is not a function of concentration. This is a consequence of the fact that ideal solutions are defined in terms of Raoult's (or Henry's) law, where concentrations are expressed in mole fraction units. On the other hand, since mole fraction and molar concentration units are not linearly related (see equation (V-21)), except at the limit of infinite dilution, the equilibrium constant expressed in molar concentration units will be constant only in very dilute solutions. A second objection to the use of ^cK lies with its dimensionality. A good thermodynamic equilibrium constant, in view of the relation $\Delta F = -RT \ln K$, should be dimensionless, whereas ^cK as defined here has the dimensions of liters/mole. It therefore seems quite clear that ^xK is the more significant quantity, especially in view of the fact that ideal behavior is usually assumed and since most measurements are made in the presence of a large excess of donor (Benesi-Hildebrand conditions). A discussion of the significance of ^xK and ^cK for the case of non-ideal solutions is given in Part E.

It was brought out in Part A that the Benesi-Hildebrand equation can be rearranged into a variety of different forms for purposes of making a linear plot. The same is true for the rigorous equations (V-18) and (V-26). These can be rearranged into the following linear forms:

$$\frac{y}{\frac{C_A C_D}{Abs}} = \frac{b}{\frac{1}{c_{\epsilon_c}}} \cdot \frac{x}{(C_A + C_D - \frac{Abs}{c_{\epsilon_c}})} + \frac{a}{\frac{1}{c_K c_{\epsilon_c}}} \quad (V-18)$$

$$\frac{C_A C_D}{Abs} \cdot \frac{1}{(C_A + C_D - \frac{Abs}{c_{\epsilon_c}})} = \frac{1}{c_K c_{\epsilon_c}} \cdot \frac{1}{(C_A + C_D - \frac{Abs}{c_{\epsilon_c}})} + \frac{1}{c_{\epsilon_c}} \quad (V-18a)$$

$$(C_A + C_D - \frac{Abs}{c_{\epsilon_c}}) = c_{\epsilon_c} \cdot \frac{C_A C_D}{Abs} - \frac{1}{c_K} \quad (V-18b)$$

$$(C_A + C_D - \frac{Abs}{c_{\epsilon_c}}) \cdot \frac{Abs}{C_A C_D} = - \frac{1}{c_K} \cdot \frac{Abs}{C_A C_D} + c_{\epsilon_c} \quad (V-18c)$$

$$\frac{C_A C_D}{Abs} \cdot \frac{1}{(C_A + C_D + C_S - \frac{Abs}{x_{\epsilon_c}})} = \frac{1}{x_{\epsilon_c}} \cdot \frac{(C_A + C_D - \frac{Abs}{x_{\epsilon_c}})}{(C_A + C_D + C_S - \frac{Abs}{x_{\epsilon_c}})} + \frac{1}{x_K x_{\epsilon_c}} \quad (V-26)$$

$$\frac{C_A C_D}{Abs} \cdot \frac{1}{(C_A + C_D - \frac{Abs}{x_{\epsilon_c}})} = \frac{1}{x_K x_{\epsilon_c}} \cdot \frac{(C_A + C_D + C_S - \frac{Abs}{x_{\epsilon_c}})}{(C_A + C_D - \frac{Abs}{x_{\epsilon_c}})} + \frac{1}{x_{\epsilon_c}} \quad (V-26a)$$

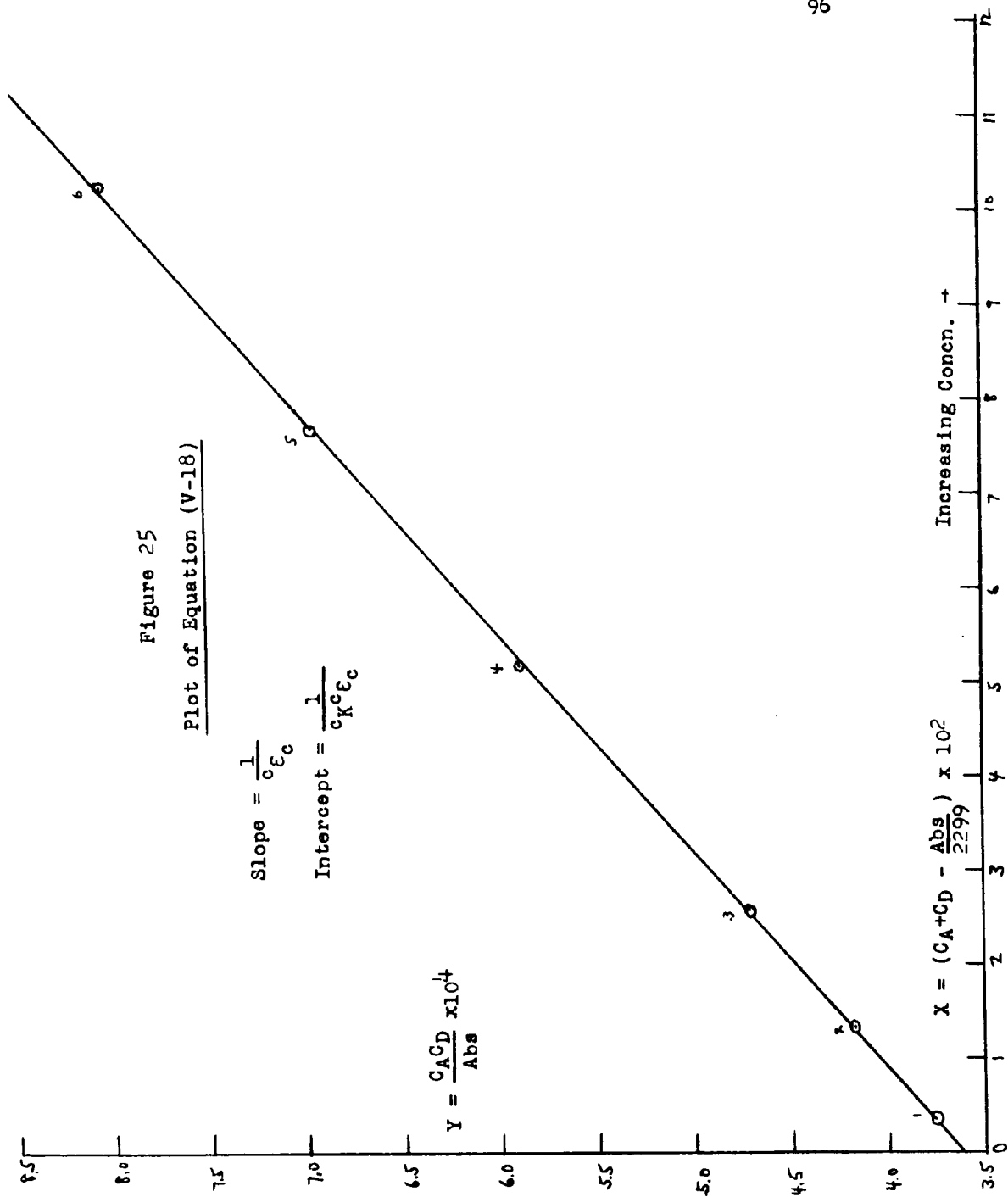
$$\frac{(C_A + C_D - \frac{Abs}{x_{\epsilon_c}})}{(C_A + C_D + C_S - \frac{Abs}{x_{\epsilon_c}})} = x_{\epsilon_c} \cdot \frac{C_A C_D}{Abs} \cdot \frac{1}{(C_A + C_D + C_S - \frac{Abs}{x_{\epsilon_c}})} - \frac{1}{x_K} \quad (V-26b)$$

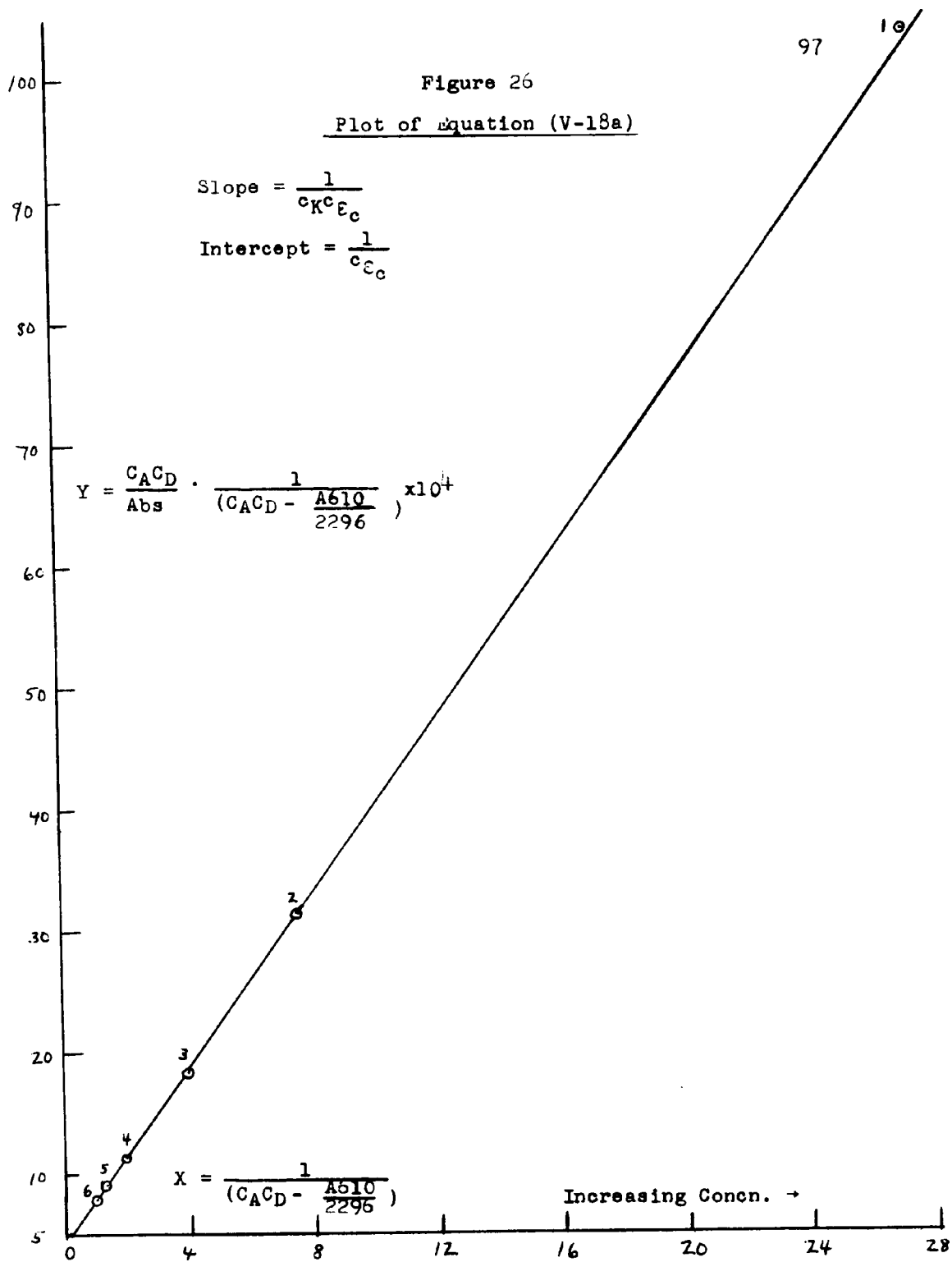
$$\frac{Abs}{C_A C_D} \cdot (C_A + C_D - \frac{Abs}{x_{\epsilon_c}}) = - \frac{1}{x_K} \cdot \frac{Abs}{C_A C_D} \cdot (C_A + C_D + C_S - \frac{Abs}{x_{\epsilon_c}}) + x_{\epsilon_c} \quad (V-26c)$$

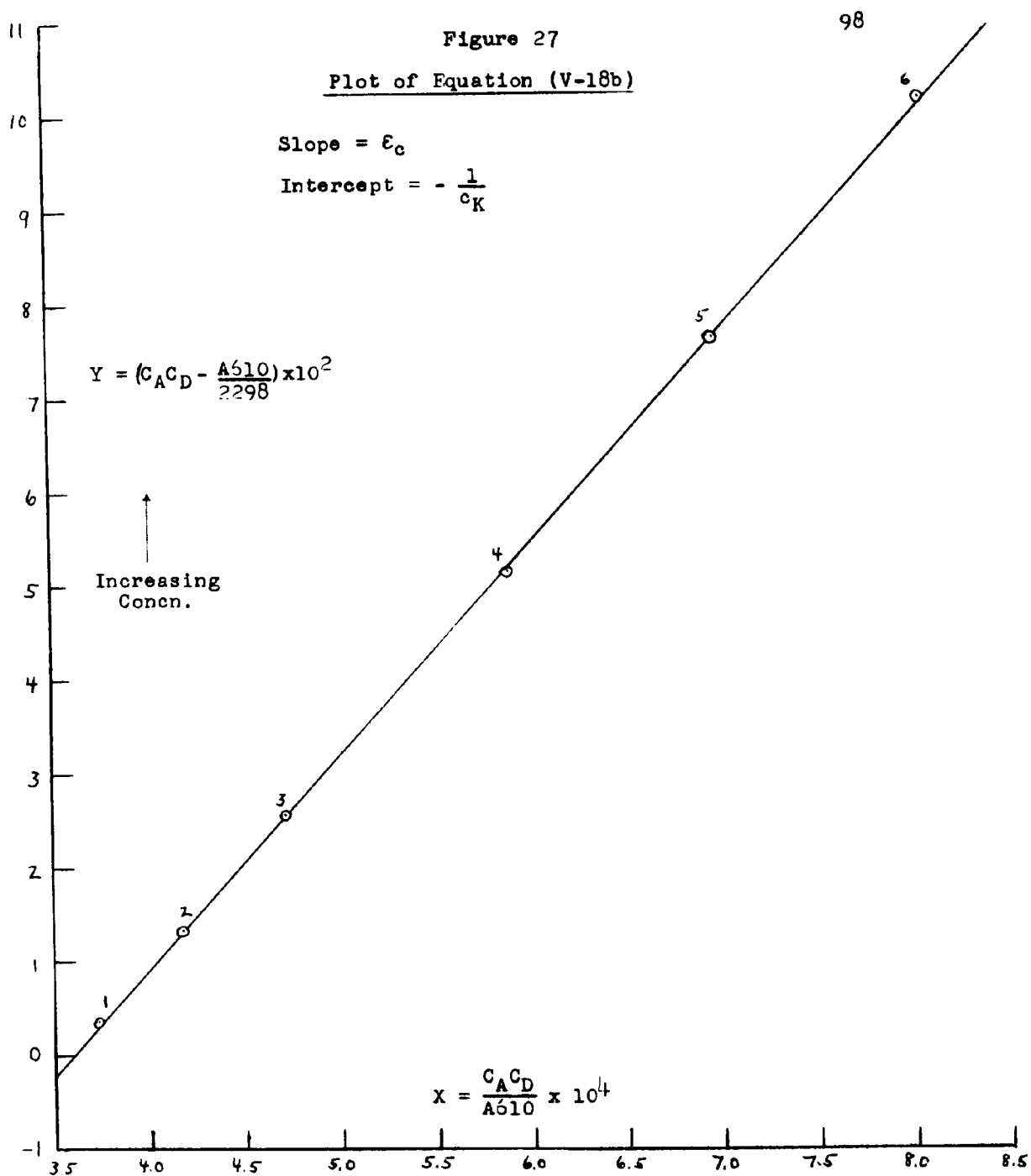
Here y and x indicate ordinate and abscissa and b and a are slope and intercept, respectively. Molar extinction coefficients of the complex are indicated by c_{ϵ_c} and x_{ϵ_c} since these will in general differ depending on whether c_K or x_K is being evaluated. Equations (V-18a) and (V-26a) are analogues of

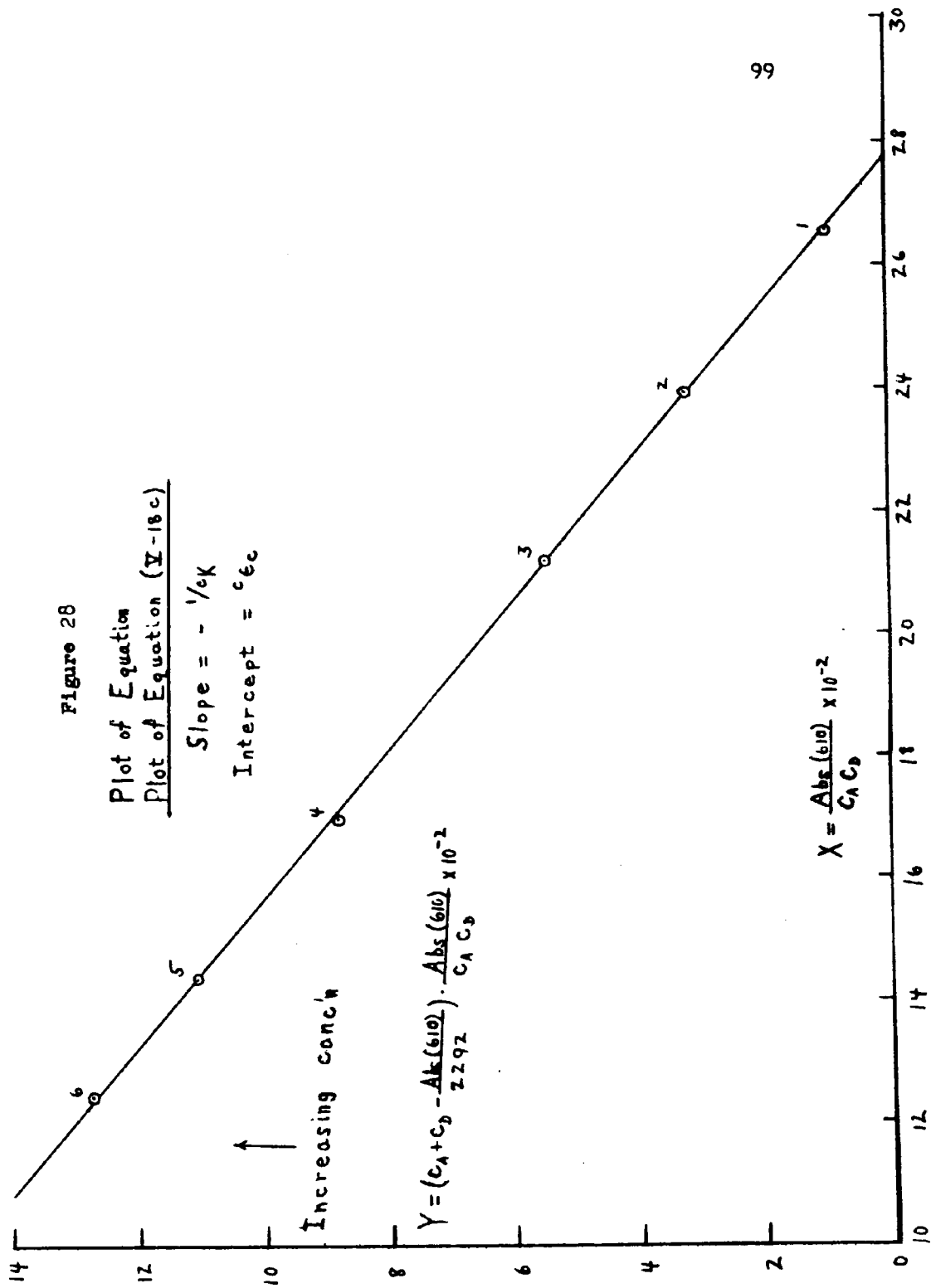
the Benesi-Hildebrand equations (V-2) and (V-4), (V-18) and (V-26) are analogues of the Scott forms, (V-6) and (V-5), of the Benesi-Hildebrand equations, and (V-18c) and (V-26c) are analogues of Buckles and Mills form (V-9) of the Benesi-Hildebrand equations.

The graphical evaluation of x_K and c_K by use of the various forms of equations (V-18) and (V-26) is illustrated in Figures 25-32. These represent plots of the data of Run 18 on TCNE-2,6-DMN. Points 1, 3, 4, 5 and 6 represent solutions whose concentrations of 2,6-DMN increase in equal increments, while point 2 represents a solution whose concentration lies midway between points 1 and 3. The following comments can be made regarding the suitability of these various plots for evaluating x_K and x_{ϵ_c} or c_K and c_{ϵ_c} . In general, it is desirable to be able to extrapolate the concentration variable to zero concentration since the initial slope thus obtained has the greatest theoretical significance. This extrapolation can be best made when zero concentration lies at the origin, rather than at infinity, as is the case for equations (V-18a) and (V-26a) (see Figures 26 and 30). These plots have the further disadvantages that the experimental points tend to crowd near the origin and that the y intercept lies close to the origin, so that small errors in a will produce large relative errors in ϵ_c . Furthermore, evaluation of K requires knowledge of ϵ_c (since $b = \frac{1}{K\epsilon_c}$) so that the uncertainty in ϵ_c is transferred to K as well.









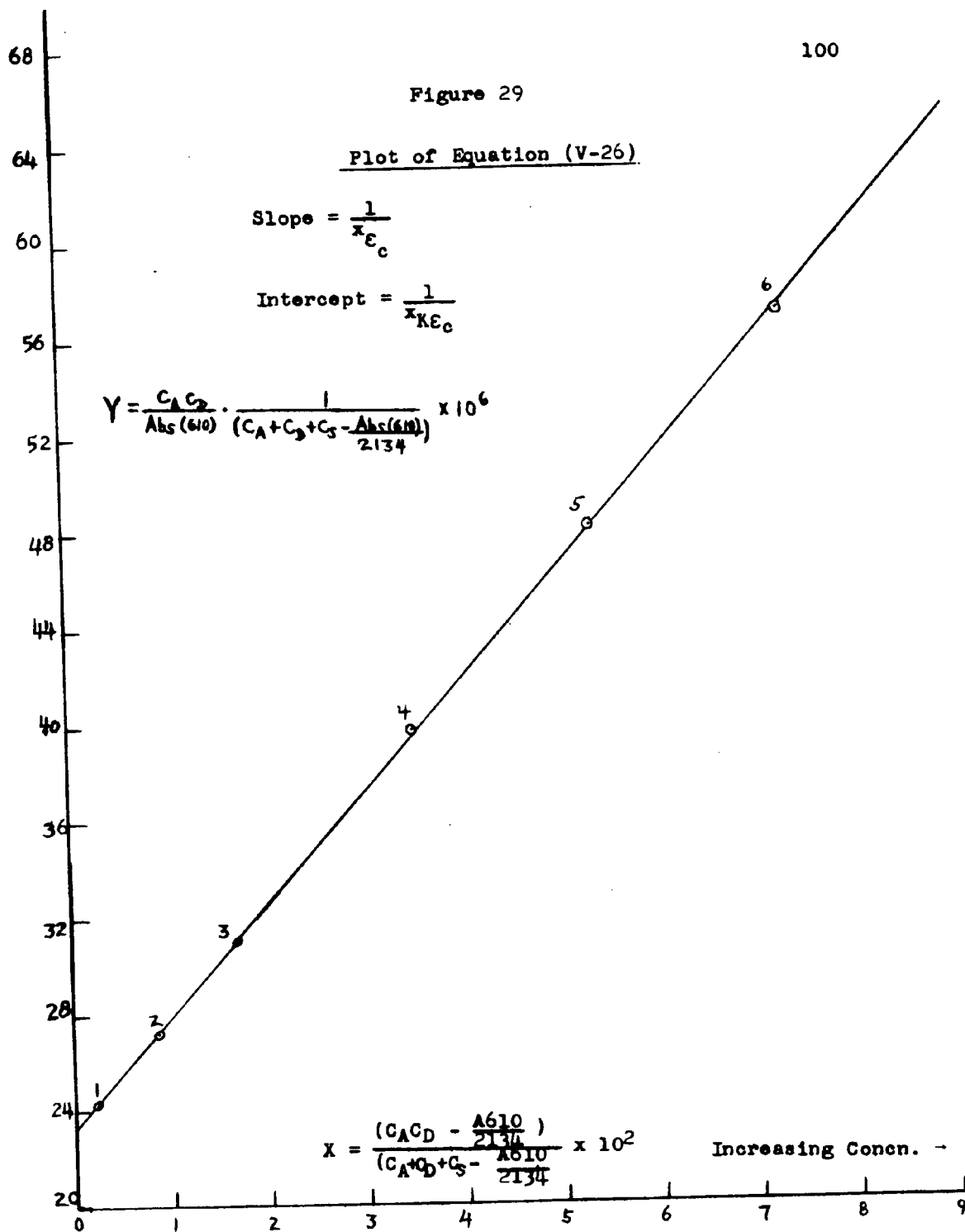


Figure 30

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Plot of Equation (Y-26a)

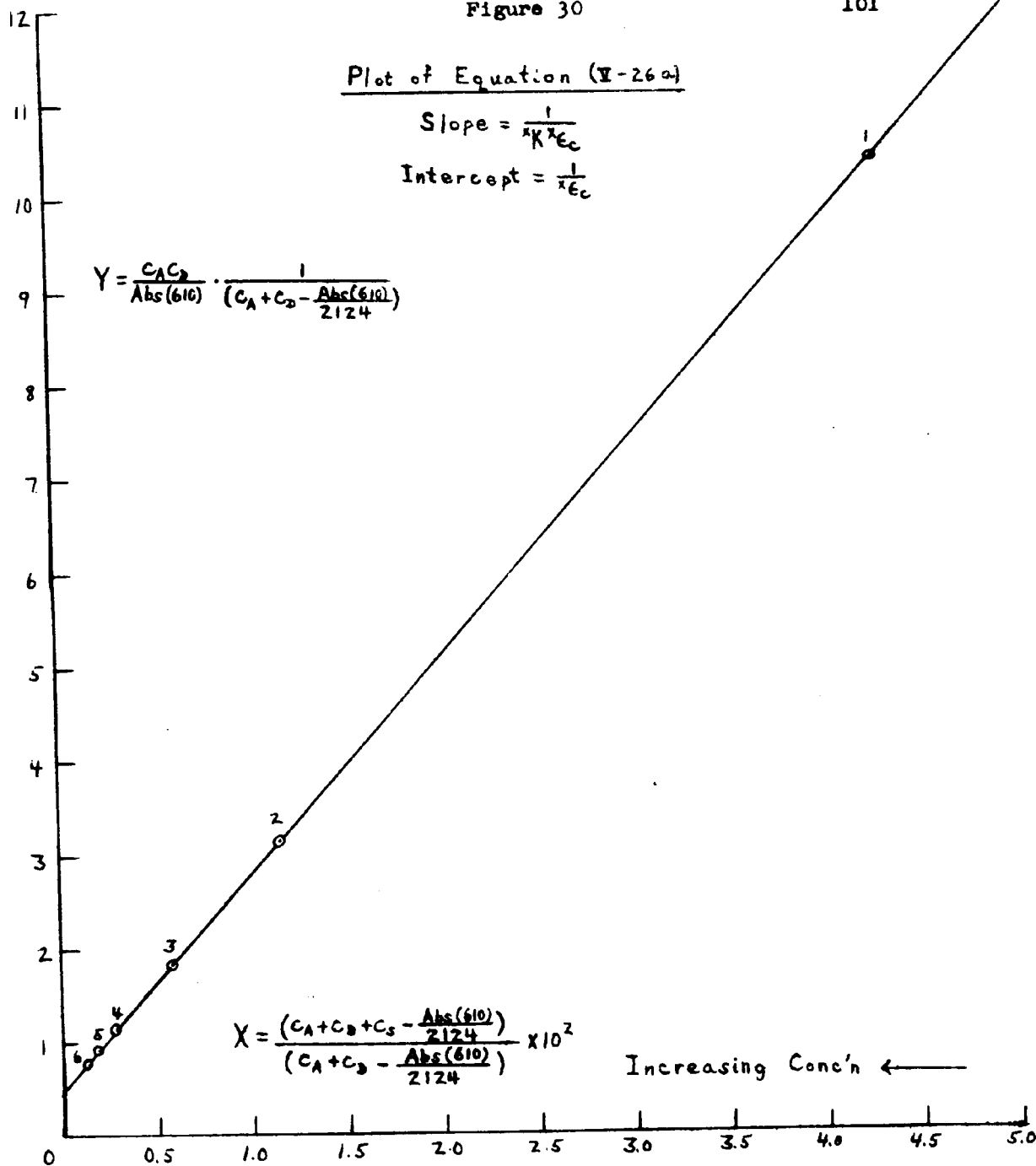
$$\text{Slope} = \frac{1}{K^2 \epsilon_c}$$

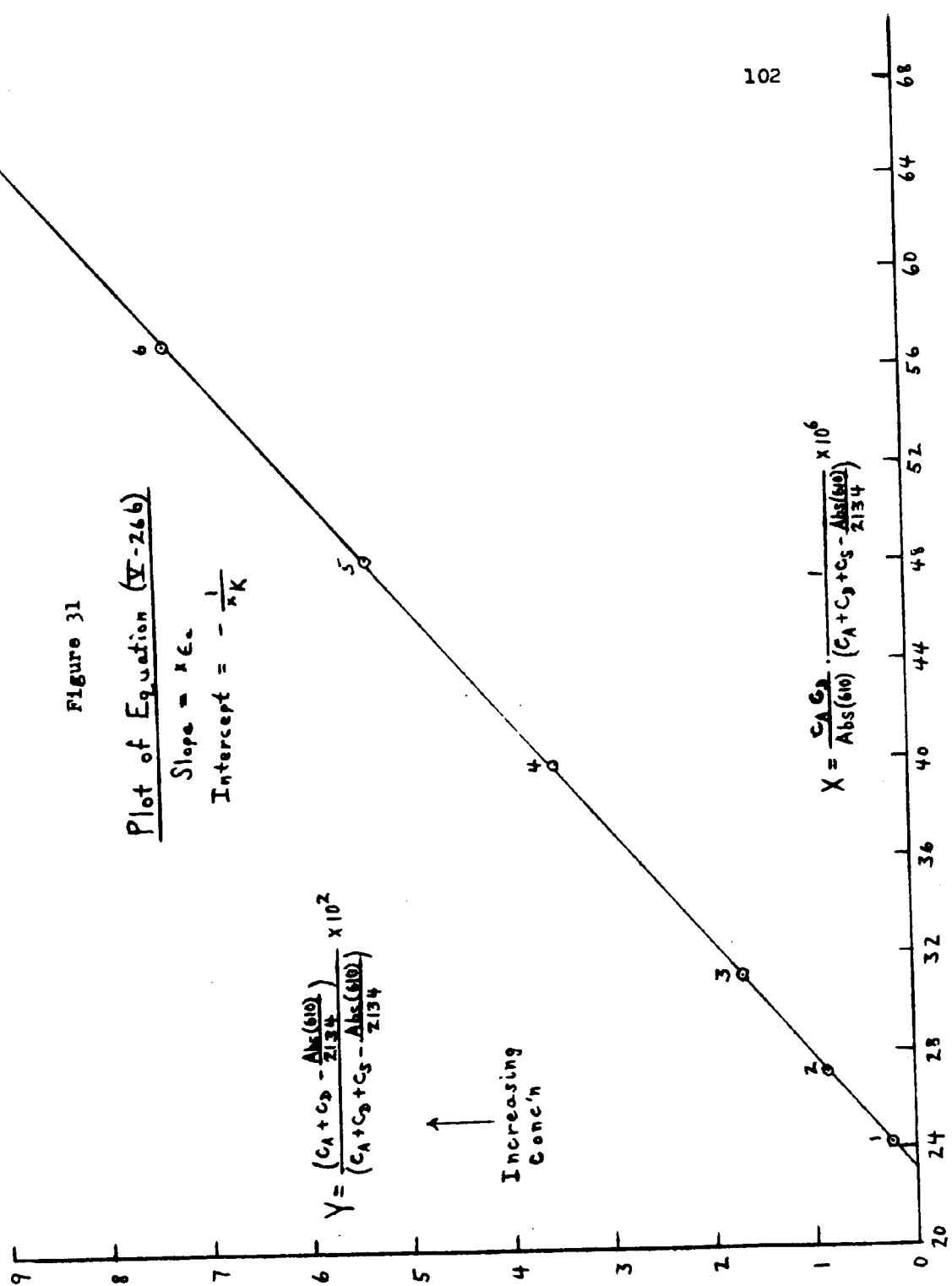
$$\text{Intercept} = \frac{1}{K^2 \epsilon_c}$$

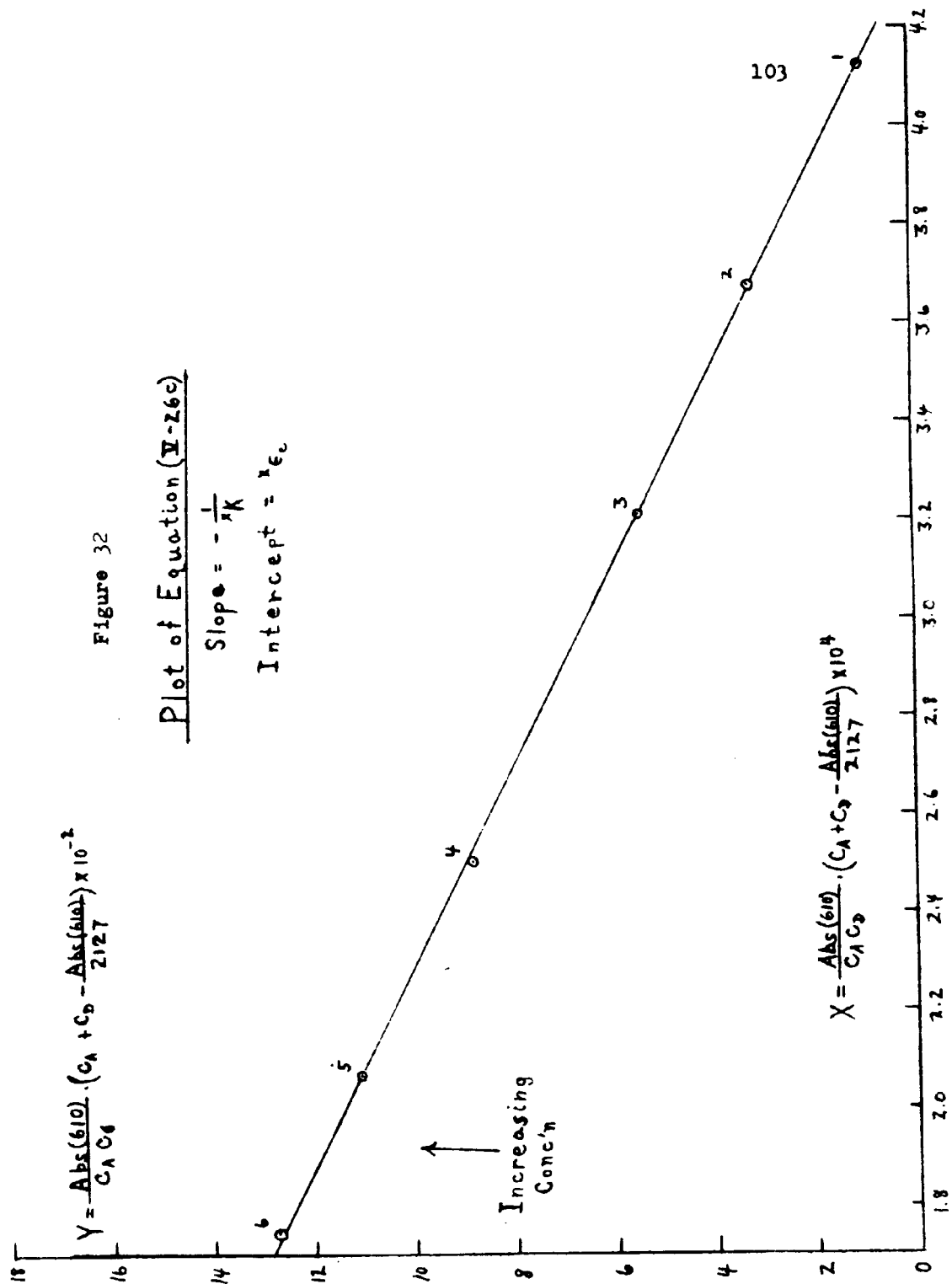
$$Y = \frac{C_A C_D}{\text{Abs}(610)} \cdot \frac{1}{(C_A + C_D - \frac{\text{Abs}(610)}{2124})}$$

$$X = \frac{(C_A + C_D + C_S - \frac{\text{Abs}(610)}{2124})}{(C_A + C_D - \frac{\text{Abs}(610)}{2124})} \times 10^2$$

Increasing Conc'n ←







Thus, equations (V-18a) and (V-26a) have nothing to recommend them.

In the case of equations (V-18b) and (V-26b) (Figures 27 and 31) the experimental points are evenly spaced but the y intercept again lies quite close to the origin. The slope, however, can be used to evaluate ϵ_c accurately.

In the case of equations (V-18) and (V-26) (Figures 25 and 29) the experimental points are again evenly spaced but the y intercept lies farther from the origin than in the case just considered. Again ϵ_c can be accurately evaluated from the slope ($b = 1/\epsilon_c$), and K can be obtained from the y intercept ($a = 1/K\epsilon_c$) with somewhat greater relative accuracy than in the previous case.

Equations (V-18c) and (V-26c) (Figures 28 and 32) represent the most favorable forms for graphical evaluation. K and ϵ_c can be obtained separately from slope and intercept, respectively, and since a lies far from the origin its relative error will be least in this form of plot. It should be noted that K can be obtained most accurately from this plot since its evaluation does not involve estimation of the intercept as in the previously considered plots. It should also be noted that the experimental points tend to be somewhat compressed at higher concentrations, but this may be advantageous in that the relatively expanded scale at low concentrations should allow a more accurate extrapolation to zero concentration in the case where the data show a significant curvature.

In applying any of the plots discussed above an iterative procedure must be used since the term Abs/ϵ_c is not known initially. A first order plot can be made either by ignoring Abs/ϵ_c or by using a reasonable estimate for ϵ_c . K and ϵ_c will normally converge to a constant value after the first iteration.

Although K and ϵ_c can be evaluated by the graphical procedures discussed above, it is far preferable that a least squares procedure be employed, especially since this allows an estimate of the precision of K and ϵ_c to be made by standard statistical methods. Liptay [68,69] has given details of a weighted least squares treatment of equation (V-18), which he writes in a rearranged form (equation (V-19)). Liptay's method cannot be applied directly to equation (V-26), however, because of the complicated nature of the latter expression. A least squares procedure which is applicable to both equations (V-18) and (V-26) is discussed below.

Consideration should first be given to the magnitudes of the experimental uncertainties associated with the various observables entering into these equations. As pointed out by Liptay, the relative errors of the measured concentrations of donor, acceptor, and solvent can be minimized by weighing of all components and careful calibration of volumetric ware. For the experiments considered here, the relative errors of these quantities are less than one part per thousand. The relative errors of the absorbance measurements are constant

(since the absorbance is held essentially constant) at about 5-6 parts per thousand (see Experimental). It is probably sufficiently accurate, therefore, to ignore the errors in the concentration terms in comparison with the error associated with Abs.

We can now consider the application of a least squares procedure to the various forms of equations (V-18) and (V-26). In its simplest form, the method of least squares considers that the absolute errors of the y variable are of the same magnitude and that errors in x are negligible (if the absolute errors in y vary considerably, the residual equations must be assigned weights, w_i , proportional to $1/\sigma_i^2$ where σ_i is the standard deviation of the measurement Y_i). Consider first equation (V-18). We are faced here with a problem of how to include the term $\text{Abs}/c\epsilon_c^2$ in the least squares treatment. Equation (V-18) can be written in the form

$$y = a + bx' - b^2z \quad (\text{V-31})$$

where $x' = (C_A + C_D)$ and $z = \text{Abs}$. This is an equation in three dimensions and is non-linear in the undetermined constants; it can be treated only by a generalized least squares method (see, for example, Wilson [73]). These methods, however, require approximate values for the undetermined constants; the problem is then treated in such a way that correction factors to these approximations are computed by the method of least squares. A large saving in computational labor can be effected by the following approximate treatment.

If equation (V-31) is written as

$$y = a + b (x' - bz) \quad (V-32)$$

and it is noted that bz (i.e. $Abs/\epsilon_c = [C]$) is always smaller than x' (i.e. $C_A + C_D$) by a factor of at least 10^2 for the data under consideration, it is apparent that the relative error in the term $(x' - bz)$ is not significantly greater than the relative error in x' . We can therefore write equation (V-32) as

$$y = a + bx \quad (V-33)$$

where, now, $x = (x' + bz)$, and use the simple least squares treatment in which only y is subject to error. Note that with this procedure we need only a good estimate for b (i.e. $1/\epsilon_c$) whereas with the more general method we require good estimates for both a and b . If our first estimate of b is not off by more than a few percent, a repetition of the least squares calculation using the new value for b does not change a and b (i.e. K and ϵ_c) by more than a few parts per million. Note also that the absolute error in $(x' - bz)$ contributed by bz is dependent on ϵ_c for the particular system under consideration and cannot in general be ignored.

The least squares treatment applied to equation (V-18) holds also for equation (V-26). These are both in the form $y = a + bx$ where the relative error in y is large compared to that in x . In this case x and y differ from those in equation (V-18) only by the relatively constant factor

$$\frac{1}{(C_A + C_D + C_S - Abs/x\epsilon_c)}$$

whose relative error is somewhat less than that of x in equation (V-18).

Equation (V-18a) is the same as equation (V-18) except that the slope and intercept have been interchanged by dividing through by the factor $(C_A + C_D - \text{Abs}/^c\epsilon_c)$. Again the relative error in y is large compared to that in x so that the least squares treatment applied to equation (V-18) holds here also. The corresponding equation for x_K , equation (V-26a) can be treated similarly.

Equation (V-18b) is written in the form $y = a + bx$ but the error in x is larger than the error in y ; thus the simple least squares treatment used for equation (V-18) does not apply. In order to apply least squares to this equation the generalized method of Wilson must be used. The same is true for equation (V-26b).

In the case of equation (V-18c), the relative errors in x and y are essentially equal. A least squares treatment for this rather special case is given by Scarborough [74]. Although this method is simpler than the generalized method described by Wilson, it requires greater computational effort than the simple least squares treatment applicable to equations (V-18) and (V-18a) and must also, because an initial estimate for ϵ_c is required, be applied iteratively. The same comments apply to equation (V-26c).

We can now inquire which of these equations (and least squares treatments) is preferred. It should be made clear that if all points fall exactly on a straight line it would

not matter which equation or least squares treatment was used; since all residuals are zero it would not matter how the residuals were weighted--all calculations would give identical results. Since, in general, the residuals are finite the equation used and the weighting of the individual observations will determine to some extent the values of the constants to be calculated. In order to test the sensitivity of K and ϵ_c to the form of the equation used in their calculation, a naive unweighted least squares calculation, in which all error was assumed to lie in y , was made for each of the various forms of equations (V-18) and (V-26) on a typical set of data (Run 18, for TCNE-2,6-DMN*). In all cases the values of K and ϵ_c were constant to within 5 parts per million after the first iteration. The results are given below in Table 10.

It can be seen that although there is some variation in K and ϵ_c as a function of the equation employed, these values are essentially constant (to within 1%). This result is a considerable improvement over that noted previously for Run 3 on TCNE-N (Table 7), where least squares calculations of ^xK from both the Benesi-Hildebrand and Scott equations gave results differing by more than 10%. This improvement may be due either to use of the more exact equations (V-18) and (V-26) or/and more precise data.

*Plots of this data for each of these equations are shown in Figures 25-32. The straight lines drawn in these figures were determined by the least squares calculations referred to.

It is also apparent from Table 10 that K and ϵ_c are more sensitive to the form of the equation used than to any differences in the least squares treatment. Thus, application to equation (V-26c) of both the simple least squares method and the more appropriate method of Scarborough gave results identical to 1 part in 2 million.

TABLE 10

Calculation of K and ϵ_c via the Various Forms
of Equations (V-18) and (V-26)

<u>Eqn.</u>	<u>Least Squares Method</u>	<u>c_K</u>	<u>x_K</u>	<u>c_{ϵ_c}</u>	<u>x_{ϵ_c}</u>
V-18	Simple, Unweighted	1.206		2299	
V-18a	Simple, Unweighted	1.209		2296	
V-18b	Simple, Unweighted	1.206		2298	
V-18c	Simple, Unweighted	1.211		2292	
V-26	Simple, Unweighted		20.17		2134
V-26a	Simple, Unweighted		20.32		2124
V-26b	Simple, Unweighted		20.18		2134
V-26c	Simple, Unweighted		20.29		2127
V-26c	Method of Scarborough [74]		20.29		2127

Since there is no a-priori reason for preferring any particular form of equations (V-18) and (V-26), the form admitting of the simplest least squares treatment can be chosen. It was observed previously that both equations (V-18) and (V-18a) as well as (V-26) and (V-26a) could legitimately

be treated by the simple least squares method. We prefer to use equations (V-18) and (V-26) because the experimental points are linearly distributed as a function of concentration, whereas in (V-18a) and (V-26a) x is an inverse function of concentration and experimental points tend to be crowded near the origin.

It should be pointed out that in applying the simple least squares method to equations (V-18) and (V-26) weighted residuals should in general be used. This is so because although the relative error in y is constant (since measurements are made with Abs essentially constant), its absolute error varies. Thus, following Wilson [73], weights w_i should be assigned to the residual equations according to

$$w_i = (c^2 Y_i^2)^{-1} \quad (V-34)$$

where the Y_i are measured values of y and c is the (constant) relative error in Y_i .

Once the constants a and b have been calculated via least squares, estimates of their precision can be made by standard statistical procedures. The standard error of estimate s gives a measure of the closeness of fit of the data to the calculated least squares line. The variances of a and b can also be computed, and from them, by application of the law of propagation of errors, the variances of K and ϵ_c can be obtained. Knowing these, confidence intervals for a , b , K and ϵ_c can be estimated by use of Student's

t distribution. Details of the least squares treatments and methods of error estimation used in this dissertation are given in Appendix I.

Part D. Experimental Results for K and ϵ_c

Data for the various experimental runs made on TCNE-N and TCNE-2,6-DMN and resultant values of K^* and $\epsilon_c^{*(1)}$, together with their estimated uncertainties, are given in Tables 11-19. In making these runs, each solution was prepared individually before its spectrum was scanned (see Procedure C under Experimental), thus minimizing the effect of any slow time dependence in the absorption spectrum of the solution.

The data were analyzed by application of the simple, unweighted least squares procedure described in Appendix I. Since the absolute error in y varies, it would have been more rigorously correct to use the weighted least squares method applicable to the case of a constant relative error (see Appendix I). However, the absolute error in y varies by less than a factor of 2, and in view of the fact that K^* and ϵ_c^* do not appear to be particularly sensitive to the least squares treatment used (see Table 10), the unweighted treatment is probably sufficiently accurate. Initial estimates of ϵ_c^* used in the least squares calculations were obtained by solution of equations (V-18) or (V-26) for representative pairs of points. Provided that ϵ_c^* obtained on the first application of the least squares procedure did not differ from the initial estimate by more than about 10%, a second

(1) For the purposes of the ensuing discussion, values of K and ϵ_c obtained from a least-squares fit to equations (V-18) and (V-26) will be designated by a star.

TABLE 11

Run 12

TCNE-N Complex

Temp. 21.80°C

Soln. No.	$C_A \times 10^3$	C_D	C_S	$Abs(\lambda_1)^{(1)}$	$Abs(\lambda_2)^{(1)}$
1	68.9927	0.01392	15.3893	0.802	0.726
2	44.1624	0.02191	15.4116	0.833	0.753
3	31.7187	0.03249	15.4269	0.891	0.806
4	18.1635	0.05497	15.4295	0.867	0.786
5	9.7288	0.10000	15.3219	0.839	0.762
6	6.7132	0.16610	15.2565	0.938	0.849
7	3.9671	0.29458	14.9608	0.951	0.861
8	2.4264	0.48373	14.6193	0.897	0.812
9	1.6374	0.82885	13.9542	0.937	0.844
10	1.2033	1.20062	13.2701	0.902	0.812
11	0.9277	1.85157	11.9758	0.936	0.838
12	0.8123	2.40952	10.8959	0.964	0.862

(1) Absorbances are corrected for any absorption due to the components.

Analysis of Residuals

[illegible]

(1) Omitted from least squares calculation.

TABLE 11 (Continued)

Calculated Results for K^* , ϵ_c^* , a, b and s

All uncertainties are for a 95% confidence level.

<u>Results for $x_K^*(\lambda_1)$</u>	<u>Results for $c_K^*(\lambda_1)$</u>
$x_K^*(\lambda_1) = 6.162 \pm 0.117$	$c_K^*(\lambda_1) = 0.3369 \pm 0.0083$
$x_{\epsilon_c^*}(\lambda_1) = 2239 \pm 39$	$c_{\epsilon_c^*}(\lambda_1) = 2633 \pm 61$
$a = 7.249 \times 10^{-5} \pm 0.058 \times 10^{-5}$	$a = 1.1272 \times 10^{-3} \pm 0.0091 \times 10^{-3}$
$b = 4.466 \times 10^{-4} \pm 0.077 \times 10^{-4}$	$b = 3.798 \times 10^{-4} \pm 0.088 \times 10^{-4}$
$s = 0.6485 \times 10^{-6}$	$s = 0.1001 \times 10^{-4}$

TABLE 12

Run 13		TCNE-N Complex		Temp. 21.80°C	
Soln. No.	$C_A \times 10^3$	C_D	C_S	$Abs(\lambda_1)^{(1)}$	$Abs(\lambda_2)^{(1)}$
1	45.0775	0.02169	15.4190	0.839	0.759
2	73.7610	0.01369	15.3925	0.856	0.773
3	33.0624	0.03172	15.4150	0.901	0.817
4	34.2096	0.05461	15.3617	1.627	1.465
5	9.7884	0.10016	15.3208	0.843	0.763
6	7.1764	0.16511	15.1900	0.921	0.833
7	4.2337	0.29353	14.9917	0.900	0.813
8	2.7218	0.48354	14.6178	0.901	0.813
9	1.7657	0.82633	13.9717	0.912	0.823
10	1.3371	1.19927	13.2682	0.896	0.805
11	0.9974	1.84110	11.9855	0.923	0.827
12	0.8522	2.39913	10.9310	0.933	0.838

(1) Absorbances are corrected for any absorption due to the components.

Analysis of Residuals for $c_K^*(\lambda_1)$

Soln. No.	$Y(\lambda_1) \times 10^4$	$y(\lambda_1) \times 10^4$	$\delta \times 10^4$
1	11.654	11.572	+0.082
2	11.800	11.651	+0.149
3	11.639	11.564	+0.075
4	11.483	11.655	-0.172
5	11.630	11.737	-0.107
6	11.849	11.974	-0.125
7	12.427	12.455	-0.028
8	13.161	13.178	-0.017
9	14.591	14.489	+0.102
10	16.035	15.916	+0.119
11	18.363	18.375	-0.012
12	20.444	20.513	-0.069

$$\Sigma = -0.001$$

$$\bar{\delta} = 0.088$$

Results⁽¹⁾ for $c_K^*(\lambda_1)$

$$c_K^*(\lambda_1) = 0.3386 \pm 0.0088 \quad a = 1.1317 \times 10^{-3} \pm 0.0093 \times 10^{-3}$$

$$c_{\epsilon}^*(\lambda_1) = 2609 \pm 64 \quad b = 3.832 \times 10^{-4} \pm 0.094 \times 10^{-4}$$

$$s = 0.1103 \times 10^{-4}$$

(1) All uncertainties are for a 95% confidence level.

TABLE 12A

Results⁽¹⁾ for $c_K^*(\lambda_1)$ for Combined Data of Runs 12, 13 and 14

$c_K^*(\lambda_1)$	0.3366 ± 0.0047
$c_{\epsilon_c}^*(\lambda_1)$	2632 ± 35
a	$1.1286 \times 10^{-3} \pm 0.0055 \times 10^{-3}$
b	$3.799 \times 10^{-4} \pm 0.050 \times 10^{-4}$
s	0.1077×10^{-4}

TABLE 12B

Summary of Results⁽¹⁾ for TCNE-N at 21.80°C

<u>Run No.</u>	<u>$c_K^*(\lambda_1)$</u>	<u>$c_{\epsilon_c}^*(\lambda_1)$</u>	<u>$s \times 10^4$</u>
12	0.3369 ± 0.0083	2633 ± 61	0.1007
13	0.3386 ± 0.0088	2609 ± 64	0.1103
14	0.3381 ± 0.0101	2634 ± 72	0.0950
Combined Results of Runs 12,13,14	0.3366 ± 0.0047	2632 ± 35	0.1077

(1) All uncertainties are for a 95% confidence level.

TABLE 13 (Continued)

Analysis of Residuals						
Soln. No.	$x_K^*(\lambda_1)$			$x_K^*(\lambda_2)$		
	$Y(\lambda_1) \times 10^6$	$y(\lambda_1) \times 10^6$	$\delta \times 10^6$	$Y(\lambda_2) \times 10^6$	$y(\lambda_2) \times 10^6$	$\delta \times 10^6$
1	74.17	74.12	+0.05	82.15	81.94	+0.21
2	77.42	78.17	-0.75	85.78	86.51	-0.73
3	83.61	83.85	-0.24	92.64	92.93	-0.29
4	96.33	95.89	+0.44	106.78	106.52	+0.26
5	108.99	108.49	+0.50	121.26	120.74	+0.52
6	123.36	122.67	+0.69	137.40	136.75	+0.65
7	135.71	135.53	+0.18	151.43	151.27	+0.16
8	150.08	150.94	-0.86	167.90	168.67	-0.77
			$\Sigma = +0.01$			
			$\bar{\delta} = 0.46$			
						$\Sigma = +0.01$
						$\bar{\delta} = 0.45$

Soln. No.	$Y(\lambda_1) \times 10^6$	$y(\lambda_1) \times 10^6$	$\delta \times 10^6$	$Y(\lambda_2) \times 10^6$	$y(\lambda_2) \times 10^6$	$\delta \times 10^6$
1	74.17	73.78	+0.39	82.15	81.63	+0.52
2	77.42	77.92	-0.50	85.78	86.29	-0.51
3	83.61	83.73	-0.12	92.64	92.82	-0.18
4	96.33	96.05	+0.28	106.78	106.67	+0.11
5	108.99	108.94	+0.05	121.26	121.15	+0.11
6	123.36	123.45	-0.09	137.40	137.45	-0.05
			$\Sigma = +0.01$			
			$\bar{\delta} = 0.24$			
						$\Sigma = 0.00$
						$\bar{\delta} = 0.25$

TABLE 13 (Continued)

Calculated Results for K^* , ϵ_c^* , a , b and s

All uncertainties are at the 95% confidence level.

<u>$cK^*(\lambda_1)$, 8 pt. calcn.</u>	<u>$cK^*(\lambda_2)$, 8 pt. calcn.</u>
$cK^*(\lambda_1) = 0.3381 \pm 0.0101$	$cK^*(\lambda_2) = 0.3466 \pm 0.0088$
$c\epsilon_c^*(\lambda_1) = 2634 \pm 72$	$c\epsilon_c^*(\lambda_2) = 2325 \pm 53$
$a = 1.123 \times 10^{-3} \pm 0.014 \times 10^{-3}$	$a = 1.241 \times 10^{-3} \pm 0.013 \times 10^{-3}$
$b = 3.797 \times 10^{-4} \pm 0.104 \times 10^{-4}$	$b = 4.301 \times 10^{-4} \pm 0.099 \times 10^{-4}$
$s = 0.09501 \times 10^{-4}$	$s = 0.09041 \times 10^{-4}$
<u>$cK^*(\lambda_1)$, 6 pt. calcn.</u>	<u>$cK^*(\lambda_2)$, 6 pt. calcn.</u>
$cK^*(\lambda_1) = 0.3493 \pm 0.0107$	$cK^*(\lambda_2) = 0.3558 \pm 0.0106$
$c\epsilon_c^*(\lambda_1) = 2562 \pm 75$	$c\epsilon_c^*(\lambda_2) = 2275 \pm 65$
$a = 1.117 \times 10^{-3} \pm 0.010 \times 10^{-3}$	$a = 1.236 \times 10^{-3} \pm 0.011 \times 10^{-3}$
$b = 3.902 \times 10^{-4} \pm 0.115 \times 10^{-4}$	$b = 4.396 \times 10^{-4} \pm 0.125 \times 10^{-4}$
$s = 0.05496 \times 10^{-4}$	$s = 0.05982 \times 10^{-4}$
<u>$xK^*(\lambda_1)$, 8 pt. calcn.</u>	<u>$xK^*(\lambda_2)$, 8 pt. calcn.</u>
$xK^*(\lambda_1) = 6.171 \pm 0.147$	$xK^*(\lambda_2) = 6.305 \pm 0.125$
$x\epsilon_c^*(\lambda_1) = 2241 \pm 46$	$x\epsilon_c^*(\lambda_2) = 1985 \pm 34$
$a = 7.231 \times 10^{-5} \pm 0.088 \times 10^{-5}$	$a = 7.989 \times 10^{-5} \pm 0.082 \times 10^{-5}$
$b = 4.462 \times 10^{-4} \pm 0.091 \times 10^{-4}$	$b = 5.037 \times 10^{-4} \pm 0.085 \times 10^{-4}$
$s = 0.6221 \times 10^{-6}$	$s = 0.5835 \times 10^{-6}$
<u>$xK^*(\lambda_1)$, 6 pt. calcn.</u>	<u>$xK^*(\lambda_2)$, 6 pt. calcn.</u>
$xK^*(\lambda_1) = 6.348 \pm 0.156$	$xK^*(\lambda_2) = 6.450 \pm 0.152$
$x\epsilon_c^*(\lambda_1) = 2190 \pm 50$	$x\epsilon_c^*(\lambda_2) = 1949 \pm 43$
$a = 7.192 \times 10^{-5} \pm 0.064 \times 10^{-5}$	$a = 7.954 \times 10^{-5} \pm 0.069 \times 10^{-5}$
$b = 4.566 \times 10^{-4} \pm 0.104 \times 10^{-4}$	$b = 5.130 \times 10^{-4} \pm 0.112 \times 10^{-4}$
$s = 0.3550 \times 10^{-6}$	$s = 0.3828 \times 10^{-6}$

TABLE 14

Run 15

TCNE-N Complex

Temp. 30.00°C

Soln. No.	$C_A \times 10^3$	C_D	C_S	$Abs(\lambda_1)^{(1)}$	$Abs(\lambda_2)^{(1)}$
1	33.5721	0.03235	15.2985	0.847	0.773
2	6.3532	0.19573	15.0198	0.939	0.856
3	3.3471	0.39044	14.6325	0.937	0.854
4	1.8354	0.78697	13.8754	0.925	0.842
5	1.3582	1.18198	13.1563	0.933	0.849
6	1.1094	1.56545	12.4102	0.932	0.845
7	0.9631	1.95103	11.6516	0.939	0.850
8	0.8521	2.35233	10.8883	0.933	0.845

(1) Absorbances are corrected for any absorption due to the components.

Analysis of Residuals

	$c_{K^*}(\lambda_1)$			$c_{K^*}(\lambda_2)$		
Soln. No.	$Y(\lambda_1) \times 10^4$	$y(\lambda_1) \times 10^4$	$\delta \times 10^4$	$Y(\lambda_2) \times 10^4$	$y(\lambda_2) \times 10^4$	$\delta \times 10^4$
1	12.823	12.790	+0.033	14.050	14.008	+0.042
2	13.243	13.313	-0.070	14.527	14.593	-0.066
3	13.947	14.049	-0.102	15.303	15.416	-0.113
4	15.615	15.567	+0.048	17.155	17.112	+0.043
5	17.207	17.082	+0.125	18.909	18.806	+0.103
6	18.635	18.554	+0.081	20.553	20.452	+0.101
7	20.011	20.034	-0.023	22.106	22.107	-0.001
8	21.484	21.575	-0.091	23.721	23.830	-0.109
		$\Sigma = +0.001$			$\Sigma = 0.000$	
		$\bar{\delta} = 0.072$			$\bar{\delta} = 0.072$	

Soln. No.	$Y(\lambda_1) \times 10^4$	$y(\lambda_1) \times 10^4$	$\delta \times 10^4$	$Y(\lambda_2) \times 10^4$	$y(\lambda_2) \times 10^4$	$\delta \times 10^4$
1	12.823	12.743	+0.080	14.050	13.960	+0.090
2	13.243	13.280	-0.037	14.527	14.559	-0.032
3	13.947	14.037	-0.090	15.303	15.402	-0.099
4	15.615	15.595	+0.020	17.155	17.140	+0.015
5	17.207	17.151	+0.056	18.909	18.875	+0.034
6	18.635	18.663	-0.028	20.553	20.561	-0.008
			$\Sigma = +0.001$			$\Sigma = 0.000$
			$\bar{\delta} = 0.052$			$\bar{\delta} = 0.046$

TABLE 14 (Continued)

Analysis of Residuals

Soln. No.	$x_K^*(\lambda_1)$			$x_K^*(\lambda_2)$		
	$Y(\lambda_1) \times 10^6$	$y(\lambda_1) \times 10^6$	$\delta \times 10^6$	$Y(\lambda_2) \times 10^6$	$y(\lambda_2) \times 10^6$	$\delta \times 10^6$
1	83.46	83.38	+0.08	91.45	91.31	+0.14
2	87.00	87.49	-0.49	95.44	95.90	-0.46
3	92.82	93.42	-0.60	101.84	102.51	-0.67
4	106.49	106.07	+0.42	116.99	116.60	+0.39
5	120.00	119.24	+0.76	131.87	131.28	+0.59
6	133.33	132.79	+0.54	147.06	146.38	+0.68
7	147.11	147.19	-0.08	162.51	162.42	+0.09
8	162.25	162.88	-0.63	179.15	179.91	-0.76
			$\Sigma = 0.00$			$\Sigma = 0.00$
			$\bar{\delta} = 0.45$			$\bar{\delta} = 0.47$

Soln. No.	$x_K^*(\lambda_1)$			$x_K^*(\lambda_2)$		
	$Y(\lambda_1) \times 10^6$	$y(\lambda_1) \times 10^6$	$\delta \times 10^6$	$Y(\lambda_2) \times 10^6$	$y(\lambda_2) \times 10^6$	$\delta \times 10^6$
1	83.46	83.05	+0.41	91.45	90.97	+0.48
2	87.00	87.26	-0.26	95.44	95.65	-0.21
3	92.82	93.32	-0.50	101.84	102.39	-0.55
4	106.49	106.24	+0.25	116.99	116.76	+0.23
5	120.00	119.70	+0.30	131.87	131.73	+0.14
6	133.33	133.54	-0.21	147.06	147.13	-0.07
			$\Sigma = -0.01$			$\Sigma = +0.02$
			$\bar{\delta} = 0.32$			$\bar{\delta} = 0.28$

TABLE 14 (Continued)

Calculated Results for K^* , ϵ_c^* , a, b, and s

All uncertainties are at the 95% confidence level.

<u>$c_{K^*}(\lambda_1)$, 8 pt. calcn.</u>	<u>$c_{K^*}(\lambda_2)$, 8 pt. calcn.</u>
$c_{K^*}(\lambda_1) = 0.3063 \pm 0.0086$	$c_{K^*}(\lambda_2) = 0.3129 \pm 0.0082$
$c_{\epsilon_c^*}(\lambda_1) = 2604 \pm 68$	$c_{\epsilon_c^*}(\lambda_2) = 2329 \pm 56$
$a = 1.254 \times 10^{-3} \pm 0.0132 \times 10^{-3}$	$a = 1.373 \times 10^{-3} \pm 0.014 \times 10^{-3}$
$b = 3.841 \times 10^{-4} \pm 0.100 \times 10^{-4}$	$b = 4.294 \times 10^{-4} \pm 0.103 \times 10^{-4}$
$s = 0.09106 \times 10^{-4}$	$s = 0.09432 \times 10^{-4}$
<u>$c_{K^*}(\lambda_1)$, 6 pt. calcn.</u>	<u>$c_{K^*}(\lambda_2)$, 6 pt. calcn.</u>
$c_{K^*}(\lambda_1) = 0.3160 \pm 0.012$	$c_{K^*}(\lambda_2) = 0.3218 \pm 0.0114$
$c_{\epsilon_c^*}(\lambda_1) = 2535 \pm 96$	$c_{\epsilon_c^*}(\lambda_2) = 2273 \pm 78$
$a = 1.248 \times 10^{-3} \pm 0.013 \times 10^{-3}$	$a = 1.367 \times 10^{-3} \pm 0.013 \times 10^{-3}$
$b = 3.945 \times 10^{-4} \pm 0.149 \times 10^{-4}$	$b = 4.399 \times 10^{-4} \pm 0.150 \times 10^{-4}$
$s = 0.07058 \times 10^{-4}$	$s = 0.07140 \times 10^{-4}$
<u>$x_{K^*}(\lambda_1)$, 8 pt. calcn.</u>	<u>$x_{K^*}(\lambda_2)$, 8 pt. calcn.</u>
$x_{K^*}(\lambda_1) = 5.631 \pm 0.119$	$x_{K^*}(\lambda_2) = 5.732 \pm 0.114$
$x_{\epsilon_c^*}(\lambda_1) = 2181 \pm 41$	$x_{\epsilon_c^*}(\lambda_2) = 1957 \pm 34$
$a = 8.142 \times 10^{-5} \pm 0.083 \times 10^{-5}$	$a = 8.913 \times 10^{-5} \pm 0.086 \times 10^{-5}$
$b = 4.584 \times 10^{-4} \pm 0.085 \times 10^{-4}$	$b = 5.109 \times 10^{-4} \pm 0.089 \times 10^{-4}$
$s = 0.5851 \times 10^{-6}$	$s = 0.6087 \times 10^{-6}$
<u>$x_{K^*}(\lambda_1)$, 6 pt. calcn.</u>	<u>$x_{K^*}(\lambda_2)$, 6 pt. calcn.</u>
$x_{K^*}(\lambda_1) = 5.779 \pm 0.158$	$x_{K^*}(\lambda_2) = 5.870 \pm 0.142$
$x_{\epsilon_c^*}(\lambda_1) = 2135 \pm 55$	$x_{\epsilon_c^*}(\lambda_2) = 1919 \pm 44$
$a = 8.105 \times 10^{-5} \pm 0.075 \times 10^{-5}$	$a = 8.875 \times 10^{-5} \pm 0.073 \times 10^{-5}$
$b = 4.684 \times 10^{-4} \pm 0.121 \times 10^{-4}$	$b = 5.210 \times 10^{-4} \pm 0.118 \times 10^{-4}$
$s = 0.4109 \times 10^{-6}$	$s = 0.4019 \times 10^{-6}$

TABLE 15

Run 16		TCNE-N Complex		Temp. 11.50°C	
Soln. No.	$C_A \times 10^3$	C_D	C_S	Abs(λ_1) ⁽¹⁾	Abs(λ_2) ⁽¹⁾
1	23.9105	0.03175	15.6201	0.768	0.688
2	4.4375	0.19593	15.3508	0.834	0.743
3	2.4028	0.39262	14.9617	0.843	0.752
4	1.3471	0.78135	14.2095	0.832	0.744
5	0.9974	1.17299	13.4753	0.818	0.729
6	0.8197	1.57132	12.7229	0.822	0.734
7	0.7394	1.96186	11.9237	0.847	0.755
8	0.6820	2.34233	11.2349	0.858	0.765

(1) Absorbances are corrected for any absorption due to the components.

Analysis of Residuals

Soln. No.	$C_K^*(\lambda_1)$			$C_K^*(\lambda_2)$		
	$Y(\lambda_1) \times 10^4$	$y(\lambda_1) \times 10^4$	$\delta \times 10^4$	$Y(\lambda_2) \times 10^4$	$y(\lambda_2) \times 10^4$	$\delta \times 10^4$
1	9.885	9.883	+0.002	11.034	11.059	-0.025
2	10.425	10.435	-0.010	11.702	11.679	+0.023
3	11.191	11.177	+0.014	12.545	12.513	+0.032
4	12.651	12.654	-0.003	14.148	14.174	-0.026
5(2)	14.303	14.145	+0.158	16.049	15.850	+0.199
6	15.669	15.663	+0.006	17.548	17.556	-0.008
7	17.126	17.151	-0.025	19.212	19.229	-0.017
8	18.617	18.601	+0.016	20.881	20.859	+0.022

 $\Sigma = 0.000$ $\Sigma = +0.001$ $\bar{\delta} = 0.011$ $\bar{\delta} = 0.022$

Soln. No.	$Y(\lambda_1) \times 10^4$	$y(\lambda_1) \times 10^4$	$\delta \times 10^4$	$Y(\lambda_2) \times 10^4$	$y(\lambda_2) \times 10^4$	$\delta \times 10^4$
1	9.885	9.883	+0.002	11.034	11.064	-0.030
2	10.425	10.435	-0.010	11.702	11.682	+0.020
3	11.191	11.178	+0.013	12.545	12.514	+0.031
4	12.651	12.657	-0.006	14.148	14.171	-0.023
5(2)	14.303	14.149	+0.154	16.049	15.843	+0.206
6	15.669	15.668	+0.001	17.548	17.545	+0.003

 $\Sigma = 0.000$ $\Sigma = +0.001$ $\bar{\delta} = 0.006$ $\bar{\delta} = 0.021$

(2) Omitted from least squares calculation.

TABLE 15 (Continued)

Analysis of Residuals

Soln. No.	$x_K^*(\lambda_1)$			$x_K^*(\lambda_2)$		
	$Y(\lambda_1) \times 10^6$	$y(\lambda_1) \times 10^6$	$\delta \times 10^6$	$Y(\lambda_2) \times 10^6$	$y(\lambda_2) \times 10^6$	$\delta \times 10^6$
1	63.06	63.05	+0.01	70.39	70.55	-0.16
2	67.04	67.14	-0.10	75.25	75.14	+0.11
3	72.87	72.76	+0.11	81.69	81.46	+0.23
4	84.39	84.36	+0.03	94.37	94.49	-0.12
5(2)	97.64	96.59	+1.05	109.56	108.23	+1.33
6	109.61	109.66	-0.05	122.76	122.91	-0.15
7	123.33	123.39	-0.06	138.36	138.34	+0.02
8	137.12	137.06	+0.06	153.79	153.70	+0.09

$$\Sigma = 0.00$$

$$\Sigma = +0.02$$

$$\bar{\delta} = 0.06$$

$$\bar{\delta} = 0.13$$

Soln. No.	$x_K^*(\lambda_1)$			$x_K^*(\lambda_2)$		
	$Y(\lambda_1) \times 10^6$	$y(\lambda_1) \times 10^6$	$\delta \times 10^6$	$Y(\lambda_2) \times 10^6$	$y(\lambda_2) \times 10^6$	$\delta \times 10^6$
1	63.06	63.06	0.00	70.39	70.60	-0.21
2	67.04	67.15	-0.11	75.25	75.17	+0.08
3	72.87	72.77	+0.10	81.69	81.47	+0.22
4	84.39	84.36	+0.03	94.37	94.45	-0.08
5(2)	97.64	96.58	+1.06	109.56	108.14	+1.42
6	109.61	109.64	-0.03	122.76	122.77	-0.01

$$\Sigma = -0.01$$

$$\Sigma = 0.00$$

$$\bar{\delta} = 0.06$$

$$\bar{\delta} = 0.12$$

(2) Omitted from least squares calculation.

TABLE 15 (Continued)

Calculated Results for K^* , ϵ_c^* , a, b and s.

All uncertainties are at the 95% confidence level.

<u>$c_{K^*}(\lambda_1)$, 7 pt. calcn.</u>	<u>$c_{K^*}(\lambda_2)$, 7 pt. calcn.</u>
$c_{K^*}(\lambda_1) = 0.3940 \pm 0.0021$	$c_{K^*}(\lambda_2) = 0.3959 \pm 0.0033$
$c_{\epsilon_c^*}(\lambda_1) = 2624 \pm 17$	$c_{\epsilon_c^*}(\lambda_2) = 2334 \pm 17$
$a = 9.672 \times 10^{-4} \pm 0.024 \times 10^{-4}$	$a = 10.822 \times 10^{-4} \pm 0.042 \times 10^{-4}$
$b = 3.811 \times 10^{-4} \pm 0.018 \times 10^{-4}$	$b = 4.284 \times 10^{-4} \pm 0.031 \times 10^{-4}$
$s = 0.01593 \times 10^{-4}$	$s = 0.02715 \times 10^{-4}$
<u>$c_{K^*}(\lambda_1)$, 5 pt. calcn.</u>	<u>$c_{K^*}(\lambda_2)$, 5 pt. calcn.</u>
$c_{K^*}(\lambda_1) = 0.3945 \pm 0.0029$	$c_{K^*}(\lambda_2) = 0.3948 \pm 0.0077$
$c_{\epsilon_c^*}(\lambda_1) = 2621 \pm 18$	$c_{\epsilon_c^*}(\lambda_2) = 2340 \pm 44$
$a = 9.672 \times 10^{-4} \pm 0.022 \times 10^{-4}$	$a = 10.827 \times 10^{-4} \pm 0.064 \times 10^{-4}$
$b = 3.815 \times 10^{-4} \pm 0.027 \times 10^{-4}$	$b = 4.274 \times 10^{-4} \pm 0.080 \times 10^{-4}$
$s = 0.01016 \times 10^{-4}$	$s = 0.03039 \times 10^{-4}$
<u>$x_{K^*}(\lambda_1)$, 7 pt. calcn.</u>	<u>$x_{K^*}(\lambda_2)$, 7 pt. calcn.</u>
$x_{K^*}(\lambda_1) = 7.119 \pm 0.025$	$x_{K^*}(\lambda_2) = 7.150 \pm 0.046$
$x_{\epsilon_c^*}(\lambda_1) = 2284 \pm 7$	$x_{\epsilon_c^*}(\lambda_2) = 2033 \pm 11$
$a = 6.151 \times 10^{-5} \pm 0.012 \times 10^{-5}$	$a = 6.882 \times 10^{-5} \pm 0.025 \times 10^{-5}$
$b = 4.379 \times 10^{-4} \pm 0.013 \times 10^{-4}$	$b = 4.920 \times 10^{-4} \pm 0.026 \times 10^{-4}$
$s = 0.08053 \times 10^{-6}$	$s = 0.1663 \times 10^{-6}$
<u>$x_{K^*}(\lambda_1)$, 5 pt. calcn.</u>	<u>$x_{K^*}(\lambda_2)$, 5 pt. calcn.</u>
$x_{K^*}(\lambda_1) = 7.114 \pm 0.060$	$x_{K^*}(\lambda_2) = 7.119 \pm 0.110$
$x_{\epsilon_c^*}(\lambda_1) = 2285 \pm 18$	$x_{\epsilon_c^*}(\lambda_2) = 2040 \pm 29$
$a = 6.152 \times 10^{-5} \pm 0.019 \times 10^{-5}$	$a = 6.887 \times 10^{-5} \pm 0.039 \times 10^{-5}$
$b = 4.377 \times 10^{-4} \pm 0.034 \times 10^{-4}$	$b = 4.903 \times 10^{-4} \pm 0.070 \times 10^{-5}$
$s = 0.09220 \times 10^{-6}$	$s = 0.1885 \times 10^{-6}$

TABLE 16

Run 17		TCNE-N Complex		Temp. 0.72°C	
Soln. No.	$C_A \times 10^3$	C_D	C_S	Abs(λ_1) ⁽¹⁾	Abs(λ_2) ⁽¹⁾
1	27.9829	0.02786	15.8343	0.930	0.816
2	4.1712	0.20082	15.5591	0.936	0.823
3	2.2474	0.39121	15.1899	0.904	0.795
4	1.2772	0.78070	14.4510	0.879	0.773
5	0.9633	1.17684	13.6506	0.878	0.770
6	0.8106	1.56806	12.9227	0.878	0.770
7	0.7165	1.95186	12.1435	0.885	0.773
8	0.6523	2.34189	11.4099	0.885	0.775

(1) Absorbances are corrected for any absorption due to the components.

Analysis of Residuals

Soln. No.	$c_{K^*}(\lambda_1)$			$c_{K^*}(\lambda_2)$		
	$y(\lambda_1) \times 10^4$	$y(\lambda_1) \times 10^4$	$\delta \times 10^4$	$y(\lambda_2) \times 10^4$	$y(\lambda_2) \times 10^4$	$\delta \times 10^4$
1	8.382	8.432	-0.050	9.553	9.583	-0.030
2	8.949	9.015	-0.066	10.178	10.253	-0.075
3	9.726	9.752	-0.026	11.059	11.099	-0.040
4	11.344	11.271	+0.073	12.900	12.843	+0.057
5	12.912	12.818	+0.094	14.723	14.620	+0.103
6	14.477	14.347	+0.130	16.508	16.376	+0.132
7	15.803	15.847	-0.044	18.093	18.099	-0.006
8	17.260	17.371	-0.111	19.710	19.850	-0.140
			$\Sigma = 0.000$			$\Sigma = +0.001$
			$\bar{\delta} = 0.074$			$\bar{\delta} = 0.073$

Soln. No.	$y(\lambda_1) \times 10^4$	$y(\lambda_1) \times 10^4$	$\delta \times 10^4$	$y(\lambda_2) \times 10^4$	$y(\lambda_2) \times 10^4$	$\delta \times 10^4$
1	8.382	8.371	+0.011	9.553	9.520	+0.032
2	8.949	8.974	-0.025	10.178	10.210	-0.032
3	9.726	9.736	-0.010	11.059	11.082	-0.023
4	11.344	11.308	+0.036	12.900	12.879	+0.021
5	12.912	12.909	+0.003	14.723	14.710	+0.013
6	14.477	14.491	-0.014	16.508	16.519	-0.011
			$\Sigma = +0.001$			$\Sigma = 0.000$
			$\bar{\delta} = 0.017$			$\bar{\delta} = 0.022$

TABLE 16 (Continued)

Analysis of Residuals						
Soln. No.	$x_K^*(\lambda_1)$			$x_K^*(\lambda_2)$		
	$Y(\lambda_1) \times 10^6$	$y(\lambda_1) \times 10^6$	$\delta \times 10^6$	$Y(\lambda_2) \times 10^6$	$y(\lambda_2) \times 10^6$	$\delta \times 10^6$
1	52.75	53.08	-0.33	60.12	60.32	-0.20
2	56.77	57.24	-0.47	64.57	65.10	-0.53
3	62.41	62.62	-0.21	70.97	71.26	-0.29
4	74.47	74.06	+0.41	84.69	84.39	+0.30
5	87.08	86.39	+0.69	99.29	98.53	+0.76
6	99.90	99.04	+0.86	113.92	113.05	+0.87
7	112.11	112.31	-0.20	128.36	128.28	+0.08
8	125.51	126.27	-0.76	143.33	144.29	-0.96
			$\Sigma = -0.01$			$\Sigma = +0.01$
			$\bar{\delta} = 0.49$			$\bar{\delta} = 0.50$

Soln. No.	$Y(\lambda_1) \times 10^6$	$y(\lambda_1) \times 10^6$	$\delta \times 10^6$	$Y(\lambda_2) \times 10^6$	$y(\lambda_2) \times 10^6$	$\delta \times 10^6$
1	52.75	52.66	+0.09	60.12	59.89	+0.23
2	56.77	56.95	-0.18	64.57	64.79	-0.22
3	62.41	62.49	-0.08	70.97	71.12	-0.15
4	74.47	74.28	+0.19	84.69	84.60	+0.09
5	87.08	86.99	+0.09	99.29	99.12	+0.17
6	99.90	100.02	-0.12	113.92	114.02	-0.10
			$\Sigma = -0.01$			$\Sigma = +0.02$
			$\bar{\delta} = 0.12$			$\bar{\delta} = 0.16$

TABLE 16 (Continued)

Calculated Results for K^* , ϵ_c^* , a , b and s

All uncertainties are at the 95% confidence level.

<u>$cK^*(\lambda_1)$, 8 pt. calcn.</u>	<u>$cK^*(\lambda_2)$, 8 pt. calcn.</u>
$cK^*(\lambda_1) = 0.4758 \pm 0.0148$	$cK^*(\lambda_2) = 0.4810 \pm 0.0137$
$c\epsilon_c^*(\lambda_1) = 2558 \pm 67$	$c\epsilon_c^*(\lambda_2) = 2227 \pm 54$
$a = 8.215 \times 10^{-4} \pm 0.136 \times 10^{-4}$	$a = 9.334 \times 10^{-4} \pm 0.143 \times 10^{-4}$
$b = 3.909 \times 10^{-4} \pm 0.103 \times 10^{-4}$	$b = 4.490 \times 10^{-4} \pm 0.108 \times 10^{-4}$
$s = 0.09389 \times 10^{-4}$	$s = 0.09870 \times 10^{-4}$
<u>$cK^*(\lambda_1)$, 6 pt. calcn.</u>	<u>$cK^*(\lambda_2)$, 6 pt. calcn.</u>
$cK^*(\lambda_1) = 0.4966 \pm 0.0068$	$cK^*(\lambda_2) = 0.4993 \pm 0.0071$
$c\epsilon_c^*(\lambda_1) = 2472 \pm 28$	$c\epsilon_c^*(\lambda_2) = 2162 \pm 28$
$a = 8.146 \times 10^{-4} \pm 0.045 \times 10^{-4}$	$a = 9.264 \times 10^{-4} \pm 0.053 \times 10^{-4}$
$b = 4.045 \times 10^{-4} \pm 0.051 \times 10^{-4}$	$b = 4.625 \times 10^{-4} \pm 0.060 \times 10^{-4}$
$s = 0.02423 \times 10^{-4}$	$s = 0.02872 \times 10^{-4}$
<u>$xK^*(\lambda_1)$, 8 pt. calcn.</u>	<u>$xK^*(\lambda_2)$, 8 pt. calcn.</u>
$xK^*(\lambda_1) = 8.511 \pm 0.236$	$xK^*(\lambda_2) = 8.595 \pm 0.224$
$x\epsilon_c^*(\lambda_1) = 2279 \pm 49$	$x\epsilon_c^*(\lambda_2) = 1987 \pm 40$
$a = 5.155 \times 10^{-5} \pm 0.089 \times 10^{-5}$	$a = 5.857 \times 10^{-5} \pm 0.096 \times 10^{-5}$
$b = 4.387 \times 10^{-4} \pm 0.095 \times 10^{-4}$	$b = 5.034 \times 10^{-4} \pm 0.102 \times 10^{-4}$
$s = 0.6305 \times 10^{-6}$	$s = 0.6782 \times 10^{-6}$
<u>$xK^*(\lambda_1)$, 6 pt. calcn.</u>	<u>$xK^*(\lambda_2)$, 6 pt. calcn.</u>
$xK^*(\lambda_1) = 8.852 \pm 0.109$	$xK^*(\lambda_2) = 8.898 \pm 0.123$
$x\epsilon_c^*(\lambda_1) = 2211 \pm 24$	$x\epsilon_c^*(\lambda_2) = 1935 \pm 24$
$a = 5.108 \times 10^{-5} \pm 0.029 \times 10^{-5}$	$a = 5.808 \times 10^{-5} \pm 0.038 \times 10^{-5}$
$b = 4.522 \times 10^{-4} \pm 0.049 \times 10^{-4}$	$b = 5.168 \times 10^{-4} \pm 0.063 \times 10^{-4}$
$s = 0.1614 \times 10^{-6}$	$s = 0.2080 \times 10^{-6}$

TABLE 17

Run 18	TCNE-2,6-DMN Complex			Temp. 21.80°C	
Soln. No.	$C_A \times 10^3$	C_D	C_S	Abs(λ_1) ⁽¹⁾	Abs(λ_2) ⁽¹⁾
1	18.3635	0.01821	15.4690	0.889	0.781
2	2.9250	0.13019	15.2149	0.912	0.798
3	1.6442	0.25602	14.9004	0.892	0.781
4	1.0184	0.51749	14.2627	0.894	0.781
5	0.8088	0.76891	13.6423	0.893	0.776
6	0.7015	1.02416	13.0452	0.893	0.774
7	0.6399	1.29623	12.3320	0.912	0.788
8	0.6080	1.53464	11.8143	0.928	0.802

(1) Absorbances are corrected for any absorption due to the components.

Analysis of Residuals

	$x_K^*(\lambda_1)$			$x_K^*(\lambda_2)$		
Soln. No.	$y(\lambda_1) \times 10^6$	$y(\lambda_1) \times 10^6$	$\delta \times 10^6$	$y(\lambda_2) \times 10^6$	$y(\lambda_2) \times 10^6$	$\delta \times 10^6$
1	24.262	24.317	-0.055	27.617	27.656	-0.039
2	27.207	27.275	-0.068	31.093	31.100	-0.007
3	31.135	31.176	-0.041	35.560	35.641	-0.081
4	39.882	39.647	+0.235	45.653	45.503	+0.150
5	48.322	48.234	+0.088	55.607	55.501	+0.106
6	57.181	57.339	-0.158	65.972	66.101	-0.129
			$\Sigma = +0.001$			$\Sigma = 0.000$
			$\bar{\delta} = 0.108$			$\bar{\delta} = 0.085$

TABLE 17 (Continued)

Calculated Results for K^* , ϵ_c^* , a, b and s

<u>$c_K^*(\lambda_1)$, 8 pt. calcn.</u>	<u>$c_K^*(\lambda_2)$, 8 pt. calcn.</u>
$c_K^*(\lambda_1) = 1.155 \pm 0.033$	$c_K^*(\lambda_2) = 1.190 \pm 0.037$
$c_{\epsilon_c^*}(\lambda_1) = 2371 \pm 57$	$c_{\epsilon_c^*}(\lambda_2) = 2027 \pm 44$
$a = 3.652 \times 10^{-4} \pm 0.088 \times 10^{-4}$	$a = 4.147 \times 10^{-4} \pm 0.093 \times 10^{-4}$
$b = 4.218 \times 10^{-4} \pm 0.101 \times 10^{-4}$	$b = 4.933 \times 10^{-4} \pm 0.107 \times 10^{-4}$
$s = 0.06079 \times 10^{-4}$	$s = 0.06408 \times 10^{-4}$
<u>$c_K^*(\lambda_1)$, 6 pt. calcn.</u>	<u>$c_K^*(\lambda_2)$, 6 pt. calcn.</u>
$c_K^*(\lambda_1) = 1.206 \pm 0.023$	$c_K^*(\lambda_2) = 1.237 \pm 0.015$
$c_{\epsilon_c^*}(\lambda_1) = 2299 \pm 35$	$c_{\epsilon_c^*}(\lambda_2) = 1971 \pm 19$
$a = 3.608 \times 10^{-4} \pm 0.039 \times 10^{-4}$	$a = 4.100 \times 10^{-4} \pm 0.029 \times 10^{-4}$
$b = 4.350 \times 10^{-4} \pm 0.067 \times 10^{-4}$	$b = 5.073 \times 10^{-4} \pm 0.050 \times 10^{-4}$
$s = 0.02078 \times 10^{-4}$	$s = 0.01550 \times 10^{-4}$
<u>$x_K^*(\lambda_1)$, 6 pt. calcn.</u>	<u>$x_K^*(\lambda_2)$, 6 pt. calcn.</u>
$x_K^*(\lambda_1) = 20.17 \pm 0.39$	$x_K^*(\lambda_2) = 20.67 \pm 0.27$
$x_{\epsilon_c^*}(\lambda_1) = 2134 \pm 32$	$x_{\epsilon_c^*}(\lambda_2) = 1833 \pm 18$
$a = 2.322 \times 10^{-5} \pm 0.028 \times 10^{-5}$	$a = 2.638 \times 10^{-5} \pm 0.022 \times 10^{-5}$
$b = 4.685 \times 10^{-4} \pm 0.070 \times 10^{-4}$	$b = 5.455 \times 10^{-4} \pm 0.055 \times 10^{-4}$
$s = 0.1560 \times 10^{-6}$	$s = 0.1207 \times 10^{-6}$

TABLE 18

Run 19	TCNE-2,6-DMN Complex			Temp. 30.00 °C	
Soln. No.	$C_A \times 10^3$	C_D	C_S	Abs(λ_1) ⁽¹⁾	Abs(λ_2) ⁽¹⁾
1	19.6642	0.01860	15.2992	0.838	0.745
2	3.0638	0.13137	15.0434	0.848	0.750
3	1.7664	0.25730	14.7506	0.857	0.757
4	1.0712	0.51306	14.1452	0.854	0.752
5	0.8488	0.76879	13.4807	0.869	0.762
6	0.7407	1.02637	12.8769	0.884	0.773
7	0.6681	1.28619	12.2358	0.892	0.778
8	0.6403	1.53758	11.5932	0.926	0.807

(1) Absorbances are corrected for any absorption due to the components.

Analysis of Residuals

	$x_K^*(\lambda_1)$			$x_K^*(\lambda_2)$		
Soln. No.	$Y(\lambda_1) \times 10^6$	$y(\lambda_1) \times 10^6$	$\delta \times 10^6$	$Y(\lambda_2) \times 10^6$	$y(\lambda_2) \times 10^6$	$\delta \times 10^6$
1	28.451	28.426	+0.025	32.003	31.999	+0.004
2	31.273	31.417	-0.144	35.359	35.462	-0.103
3	35.334	35.367	-0.033	40.002	40.036	-0.034
4	43.987	43.771	+0.216	49.953	49.768	+0.185
5	52.696	52.640	+0.056	60.095	60.038	+0.057
6	61.858	61.977	-0.119	70.740	70.850	-0.110
			$\Sigma = +0.001$			$\Sigma = -0.001$
			$\bar{\delta} = 0.099$			$\bar{\delta} = 0.082$

Analysis of Residuals

Soln. No.	$Y(\lambda_1) \times 10^4$	$y(\lambda_1) \times 10^4$	$\delta \times 10^4$	$Y(\lambda_2) \times 10^4$	$y(\lambda_2) \times 10^4$	$\delta \times 10^4$
1	4.364	4.356	+0.008	4.908	4.904	+0.004
2	4.745	4.770	-0.024	5.367	5.384	-0.017
3	5.304	5.307	-0.003	6.004	6.008	-0.004
4	6.436	6.405	+0.031	7.309	7.283	+0.026
5	7.509	7.506	+0.003	8.564	8.560	+0.004
6	8.600	8.614	-0.014	9.835	9.848	-0.013
			$\Sigma = +0.001$			$\Sigma = 0.000$
			$\bar{\delta} = 0.014$			$\bar{\delta} = 0.011$

TABLE 18 (Continued)

Calculated Results for K^* , ϵ_c^* , a, b and s

All uncertainties are at the 95% confidence level.

$c_{K^*}(\lambda_1)$, 8 pt. calcn.

$$c_{K^*}(\lambda_1) = 0.9953 \pm 0.0254$$

$$c_{\epsilon_c^*}(\lambda_1) = 2377 \pm 46$$

$$a = 4.226 \times 10^{-4} \pm 0.070 \times 10^{-4}$$

$$b = 4.207 \times 10^{-4} \pm 0.081 \times 10^{-4}$$

$$s = 0.04856 \times 10^{-4}$$

$c_{K^*}(\lambda_2)$, 8 pt. calcn.

$$c_{K^*}(\lambda_2) = 1.030 \pm 0.025$$

$$c_{\epsilon_c^*}(\lambda_2) = 2044 \pm 36$$

$$a = 4.751 \times 10^{-4} \pm 0.076 \times 10^{-4}$$

$$b = 4.892 \times 10^{-4} \pm 0.087 \times 10^{-4}$$

$$s = 0.05215 \times 10^{-4}$$

$c_{K^*}(\lambda_1)$, 6 pt. calcn.

$$c_{K^*}(\lambda_1) = 1.027 \pm 0.019$$

$$c_{\epsilon_c^*}(\lambda_1) = 2322 \pm 36$$

$$a = 4.193 \times 10^{-4} \pm 0.039 \times 10^{-4}$$

$$b = 4.307 \times 10^{-4} \pm 0.068 \times 10^{-4}$$

$$s = 0.02098 \times 10^{-4}$$

$c_{K^*}(\lambda_2)$, 6 pt. calcn.

$$c_{K^*}(\lambda_2) = 1.061 \pm 0.014$$

$$c_{\epsilon_c^*}(\lambda_2) = 2000 \pm 22$$

$$a = 4.714 \times 10^{-4} \pm 0.032 \times 10^{-4}$$

$$b = 5.000 \times 10^{-4} \pm 0.055 \times 10^{-4}$$

$$s = 0.01711 \times 10^{-4}$$

$x_{K^*}(\lambda_1)$, 6 pt. calcn.

$$x_{K^*}(\lambda_1) = 17.24 \pm 0.29$$

$$x_{\epsilon_c^*}(\lambda_1) = 2127 \pm 30$$

$$a = 2.726 \times 10^{-5} \pm 0.027 \times 10^{-5}$$

$$b = 4.701 \times 10^{-4} \pm 0.066 \times 10^{-4}$$

$$s = 0.1469 \times 10^{-6}$$

$x_{K^*}(\lambda_2)$, 6 pt. calcn.

$$x_{K^*}(\lambda_2) = 17.76 \pm 0.22$$

$$x_{\epsilon_c^*}(\lambda_2) = 1837 \pm 19$$

$$a = 3.066 \times 10^{-5} \pm 0.023 \times 10^{-5}$$

$$b = 5.443 \times 10^{-4} \pm 0.055 \times 10^{-4}$$

$$s = 0.1239 \times 10^{-6}$$

TABLE 19

Run 20 TCNE-2,6-DMN Complex Temp. 0.68°C

Soln. No.	$C_A \times 10^3$	C_D	C_S	$Abs(\lambda_1)^{(1)}$	$Abs(\lambda_2)^{(1)}$
1	15.3780	0.015171	15.8902	0.911	0.779
2	2.5721	0.097393	15.7449	0.877	0.749
3	1.4921	0.196678	15.4704	0.891	0.759
4	0.9331	0.387486	15.0238	0.872	0.742
5	0.7512	0.581776	14.5191	0.881	0.745
6	0.6583	0.792888	14.0095	0.894	0.756

(1) Absorbances are corrected for any absorption due to the components.

Analysis of Residuals

Soln. No.	$cK^*(\lambda_1)$			$cK^*(\lambda_2)$		
	$Y(\lambda_1) \times 10^4$	$y(\lambda_1) \times 10^4$	$\delta \times 10^4$	$Y(\lambda_2) \times 10^4$	$y(\lambda_2) \times 10^4$	$\delta \times 10^4$
1	2.561	2.570	-0.009	2.995	3.003	-0.008
2	2.856	2.869	-0.013	3.345	3.360	-0.015
3	3.294	3.293	+0.001	3.866	3.866	+0.000
4	4.147	4.113	+0.034	4.873	4.845	+0.028
5	4.960	4.950	+0.010	5.866	5.844	+0.022
6	5.839	5.860	-0.021	6.904	6.930	-0.026
			$\Sigma = +0.002$			$\Sigma = +0.001$
			$\bar{\delta} = 0.015$			$\bar{\delta} = 0.017$

Soln. No.	$xK^*(\lambda_1)$			$xK^*(\lambda_2)$		
	$Y(\lambda_1) \times 10^6$	$y(\lambda_1) \times 10^6$	$\delta \times 10^6$	$Y(\lambda_2) \times 10^6$	$y(\lambda_2) \times 10^6$	$\delta \times 10^6$
1	16.086	16.139	-0.053	18.811	18.853	-0.042
2	18.028	18.131	-0.103	21.109	21.229	-0.120
3	21.021	21.006	+0.015	24.677	24.659	+0.018
4	26.905	26.701	+0.204	31.618	31.452	+0.166
5	32.847	32.767	+0.080	38.844	38.688	+0.156
6	39.443	39.586	-0.143	46.643	46.822	-0.179
			$\Sigma = 0.000$			$\Sigma = -0.001$
			$\bar{\delta} = 0.100$			$\bar{\delta} = 0.114$

TABLE 19 (Continued)

Calculated Results for K^* , ϵ_c^* , a, b and s

All uncertainties are at the 95% confidence level.

 $c_K^*(\lambda_1)$, 6 pt. calcn.

$$c_K^*(\lambda_1) = 1.767 \pm 0.048$$

$$c_{\epsilon c}^*(\lambda_1) = 2319 \pm 45$$

$$a = 2.440 \times 10^{-4} \pm 0.041 \times 10^{-4}$$

$$b = 4.312 \times 10^{-4} \pm 0.029 \times 10^{-4}$$

$$s = 0.02194 \times 10^{-4}$$

 $c_K^*(\lambda_2)$, 6 pt. calcn.

$$c_K^*(\lambda_2) = 1.807 \pm 0.044$$

$$c_{\epsilon c}^*(\lambda_2) = 1943 \pm 37$$

$$a = 2.848 \times 10^{-4} \pm 0.044 \times 10^{-4}$$

$$b = 5.147 \times 10^{-4} \pm 0.099 \times 10^{-4}$$

$$s = 0.02365 \times 10^{-4}$$

 $x_K^*(\lambda_1)$, 6 pt. calcn.

$$x_K^*(\lambda_1) = 29.69 \pm 0.77$$

$$x_{\epsilon c}^*(\lambda_1) = 2204 \pm 43$$

$$a = 1.528 \times 10^{-5} \pm 0.026 \times 10^{-5}$$

$$b = 4.536 \times 10^{-4} \pm 0.089 \times 10^{-4}$$

$$s = 0.1432 \times 10^{-6}$$

 $x_K^*(\lambda_2)$, 6 pt. calcn.

$$x_K^*(\lambda_2) = 30.35 \pm 0.74$$

$$x_{\epsilon c}^*(\lambda_2) = 1848 \pm 33$$

$$a = 1.783 \times 10^{-5} \pm 0.029 \times 10^{-5}$$

$$b = 5.411 \times 10^{-4} \pm 0.098 \times 10^{-4}$$

$$s = 0.1586 \times 10^{-6}$$

least squares calculation gave values of K^* , ϵ_c^* , a and b which were in agreement with those from the first calculation to within 1 or 2 parts in 10^6 .

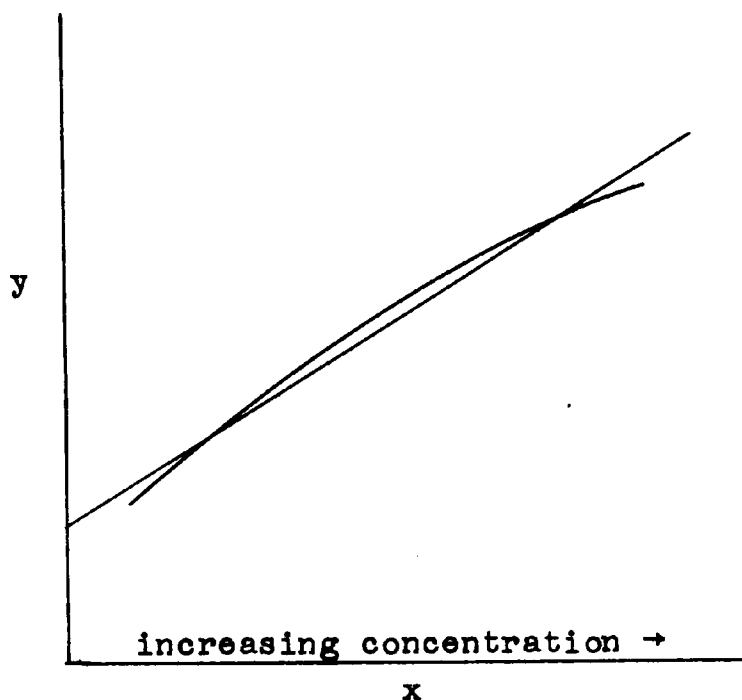
Several of the concentration terms listed in Tables 11-19 are given to six significant figures, which is one or sometimes two figures in excess of the accuracy with which these quantities are known. This is done because (see, for example, Scarborough [71]) the various measured quantities (i.e. the weights, molecular weights and volumes) which are used in a least squares treatment must be considered as exact numbers and computations carried through with a number of significant figures equal to $p + q + 1$; here p is the desired number of significant figures in the result (4 in the present case) and q is the number of significant figures lost by subtraction (1 in the present case).

Three runs, numbers 12, 13 and 14, were made on the TCNE-N complex at 21.80°C. Runs 12 and 13 (Tables 11 and 12) employed 12 data points, while for Run 14 (Table 13) only 8 points (covering the same range of concentrations) were used. The calculated values of $^cK^*$ and $^c\epsilon_c^*$ for these runs, together with values derived from the combined data, are given in Table 12B. It is apparent that the reproducibility is quite good, the relative range of values of $^cK^*$ and $^c\epsilon_c^*$ being less than 1%. In view of the fact that the results for Run 14 appear equally as good as those for the somewhat more elaborate Runs 12 and 13, as measured by s or $\bar{\delta}$, all subsequent runs were

made, as was Run 14, using concentrations of donor chosen to give points equally spaced on a plot of equations (V-18) or (V-26) (see, for example, Figures 25, 29).

It was pointed out in Part C that the existence of any non-ideality effects, which are expected at high concentrations of donor, might be ascertained by the presence of systematic deviations of the data from the least squares straight line. The occurrence of such deviations can be most conveniently demonstrated upon examination of the residuals to the least squares fits, as listed in Tables 11-19 for the data of Runs 12-20, respectively. It is apparent from these tables that the data fit their least squares lines quite closely, the relative deviation in y usually being less than 0.5% and rarely as much as 1%. This compares favorably with the estimated uncertainty in y , 5-6 parts per thousand, due to the uncertainty in absorbance measurements. Although there are no striking deviations from linearity, a definite trend in the curvature of the data is apparent at high concentrations; as the concentration of donor increases, δ goes from negative values, through several positive values, and back to negative values, as shown in a highly magnified fashion in the schematic diagram below (Figure 33).

Figure 33

Behavior of Deviations from Least Squares Line

The effect of this curvature is to reduce the slope of the least squares line from the limiting value it would have at low concentrations; reference to equations (V-18) or (V-26) shows that this operates to increase ϵ_c^* and decrease K^* from their low concentration values. This effect can be further seen by a comparison (see Tables 20, 21) of values of K^* and ϵ_c^* calculated from all 8 experimental points with those calculated using the first 6 points; inclusion of the high concentration data results in an increase in ϵ_c^* of 2-4% while K^* decreases by 2-5%. There is one exception to the trends described above. The data of Run 16 (Table 15) are anomal-

TABLE 20

Summary of Results for TCNE-N⁽¹⁾

Run No.	Temp.	No. of Points	$c_K^*(\lambda_1)$	$c_{\epsilon_c}^*(\lambda_1)$	$c_K^*(\lambda_2)$	$c_{\epsilon_c}^*(\lambda_2)$
15	30.00	8	0.3063 $\pm$ 0.0086	2604 $\pm$ 68	0.3129 $\pm$ 0.0082	2329 $\pm$ 56
	± 0.02	6	0.3160 $\pm$ 0.0124	2535 $\pm$ 96	0.3218 $\pm$ 0.0114	2273 $\pm$ 78
14	21.80	8	0.3381 $\pm$ 0.0101	2634 $\pm$ 72	0.3466 $\pm$ 0.0088	2325 $\pm$ 54
	± 0.02	6	0.3493 $\pm$ 0.0108	2562 $\pm$ 75	0.3558 $\pm$ 0.0106	2275 $\pm$ 65
16	11.50	7	0.3940 $\pm$ 0.0021	2624 $\pm$ 17	0.3959 $\pm$ 0.0033	2334 $\pm$ 17
	± 0.03	5	0.3945 $\pm$ 0.0029	2621 $\pm$ 18	0.3948 $\pm$ 0.0072	2340 $\pm$ 44
17	0.72	8	0.4758 $\pm$ 0.0148	2558 $\pm$ 67	0.4810 $\pm$ 0.0137	2227 $\pm$ 54
	± 0.04	6	0.4966 $\pm$ 0.0068	2472 $\pm$ 28	0.4993 $\pm$ 0.0071	2162 $\pm$ 28

Run No.	Temp.	No. of Points	$x_K^*(\lambda_1)$	$x_{\epsilon_c}^*(\lambda_1)$	$x_K^*(\lambda_2)$	$x_{\epsilon_c}^*(\lambda_2)$
15	30.00	8	5.631 $\pm$ 0.119	2181 $\pm$ 41	5.732 $\pm$ 0.114	1957 $\pm$ 34
	± 0.02	6	5.780 $\pm$ 0.158	2135 $\pm$ 55	5.870 $\pm$ 0.142	1919 $\pm$ 44
14	21.80	8	6.171 $\pm$ 0.147	2241 $\pm$ 46	6.305 $\pm$ 0.125	1985 $\pm$ 34
	± 0.02	6	6.348 $\pm$ 0.156	2190 $\pm$ 50	6.450 $\pm$ 0.152	1949 $\pm$ 43
16	11.50	7	7.119 $\pm$ 0.025	2284 $\pm$ 6	7.150 $\pm$ 0.046	2032 $\pm$ 11
	± 0.03	5	7.115 $\pm$ 0.060	2285 $\pm$ 18	7.119 $\pm$ 0.110	2040 $\pm$ 29
17	0.72	8	8.511 $\pm$ 0.236	2279 $\pm$ 50	8.595 $\pm$ 0.224	1987 $\pm$ 40
	± 0.04	6	8.852 $\pm$ 0.109	2212 $\pm$ 24	8.898 $\pm$ 0.123	1935 $\pm$ 24

(1) All uncertainties are for a 95% confidence level.

TABLE 21

Summary of Results for TCNE-2,6-DMN (1)

Run No.	Temp.	No. of Points	$c_{K^*}(\lambda_1)$	$c_{\epsilon_c^*}(\lambda_1)$	$c_{K^*}(\lambda_2)$	$c_{\epsilon_c^*}(\lambda_2)$
19	30.00	8	0.995 ± 0.025	2377 ± 46	1.030 ± 0.025	2044 ± 36
	± 0.02	6	1.027 ± 0.019	2322 ± 36	1.061 ± 0.014	2000 ± 22
18	21.80	8	1.155 ± 0.039	2371 ± 57	1.190 ± 0.037	2027 ± 44
	± 0.02	6	1.206 ± 0.023	2299 ± 35	1.237 ± 0.015	1971 ± 19
20	0.68	6	1.767 ± 0.048	2319 ± 45	1.807 ± 0.044	1943 ± 37
	± 0.03					

Run No.	Temp.	No. of Points	$x_{K^*}(\lambda_1)$	$x_{\epsilon_c^*}(\lambda_1)$	$x_{K^*}(\lambda_2)$	$x_{\epsilon_c^*}(\lambda_2)$
19	30.00	6	17.24 ± 0.29	2127 ± 30	17.76 ± 0.22	1837 ± 19
	± 0.02					
18	21.80	6	20.17 ± 0.39	2134 ± 32	20.67 ± 0.27	1833 ± 18
	± 0.02					
20	0.68	6	29.69 ± 0.77	2205 ± 43	30.35 ± 0.74	1848 ± 34
	± 0.03					

(1) All uncertainties are for a 95% confidence level.

ously "good" in that their residuals δ are quite small (except for point 5, which has been excluded from the least squares calculation--inclusion of this point alters K^* and ϵ_c^* by less than 0.1%) and show no detectable curvature. The closeness of fit in this case is probably fortuitous.

The various values of K^* and ϵ_c^* obtained for the runs on TCNE-N and TCNE-2,6-DMN are summarized in Tables 20 and 21, respectively. Table 22 presents approximate values of K^* and ϵ_c^* derived from two measurements, at high and low concentrations of donor, for several other TCNE complexes. The uncertainties of these results are not known directly, but they are probably accurate to within 10%. These complexes were not studied in greater detail because the intensity of their charge-transfer spectrum decreased with time (several per cent in a few minutes, in the case of TCNE-1MN solutions with a high concentration of donor), together with the attendant appearance of an intense absorption band centered at 453 m μ , giving the resultant solution a yellow coloration. These phenomena are discussed further in Section III.

It is interesting to note the behavior of the ratio x_{K^*}/c_{K^*} in relation to the strength of the complex, as measured by x_{K^*} (see Table 23). It is apparent that $x_{K^*}/c_{K^*} > 1/V_S$ in contrast to the opposite prediction of equation (V-28), i.e. $x_{K^*}/c_{K^*} = 1/\bar{V}_{av}$; for the data under consideration $\bar{V}$ increases with concentration so that $1/\bar{V}_{av}$ should be less than $1/V_S$. However, x_{K^*}/c_{K^*} approaches $1/V_S$ as the stability of

TABLE 22

Approximate Values^(1,2) of K^* , ϵ_c^* for Other Complexes

<u>TCNE-1-MN Complex</u>			
<u>$c_{K^*}(\lambda_1)$</u>	<u>$c_{\epsilon_c^*}(\lambda_1)$</u>	<u>$x_{K^*}(\lambda_1)$</u>	<u>$x_{\epsilon_c^*}(\lambda_1)$</u>
0.674	2210	11.6	1990
0.652	2280		
<u>TCNE-2-MN Complex</u>			
<u>$c_{K^*}(\lambda_1)$</u>	<u>$c_{\epsilon_c^*}(\lambda_1)$</u>	<u>$x_{K^*}(\lambda_1)$</u>	<u>$x_{\epsilon_c^*}(\lambda_1)$</u>
0.731	2130	12.6	1930
<u>TCNE-1,6-DMN Complex</u>			
<u>$c_{K^*}(\lambda_1)$</u>	<u>$c_{\epsilon_c^*}(\lambda_1)$</u>	<u>$x_{K^*}(\lambda_1)$</u>	<u>$x_{\epsilon_c^*}(\lambda_1)$</u>
1.06	2380	17.8	2190
<u>TCNE-2,3-DMN Complex</u>			
<u>$c_{K^*}(\lambda_1)$</u>	<u>$c_{\epsilon_c^*}(\lambda_1)$</u>	<u>$x_{K^*}(\lambda_1)$</u>	<u>$x_{\epsilon_c^*}(\lambda_1)$</u>
1.35	2300	22.4	2150
1.34	2310		

(1) Uncertainties are probably of the order of 10%.

(2) Temperature of measurement 21.80°C.

TABLE 23

Dependence of $x_K^*V_s/c_K^*$ and $c_{\epsilon_c}^*/x_{\epsilon_c}^*$ on Complex Stability

Complex	Run No.	No. of Points	Temp.	x_K^* (λ_1)	x_K^* (c_K^*) λ_1	x_K^* (c_K^*) λ_2	$\frac{1}{V_s}$	$x_K^*V_s$ ($-c_K^*$) λ_1	$x_K^*V_s$ ($-c_K^*$) λ_2	$c_{\epsilon_c}^*$ ($x_{\epsilon_c}^*$) λ_1	$c_{\epsilon_c}^*$ ($x_{\epsilon_c}^*$) λ_2
TCNE-N	15	8	30.00	5.63	18.37	18.31	15.40	1.193	1.189	1.194	1.191
				5.78	18.28	18.25	15.40	1.187	1.185	1.187	1.185
TCNE-N	14	8	21.80	6.17	18.25	18.20	15.57	1.173	1.170	1.174	1.172
				6.35	18.18	18.14	15.57	1.167	1.165	1.170	1.167
TCNE-N	16	8	11.50	7.12	18.08	18.06	15.80	1.148	1.143	1.149	1.148
				7.11	18.04	18.04	15.80	1.142	1.142	1.147	1.148
TCNE-N	17	8	0.72	8.51	17.89	17.87	16.03	1.116	1.115	1.123	1.122
				8.85	17.84	17.85	16.03	1.113	1.113	1.117	1.117
TCNE-1MN	2	2	21.80	11.59	17.21		15.57	1.106		1.108	
TCNE-2MN	2	2	21.80	12.59	17.22		15.57	1.106		1.106	
TCNE-2,6-DMN	19	6	30.00	17.24	16.79	16.75	15.40	1.090	1.088	1.093	1.089
TCNE-1,6-DMN	2	2	21.80	17.83	16.85		15.57	1.083		1.084	
TCNE-2,6-DMN	18	6	21.80	20.17	16.74	16.71	15.57	1.076	1.074	1.077	1.076
TCNE-2,3-DMN	2	2	21.80	22.42	16.59		15.57	1.065		1.066	
TCNE-2,6-DMN	20	6	0.68	29.69	16.82	16.78	16.04	1.050	1.047	1.052	1.053

the complex increases. Furthermore, the ratios $x_K^* V_S / c_K^*$ and $c_{\epsilon_c}^* / x_{\epsilon_c}^*$ are essentially identical and vary quite regularly with x_K^* , appearing to approach a limiting value of unity as the stability of the complex increases. These regularities are remarkable in view of the fact that data for several different complexes and at several different temperatures are compared. A further discussion of these regularities is given in Part E, where it is shown that they arise as a consequence of a nearly linear relationship between $1/\bar{V}$ and $(C_A + C_D - \text{Abs}/c_{\epsilon_c})$.

The most important relationships evident from Tables 20-23 are summarized below:

1. Stability of the TCNE complexes, as measured by c_K^* or x_K^* , increases in the order naphthalene < methyl naphthalenes < dimethyl naphthalenes. This is the order to be expected on the basis of increasing π -electron density (i.e. π -electron donating ability) in the alkyl substituted compounds, and parallels the results obtained by Merrifield and Phillips [20] for the methylated benzenes.
2. The fit of all sets of data to the calculated least squares curves is quite good, the relative deviations in y , δ_i/y_i , being usually less than 0.5% and rarely exceeding 1% (Run 16 is anomalously good, except for point 5 where $\delta_i/y_i > 1\%$). This is reflected in the relatively small uncertainties in K and ϵ_c , even at a 95%

- confidence level (the relative uncertainties are almost all within the range of 2-3%).
3. A definite trend in the curvature of the data is apparent at high concentrations of donor. This operates to decrease the slope and raise the intercept (i.e. to increase ϵ_c^* and decrease K^*) of the least squares line from the values they would have at the limit of low concentrations.
 4. The fit of the data to the least squares curves is (except for three rather close cases) uniformly better for the 6 point calculations, as measured by $\bar{\delta}_1$ or by s . However, the error limits increase somewhat unless there has been a great improvement in s (by a factor >3).
 5. Except for the anomalously "good" Run 16, K^* as calculated for the first 6 points is greater than K^* for all 8 points by 2-5%. For the same cases, ϵ_c^* (6 points) $<$ ϵ_c^* (8 points) by 2-4%.
 6. $^c\epsilon_c^*$ is uniformly greater than $^x\epsilon_c^*$. The ratio $^c\epsilon_c^*/^x\epsilon_c^*$ is greater for TCNE-N than for TCNE-2,6-DMN and approaches unity as K^* increases. The ratio $^xK^*V_S/^cK^*$ behaves similarly.
 7. $K^*(\lambda_2)$ is uniformly greater than $K^*(\lambda_1)$. It is pointed out in Part E that this is a consequence of the fact that the absorbance ratio $Abs(\lambda_2)/Abs(\lambda_1)$ decreases uniformly with increasing concentration of donor (cf. Table 29). The latter behavior has been interpreted in terms

of the presence of higher order complexes (e.g. D_2A) in concentrated solutions of donor (see further discussion in Part E-3).

A further discussion of points 3, 4, 5 and 6, in terms of deviation from ideal behavior, is given below in Part E.

Part E. Discussion of Results

The most significant facts to be noted from the data and results presented in Part D are:

- (1) the inequalities $c_{\epsilon_c}^* > x_{\epsilon_c}^*$ and $c_K^* < x_K^* v_S$
- (2) the curvature in the data plots.

Although curvature in the data plots for c_K could be anticipated, even for ideal solutions, on the basis of the argument given in Part C, the curvature exhibited by the data for x_K indicates that non-ideality effects are important over the range of concentrations studied. Points 1 and 2 above are discussed below in some detail; firstly under the assumption that the systems investigated exhibit ideal behavior, and secondly, recognizing that non-ideality plays an important role in causing the observed non-linear plots.

1. Ideal Behavior

It was shown in Part C that x_K and c_K are not simply related except at infinite dilution and that c_K is not a rigorous thermodynamic constant but varies with $\bar{V}$ in accordance with

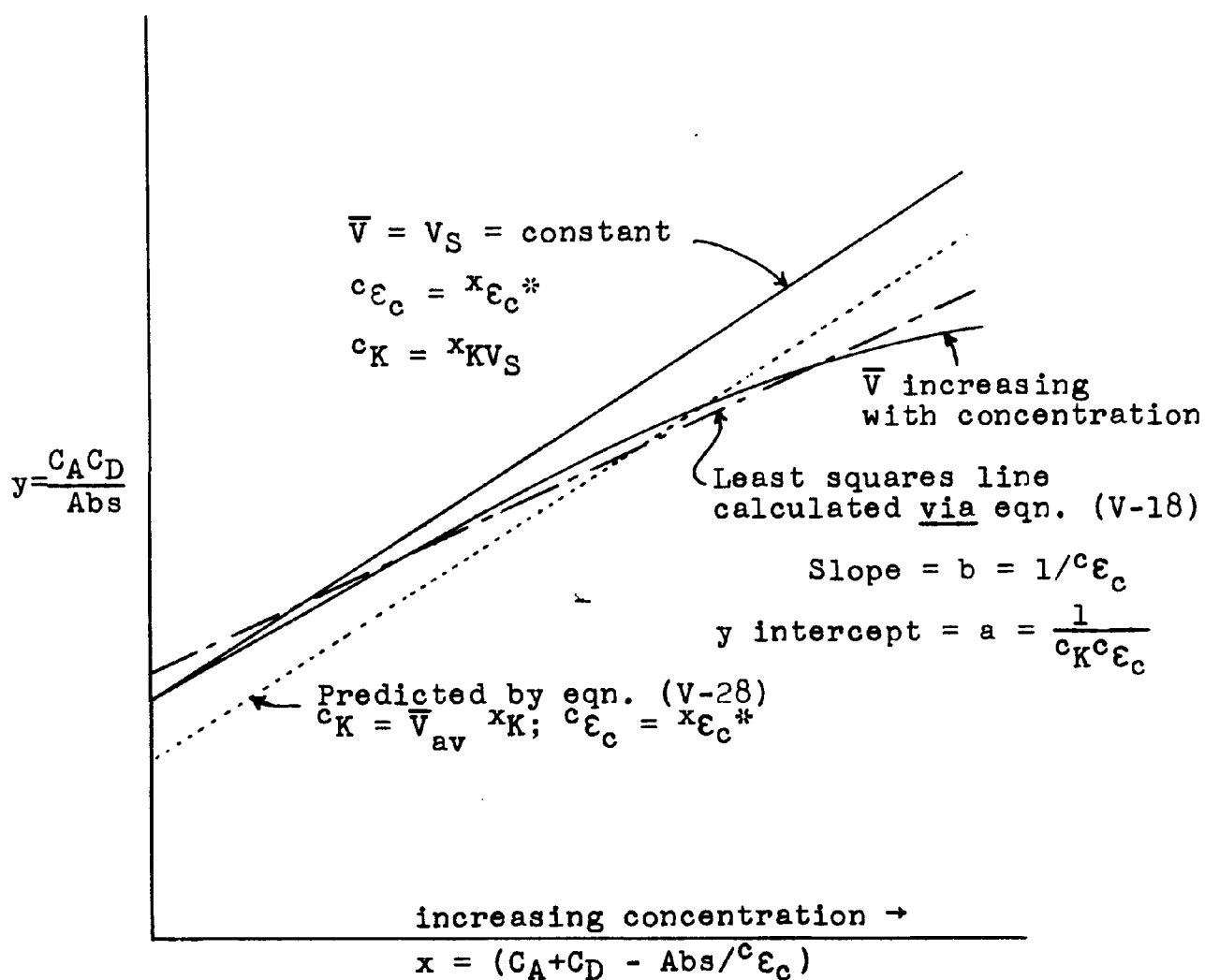
$$c_K = x_K \bar{V} \quad (V-23)$$

Consequently, a plot of equation (V-18) can be expected to show curvature to a degree depending on the variation of $\bar{V}$ with concentration. In the case of the data under discussion here $1/\bar{V}$ decreases with increasing concentration; therefore c_K should increase as the concentration of donor increases. The effect of such an increase in c_K on a plot of equation

(V-18) is shown schematically in Figure 34. For the case where $\bar{V}$ is a constant, $\bar{V} = V_S$ and a straight line is obtained whose slope gives a value of c_{ϵ_c} in agreement

Figure 34

Plot of Equation (V-18)
for the Case of $\bar{V}$ Increasing with Concentration



with $x_{\epsilon_c}^*$ as obtained from equation (V-26). If $\bar{V}$ increases with concentration a line falling below that for $\bar{V} = V_S$, and showing negative curvature (concave downward), is obtained. This is in agreement with the behavior predicted by equation (V-28), that $c_K = x_K \bar{V}_{av}$, provided that c_{ϵ_c} is held constant at $c_{\epsilon_c} = x_{\epsilon_c}^*$. This last condition is equivalent to imposing the constraint that the least squares line fitted to the data be parallel to the straight line obtained when $\bar{V} = V_S$; the line obeying this condition is indicated by the dotted line in Figure 34. The least squares line actually calculated by fitting the data to equation (V-18), indicated by the dashed line in Figure 34, is not subject to this constraint, however, and both c_K^* and $c_{\epsilon_c}^*$ change simultaneously as $\bar{V}$ changes from $\bar{V} = V_S$. The effect of this simultaneous change, as can be seen from the slope and intercept of the dashed line, is as follows: the value of $c_{\epsilon_c}^*$ obtained from equation (V-18) is greater than $x_{\epsilon_c}^*$ and increases the more rapidly $\bar{V}$ increases with concentration. Also, since both the y intercept and $c_{\epsilon_c}^*$ increase, c_K^* as given by equation (V-18) must decrease below the value $c_K^* = x_K^* V_S$ which would hold if $\bar{V}$ were constant. In other words, if $\bar{V}$ increases with concentration, the values $c_{\epsilon_c}^*$ and c_K^* obtained from a least squares fit to equation (V-18) obey the inequalities $c_{\epsilon_c}^* > x_{\epsilon_c}^*$ and $c_K^* < x_K^* V_S$, where $x_{\epsilon_c}^*$ and x_K^* denote values obtained from a least squares fit to equation (V-26). This is just the behavior shown by the results obtained in Part D.

It should be emphasized that the apparent violation of equations (V-23) and (V-28) is a consequence of the fact that both c_K^* and $c_{\epsilon_c}^*$ change with concentration; if $c_{\epsilon_c}^*$ were held constant at $c_{\epsilon_c}^* = x_{\epsilon_c}^*$ equations (V-23) and (V-28) would be obeyed.

The above argument has established that a plot of equation (V-18) for the systems under consideration should show negative curvature from the increase of $\bar{V}$ with concentration. It was pointed out in Part D that both the data for c_K^* and x_K^* , plotted according to equations (V-18) and (V-26) respectively, show a slight negative curvature. In the case of x_K^* this curvature should be due only to non-ideality effects, while in the case of c_K^* there should be contributions from both non-ideality and change in $\bar{V}$ with concentration. It will be shown below in the discussion on non-ideal behavior that the degree of departure from ideality is the same for both molar concentration and mole fraction units; consequently the negative curvature exhibited by the data for c_K^* should be greater than that for x_K^* .

Two measures of the degree of curvature suggest themselves:

1. The relative uncertainties in the least squares values K^* and ϵ_c^* .
2. Some appropriate function of the observed deviations in y . It is convenient to define the relative curvature

(R.C.) as

$$\text{R.C.} = \frac{|\delta_a|}{y_a} + \frac{|\delta_b|}{y_b} + \frac{|\delta_c|}{y_c} \quad (\text{V-35})$$

where δ_a , δ_b , and δ_c are the maximum -, +, and - deviations, respectively, over the portion of the curve showing a smooth curvature.

Of these two criteria, number 2 seems to be the more appropriate since number 1 measures random deviations as well as those showing a smoothly varying behavior. The first criterion applied to the TCNE-N complex data indicates that the fit to equation (V-26) is better than to equation (V-18); relative uncertainties in x_K^* and $x_{\epsilon_c}^*$ are uniformly significantly less than those in c_K^* and $c_{\epsilon_c}^*$. The uncertainties for the TCNE-2,6-DMN complex, however, are all of comparable magnitude and no clear distinction as to the better fit can be made. According to the second criterion, the relative curvatures for all data, both TCNE-N and TCNE-2,6-DMN complexes, are about the same for both equations; however, for TCNE-N there appears to be a slight bit more curvature in the case of equation (V-18). It can be concluded that the curvatures in plots for c_K^* and x_K^* are very nearly the same, except that in the case of TCNE-N there may be somewhat more curvature in the plot for c_K^* .

The fact that there is only a slight curvature in the plot for c_K^* due to the change in $\bar{V}$ is somewhat surprising, in view of the fact that $1/\bar{V}$ varies by as much as 10% over

the range of concentrations studied. This behavior implies that there is an essentially linear relationship between $1/\bar{V}$ and the value of the abscissa in Figure 34, $x = (C_A + C_D - \text{Abs}/^c\epsilon_c)$. That is

$$1/\bar{V} = -kx + k' \quad (\text{V-36})$$

Plots of $1/\bar{V}$ vs. x for the various sets of data confirm this linearity; a typical plot, for the data of Run 14 on TCNE-N, is shown in Figure 35. Since $1/\bar{V} = (C_S + C_A + C_D - \text{Abs}/^x\epsilon_c)$ it is apparent that the y intercept, k' , should be identical with $1/V_S$. Denoting this extrapolated value for the molar volume of the solvent as V_S' , equation (V-36) becomes

$$1/\bar{V} = -kx + 1/V_S' \quad (\text{V-37})$$

This equation allows the derivation of some interesting relationships between $^xK^*$ and ^cK , the value of ^cK at infinite dilution.

Equation (V-18) can be written as

$$y = \frac{1}{^c\epsilon_c} x + \frac{1}{^cK^c\epsilon_c} \quad (\text{V-38})$$

^cK can be replaced by $^xK\bar{V}$ provided that $^c\epsilon_c = ^x\epsilon_c = ^\infty\epsilon_c$, where $^\infty\epsilon_c$ is the value of $^c\epsilon_c$ (ordinarily a function of concentration) at infinite dilution. Equation (V-38) then becomes

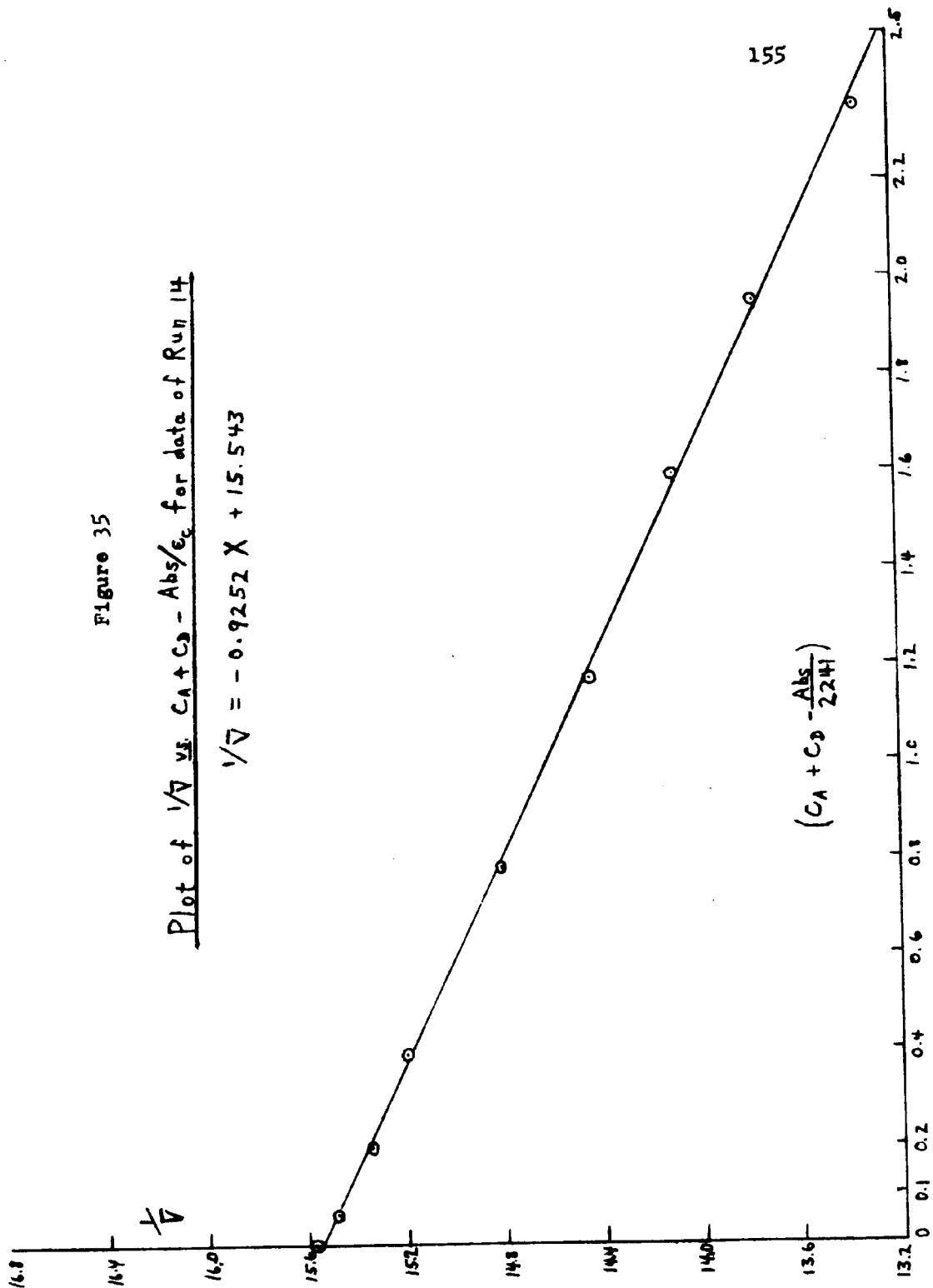
$$y = \frac{1}{^\infty\epsilon_c} x + \frac{1}{^xK\bar{V}^\infty\epsilon_c} \quad (\text{V-39})$$

Substituting for $1/\bar{V}$ from (V-37) and rearranging gives

Figure 35

Plot of $1/\bar{V}$ vs. $C_A + C_B - \text{Abs}/e_c$ for data of Run 14

$$1/\bar{V} = -0.9252 X + 15.543$$



$$y = \left[\frac{x_{K-k}}{x_K \omega_{\epsilon_c}} \right] x + \frac{1}{x_{KV_S'} \omega_{\epsilon_c}} \quad (V-40)$$

It can thus be seen that the values $\omega_{\epsilon_c}^*$ and c_K^* obtained from a least squares fit to equation (V-18) are, to a good approximation, given by

$$\omega_{\epsilon_c}^* \cong \omega_{\epsilon_c} \left[\frac{x_K}{x_{K-k}} \right]; \quad c_K^* \cong v_{S'} x_K \left[\frac{x_{K-k}}{x_K} \right] \quad (V-41)$$

These expressions are not exact because of the fact that in equations (V-18) and (V-37) x is given by $(C_A + C_D - \text{Abs}/\omega_{\epsilon_c})$ while in (V-39) $x = (C_A + C_D - \text{Abs}/\omega_{\epsilon_c})$; however, the numerical differences between these expressions are usually negligible. Now, for ideal solutions, x_K can be replaced by x_K^* and $v_{S'} x_K \cong v_S x_K = \omega_K$. Substitution in (V-41) then gives the following expressions for $\omega_K^\dagger$ and $\omega_{\epsilon_c}^\dagger$

$$\omega_K^\dagger \cong c_K^* \left[\frac{x_K^*}{x_{K-k}^*} \right] \quad (V-42)$$

$$\omega_{\epsilon_c}^\dagger \cong \omega_{\epsilon_c}^* \left[\frac{x_K^* - k}{x_K^*} \right] \quad (V-43)$$

where the dagger is used to distinguish the values of ω_K and ω_{ϵ_c} given by (V-42) and (V-43) from those given by other expressions below. Equations (V-42) and (V-43) allow calculation of ω_K and ω_{ϵ_c} at infinite dilution from the values c_K^* , x_K^* and $\omega_{\epsilon_c}^*$ obtained from a least squares fit to equations (V-18) and (V-26), together with k , which is obtained from a plot of $1/\bar{V} = (C_S + C_A + C_D - \text{Abs}/x_{\epsilon_c})$ vs. $(C_A + C_D - \text{Abs}/\omega_{\epsilon_c})$. It should be pointed out that ω_K does obey the thermodynamic

equation ${}^cK = x_{KV_S}$ which Scott notes should hold at infinite dilution, and that ${}^c\epsilon_c = x_{\epsilon_c}$.

Equations (V-42) and (V-43) explain the regularities previously noted (Part D) between x_{K^*} and the ratios ${}^c\epsilon_c^*/x_{\epsilon_c}^*$ and $x_{K^*}V_S/c_{K^*}$. Although (V-42) and (V-43) are derived for systems exhibiting ideal behavior, the complexes under discussion show only a slight curvature in their data for x_K , so that they can be treated as ideal, to a first approximation. If it is noted that for ideal solutions ${}^c\epsilon_c = x_{\epsilon_c}^*$ and ${}^cK = x_{K^*}V_S$, equations (V-42) and (V-43) rearrange to

$$\frac{x_{K^*}V_S}{c_{K^*}} \approx \frac{x_{K^*}}{x_{K^*-k}} \quad (V-44)$$

$$\frac{{}^c\epsilon_c^*}{x_{\epsilon_c}^*} \approx \frac{x_{K^*}}{x_{K^*-k}} \quad (V-45)$$

These expressions account for the essentially identical values of $x_{K^*}V_S/c_{K^*}$ and ${}^c\epsilon_c^*/x_{\epsilon_c}^*$ noted previously. Also, since k does not vary appreciably for the complexes studied, these expressions explain the regular variation of $x_{K^*}V_S/c_{K^*}$ and ${}^c\epsilon_c^*/x_{\epsilon_c}^*$ with x_{K^*} and the approach of these ratios to a limiting value of unity as the stability of the complex increases.

In addition to equation (V-42) above, two other expressions can be used to obtain ${}^cK$. From (V-42) and (V-43),

$${}^c\epsilon_c^{\dagger} {}^cK^{\dagger} \approx {}^c\epsilon_c^* c_{K^*} \quad (V-46)$$

Now, for ideal solutions, ${}^c\epsilon_c = x_{\epsilon_c}$, so that (V-46) becomes

$${}^cK^{\dagger} \approx \frac{{}^c\epsilon_c^* c_{K^*}}{x_{\epsilon_c}^*} \quad (V-47)$$

Finally, c_K can be calculated directly from

$$c_K^{\S} = x_K^* v_S \quad (V-48)$$

The superscripts † , * and § have been used to distinguish values of c_K obtained from equations (V-42), (V-47) and (V-48), respectively. It should be noted that (V-42) and (V-46) are obtained on the basis of a linear relationship between $1/\bar{V}$ and $x = (C_A + C_D - \text{Abs}/c_{\mathcal{E}_C})$, while for equation (V-48) this assumption is not required.

Although the complexes under discussion here do not show strictly ideal behavior, it is interesting to compare the results obtained from equations (V-42), (V-43), (V-47) and (V-48). Values of k and $1/V_S'$ obtained from equation (V-37), together with values of $1/V_S$ calculated from literature data [29] are given in Table 24. Agreement between $1/V_S'$ and $1/V_S$, although not always exact, is well within 1%. A comparison of $x_{\mathcal{E}_C}^*$ and $c_{\mathcal{E}_C}^{\dagger}$, as calculated from equation (V-43), is given in Table 25; the agreement is quite good (within 0.3%). Values of $c_K^{\dagger}$, c_K^* and $c_K^{\S}$ are listed in Table 26; again the agreement is well within 1% (in the case of $c_K^{\S}$, V_S' was used in place of V_S in the calculation). It is apparent from these results that the discrepancies noted by Scott between c_K^* and $x_K^* v_S$ and between $c_{\mathcal{E}_C}^*$ and $x_{\mathcal{E}_C}^*$ can be accounted for when the change in $\bar{V}$ with concentration is taken into consideration.

It is instructive to consider further the significance of k in equation (V-37). If the terms in C_A and $\text{Abs}/\mathcal{E}_C$ are ignored, (V-37) can be written

TABLE 24

Values of k and $1/V_S'$ from Equation (V-37)
and Literature Values of $1/V_S$

<u>Complex</u>	<u>Run No.</u>	<u>Temp.</u>	<u>No. of Points</u>	<u>k</u>	<u>$1/V_S'$</u>	<u>$1/V_S$</u>
TCNE-N	15	30.00	8	0.9145	15.40	15.40
	14	21.80	8	0.9252	15.54	15.57
	16	11.50	8	0.9200	15.72	15.80
	17	0.72	8	0.9360	15.94	16.04
TCNE-2,6-DMN	19	30.00	8	1.479	15.40	15.40
	18	21.80	8	1.466	15.57	15.57
	20	0.68	6	1.542	16.02	16.04
TCNE-1-MN		21.80	2	1.134	15.52	15.57
TCNE-2-MN		21.80	2	1.198	15.58	15.57
TCNE-1,6-DMN		21.80	2	1.378	15.54	15.57
TCNE-2,3-DMN		21.80	2	1.400	15.56	15.57

TABLE 25

Comparison of $x_{\epsilon_c}^*$ and $c_{\epsilon_c}^{\dagger}$

Complex	Run No.	No. of Points	$x_{\epsilon_c}^*$ (λ_1)	$c_{\epsilon_c}^{\dagger}$ (λ_1)	$x_{\epsilon_c}^*$ (λ_2)	$c_{\epsilon_c}^{\dagger}$ (λ_2)
TCNE-N	15	8	2181	2181	1957	1957
		6	2135	2134	1919	1919
	14	8	2241	2239	1985	1984
		6	2190	2189	1949	1948
	16	8	2284	2284	2033	2034
		6	2285	2282	2040	2037
	17	8	2279	2277	1987	1985
		6	2212	2209	1935	1935
TCNE-2,6-DMN	19	6	2127	2123	1837	1833
	18	6	2134	2132	1833	1831
	20	6	2205	2199	1848	1844
TCNE-1-MN		2	1991	1993		
TCNE-2-MN		2	1926	1927		
TCNE-1,6-DMN		2	2194	2194		
TCNE-2,3-DMN		2	2152	2152		

TABLE 26

Complex	Run No.	No. of Points	Comparison of c_K^+ , c_K^+ , and c_K^s					
			c_K^+ (λ_1)	c_K^+ (λ_1)	c_K^s (λ_1) (1)	c_K^+ (λ_2)	c_K^+ (λ_2)	c_K^s (λ_2) (1)
TCNE-N	15	8	.3657	.3656	.3656	.3722	.3722	.3722
	6	6	.3753	.3752	.3753	.3812	.3811	.3812
14	8	8	.3978	.3973	.3970	.4062	.4059	.4057
	6	6	.4089	.4086	.4084	.4153	.4151	.4150
16	8	8	.4525	.4527	.4529	.4544	.4547	.4548
	6	6	.4530	.4525	.4526	.4533	.4528	.4529
17	8	8	.5346	.5341	.5339	.5398	.5393	.5392
	6	6	.5553	.5551	.5554	.5580	.5579	.5582
TCNE-2,6-DMN	19	6	1.124	1.121	1.120	1.157	1.155	1.153
	6	6	1.300	1.298	1.296	1.332	1.331	1.327
20	6	6	1.864	1.859	1.851	1.904	1.900	1.893
TCNE-1MN	2	2	.746	.747	.747			
TCNE-2-MN	2	2	.808	.808	.808			
TCNE-1,6-DMN	2	2	1.147	1.147	1.147			
TCNE-2,3-DMN	2	2	1.142	1.142	1.141			

(1) Calculated from $c_K^s = x_K^* v_s$

$$1/\bar{V} \cong C_S + C_D \cong -kC_D + 1/V_S' \quad (V-49)$$

If it is further assumed that in solutions of donor the molar volumes of solvent and donor are additive, C_S can be written as

$$C_S \cong 1/V_S - (V_D/V_S)C_D \quad (V-50)$$

where V_D is the molar volume of pure donor. k can now be identified as

$$k \cong \frac{V_D}{V_S} - 1 \quad (V-51)$$

It is apparent from (V-51) that k depends on the relative size of donor and solvent molecules and so is positive for aromatic hydrocarbon donors in solvents such as CCl_4 . If expression (V-51) for k is substituted into equations (V-42) and (V-43), equations (V-29) and (V-30), previously derived by Ogimachi, Andrews and Keefer [72], result. The latter equations can thus be considered as special cases of equations (V-42) and (V-43) respectively.

It should be emphasized that it is preferable that ^xK , rather than ^cK , be determined experimentally. Then, if desired, ^cK or ^cK (at any concentration) are given rigorously by $^cK = ^xK\bar{V}$. If ^cK is measured experimentally, ^xK and ^cK can be obtained from equations (V-29) and (V-42), but these are only approximations and depend on fulfillment of the linear relationship (V-37) and additivity of the volumes of solvent and donor. Also, $^x\epsilon_c$ gives the "true" value of ϵ_c and it is preferable that this be obtained directly rather than from the approximate relations (V-30) or (V-43).

The dependence of ϵ_K and ϵ_c on the magnitudes of x_K and k is of interest in regard to the failure of one of the predictions of the simplest form of Mulliken's charge-transfer theory. The Mulliken theory predicts [3,8,79] that if the complexes between a given acceptor and a series of similar donors have a common geometrical structure the intensity of the charge-transfer band will increase as the stability of the complex increases. Although this predicted relationship is sometimes approximately obeyed (e.g. for complexes of chloranil with methylated benzenes [80]), it has been pointed out [8-10,16,50,79,81,82] that the opposite behavior is usually observed, particularly for complexes of the methylated benzenes with I_2 [83,84] and ICl [72,83,85].

Several explanations of this apparent failure of the Mulliken theory have been advanced. The most attractive of these is the contact charge-transfer theory of Orgel and Mulliken [50] which attributes a large part of the intensity in the case of components which form weak complexes to absorption by random contact-pairs rather than stable complexes. Orgel and Mulliken's treatment incorporates an earlier suggestion by Evans [86] regarding the possibility of absorption by contact pairs, together with a consideration of the absorption by a whole ensemble of orientation isomers. An explanation in terms of the latter had been previously proposed by Murakami [87]. Murrell [9,81] has shown that large contributions to the charge-transfer intensity may be due to intensity borrowing (see, for example, Murrell [88]) from

transitions localized on the donor or acceptor molecules, provided that the symmetry of the complex or contact pair allows mixing between the charge-transfer and donor or acceptor excited states. The latter condition can be most readily fulfilled by weak complexes or contact pairs--hence these may be expected to show a greater charge-transfer intensity than strong complexes. Finally, Carter, Murrell and Rosch [82] have recently shown that if the complex and its components are assumed to have definite solvation shells a modification of the Benesi-Hildebrand equation allows calculation of new K and ϵ_c values such that ϵ_c is a linear function of K for a given series of complexes.

It is important when examining the relationship between complex stability and charge-transfer band intensity for a series of complexes that appropriate values of K and ϵ_c be used. Most writers [8-10,16,50,79,81,82] who have commented on the apparent failure of the predicted relationship have compared values of $^cK^*$ and $^c\epsilon_c^*$. However, as shown above, these quantities are not good thermodynamic constants; the quantities which should be compared, for ideal solutions, are $^xK^*$ and $^x\epsilon_c^*$ or ^c_cK and $^c_c\epsilon_c$. The error introduced by the use of $^cK^*$ and $^c\epsilon_c^*$ operates to magnify any disagreement with the predicted relationship; that is, as the complexes become weaker $^c\epsilon_c^*$ increasingly overestimates $^c_c\epsilon_c$ and $^cK^*$ increasingly underestimates ^c_cK , assuming that k remains constant. Actually, for the methylated benzenes, k decreases as $^xK^*$ decreases, so that the error is not as great as it would

be for a constant k . However, for cases where x_K^* is small and k large (e.g. iodine complexes with benzene derivatives having 3 or more bulky alkyl groups) considerable error can result; for the iodine complex of hexaethylbenzene, for example, $c_{\mathcal{E}_c}^*$ is almost 3 times $c_{\mathcal{E}_c}^\dagger$. It is not claimed here that use of c_K^* and $c_{\mathcal{E}_c}^*$ rather than x_K^* and $x_{\mathcal{E}_c}^*$ can completely account for the apparent failure of the predicted relationship between intensity and stability; however, c_K^* and $c_{\mathcal{E}_c}^*$ are not appropriate quantities for comparison with theory, and their use can contribute significantly to the disparity between predicted and experimentally observed behavior.

2. Non-Ideal Behavior

Since the solutions under study have been shown to exhibit non-ideal behavior, it is desirable to determine the initial slope and intercept of the data at infinite dilution; these should give the best approximations to the true thermodynamic values. The behavior of the ratio c_K/x_K as a function of concentration is also of interest, since as infinite dilution is approached, $\bar{V} \rightarrow V_S$, $c_K/x_K \rightarrow V_S$ and $x_{\mathcal{E}_c}$ and $c_{\mathcal{E}_c}$ should become identical. It is not possible to determine the initial slope graphically, since the deviations of the data from a straight line are small. It is possible, however, to solve analytically equations (V-18) and (V-26) for various pairs of data points as a function of concentration. The variation of c_K and x_K with concentration

proceeds smoothly at high and intermediate concentrations. However, at low concentrations, the data points show considerable scatter and fall on both sides of the least squares line; consequently such calculations become meaningless at low concentrations and as infinite dilution is approached. The results of a calculation of ^cK and ^xK as a function of concentration using the data of Run 12 (Table 11) taken pairwise is given in Table 27. It can be seen from this table that ^xK and ^cK increase with dilution and that $^xK/^cK$ and $^c\epsilon_c/^x\epsilon_c$ tend to change in the direction of their expected values at infinite dilution, 15.57 and 1, respectively. If data points for more dilute solutions (points 1-6) are used, ^xK and ^cK behave erratically and make a meaningful extrapolation to infinite dilution impossible. It is apparent, therefore, that for the data under discussion the true thermodynamic equilibrium constant can be obtained only if deviations from ideality are taken quantitatively into account.

TABLE 27

K and ϵ_c from the Data of Run 12 Taken Pairwise

<u>Data Points</u>	<u>C_A+C_D</u>	<u>$^c\epsilon_c$</u>	<u>$^x\epsilon_c$</u>	<u>^cK</u>	<u>^xK</u>	<u>$^xK/^cK$</u>	<u>$^c\epsilon_c/^x\epsilon_c$</u>
11,12	2.410	2859	2374	0.2946	5.521	18.74	1.204
10,11	1.852	2786	2310	0.3067	5.792	18.89	1.207
9,10	1.202	2424	2115	0.3731	6.619	17.74	1.147
8,9	.830	2460	2114	0.3657	6.622	18.11	1.164
7,8	.486	2356	2072	0.3850	6.788	17.63	1.138

Scott [53] and Liptay [69] have modified equations (V-5) and (V-6), and (V-19) and (V-20), respectively, to include activity coefficients and have given relations between the true thermodynamic values of K and ϵ_c and those calculated via equations (V-5), (V-6), (V-19) and (V-20). In order for these modified equations to be of any use, however, values of the activity coefficients or the absolute concentration of the complex must be determined by an independent method. Insofar as no practical method for doing this is at present available, there remains an important experimental uncertainty in K and ϵ_c . It would be possible, in principle, to write expressions for the activity coefficients in terms of polynomial expansion in the concentration variables. Then if the first two terms, say, in these expressions are retained, a total of 2×3 unknowns are added to the residual equations in addition to K and ϵ_c . If a sufficiently large number of experimental points are measured with very high precision an evaluation of all constants should be possible. In practice, however, such a calculation would be very laborious, and could probably not be justified on the basis of the precision of the data. It must be concluded, therefore, that the observed non-ideal behavior cannot be treated quantitatively. Several observations on the nature of the interactions leading to this non-ideal behavior can, however, be made. In the following discussion, non-ideality is first considered in a generalized, thermodynamic fashion; specific contributions to non-ideality are then treated separately.

Consider first the significance of x_K and c_K for solutions showing non-ideal behavior, and the relationship between them. The equilibrium constant written in terms of activities and measured in mole fraction units, x_{K_a} , is defined by

$$x_{K_a} \equiv \frac{x_{a_c}}{x_{a_A} \cdot x_{a_D}} = \frac{(X_c)_{eq.}}{(X_A)_{eq.} \cdot (X_D)_{eq.}} \cdot \frac{x_{\gamma_c}}{x_{\gamma_A} \cdot x_{\gamma_D}} = x_K \cdot x_{K_Y} = c_K \frac{1}{V} x_{K_Y} \quad (V-52)$$

and similarly

$$c_{K_a} \equiv \frac{c_{a_c}}{c_{a_A} \cdot c_{a_D}} = \frac{[C]}{[A][D]} \cdot \frac{c_{\gamma_c}}{c_{\gamma_A} \cdot c_{\gamma_D}} = c_K \cdot c_{K_Y} \quad (V-53)$$

Here x_{a_A} etc. and c_{a_A} etc. are the activities in mole fraction and molar concentration units of components A, etc.; x_{γ_A} etc. and c_{γ_A} etc. are the activity coefficients in mole fraction and molar concentration units of A etc., and x_{K_Y} and c_{K_Y} are defined by

$$x_{K_Y} \equiv \frac{x_{\gamma_c}}{x_{\gamma_A} \cdot x_{\gamma_D}} ; c_{K_Y} \equiv \frac{c_{\gamma_c}}{c_{\gamma_A} \cdot c_{\gamma_D}} \quad (V-54)$$

The activity coefficients are defined by

$$\lim_{\substack{x_i \rightarrow 0 \\ c_i \rightarrow 0}} x_{\gamma_i} = \lim_{\substack{x_i \rightarrow 0 \\ c_i \rightarrow 0}} c_{\gamma_i} = 1 \quad (V-55)$$

or, in other words, ideal behavior is measured in terms of adherence to Henry's law.

The relationship between x_{K_a} and c_{K_a} and between x_{γ_i} and c_{γ_i} can be chosen in either of two ways.

1. The relation between x_K and c_K can be preserved if we write

$$c_{K_A} = x_{K_A} \bar{V} \quad (V-56)$$

Then, from equations (V-52) and (V-53) we get

$$x_{K_Y} = c_{K_Y} \quad (V-57)$$

$$\text{and } x_{Y_i} = c_{Y_i} \quad (V-58)$$

In this case x_{K_A} is a true thermodynamic constant but c_{K_A} , as in the case of c_K , is not a constant but varies with $\bar{V}$.

2. We can force c_{K_A} to remain constant and determine the relationships between x_{K_A} and c_{K_A} and between x_{Y_i} and c_{Y_i} by the following argument (after Denbigh [89]).

The Gibbs free energies for complex formation in mole fraction and molar concentration units, respectively,

are

$$\Delta F^* = -RT \ln x_{K_A} = -RT \ln x_K \cdot x_{K_Y}$$

$$\Delta F^\diamond = -RT \ln c_{K_A} = -RT \ln c_K \cdot c_{K_Y}$$

combining

$$\Delta F^* - \Delta F^\diamond = RT \ln \frac{c_K \cdot c_{K_Y}}{x_K \cdot x_{K_Y}} \quad (V-59)$$

at infinite dilution,

$$c_{K_Y} = x_{K_Y} = 1$$

$$\text{and } c_K = \bar{V} x_K = V_S x_K$$

Equation (V-59) then becomes

$$\Delta F^* - \Delta F^\diamond = RT \ln V_S \quad (V-60)$$

Now, since $\Delta F^* - \Delta F^\diamond$ must be constant independent of concentration, (V-59) and (V-60) lead to

$$c_{K_A} = x_{K_A} V_S \quad (V-61)$$

and since

$$c_K = x_K \bar{V},$$

$$c_{K_Y} = \frac{V_S}{\bar{V}} x_{K_Y} \quad (V-62)$$

$$\text{or } c_{Y_i} = \frac{\bar{V}}{V_S} x_{Y_i} \quad (V-63)$$

Equations (V-62) and (V-63) are the analogues of equations (V-57) and (V-58) above and are the equations used by Liptay [68,69]. Although the choice between these two sets of expressions is a matter of personal preference, this writer prefers use of the former for the following reasons:

- (1) The relation between c_K and x_K for the case of ideal behavior is preserved.
- (2) It seems desirable that activity coefficients remain constant for any particular system and not be a function of the choice of concentration units.

The relationships between c_{K_a} and x_{K_a} deduced above help to clarify the role played by non-ideality in causing the discrepancies, first pointed out by Scott [53], between c_K and x_{KV_S} (and between $c_{\mathcal{E}_c}$ and $x_{\mathcal{E}_c}$). Scott, in his analysis, ascribed the inequality of c_K and x_{KV_S} to a concentration dependence of the equilibrium constants due to the effects on non-ideality, and did not consider separately the non-constancy of $\bar{V}$. It has already been shown (Part C) that for ideal solutions x_K will be a constant and c_K will vary in accord with $c_K = x_K \bar{V}$, so that in this case the inequality

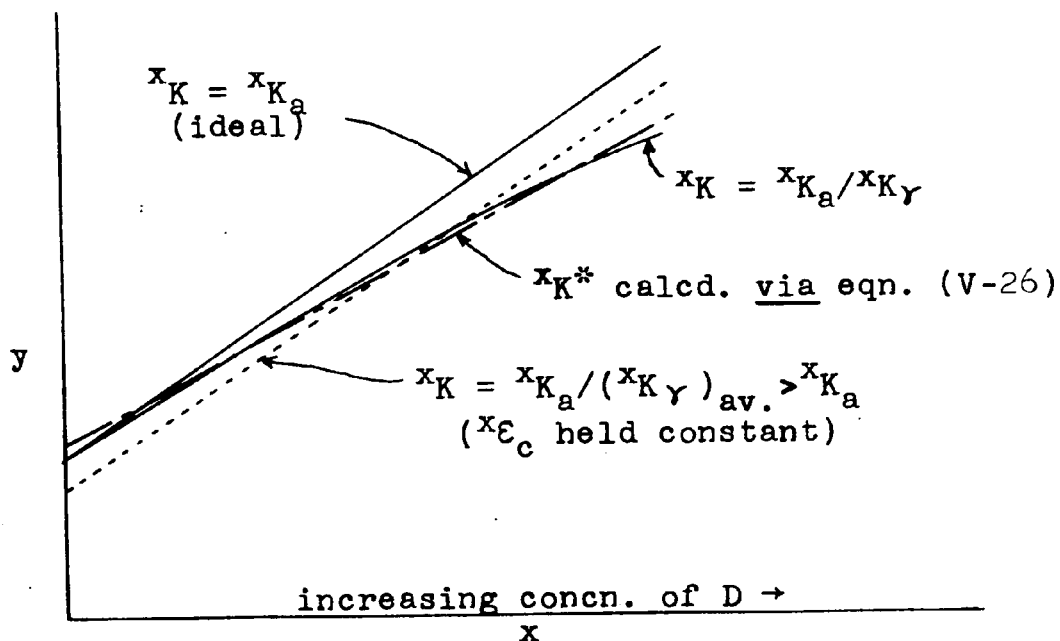
$c_K \neq x_{KV_S}$ is seen to be due to the variation with concentration of $\bar{V}$. For the non-ideal case, under choice 1 above the activity coefficients for both systems of concentration units are equal, so that again any discrepancy between c_K and x_{KV_S} must be due to the non-constancy of $\bar{V}$. On the other hand, choice 2 somewhat arbitrarily includes the variation of $\bar{V}$ in the relationship between c_{Y_1} and x_{Y_1} , so that the different concentration dependencies of c_K and x_K appear to be due to differing activity coefficients in the two systems of concentration units. Choice 2, in effect, establishes two different definitions of ideality, one for mole fraction units and another for molar concentrations, and it is only in this special sense that non-ideal behavior can be considered to account for the discrepancy between c_K and x_{KV_S} . It should be emphasized that if a consistent definition of ideality (e.g. Henry's law) is used for both systems of concentration units, non-ideal behavior plays no part in causing a discrepancy between c_K and x_{KV_S} , but that this discrepancy is due entirely to the non-linear relationship between mole fraction and molar concentration units.

We next consider how the activity coefficients Y_1 behave with increasing concentration of donor and the nature of the deviations from ideality responsible for this behavior. The relationships between K , K_a , and the calculated values K^* are shown, for the case of negative curvature of

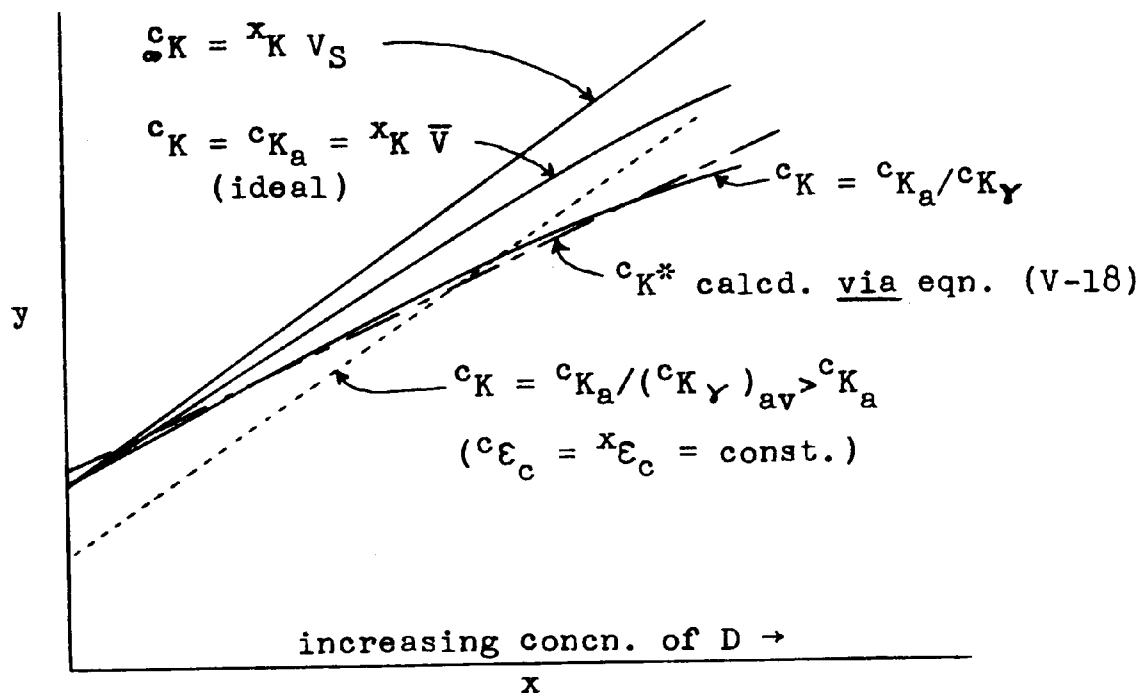
the data, in Figures 36(a) and (b). In these figures the dashed lines represent the least squares lines calculated via equations (V-18) and (V-26) and the dotted lines represent the lines which would be obtained if ϵ_c were held constant at its ideal solution value. It is apparent, since these dotted lines have y intercepts less than those of the lines representing ideal behavior, that negative curvature of the data corresponds to an increase of x_K and c_K with increasing concentration, and that x_{K_Y} and c_{K_Y} decrease with increasing concentration. The behavior of the individual activity coefficients is difficult to assess since the solutions studied are multicomponent systems in which the concentration of one of the components, C_D , varies considerably (X_D lies between 0.001 and 0.14). As a reasonable first approximation it may be assumed that γ_c is independent of concentration (or at least has the smallest concentration dependence), since in all solutions studied the concentration of complex was quite small (<0.001 M) and essentially constant. Consequently, the decrease in K_Y must be due to an increase in the product $\gamma_D \gamma_A$. Now, in the solutions studied, C_A decreased while C_D increased, so that either γ_D increases with increasing C_D , or γ_A increases with decreasing C_A , or both. Since an increase in γ with concentration corresponds to a negative deviation from Raoult's law, it can be seen that the observed negative curvature implies that D exhibits a negative deviation from Raoult's law, or that A exhibits a positive deviation, or both.

Figure 36

Relationship between K_a and K^*



(a) Plot of equation (V-26)



(b) Plot of equation (V-18)

An estimate of any departure from ideal behavior by solutions of naphthalene or TCNE in CH_2Cl_2 can be obtained from a consideration of the solubilities of these substances. Their ideal solubilities can be calculated by means of the following relation (see, for example, Denbigh [90])

$$\log X_2 = \frac{\Delta H_f}{2.303R} \left[\frac{1}{T_M} - \frac{1}{T} \right] \quad (\text{V-64})$$

where ΔH_f is the heat of fusion of component 2 (solute), T_M is its melting point and T is the temperature of its saturated solution. For naphthalene, taking $\Delta H_f = 4440 \text{ cal mole}^{-1}$ [91] and $T_M = 273.2 + 80.2 \text{ }^\circ\text{K}$, the ideal solubilities given in Table 28 are obtained. The measured solubilities listed in Table 28 indicate that naphthalene in CCl_4 exhibits a positive deviation from Raoult's law, while solutions in CHCl_3 and CH_2Cl_2 show negative deviations. In the case of TCNE, ΔH_f is not known, but $1/2 \Delta H$ (sublimation) can serve as an upper bound. Taking $\Delta H \text{ sub.} = 18,650 \text{ cal mole}^{-1}$ [95] and $T_M = 273.2 + 199.0$, a lower bound to the ideal solubility of TCNE at 21.8°C is $X_2 (\text{ideal}) = 0.0329$. The measured

TABLE 28

Ideal and Measured Solubilities of Naphthalene

<u>Temp.</u>	<u>X_2 (ideal)</u>	<u>X_2 (CCl_4)</u>	<u>X_2 (CHCl_3)</u>	<u>X_2 (CH_2Cl_2)</u>
0.7°C	0.160			>0.170
20.0	0.273	0.231 [92] 0.205 [93]	0.302 [92] 0.295 [94]	
21.8	0.286			>0.248 and <0.331
25.0	0.310	0.264 [92]	0.335 [94]	

solubility of TCNE in CH_2Cl_2 is $<0.1 \text{ M}$ or $X_2 < 0.00637$; thus TCNE apparently shows a marked positive deviation from Raoult's law.

It is generally believed that positive deviations from Raoult's law in two component systems can be attributed to differences in internal pressure, polarity, or molecular size of the components, or to self-association of one of them, whereas negative deviations imply association of one component with the other. These considerations indicate that positive deviations are usually to be expected and that negative deviations will occur only when the degree of association between the two components is large enough to override the contributions toward positive deviation due to differences in polarity, etc. The solubility of naphthalene in CH_2Cl_2 thus indicates a fairly strong association between these molecules. Since the concentrations of A and complex are usually small in comparison with D, it seems reasonable that in the solutions studied D should show a negative deviation from Raoult's law; this is in accord with the behavior of γ_D inferred from the curvature in plots of equations (V-18) and (V-26). The behavior of γ_A and γ_C is less certain. Although TCNE in pure CH_2Cl_2 shows a strong positive deviation, complex formation with D, which is present in rather high concentration in the solutions studied, would tend to cause a negative deviation. In the case of the complex, its somewhat polar nature would tend to make its solubility greatest in pure CH_2Cl_2 ; γ_C would therefore increase

with concentration of D. On the other hand, if there were a tendency toward formation of higher order complexes (e.g. AD_2), the solubility of complex would increase with concentration of D and γ_C would decrease.

It can be concluded from the foregoing that association between solvent and donor plays an important role in causing the observed curvature in plots of equations (V-18) and (V-26). A positive deviation from Raoult's law by solutions of TCNE, or formation of complexes involving two molecules of donor, may also contribute toward this behavior, but the importance of these effects is uncertain.

The preceding discussion has considered non-ideality in a general, thermodynamic sense. It is instructive, however, to consider separately the several specific interactions which might be expected to contribute to non-ideal behavior; according to this point of view the observed non-linearity in the data may be due simply to the fact that one or more important competing equilibria have been ignored. The specific effects which might be important in causing non-linearity can be listed as follows:

- a) In the case of evaluation of ^cK (equation (V-18)), the non-constancy of $\bar{V}$.
- b) A multiplicity of 1:1 complexes and/or 1:1 contact charge-transfer pairs formed between D and A.
- c) Complexing between solvent and A (or D).

- d) Self-complex formation between molecules of D (or, less likely, A).
- e) Formation of higher order complexes between D and A (e.g. AD_2).
- f) van der Waals forces (dipole forces, dispersion forces), which are responsible for non-ideal behavior in solutions where no other specific interactions exist.

Possibility a) above has previously been shown to be of minor importance for the data under discussion. Possibility f) serves as a catch-all since van der Waals forces can be invoked to explain any effects which cannot be rationalized by the other possibilities. The effects to be expected from possibilities b) through e) are discussed below.

b) Multiple 1:1 Complexes and/or Contact Pairs

The effect of the presence of multiple 1:1 complexes and/or contact pairs on the Benesi-Hildebrand method for determining K and ϵ_c was thoroughly discussed by Orgel and Mulliken [50] and is summarized in Part A. They showed that equations formally identical with the Benesi-Hildebrand equations ((V-2) and (V-4)) can be derived for the most general case--presence of both 1:1 complexes and contact pairs. In view of this fact, a Benesi-Hildebrand plot would retain its linearity under these circumstances even though the significance of K and ϵ_c would be somewhat different than in the case of a single 1:1 complex. A derivation analogous to that of Orgel and Mulliken can be given (Appendix II) to show that

the rigorously correct equations (V-18) and (V-26) also retain their form when multiple complexes and contact pairs are present. These become

$$\frac{C_A C_D}{\text{Abs}} = \frac{1}{\epsilon_c''} (C_A + C_D - \frac{\text{Abs}}{c \epsilon_c''}) + \frac{1}{c_{K'} \epsilon_c''} \quad (\text{V-18}')$$

$$\text{and } \frac{C_A C_D}{\text{Abs}} \bar{V}' = \frac{\bar{V}'}{\epsilon_c''} (C_A + C_D - \frac{\text{Abs}}{x \epsilon_c''}) + \frac{1}{x_{K'} \epsilon_c''} \quad (\text{V-26}')$$

$$\text{where } c_{K'} = \sum c_{K_i}; \quad x_{K'} = \sum x_{K_i}; \quad \bar{V}' = 1/(C_S + C_A + C_D - \frac{\text{Abs}}{\epsilon_c''}) \quad (\text{V-65})$$

$$\epsilon_c'' = \frac{1}{c_{K'}} (c_a \bar{\epsilon}_{DA} + \sum c_{K_i} \epsilon_{c_i}) = \frac{1}{x_{K'}} (x_a \bar{\epsilon}_{DA} + \sum x_{K_i} \epsilon_{c_i}). \quad (\text{V-66})$$

If there is no contribution from contact charge-transfer absorption, ϵ_c'' can be replaced by ϵ_c' , given by

$$\epsilon_c' = \frac{\sum x_{K_i} \epsilon_{c_i}}{x_{K'}} = \frac{\sum c_{K_i} \epsilon_{c_i}}{c_{K'}}.$$

Again, the presence of more than one 1:1 complex (or contact C-T pair) will have no effect on the linearities of equations (V-18) and (V-26) although the significance of K and ϵ_c is changed. As pointed out by Orgel and Mulliken, $c_{K'}$ and $x_{K'}$ are total equilibrium constants and as such are valid thermodynamic measures of the amount of 1:1 complexing taking place while, on the other hand, ϵ_c' and ϵ_c'' are weighted average extinction coefficients and cannot be compared directly with the predictions made by the Mulliken charge-transfer theory. It can be concluded that equations (V-18) and (V-26) cannot distinguish between the presence of one or many 1:1 complexes and/or contact C-T pairs.

c) Complexing between Solvent and A (or D).

It has been proposed by several authors [20,62] that complexes between solvent and acceptor may be important and can explain curvature in ^cK as a function of concentration. Tamres [62] has given an approximate expression for ^cK in the case of competition of the solvent for A. Rigorous expressions for both ^cK and ^xK for the general case of several 1:1 DA complexes and/or C-T pairs plus complex formation between solvent and A (or D) are derived in Appendix III-A.

These are

$$\frac{1}{^cK'} = \frac{1}{1 + ^cK_{SA}(C_S - [C_{SA}])} \left[\frac{C_A C_D}{Abs} \epsilon_c'' - C_A - C_D + \frac{Abs}{\epsilon_c''} \right] \quad (V-67)$$

$$\text{and } \frac{1}{^xK'} = \frac{1}{1/\bar{V}'' + ^xK_{SA}(C_S - [C_{SA}])} \left[\frac{C_A C_D}{Abs} \epsilon_c'' - C_A - C_D + \frac{Abs}{\epsilon_c''} \right] \quad (V-68)$$

$$\text{where } 1/\bar{V}'' = C_S + C_D + C_A - [C_{SA}] - \frac{Abs}{\epsilon_c''} \quad (V-69)$$

and $^cK'$, $^xK'$ and ϵ_c'' are given by equations (V-65) and (V-66).

Comparison with equations (V-18') and (V-26') reveals that (V-67) and (V-68) can be written as

$$^cK' = [1 + ^cK_{SA}(C_S - [C_{SA}])] ^cK' \quad (V-18') \quad (V-70)$$

$$\text{and } ^xK' = (\bar{V}'/\bar{V}'')[1 + ^cK_{SA}(C_S - [C_{SA}])] ^xK' \quad (V-26') \quad (V-71)$$

where $^cK'$ (V-18') and $^xK'$ (V-26') represent values of $^cK'$ and $^xK'$ given by equations (V-18') and (V-26'), respectively, when ϵ_c'' is held fixed at its "true" or infinite dilution value.

In view of the fact that for the data under consideration ($\bar{V}'/\bar{V}''$) is essentially constant and $[C_{SA}]$ is negligible compared to C_S , it is apparent that $^cK'$ (V-18') and $^xK'$ (V-26') increase with decrease in C_S (or with increase of C_D , since, in general, C_S decreases as C_D increases). This predicted behavior of $^cK'$ (V-18') and $^xK'$ (V-26') is in accord with that observed for both TCNE-N and TCNE-2,6-DMN and indicates that association of the solvent with either A or D may contribute to the observed behavior in these systems.

d) Self-Complex Formation Between Molecules of D (or A).

Rigorous expressions for ^cK and ^xK for the general case of several 1:1 DA complexes and/or C-T pairs plus a self-complex D_2 (or A_2) are derived in Appendix III-B. These are

$$\frac{1}{^cK'} = \frac{\left[\frac{C_A C_D}{Abs} \epsilon_c'' - C_A - C_D + \frac{Abs}{\epsilon_c''} \right]}{1 + 2 ^cK_{D_2} (C_D - [C]' - 2[D_2])} \quad (V-72)$$

$$\text{and } \frac{1}{^xK'} = \frac{\left[\frac{C_A C_D}{Abs} \epsilon_c'' - C_A - C_D + \frac{Abs}{\epsilon_c''} \right]}{1/\bar{V}''' + 2 ^xK_{D_2} (C_D - [C]' - 2[D_2])} \quad (V-73)$$

$$\text{where } 1/\bar{V}''' = C_S + C_D + C_A - [D_2] - \frac{Abs}{\epsilon_c''} \quad (V-74)$$

and $^cK'$, $^xK'$ and ϵ_c'' are given by equations (V-65) and (V-66). Equations (V-72) and (V-73) can be written as

$$^cK' = [1 + 2 ^cK_{D_2} (C_D - [C]' - 2[D_2])] ^cK' \text{ (V-18')} \quad (V-75)$$

$$\text{and } ^xK' = (\bar{V}'/\bar{V}''') [1 + 2 ^xK_{D_2} (C_D - [C]' - 2[D_2])] ^xK' \text{ (V-26')} \quad (V-76)$$

where c_K' (V-18') and x_K' (V-26') represent values of c_K' and x_K' given by equations (V-18') and (V-26'), respectively, when ϵ_c'' is held constant at its "true" or infinite dilution value. Since, for the data under discussion, $(\bar{V}'/\bar{V}'')$ is essentially constant and $([C]'-2[D_2])$ is negligible compared to C_D , it is apparent that c_K' (V-18') and x_K' (V-26') decrease as the concentration of donor, C_D , increases. For the case of an A_2 self complex c_K' (V-18') and x_K' (V-26') would be predicted to increase with increasing concentration of donor. The observed behavior is in accord with the latter prediction. It can be concluded, therefore, that formation of A_2 may be significant in the systems studied, while formation of D_2 is of minor importance.

e) Higher-Order Complexes

Rigorous expressions for c_K and x_K for the general case of several 1:1 DA complexes and/or contact C-T pairs plus a complex D_2A (or DA_2) are derived in Appendix III-C. These are

$$\frac{1}{c_K'} = \frac{\left[\frac{C_A C_D}{\text{Abs} \epsilon_c'''} - C_A - C_D + \frac{\text{Abs}}{\epsilon_c'''} \right]}{1 + c_{D_2A} [C]' \left[2 + \frac{(C_D - [C]')}{(C_A - [C]' - [D_2A])} \right]} \quad (\text{V-77})$$

$$\text{and } \frac{1}{x_K'} = \frac{\left[\frac{C_A C_D}{\text{Abs} \epsilon_c'''} - C_A - C_D + \frac{\text{Abs}}{\epsilon_c'''} \right]}{1/\bar{V}''' + x_{D_2A} [C]' \left[2 + \frac{(C_D - [C]')}{(C_A - [C]' - [D_2A])} \right]} \quad (\text{V-78})$$

$$\text{where } 1/\bar{V}''' = C_S + C_D + C_A - 2[D_2A] - \frac{\text{Abs}}{\epsilon_c'''} \quad (\text{V-79})$$

$$[C]' = \sum [C_i] = \frac{\text{Abs}}{\epsilon_c'''}$$

and $^cK'$ and $^xK'$ are given by equations (V-65) and (V-66).

ϵ_c''' is no longer a true constant, as was ϵ_c'' , but is a function of the concentration of donor, given by

$$\epsilon_c''' = \frac{1}{^cK'} [\bar{\epsilon}_{AD} ^c c_a + \sum \epsilon_{C_i} ^c K_i + \epsilon_{D_2A} ^c K'_{D_2A} [D] = \epsilon_c'' + \epsilon_{D_2A} ^c K'_{D_2A} [D] \quad (V-80)$$

In view of equations (V-18'), (V-26'), (V-77) and (V-78) can be written as

$$^cK' = \left\{ 1 + ^cK_{D_2A} [C]' \left[2 + \frac{(C_D - [C]')}{(C_A - [C]' - [D_2A])} \right] \right\} ^cK' (V-18') f[D] \quad (V-81)$$

and

$$^xK' = (\bar{V}' / \bar{V}''') \left\{ 1 + ^cK_{D_2A} [C]' \left[2 + \frac{(C_D - [C]')}{(C_A - [C]' - [D_2A])} \right] \right\} ^xK' (V-26') f[D] \quad (V-82)$$

where $^cK' (V-18')$ and $^xK' (V-26')$ represent values of $^cK'$ and $^xK'$ given by equations (V-18') and (V-26'), respectively, when ϵ_c'' is held constant at its "true" or infinite dilution value, and where $f[D]$ is given by

$$f[D] = \frac{\left[\frac{C_A C_D}{Abs} \epsilon_c'' - C_D - C_A + \frac{Abs}{\epsilon_c''} \right]}{\left[\frac{C_A C_D}{Abs} \epsilon_c''' - C_D - C_A + \frac{Abs}{\epsilon_c'''} \right]} .$$

The behavior of $^cK' (V-18')$ and $^xK' (V-26')$ with increase in C_D is not obvious in this case since the term in braces increases with C_D while, if $\epsilon_c''' > \epsilon_c''$, $f[D]$ decreases. The behavior of the product of these two terms depends strongly on the magnitude of ϵ_{D_2A} and somewhat less strongly on $^cK_{D_2A}$. Thus, if the data for a typical run (e.g. Run 14) are

examined, it is found that $^cK'$ (V-18') and $^xK'$ (V-26') decrease with increasing C_D for $\epsilon_{D_2A} < 0.1 \epsilon_c''$, while, for $\epsilon_{D_2A} > 0.3 \epsilon_c''$, $^cK'$ (V-18') and $^xK'$ (V-26') increase with increasing C_D (this result holds for $^cK_{D_2A}$ between 1 and 0.001). A similar analysis for the case of formation of a complex DA_2 indicates that $^cK'$ (V-18') and $^xK'$ (V-26') decrease with increasing C_D if $\epsilon_{DA_2} > 0.05 \epsilon_c''$. Any estimate of the relative magnitudes of ϵ_c'' and ϵ_{D_2A} (or ϵ_{DA_2}) at a given wavelength must be purely speculative, but it seems reasonable that if higher order complexes exist, their charge-transfer intensities would be comparable to those of 1:1 complexes, and lie in the same spectral region. Hence, it can be tentatively concluded that the observed increase in ^cK and ^xK with increasing C_D implies the possible presence of D_2A complexes.

The behavior of ^cK and ^xK (ϵ_c held constant) with increase in donor concentration, for each of the cases listed above, can be summarized as follows:

a)	Non-constancy of $\bar{V}$; ^cK increases, no effect on ^xK
b)	Multiple complexes and/or contact C-T pairs; no effect on $^cK, ^xK$
c)	Complexes with solvent
	SA; $^cK, ^xK$ increase
	SD; $^cK, ^xK$ increase
d)	Self-complex formation
	D_2 ; $^cK, ^xK$ decrease
	A_2 ; $^cK, ^xK$ increase
e)	Higher order complexes
	D_2A ; $^cK, ^xK$ increase
	DA_2 ; $^cK, ^xK$ decrease

- f) van der Waals forces; effect on ^cK , ^xK indeterminate, but excluding specific interactions, differences in van der Waals forces would be expected to result in a decrease in γ_1 with increase in concentration of component i (i.e. positive deviation from Raoult's law).

As pointed out previously, the contribution of a) to the negative curvature exhibited by the data is negligible. This curvature (i.e. increase of ^cK and ^xK with increase of C_D) must therefore be explained by some combination of van der Waals forces, competition of solvent for D and A, and formation of A_2 and D_2A species in the solutions studied. Of these, the effect of pure van der Waals forces is impossible to assess. Formation of a complex between solvent and donor, however, seems quite likely. In this regard, Anderson and Prausnitz [51] have reported weak charge-transfer complexes between CCl_4 and aromatics ($^cK = 0.009$ and 0.118 for benzene and mesitylene, respectively) while Reeves and Schneider [96] have reported complexes of $CHCl_3$ with benzene, toluene, and mesitylene. For the present case of CH_2Cl_2 and naphthalene, the negative deviation from Raoult's law for this system, discussed previously, indicates that association between these molecules is appreciable. Complex formation between solvent and acceptor is probably less important in the systems studied. Although Merrifield and Phillips [20] have estimated indirectly that ^xK for CH_2Cl_2 -TCNE = 0.21 , the rather large positive deviation from Raoult's law exhibited by this system indicates that any complexing is quite weak.

Formation of A_2 probably does not occur to any extent in the relatively concentrated solutions of donor, so that any contribution from this effect is unlikely.

Concerning formation of D_2A , the energy of formation of this species depends on the degree to which charge-transfer forces between D and A are saturated upon formation of DA. As pointed out by Orgel and Mulliken [50], the charge-transfer complexing ability of an acceptor molecule for a second favorably oriented partner should not be greatly diminished in weak 1:1 complexes, but should be sharply reduced as the 1:1 complex becomes more stable. Thus, curvature due to D_2A formation should be more important in the case of TCNE-N than for complexes of the methylated naphthalenes. The data show no significant difference in curvature between TCNE-N and TCNE-2,6-DMN. However, this fact cannot be taken as strong evidence against the presence of D_2A complexes, since the curvature is very slight in both cases. A more sensitive criterion for the presence of D_2A species is an increase in ϵ_c (*i.e.* ϵ_c'') with concentration of donor. An apparent change in ϵ_c is in fact observed, since the ratio $Abs(\lambda_2)/Abs(\lambda_1)$ decreases regularly with increase in C_D . This effect, however, is probably due to a solvent dependent change in the equilibrium constants concerned (see further discussion under Solvent Effects below). Although a clear-cut decision cannot be reached in regard to the relative importance of D_2A complexes in causing the observed curvature in the data, it is felt that this effect is probably second in importance compared to

association between donor and solvent, and that any contribution due to SA and A_2 complexes is probably insignificant.

The two effects which should lead to a decrease in ^cK and ^xK are not expected to be significant for the systems under discussion. The presence of D_2 complexes is improbable in view of the negative deviation from Raoult's law exhibited by the CH_2Cl_2 -naphthalene system. Complexes of type DA_2 are also unlikely to be of importance since the concentration of D is much larger than that of A in the region where the curvature is most pronounced.

It can be concluded that the specific interactions probably responsible for the observed increase in ^cK and ^xK are formation of solvent-donor complexes and, to a less certain extent, the presence of D_2A complexes. This conclusion agrees with that previously reached on the basis of a consideration of the change in activity coefficients with concentration of donor.

3. Solvent Effects: Dependence of λ_{max} and ϵ_c on Temperature, Pressure and Composition

The observed curvature in plots of equations (V-18) and (V-26) has been discussed above in terms of non-ideality and competing equilibria. It is apparent, however, that a variation in ϵ_c will also produce a non-linear plot; in particular, an increase in ϵ_c with increasing concentration of donor would give rise to a negative curvature, in agreement with the present results. It has been implicitly assumed, in the

preceding discussion and in the derivation of all equations for K and ϵ_c , that ϵ_c is a characteristic constant of the absorbing species and is independent of its concentration and of the composition of the solvent (i.e. Beer's law is obeyed). The validity of this assumption must be examined with some care in view of the slight but definite changes which occur in the absorption spectrum of the complex with changes in temperature or concentration of donor.

It can be seen from the data in Table 29 that the intensity of absorption at λ_1 increases with respect to that at λ_2 both as the concentration of donor increases and as the temperature decreases. In addition to this change in absorption intensity, slight shifts in wavelength of the absorption maxima, λ_1 and λ_2 , are observed--these show a blue shift with increasing concentration of donor (this is somewhat more pronounced for TCNE-2,6-DMN than for TCNE-N) and a red shift with decrease in temperature. Effects similar to these have been observed [97] upon increasing the external pressure on the system. It will be attempted, below, to rationalize these various effects within the framework of the Mulliken charge-transfer theory, and, concomitantly, to infer something about the nature of the absorbing species.

Consider first the factors which might cause a shift in λ_{max} .

1) General solvent shift. A number of theories have been advanced which attempt to predict the shift in wavelength of a purely electronic transition (i.e. the 0,0 band of a vibronic

TABLE 29

Concentration and Temperature Dependence of Absorption Maxima

<u>Soln. #</u> ⁽¹⁾	<u>TCNE-N</u>			
	<u>(Abs(λ_2)/Abs(λ_1))</u>			
	<u>30.00°C</u>	<u>21.80°C</u>	<u>11.50°C</u>	<u>0.72°C</u>
	<u>(Run #15)</u>	<u>(Run #14)</u>	<u>(Run #16)</u>	<u>(Run #17)</u>
1	0.913	0.903	0.896	0.877
2	0.912	0.903	0.891	0.879
3	0.911	0.902	0.892	0.879
4	0.910	0.903	0.891	0.879
5	0.910	0.899	0.894	0.877
6	0.907	0.898	0.893	0.877
7	0.905	0.894	0.891	0.873
8	0.906	0.896	0.892	0.876

<u>Soln. #</u> ⁽¹⁾	<u>TCNE-2,6-DMN</u>		
	<u>(Abs(λ_2)/Abs(λ_1))</u>		
	<u>30.00°C</u>	<u>21.80°C</u>	<u>0.68°C</u>
	<u>(Run #19)</u>	<u>(Run #18)</u>	<u>(Run #20)</u>
1	0.889	0.879	0.855
2	0.884	0.876	0.854
3	0.883	0.876	0.852
4	0.881	0.874	0.851
5	0.877	0.871	0.846
6	0.874	0.869	0.846
7	0.872	0.866	
8	0.872	0.866	

(1) Concentration of solute increases with increasing Soln. #.

band envelope), upon going from the vapor phase to solution, in terms of the continuum properties of the solvent. These have been reviewed recently by S. Basu [99]. Such theories, for example those of McRae [99] and Bakhshiev [100], treat the solvent shift as the sum of dispersive and electrostatic (permanent and induced dipole interaction) contributions and result in expressions for the shift in terms of the refractive index and dipole moment of the solvent. In the case of the molecular complexes being considered here, where absorption is accompanied by an increase in dipole moment, these theories predict [9,11,101,102] a red shift with increase in solvent polarity. It should be emphasized, however, that these expressions refer to the pure electronic transition and are not strictly applicable to λ_{max} of the charge-transfer absorption.

2) Franck-Condon effect. It is quite possible that the shapes of the potential energy curves of the ground and excited electronic states of a molecular complex may change somewhat as the properties of the solvent change, due to differences in the electrostatic interactions between solvent and solute. Such a change in shape of the potential energy curves would in turn, as a consequence of the Franck-Condon principle, lead to a redistribution of intensity within the band envelope, with the result that the Franck-Condon maximum (or λ_{max}) might shift with a change in solvent in a manner different from that of the 0,0 band.

3) Change in internal energetics of the complex. In the usual treatment of solvent effects it is assumed that the internal energies of the ground and excited states are constants characteristic of the molecule, and that they are subsequently modified by electrostatic interactions between the molecule and the solvent. In the case of charge-transfer complexes, however, the energy of the dative structure of the complex, which influences the energies of both the ground and excited states, is dependent to some extent on the dielectric constant of the medium. Thus the solvent influences the energy of the charge-transfer transition both by the usual electrostatic interaction between solvent and solute and by changing, to some degree, the nature of the absorbing species.

A change in polarity of the solvent can be seen to lead to a change in energetics of the complex as follows. The energy difference between the non-bonded and dative structures of the complex is given by (see Figure 1)

$$(W_1 - W_0) = I_D - E_A - \frac{e^2}{R_{eq.}} - W_0 \quad (V-83)$$

The third term in this expression represents the Coulombic energy of the ion-pair at its equilibrium separation and is a function of the polarity of the solvent (the dielectric constant ϵ of the medium enters the denominator). However, the ionization potential of the donor I_D and electron affinity of the acceptor E_A are also essentially Coulombic in nature, and the dielectric constant of the medium alters the magnitudes of these terms as well. The final term W_0 repre-

sents the van der Waals attraction energy between neutral D and A and can be considered to remain constant. The result, then, of an increase in solvent polarity would be an essentially proportional decrease in the first three terms and a net decrease in $(W_1 - W_0)$. This decrease in the energy separating the non-bonded and dative states leads to an increased resonance interaction between them and to a corresponding resonance stabilization of the ground state and destabilization of the excited states (cf. equations (I-3) and (I-4)). (It is assumed that H_{01} and S remain essentially constant so that the change in the energy denominator is the dominant term.) It is also apparent that the energy of the charge-transfer transition, given by

$$\begin{aligned} h\nu_{CT} &= (W_E - W_N) = (W_1 - W_0) + (R_E - R_N) \\ &= (W_1 - W_0) + \frac{\beta_0^2 + \beta_1^2}{(W_1 - W_0)} = (W_1 - W_0) + \frac{(H_{01} - SW_0)^2 + (H_{01} - SW_1)^2}{(W_1 - W_0)} \quad (V-84) \end{aligned}$$

will decrease with an increase in solvent polarity, provided that $(W_1 - W_0)^2 > [H_{01} - SW_0]^2 + [H_{01} - SW_1]^2$. The latter condition is almost certainly satisfied for the complexes under discussion here. It should be pointed out that the present analysis predicts a red shift with increasing solvent polarity, whereas Offen and Abidi [102], on the basis of similar considerations, predict a blue shift.

The factors which might be responsible for non-constancy of ϵ_c are as follows:

i) Dependence of the extinction coefficient on refractive index. In the case of a collection of simple oscillators in a vacuum the fraction of light absorbed depends only on the number of oscillators in the light path, and ϵ is therefore a true constant. (Strictly speaking, the oscillator strength f is constant while ϵ may vary due to Doppler and collisional broadening, but this broadening is normally small compared to the bandpass used in spectrophotometry so that for the purpose of the present discussion ϵ is not affected. Also, if very intense radiation is used, ϵ may vary with intensity due to saturation of the transition or to various non-linear optical effects (two photon absorption, etc.) but, again, this condition is not met with in ordinary spectrophotometry.) If the oscillators are immersed in a medium (solvent) whose refractive index is different from unity, f remains constant but ϵ depends on the magnitude of n . Chako [103] has shown that f numbers measured in solution should be corrected by a factor γ , the Lorentz-Lorenz correction.

Thus

$$f_i(\text{vac}) = \frac{2303m_e c}{\pi N e^2} \gamma \int \epsilon_i d\nu = 4.319 \times 10^{-9} \gamma \int \epsilon_i d\nu \quad (\text{V-85})$$

where

$$\gamma = \frac{9n_o}{(n_o^2 + 2)^2} < 1$$

and n_o is the refractive index of the solvent at the wavelength of the band maximum. If the band shape does not change, it is apparent that

$$\epsilon_\lambda(\text{vac}) = \epsilon_\lambda(\text{soln}) \gamma < \epsilon_\lambda(\text{soln}) \quad (\text{V-86})$$

which indicates that $\epsilon\lambda$ (soln) increases as n_0 increases. For the complexes under discussion here, equation (V-86) predicts that ϵ_c should increase as the concentration of donor increases or as the temperature decreases, and, since $n(\lambda_2)$ increases faster than $n(\lambda_1)$, that $\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)$ should increase both with increasing concentration of donor and with decreasing temperature. The observed behavior is just the opposite of this prediction, indicating that the effect of a change in refractive index is of minor importance in the systems studied.

ii) Franck-Condon effect. As pointed out above, a change in properties of the solvent can lead to a redistribution of intensity within the charge-transfer band envelope so that ϵ_c at a given wavelength may increase or decrease, depending on the detailed shapes of the potential energy curves of the ground and excited states. It should be noted that a change in shape of either potential energy curve implies a change in the manifold of vibrational states associated with it, so that the intrinsic intensity of the vibronic band will probably change as well.

iii) Change in internal energetics of the complex. A change in internal energetics can bring about a change in extinction coefficient of the complex in two distinct ways. The first involves a change in intrinsic intensity of the transition due to a change in the relative contribution of the dative structure to the ground and excited state wave-

functions of the complex, while the second involves an apparent change in ϵ_c due to a change in equilibrium constant, caused by a change in the resonance stabilization of the ground state.

a) Change in intrinsic intensity. The transition moment associated with a charge-transfer absorption band is given approximately [3] by

$$\begin{aligned}\mu_{EN} &= ea^*b(\bar{r}_D - \bar{r}_A) + (aa^* - bb^*)eS(\bar{r}_D - \bar{r}_{DA}) \\ &\approx e(\bar{r}_D - \bar{r}_A)[a^*b + 0.5S(aa^* - bb^*)]\end{aligned}\quad (V-87)$$

where e is the electronic charge; a, b, a^* and b^* are the coefficients of the wavefunctions of the pure non-bonded and dative structures of the complex entering into the ground and excited state wavefunctions of the complex (cf. equations (I-1) and (I-2)); $\bar{r}_D$ and $\bar{r}_A$ denote the average position of an electron in the donation and acceptation orbitals, ϕ_D and ϕ_A respectively, with respect to some convenient origin, while $\bar{r}_{DA}$ is the average position of an electron having a charge distribution of the form of the overlap of orbitals ϕ_D and ϕ_A , and S is the overlap integral between the non-bonded Ψ_0 and dative Ψ_1 wavefunctions of the complex. Of the two terms in equation (V-87) the first is by far the most important. It is apparent that any change in the relative contributions of Ψ_0 and Ψ_1 to the ground and excited state wavefunctions of the complex will result in a change in intensity of the charge-transfer band.

Consider the effect of an increase in dielectric constant of the solvent. The ground state wavefunction of the complex normally receives only a small contribution from the dative structure of the complex, i.e. the coefficient b is small. As the polarity of the solvent increases the dative structure is more and more stabilized and hence makes a larger contribution to the ground state wavefunction (b increases). It turns out that for the complexes considered here the increase in b is the most important change in the factors entering into equation (V-87), so that an increase in solvent polarity results in an increase in μ_{EN} (or ϵ_c). This result can be obtained in a more quantitative fashion as follows: According to the Mulliken charge-transfer theory [3] the coefficients a, b, a^* and b^* are connected by the following relations

$$a^2 + 2abS + b^2 = 1 \quad (V-88)$$

$$a^{*2} - 2a^*b^*S + b^{*2} = 1 \quad (V-89)$$

$$b/a \simeq - \frac{(H_{01} - SW_0)}{(W_1 - W_0)} \quad (V-90)$$

$$b^*/a^* \simeq - \frac{(H_{01} - W_1)}{(W_1 - W_0)} \quad (V-91)$$

from which all four coefficients can be evaluated provided W_0 , W_1 , H_{01} and S are known. Estimates of these quantities, for the case of TCNE-N complex in CCl_4 , have been calculated by Briegleb, Czekalla and Reuss [104,105]. Their values for the various parameters which describe the charge-transfer interaction are given in the second column of Table 30. The

TABLE 30

Parameters Describing the Charge-Transfer Interaction
Between TCNE and Naphthalene

	TCNE-N in <u>CCl₄ [104,105]</u>	<u>Effective Dielectric Constant Doubled</u>
$W_N = \Delta H$	-4.0 ⁽¹⁾	-6.35 ⁽¹⁾
W_O	-1.5	-1.5
R_N	-2.5	-4.85
W_E	40.6	24.7
W_1	36.0	18.0
R_E	4.6	6.75
$(W_E - W_N) = h\nu_{CT}$	44.6	31.0
$(W_1 - W_O)$	37.5	19.4
I_D	190.0	95.0
E_A	36.9	18.45
$e^2/R_{eq.}$	117.1	58.55
H_{O1}	-9.85	-9.85
S	0.1	0.1
$\beta_0 = (H_{O1} - SW_O)$	-9.7	-9.7
$\beta_1 = (H_{O1} - SW_1)$	-13.1	-11.45
$\gamma = R_N / \Delta H$	0.62	0.76
$\mu_{DA} \times 10^{18}$	1.28	
a	0.945	0.863
b	0.245	0.432
a^*	0.973	0.898
b^*	0.341	0.530
μ_{EN}	0.276 $e(\bar{r}_D - \bar{r}_A)$	0.413 $e(\bar{r}_D - \bar{r}_A)$

⁽¹⁾Energies are given in kcal mole⁻¹.

quantities in the third column have been calculated on the assumption that the effective dielectric constant of the medium has been doubled, thus halving the quantity $W_1 = I_D - E_A - e^2/R_{eq.}$. It has also been assumed that W_0 , S and H_{01} remain constant. The constancy of H_{01} is questionable, but it appears reasonable to suppose that any change in $(H_{01} - SW_0)$ will be less than the corresponding change in $(W_1 - W_0)$, so that the above results are qualitatively correct. The remaining energy terms in the third column (W_1 , W_N , W_E , R_N , R_E) were calculated by use of equations (I-3), (I-4) and (V-83), while a , b , a^* , b^* and μ_{EN} were calculated via equations (V-87)-(V-91). Although the results of these calculations cannot be interpreted as more than qualitatively correct, they provide a sufficient indication that an increase in solvent polarity should result in an increase in both complex stability and overall charge-transfer intensity.

b) Apparent change in ϵ_c due to a change in equilibrium constant. As can be seen from Table 30 an increase in solvent polarity results in an increased stabilization of the ground state and a corresponding increase in ΔH (ΔH is a negative quantity, indicating evolution of heat). Assuming that this change in ΔH is not due solely to a change in the entropy term $T\Delta S$ in the relation $\Delta H = \Delta F + T\Delta S$, it follows that as ΔH becomes more negative, ΔF does likewise. (A parallelism between changes in ΔH and ΔF has been observed for TCNE complexes of aromatics by Briegleb, Czekalla and Reuss [104].) In view of the relation $-\Delta F = RT \ln^x K$, this change

in ΔF in turn implies an increase in ^XK and, consequently, an increase in absorbance due to the complex, as the solvent polarity increases. This solvent dependent increase in absorbance may be considered to be an apparent increase in ϵ_c (i.e. if ^XK is assumed to remain constant). However, it is more properly regarded as a solvent dependent change in the equilibrium constant.

It should be noted here that an apparent dependence of ϵ_c on the composition of the solution may also be due to participation of the light absorbing species in some equilibrium which has not been taken into account, or to non-ideality effects in general. In particular, it has already been pointed out that if higher order complexes are present ϵ_c''' will vary with the composition of the solution. This behavior is also more properly considered as a concentration dependence of the equilibrium constant involved.

At this point it is appropriate to give some consideration to the nature of the species responsible for the double absorption bands. Orgel and Mulliken [50] have pointed out that, in general, absorption can originate from donor-acceptor pairs whose components may have a wide range of separations and orientations relative to each other, representing anything from a relatively stable complex to a statistical collision pair. The relative stabilities and absorption intensities of these complexes are determined, according to the orientation and overlap principle [3,8,79], by the symmetries

of the donor and acceptor MO's, and the extent of overlap between them. For the π - π complexes considered here, the most stable configuration is undoubtedly a sandwich structure, with the planes of donor and acceptor parallel to each other. The measured heats of formation ($2-3 \text{ kcal mole}^{-1}$, see Section VI) are several times the value of RT ($\sim 600 \text{ cal mole}^{-1}$), indicating that the complexes formed are relatively stable and implying that light absorption is due to a relatively small number of complexes having definite geometries rather than to a whole ensemble of random donor-acceptor pairs. It should be recognized, however, that molecules bound in even a stable complex may undergo comparatively large amplitude vibrations and torsional motions relative to each other, due to thermal buffeting by neighboring molecules; this effect is probably responsible for the broad, structureless appearance of charge-transfer bands.

In order to facilitate further discussion, consider the observed double-banded absorption to originate from one of the following three possibilities:

- (a) A single complex having only one electronic transition.
- (b) A single complex with two separate electronic transitions.
- (c) Two complexes, each with its own electronic transition.

These represent increasing degrees of generality in that the number of variables in terms of which the observed behavior can be described increases on going from (a) to (b) to (c); thus (a) involves only one ground and one excited state while (b) involves one ground and two excited states and (c) involves two ground states and two excited states.

The first possibility can be eliminated immediately since it cannot easily account for the large changes in $\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)$ observed with changes in temperature and pressure. At least one of the combining states would have to have a potential energy curve with two minima, each of which is affected differently by changes in temperature and pressure; changes in λ_{max} and $\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)$ might then become explicable in terms of changing Franck-Condon factors. A choice between the two remaining possibilities is somewhat more difficult to make. Although the possibility that both charge-transfer bands may arise from a single complex cannot be definitely excluded, the considerable amount of experimental evidence available regarding the TCNE-N complex [97, 102, 104, 106-110] points strongly toward the existence of two conformational isomers in this case. A discussion of the effects on the wavelengths and intensities of the charge-transfer bands of TCNE-N caused by changes in temperature, pressure and composition of the solution is given below, on the assumption that each of the two charge-transfer bands is due to a different conformational isomer.

In order to allow a simplified comparison between the two isomeric complexes and to permit semiquantitative calculations, it will be assumed that these complexes differ principally only in donor ionization potential, I_D . This is equivalent to the assumption that different donor MO's are involved in the charge-transfer interaction in each case

(see further discussion in Section VII). The quantities W_0 , E_A , $e^2/R_{eq.}$, S and H_{01} will be taken, as a first approximation, as equal in both cases.

Temperature Effects

The presently observed effects of a change in temperature on the charge-transfer spectra of TCNE-N and TCNE-2,6-DMN are as follows (cf. Table 29):

- (a) A slight red shift in the wavelengths of the absorption maxima, λ_1 and λ_2 , with decreasing temperature.
- (b) A decrease in the ratio $Abs(\lambda_2)/Abs(\lambda_1)$ with decreasing temperature.

The occurrence of these effects can be understood in terms of the possible contributing factors discussed above. In the case of the wavelength shift these factors are:

1) General solvent shift. Since the dielectric constant ϵ of the solvent increases with decreasing temperature, a general red shift is predicted.

2) Franck-Condon effect. The shapes of the ground and excited state potential energy curves are unknown, hence the contribution from this factor is uncertain.

3) Change in internal energetics of the complex. As previously discussed, an increase in solvent polarity should decrease the energy of the charge-transfer transition so that a red shift is to be expected.

The observed red shift is thus seen to be in accord with predicted behavior.

In the case of the intensity effect, the most important factor is undoubtedly the temperature dependent shift in the equilibrium of the complex formation reaction. Since the heats of formation of the complexes are negative quantities, the van't Hoff equation $-\Delta H = R \partial \ln x_K / \partial (1/T)$ indicates that x_K , and hence Abs, will increase as the temperature decreases. If two complexes are present, each having a different value of ΔH , the more stable complex will show a faster increase in Abs. The observed decrease in $\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)$ therefore indicates that the complex absorbing at λ_1 is the more stable of the two. This conclusion is in agreement with the prediction that the complex having the longest wavelength charge-transfer transition should be the most stable. This prediction follows from the fact that the ground state resonance energy R_N is approximately inversely proportional to the energy of the charge-transfer transition. Thus

$$\Delta H = W_N = W_0 + R_N$$

$$R_N = \frac{-\beta_0^2}{(W_1 - W_0)} \simeq \frac{-\beta_0^2}{(W_E - W_N)} = \frac{-\beta_0^2}{h\nu_{CT}}$$

so that if W_0 and β_0 can be regarded as approximately constant for a series of complexes, ΔH will become more negative as the charge-transfer band moves toward longer wavelengths.

The following factors may also affect the intensities:

i) Dependence of the extinction coefficient on refractive index. As discussed previously ϵ_c should increase with an increase in refractive index, and since $n(\lambda_2)$ increases faster than $n(\lambda_1)$, $\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)$ would be expected to increase. Since the observed behavior is contrary to this prediction, this factor must be of minor importance in the systems studied.

ii) Franck-Condon effect. Again, the relative importance of this effect is uncertain.

iii) Change in internal energetics of the complex.

a) Change in intrinsic intensity. As discussed above, an increase in solvent polarity should result in an increased intensity of the charge-transfer transition; it remains to be determined whether the increase in intensity will be greater at λ_1 or at λ_2 . The intensity of the charge-transfer transition is governed chiefly by the ratio of the MO coefficients a and b as given by equation (V-90). An increase in this ratio corresponds to an increase in intensity. If two complexes are present, they will have different values for the energies of their dative states, $W_1 = I_D - E_A - e^2/R_{eq.}$. Since all three terms determining W_1 are essentially Coulombic in nature, the relative decreases in W_1 brought about by an increase in dielectric constant will be the same for both complexes. The relative decrease in $(W_1 - W_0)$, however, will be

slightly greater for complex $\lambda_2^{(1)}$, due to the fact that for these complexes W_0 is a negative quantity (see Table 30). If β_0 and W_0 are considered to remain constant independent of the increase in dielectric constant, it is apparent that b/a will increase slightly faster for complex λ_2 and hence $\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)$ would be expected to increase. The effect of this factor is probably of minor importance, however, since the change in dielectric constant is small and because W_0 is small in comparison with W_1 .

iii b) Apparent change in ϵ_c due to a change in equilibrium constant. In addition to the shift in equilibrium due to the change in temperature, there will also be an increase in ^xK due to the increased ground state resonance energy of the complex brought about by the increase in solvent polarity. The ground state resonance energy R_N is given by equation

$$(V-92) \quad R_N \cong - \frac{\beta_0^2}{(W_1 - W_0)} = - \frac{(H_{01} - SW_0)^2}{(W_1 - W_0)} \quad (V-92)$$

By the same argument used in iii a) it follows that the relative increase in R_N is slightly faster for the complex absorbing at λ_2 . It is the absolute increase in R_N , however, which determines the behavior of the ratio $\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)$. From the relation $-\Delta F = RT \ln ^xK$ it follows that

$$\Delta F(\lambda_1) - \Delta F(\lambda_2) = RT \ln \frac{{}^xK(\lambda_2)}{{}^xK(\lambda_1)} = RT \frac{\text{Abs}(\lambda_2)/\epsilon_c(\lambda_2)}{\text{Abs}(\lambda_1)/\epsilon_c(\lambda_1)}$$

(1) "Complex λ_1 " and "complex λ_2 " are used as shorthand expressions for "the complex absorbing at λ_1 " and "the complex absorbing at λ_2 ", respectively.

If the ratio of the extinction coefficients can be assumed to remain constant, the last expression can be written

$$\Delta F(\lambda_1) - \Delta F(\lambda_2) = a RT \ln \frac{\text{Abs}(\lambda_2)}{\text{Abs}(\lambda_1)} \quad (\text{V-93})$$

If it is further assumed that the entropy change for complex formation and the van der Waals interaction energy W_0 are independent of the small change in dielectric constant, equation (V-93) becomes

$$\Delta F(\lambda_1) - \Delta F(\lambda_2) = \Delta H(\lambda_1) - \Delta H(\lambda_2) = R_N(\lambda_1) - R_N(\lambda_2) = aRT \ln \frac{\text{Abs}(\lambda_2)}{\text{Abs}(\lambda_1)} \quad (\text{V-94})$$

Bearing in mind that R_N is a negative quantity, this equation indicates that if the absolute increase in R_N is greatest for complex λ_1 , then $\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)$ should decrease with decreasing temperature, as observed. Although the relative increase in R_N should be slightly greater for complex λ_2 , the absolute increase is probably greatest for complex λ_1 because of the following:

(1) W_0 is small compared to W_1 ($W_0 \sim 0.05 W_1$) so that the relative decreases in $(W_1 - W_0)$ are very nearly the same for both complexes.

(2) $R_N(\lambda_1)$ is probably greater than $R_N(\lambda_2)$ by $\sim 30\%$ so that although the relative increases in R_N are about the same for both complexes, the largest absolute increase occurs for complex λ_1 . This is so because $(W_1 - W_0)_{\lambda_1}$ is less than $(W_1 - W_0)_{\lambda_2}$ ($(W_1 - W_0)_{\lambda_2} / (W_1 - W_0)_{\lambda_1} \approx h\nu_{CT}(\lambda_2) / h\nu_{CT}(\lambda_1) = 1.29$) while β_0 is nearly the same for both complexes.

(Actually $\beta_0(\lambda_2)$ is probably slightly less than $\beta_0(\lambda_1)$, which has the effect of increasing $R_N(\lambda_1)$ faster than $R_N(\lambda_2)$.) Thus this factor is expected to lead to a change in $\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)$ in agreement with that observed.

It can be concluded that the observed intensity effect arises principally from a temperature dependent shift in the complex formation equilibria, with a smaller contribution from iii b); i) and iii a) would give rise to the opposite effect and must therefore be considered of minor importance.

The temperature dependence of the TCNE-N spectrum has also been studied by Briegleb, Czekalla and Reuss [106,107]. These authors compared the spectra obtained at 20°C and -180°C in n-propyl ether and n-propyl ether/isopentane mixtures. In contrast to the present results, they found slight blue shifts in λ_1 and λ_2 and an increase in $\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)$ upon going to the lower temperature. They also studied the TCNE complexes of pyrene and 1,2-benzanthracene. Both of these complexes showed marked decreases in $\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)$ on going to -180°C; the pyrene complex showed blue shifts at λ_1 and λ_2 while the 1,2-benzanthracene complex showed a red shift at λ_1 .

The validity of Briegleb et al.'s results for TCNE-N can be questioned on the following grounds:

(1) Competitive complex formation between the solvent and TCNE. It is quite likely that formation of a TCNE-ether complex which absorbs in the neighborhood of λ_2 of TCNE-N has

some effect on Briegleb et al.'s results. Formation of a TCNE-diethyl ether complex ($^xK = 1.54$ in CHCl_3) with an absorption band at 3350 Å was reported by Merrified and Phillips [20]. Any interference due to the TCNE-ether charge-transfer band would be less serious in the case of the pyrene and 1,2-benzanthracene complexes since their first two charge-transfer bands lie considerably to the red of those of TCNE-N.

(2) Lack of true equilibrium conditions at -180°C . The solvents used by Briegleb et al. become viscous and solidify to rigid glasses at temperatures above -180°C . If the usual technique of quenching the sample solution in a bath of liquid nitrogen was employed, it is quite unlikely that a true equilibrium was attained.

Both factors may be responsible for the observed increase in $\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)$. The first of these, however, is probably the most important since both the pyrene and 1,2-benzanthracene complexes show the expected decrease in $\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)$ even though a true equilibrium may not have been reached at -180°C .

The blue shifts observed by Briegleb et al. for the TCNE-N and TCNE-pyrene complexes are more difficult to explain. Of the three factors previously considered to affect the energy of the charge-transfer transition the only one which might give rise to a blue shift is the Franck-Condon effect. At -180°C any "hot bands" along the red edge of the band envelope should be effectively frozen out, with a consequent blue shift in the Franck-Condon maximum. Indeed, a

loss of intensity along the red edge of the band envelope is observed in the TCNE-1,2-benzanthracene complex, but the Franck-Condon maximum nevertheless shows a red shift. Another factor which would be expected to lead to a blue shift involves strong solvation of the complex by ether. Since TCNE is known to form a complex with diethyl ether, a tightly bound TCNE-N solvate or an ether-TCNE-N sandwich 1:1:1 complex is a possibility; such a species would be especially favored at low temperature. The TCNE-N interaction would be weakened in such a complex with the result that the charge-transfer transition characteristic of TCNE-N would be blue shifted. (The effect of solvation is further discussed under "Solvent Composition Effects", below.)

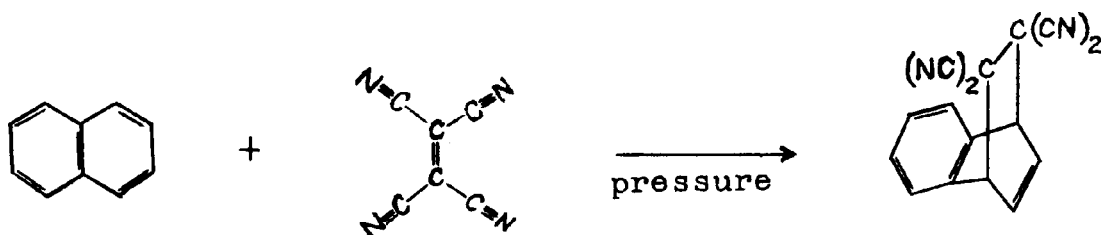
In any event, the complications introduced by use of an ether containing solvent cast doubt on Briegleb et al.'s results for TCNE-N and it is felt that the results of the present work better represent the true temperature dependence of the TCNE-N system. In agreement with the behavior presently observed for TCNE-N, Briegleb and Czekalla [111] reported a slight red shift over the temperature range 40-20°C for the quinone-dimethylaniline complex in CCl_4 .

Pressure Effects

The effects of high pressures on the TCNE-N absorption spectrum have been studied in CH_2Cl_2 [97], in polymer matrices [108], and in the polycrystalline solid [109]. The Mulliken charge-transfer theory [3,8,79] predicts that both

the stability of a charge-transfer complex and its extinction coefficient should increase with an increase in pressure, due to the increased overlap between the donor and acceptor MO's of the components. For TCNE-N in CH_2Cl_2 , Gott and Maisch [97] observed a 5-6 fold increase in absorbance upon increasing the pressure to 10 Kbars, with the long wavelength band showing an increase in intensity 30% greater than that of the short wavelength band. These authors attributed the increased absorbance principally to an increase in ϵ_c (ϵ_K was actually observed to decrease slightly in the case of TCNE-benzene) and the decrease in $\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)$ to the presence of two stable orientational isomers having slightly different molar volumes. In addition to the intensity effects, the absorption maxima of both bands showed red shifts with increasing pressure, that of the high frequency band being most pronounced. Offen and Kadhim [108] observed quite similar effects for TCNE-N in films of cellulose acetate over a pressure range of 1-25 Kbars. Again, the observed decrease in $\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)$ was attributed to the presence of orientational isomers. Bentley and Drickamer [109] found that the application of very high pressures (500-600 Kbars) produced irreversible changes in polycrystalline TCNE-N complex. After subjection to such pressures the long wavelength band of the sample disappeared while the short wavelength band remained essentially unaffected. A comparison of the infrared spectrum of the transformed sample with that of the original

material led these authors to conclude that a Diels-Alder addition of TCNE to naphthalene had occurred under the influence of pressure.



The persistence of the short wavelength band in Bentley and Drickamer's experiments can be most easily explained by assuming that there are two possible orientations of donor and acceptor within the crystal, only one of which has a geometry favorable to formation of a Diels-Alder adduct. (A further discussion of the geometries of TCNE-aromatic complexes is given in Section VII.) The red shifts and increases in intensity which occur in solutions upon increasing the pressure can be understood in terms of the considerations previously outlined.

Considering first the red shift of $\lambda_{\max}$, the possible contributing factors are:

1) General solvent shift. The dielectric constant of the solvent increases with increasing pressure; a general red shift is therefore predicted. Since the effect depends primarily on changes in the nature of the solvent, the shift should be essentially the same for both complexes.

2) Franck-Condon effect. Since the equilibrium separation of donor and acceptor probably changes significantly with large increases in pressure, a change in Franck-Condon factors may be of major importance in causing pressure dependent changes in the charge-transfer spectrum. In order to separate the effects of a change in Franck-Condon factors from those of a change in the zero-point energies of the ground or excited states, it is convenient to assume that the energy of the 0,0 band of the charge-transfer transition remains constant, and to draw the potential energy curves of the ground and excited states so that the energy separation between their minima remains unchanged. The effect on $\lambda_{\max}$ of a change in shape of the potential energy curves will then stand out clearly.

The question of whether $R_{\text{eq.}}$ increases or decreases upon going from the ground to the excited state of the complex is of central importance in determining whether a red or a blue shift in $\lambda_{\max}$ will occur with an increase in pressure. Mulliken [7], although pointing out that this is still an open question, prefers to draw the potential energy curves so that $R_{\text{eq.}}$ increases on going to the excited state (see Figure 37-(a)); the broadness of most observed charge-transfer spectra can then be explained in terms of transitions terminating on the steep repulsive portion of the excited state potential energy curve. Consider now the effect of an increase in pressure. The change in the potential energy curves can be

Figure 37

Effect of Increasing Pressure on Potential Energy Curves

$$R_{eq.} \text{ (excited state)} > R_{eq.} \text{ (ground state)}$$

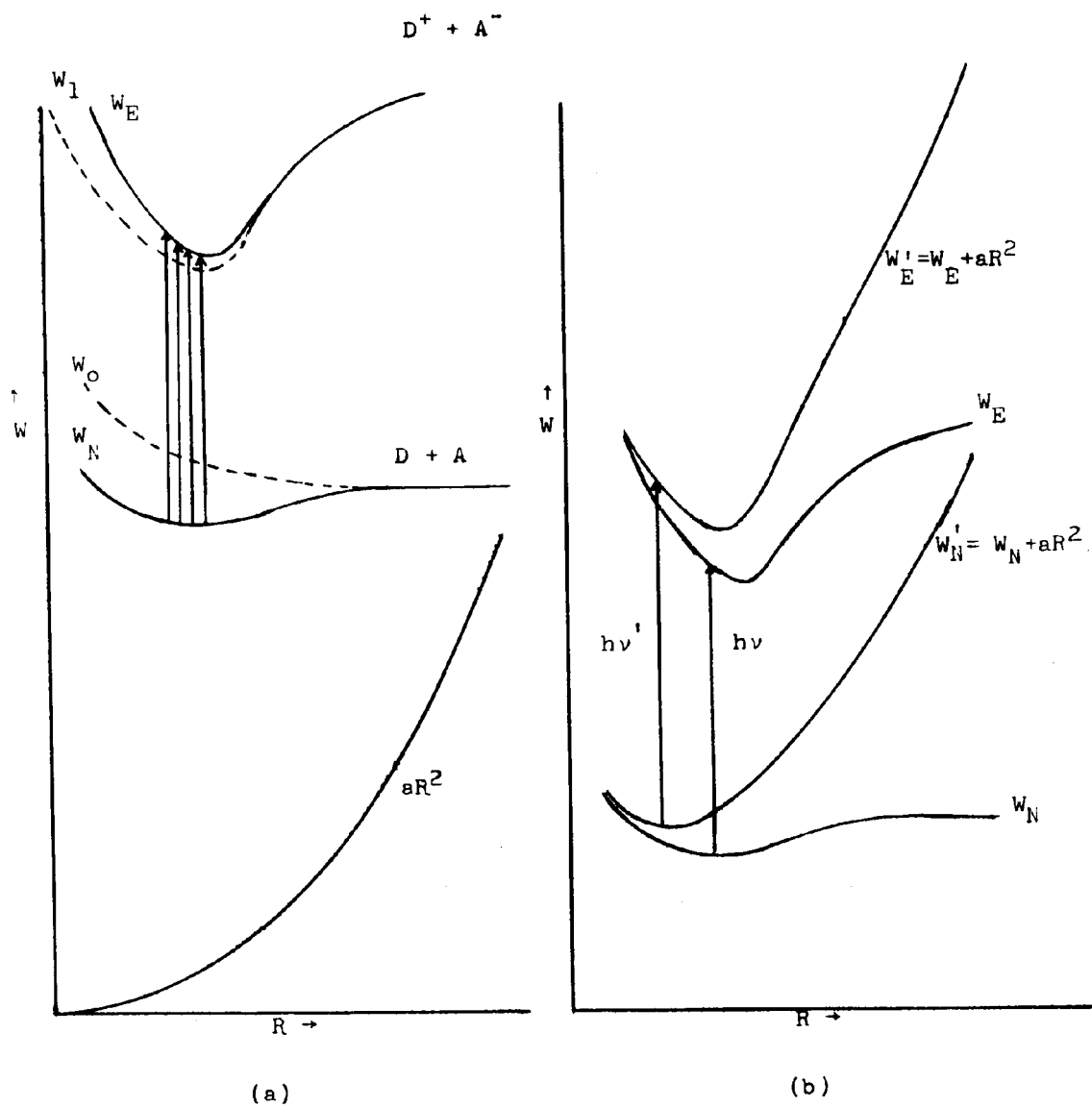
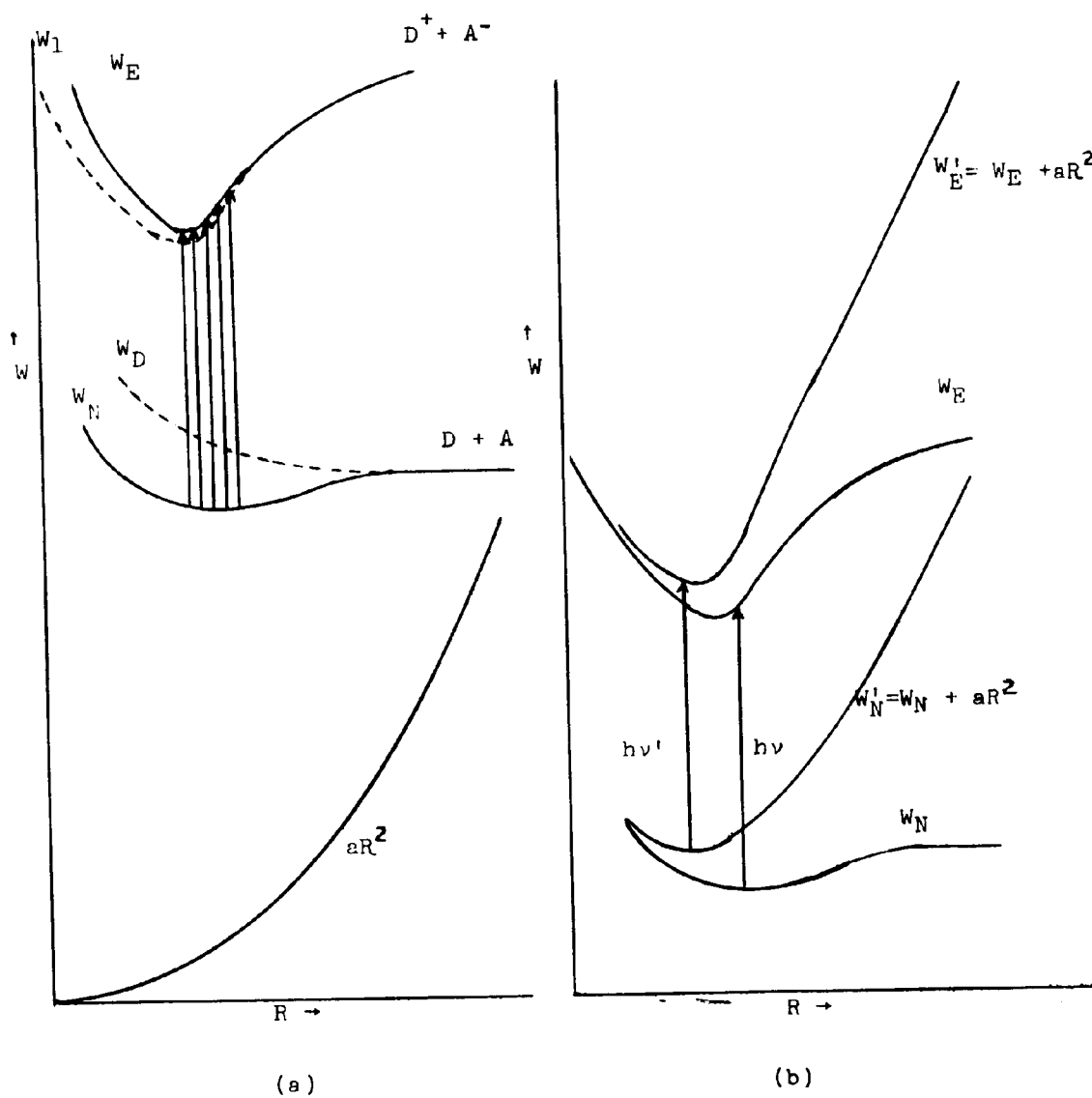


Figure 38

Effect of Increasing Pressure on Potential Energy Curves $R_{eq.} \text{ (excited state)} < R_{eq.} \text{ (ground state)}$ 

approximated by the addition to each of a repulsion term which increases with R (for example, aR^2). Since the W_E curve is much steeper on both sides of the minimum than is the curve for W_N , it is apparent that, with increasing pressure, $R_{eq.}$ will decrease much more rapidly in the ground state than in the excited state (see Figure 37-(b)). As a result of this differential decrease in $R_{eq.}$, λ_{max} would be expected to exhibit a blue shift. On the other hand, if $R_{eq.}$ decreases upon excitation, a red shift in λ_{max} would be predicted (see Figure 38).

The argument given above is admittedly oversimplified in that it assumes that the most intense portion of the charge-transfer band, corresponding to λ_{max} , originates from the vibrationless level of the ground state. This neglects the possibility of a redistribution of intensity within the charge-transfer band due to a change in overlap between the vibrational wavefunctions of the ground and excited states. Since it is not possible to take this factor into account without a detailed knowledge of the vibrational wavefunctions involved, it seems reasonable, as a first approximation, to assume that the intensities of the various vibronic components vary in accordance with the Boltzmann populations of their initial vibrational levels.

Whether $R_{eq.}$ increases or decreases on excitation depends on the relative importance of the following opposing factors:

(a) Increased Coulombic and covalent binding forces in the excited state. Since the excited state of the complex is essentially an ion-pair, the attractive Coulombic forces between the ions act to decrease $R_{eq.}$ below its ground state value. In addition, the binding forces associated with the weak covalent bond formed between donor and acceptor in the excited state would favor a decrease in $R_{eq.}$

(a) Increased repulsive forces between D and A in the excited state due to an increase in size of the acceptor. Since TCNE is a closed-shell molecule, the acceptor anion formed upon excitation of the complex would be expected to have a van der Waals volume somewhat larger than that of the neutral molecule. The increased exchange repulsion in the excited state would then lead to an increase in $R_{eq.}$ As pointed out by Mulliken [79], the magnitude of this effect should be greatest when the acceptation orbital involved is strongly antibonding. In the case of TCNE, however, Hückel MO calculations [112,113] indicate that the acceptation orbital is slightly bonding. A large increase in van der Waals volume is therefore unlikely.

An unequivocal decision as to which of these two competing factors should predominate is not possible. A resultant decrease in $R_{eq.}$, however, is the more attractive of the two possibilities since it allows an explanation of the unusual pressure dependent shifts in λ_{max} exhibited by the TCNE complexes of some polymethylated benzenes. The

TCNE-hexamethylbenzene complex [97,108] shows an initial red shift with increasing pressure, but, as the pressure continues to increase, this trend reverses, until, at pressures greater than 10 Kbars, a net blue shift results. The TCNE-durene complex [108] shows qualitatively the same behavior, but the effect is much less pronounced. In hexamethylbenzene the methyl groups probably occupy staggered, out-of-plane positions due to steric crowding; as a result $R_{eq.}$ in both ground and excited states might be expected to be considerably greater than for TCNE-benzene. Since, upon compression, $R_{eq.}$ should decrease much more rapidly in the ground state, it might be possible that in this case $R_{eq.}$ in the ground state eventually becomes equal to, and finally less than, that in the excited state. As this occurs, λ_{max} would be expected to go through a maximum and then decrease as observed. This same effect may occur, but to a lesser degree, with TCNE-durene.

Assuming that the observed red shifts in λ_{max} do occur by the mechanism discussed above, it remains to be determined which of the two isomeric TCNE-N complexes should show the greatest change with increasing pressure. It was previously pointed out that the ground state resonance energy R_N should be greatest for complex λ_1 ; the ground state potential energy curve for this complex should therefore have the deepest minimum. Since the effect of an increase in pressure in causing a decrease in $R_{eq.}$ is greater the shallower the

potential energy minimum, $R_{eq.}$ should decrease fastest for complex λ_2 and thus λ_{max} should red shift fastest for this complex. The observed behavior is in agreement with this prediction.

It can be concluded that a decrease in $R_{eq.}$ seems likely upon charge-transfer excitation; if this is the case, the shifts in λ_{max} accurately follow predicted behavior.

3) Change in internal energetics of the complex. The principal effects of an increase in pressure are a decrease in the equilibrium separation $R_{eq.}$ of donor and acceptor and an increase in overlap between the donation and acceptation orbitals. The energy of the charge-transfer transition, given by equation (V-84), is altered by both of these effects. According to equation (V-83), the decrease in $R_{eq.}$ operates to decrease the energy difference ($W_1 - W_0$) between the dative and no-bond states of the complex by increasing the Coulombic energy in the dative state. The first term in equation (V-84) therefore predicts a red shift with increasing pressure. The behavior of the second term in this equation, however, gives rise to a blue shift. This occurs for two reasons: (a) the magnitude of H_{01} increases roughly in proportion to S [79], and β_0^2 and β_1^2 therefore increase, while, simultaneously (b) the denominator ($W_1 - W_0$) decreases. Whether a net red or blue shift results depends on how fast S (or H_{01}) increases with decreasing $R_{eq.}$ For TCNE-N, $e^2/R_{eq.}$ is large (+117.1 kcal. mole⁻¹), hence a small decrease in $R_{eq.}$ could cause a rela-

tively large red shift. On the other hand, it appears that a small relative change in $R_{eq.}$ will be accompanied by a large relative change in S (and in H_{O1}), which operates to increase β_0^2 and β_1^2 , leading to a blue shift. It is difficult to decide which effect will predominate. Making a rough calculation from the parameters determined by Briegleb et al. [104, 105] for TCNE-N in CCl_4 (see Table 30), and assuming that the relative changes in H_{O1} and S are equal, it turns out that for a 5% decrease in $R_{eq.}$ there will be a blue shift if S increases by >26% or a red shift if S increases by <26%. Similarly, for a 10% decrease in $R_{eq.}$, S must increase by >43% in order to produce a blue shift. Although the sensitivity of S to a change in $R_{eq.}$ is not known, a strong blue shift is unlikely; zero shift or a slight red shift might reasonably be expected.

In addition to producing a decrease in $R_{eq.}$, an increase in pressure compresses the solvent to some extent, causing an increase in the dielectric constant ϵ . This results in a decrease in $(W_1 - W_0)$ and, if this effect is considered independently from the decrease in $R_{eq.}$, leads to a small red shift in λ_{max} , in a manner previously discussed. Since the shifts produced by a decrease in $R_{eq.}$ or an increase in ϵ , considered separately, should be approximately additive, the net result of an increase in pressure should be a small red shift.

We wish next to determine which of the two isomeric complexes should show the greater wavelength shift with an in-

crease in pressure. Consider first the effect of the increase in ϵ . The energies of the dative (W_1) states of both complexes will decrease by the same proportion; since W_1 is largest for complex λ_2 , the absolute decrease in W_1 will be largest for this complex. Now, the energy of the charge-transfer band is given principally by the first term in equation (V-84). Since the decrease in this term is greatest for complex λ_2 , the red shift in $\lambda_{\max}$ should be greatest for this complex. This prediction is in agreement with the observed behavior.

Consider next the energy changes caused by the decrease in R_{eq} . Two separate cases will be distinguished. In the first case R_{eq} is initially the same for both complexes and upon compression decreases at the same rate for both. In the second case R_{eq} is initially the same for both but upon compression decreases somewhat faster for complex λ_2 ; this case corresponds to the behavior of R_{eq} predicted above in the discussion of the Franck-Condon effect.

Case 1. Since the decrease in R_{eq} is the same for both complexes, the increase in Coulombic energy and decrease in W_1 is also equal for both. Consequently, the first term in equation (V-84) predicts equal red shifts for both complexes. The second term in this equation, however, predicts a blue shift, which should be largest for complex λ_1 . The behavior of this term is governed chiefly by the relative decrease in the denominator ($W_1 - W_0$). This is largest for complex λ_1 , because W_1 is smallest for this complex. The numerator ($\beta_0^2 + \beta_1^2$)

increases with pressure since H_{01} and S increase as $R_{eq.}$ decreases, but the relative changes in this factor are essentially equal for both complexes. (Actually, $(\beta_0^2 + \beta_1^2)$ increases slightly faster for complex λ_2 but this effect is quite small.) Whether a net red shift or blue shift results depends on how fast S (and H_{01}) increase with decrease in $R_{eq.}$, as discussed above. The relative shifts at λ_1 and λ_2 are correctly predicted, however, since the energy separation between λ_1 and λ_2 is predicted to decrease as the pressure increases.

Case 2. Since $R_{eq.}$ decreases fastest for complex λ_2 , the Coulombic energy increases fastest for this complex. W_1 and $(W_1 - W_0)$ therefore decrease most rapidly at λ_2 and, consequently, the first term of equation (V-84) predicts that complex λ_2 will show the largest red shift. The change with pressure of the second term in equation (V-84) again leads to blue shifts. Depending on how fast $R_{eq.}$ decreases for complex λ_2 compared to complex λ_1 the blue shift may be largest for either complex. If the rates of decrease are nearly equal, complex λ_1 will show the largest blue shift, as in Case 1. If the rates of decrease are sufficiently different, the blue shift will be larger for complex λ_2 . Again, the behavior of the net shifts in λ_{max} are ambiguous and depend on how fast S and H_{01} increase with decrease in $R_{eq.}$ as well as on the rates of decrease of $R_{eq.}$ for the two complexes.

In summary, red shifts may arise from any of the three factors discussed. Factor 1) predicts small red shifts at

λ_1 and λ_2 . Factor 2) could be responsible for large red shifts, provided $R_{eq.}(\text{excited state}) < R_{eq.}(\text{ground state})$; this factor predicts that $R_{eq.}$ should decrease fastest for complex λ_2 , so that the red shift should be greatest at λ_2 , as observed. In the case of factor 3), the direction and magnitude of the wavelength shift is dependent on the rate of increase of H_{01} and S with decreasing $R_{eq.}$, but a red shift seems most likely. In any event, the energy separation between λ_1 and λ_2 should decrease, in agreement with observation; this effect should be most pronounced if $R_{eq.}$ decreases at the same rate for both complexes.

Consider next the factors which may contribute to the observed increases in charge-transfer intensity.

i) Dependence of the extinction coefficient on refractive index. The refractive index increases with increasing pressure and ϵ_c would therefore be expected to increase. Since $n(\lambda_2)$ increases faster than $n(\lambda_1)$, the ratio $Abs(\lambda_2)/Abs(\lambda_1)$ should increase as well. The observed behavior, however, is contrary to this prediction, indicating that this factor is of minor importance in the systems studied.

ii) Franck-Condon effect. Since the shapes of both ground and excited state potential energy curves might reasonably be expected to change more drastically with large changes in pressure than with changes in temperature or solvent composition, this factor probably plays a more important

role in producing the observed pressure effects than it does in the cases of the related temperature or solvent composition effects. If the analysis given above in the discussion of the wavelength shift is correct, i.e. if $R_{eq.}$ (excited state) $< R_{eq.}$ (ground state) and if $R_{eq.}$ (ground state) decreases more rapidly upon compression than does $R_{eq.}$ (excited state), ϵ_c would be expected to increase with increasing pressure, in agreement with observation. ϵ_c should increase in this case because, as $R_{eq.}$ becomes nearly equal in both ground and excited states, the vibrational overlap between these states, and hence also the Franck-Condon factor, should reach a maximum value. The behavior of the ratio $Abs(\lambda_2)/Abs(\lambda_1)$ due to this factor is more difficult to predict. If the ground state equilibrium separation decreases more rapidly with pressure for complex λ_2 , as previously predicted, $Abs(\lambda_2)/Abs(\lambda_1)$ would be expected to increase with pressure, contrary to observed behavior. In making this deduction, however, it is assumed that the shapes of the ground and excited state potential energy curves, and their respective $R_{eq.}$ values, are initially exactly the same (or nearly so) for both isomeric complexes; this assumption is probably not justified.

iii) Change in internal energetics of the complex.

a) Change in intrinsic intensity. As discussed above, the intrinsic intensity of the charge-transfer transition is governed chiefly by the ratio of the MO coefficients b/a as

given by equation (V-90). In the present case a large increase in intensity is expected since b/a increases due to each of several different factors: (1) As $R_{eq.}$ decreases, the Coulombic energy of the dative state increases and thus W_1 decreases; the denominator $(W_1 - W_0)$ in equation (V-90) therefore decreases and b/a increases. (2) Since the dielectric constant of the medium increases with increasing pressure, all terms entering into equation (V-83) for W_1 decrease; W_1 and $(W_1 - W_0)$ therefore decrease and b/a increases. (3) H_{01} increases (i.e. becomes more negative) as $R_{eq.}$ decreases; since this term is much larger than SW_0 , the numerator in equation (V-90) increases and therefore b/a increases.

The behavior of the ratio $Abs(\lambda_2)/Abs(\lambda_1)$ remains to be determined. Two different cases will again be considered.

Case 1. $R_{eq.}$ is initially the same for both complexes and decreases at the same rate for both upon compression. The increase in dielectric constant should cause no significant change in $Abs(\lambda_2)/Abs(\lambda_1)$ because the relative change in W_1 due to this effect is the same for both complexes; since W_0 is small compared to W_1 , the relative changes in $(W_1 - W_0)$ should be essentially equal for both complexes and $Abs(\lambda_2)/Abs(\lambda_1)$ should therefore remain essentially unchanged. The decrease in $R_{eq.}$, however, leads to a decrease in $Abs(\lambda_2)/Abs(\lambda_1)$. Since the absolute decrease in W_1 due to a decrease in $R_{eq.}$ is the same for both complexes, the relative decrease in W_1 and in $(W_1 - W_0)$ is greatest for complex λ_1 . The rela-

tive increase in the numerator - $(H_{01} - SW_0)$ is the same for both complexes. As a result, $Abs(\lambda_1)$ increases faster with a decrease in $R_{eq.}$ than does $Abs(\lambda_2)$, and the ratio $Abs(\lambda_2)/Abs(\lambda_1)$ decreases with increasing pressure, in agreement with observation.

Case 2. $R_{eq.}$ is initially the same for both complexes but decreases faster for complex λ_2 ; S and H_{01} therefore increase faster for complex λ_2 . As for Case 1, the increase in dielectric constant should cause no significant change in $Abs(\lambda_2)/Abs(\lambda_1)$. Since H_{01} is much larger than SW_0 , the relative increase in the numerator - $(H_{01} - SW_0)$ is largest for complex λ_2 . The relative decrease in W_1 and in the denominator $(W_1 - W_0)$ may be greater for either complex, depending upon how much faster $R_{eq.}$ decreases for complex λ_2 than for complex λ_1 . In general, the rates of decrease should be similar so that although the relative decrease in $(W_1 - W_0)$ for complex λ_2 will be larger in comparison to that for complex λ_1 than it was in Case 1, it will still be somewhat larger for complex λ_1 . Considering changes in both numerator and denominator, $Abs(\lambda_2)$ may increase faster than $Abs(\lambda_1)$, depending on the rates of decrease of $R_{eq.}$ for the two complexes; $Abs(\lambda_2)/Abs(\lambda_1)$ would then increase. In any event, the ratio $Abs(\lambda_2)/Abs(\lambda_1)$ will decrease less rapidly with increase in pressure than it did in Case 1.

iii b) Apparent change in ϵ_c due to a change in equilibrium constant. The equilibrium constant ^xK will increase

with increasing pressure due to an increase in complex stability, as measured by the ground state resonance energy R_N . The expression, equation (V-92), for R_N contains the same terms as does equation (V-90) for b/a and it is therefore apparent that the same three factors, discussed above in iii a), which contribute to the increase in b/a will in this case cause R_N to increase.

The behavior of the ratio $Abs(\lambda_2)/Abs(\lambda_1)$ is determined, according to equation (V-94), by the numerical difference between the R_N values for the two complexes. Consider the same two cases discussed in iii a) above.

Case 1. In view of the similarities between equations (V-90) and (V-92), the reasoning utilized above to show that the relative increase in b/a is greatest for complex λ_2 applies here as well. Thus, the relative increases in R_N , due to either an increase in the numerator or a decrease in the denominator because of increasing dielectric constant, are equal for both complexes. The relative decrease in the denominator due to a decrease in $R_{eq.}$, however, is greatest for complex λ_1 , and as a result the relative increase in R_N is greatest for complex λ_1 . Since, at atmospheric pressure, $R_N(\lambda_1) > R_N(\lambda_2)$, it is apparent that the absolute increase in R_N is greatest for complex λ_1 . Consequently, according to equation (V-94), the ratio $Abs(\lambda_2)/Abs(\lambda_1)$ should decrease with increasing pressure. This prediction is in agreement with the observed behavior.

Case 2. Here again, the relative increases in R_N for each of the two complexes parallel the increases in b/a discussed above in iii a). The relative increase due to an increase in dielectric constant should be the same for both complexes. The relative increase in the numerator of equation (V-92) is greatest for complex λ_2 (since $(H_{01}-SW_0)$ is raised to the second power in equation (V-92), this equation is more sensitive to a change in $R_{eq.}$ than was equation (V-90)). Again, the absolute decrease in (W_1-W_0) will be larger for complex λ_2 , but the relative decrease in this term may be larger for either complex, depending on how fast $R_{eq.}$ decreases for each. As a result, the relative increase in R_N may be larger for either complex. In general, however, provided the rates of decrease of $R_{eq.}$ are similar for both complexes, the relative increase in R_N will still be larger for complex λ_1 . Accordingly, the absolute increase in R_N will be greatest for complex λ_1 and the ratio $Abs(\lambda_2)/Abs(\lambda_1)$ will again decrease with increasing pressure, as experimentally observed. The decrease in $Abs(\lambda_2)/Abs(\lambda_1)$, however, will be less pronounced in this case than in Case 1 above.

In summary, all three factors discussed above, i), ii) and iii a) and b), correctly predict an increase in absorbance with increasing pressure. The first factor, however, incorrectly predicts an increase in the ratio $Abs(\lambda_2)/Abs(\lambda_1)$, as does the second factor α if $R_{eq.}$ decreases more rapidly for complex λ_2 than for complex λ_1 . Factors iii a) and b) must

therefore be primarily responsible for the decrease observed in $\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)$; the decrease due to each of these factors is more pronounced if the rate of decrease of $R_{\text{eq.}}$ is the same for both complexes (Case 1 above) than if, as previously predicted, $R_{\text{eq.}}$ decreases more rapidly for complex λ_2 (Case 2).

In the event that the viscosity of the medium hinders the rapid attainment of equilibrium, the effect of factor iii b) is nullified. This is probably the case for TCNE-N in cellulose acetate film since the pressure sensitivity of TCNE-N in this medium is only fractionally as great as in liquid CH_2Cl_2 . The decrease in $\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)$ observed in this case must be due almost wholly to iii a).

Solvent Composition Effects

The effect of a change in solvent properties on the energies and intensities of charge-transfer bands can be most conveniently discussed by dividing these effects into two classes, depending on the composition of the solvent:

- (1) Single component solvent. In this case the solvent is a fourth molecular species present in large excess compared to donor, acceptor and complex; it acts ideally as an "inert" diluent and is not involved in any equilibria with the other components.
- (2) Two component solvent. In this case one of the complex components, usually the donor, is present in large excess compared to the other; if its mole fraction is appreciable compared to that of the "inert" solvent, its properties help to determine the properties of the bulk medium and it can be conveniently regarded as one component of a mixed solvent. This case arises typically in the Benesi-Hildebrand and similar procedures, where a large excess of donor is employed in the determination of equilibrium constants. The interpretation of effects due to the solvent is complicated, in this case, by the possible formation of higher order complexes between donor and acceptor.

The solvent effects observed in the present study belong in the second category. In addition to these results, the effects of several solvents of Class 1 on the charge-transfer

spectrum of TCNE-N have been studied by other workers [102, 107, 110]; these will be commented on later.

Consider first the present results. These are as follows:

- (a) Slight blue shifts in the absorption maxima at λ_1 and λ_2 with increasing C_D .
- (b) A decrease of the ratio $\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)$ with increasing C_D (see Table 29).

The factors which may contribute to a change in energy of the charge-transfer maximum are:

1) General solvent shift. The dielectric constant of the medium decreases with increasing concentration of donor, hence a blue shift should result.

2) Franck-Condon effect. Since any change in the shapes of ground and excited state potential energy curves with a change in solvent properties cannot be readily predicted, the contribution due to this factor remains uncertain.

3) Change in internal energetics of the complex. Since the dielectric constant decreases with increasing C_D , W_1 , and hence $(W_1 - W_0)$, should increase. Consider the second term in equation (V-84) for the energy of the charge-transfer band; the denominator increases, β_0^2 remains constant, and β_1^2 increases. The relative increase in the numerator ($\beta_0^2 + \beta_1^2$), however, is less than that in the denominator, so that, on balance, the second term in (V-84) decreases. Since, however, $(W_1 - W_0)^2 > (\beta_0^2 + \beta_1^2)$, the absolute increase in the first term in equation (V-84), $(W_1 - W_0)$, will be larger than the

absolute decrease in the second term; $(W_E - W_N)$ will therefore increase and a blue shift should result.

Thus, the first and third factors should both contribute to the observed blue shift while the effect of the second factor is indeterminate.

In the case of the intensity effect the possible factors are:

i) Dependence of the extinction coefficient on refractive index. Since the refractive index increases with increasing C_D , the extinction coefficient, and hence the measured absorbance, should also increase. Moreover, since n_D increases faster at λ_2 than at λ_1 , the ratio $Abs(\lambda_2)/Abs(\lambda_1)$ should increase as well. This prediction is contrary to the observed behavior.

ii) Franck-Condon effect. As pointed out above, the contribution due to this factor is indeterminate.

iii) Change in internal energetics of the complex.

a) Change in intrinsic intensity. As previously discussed, the intrinsic intensity of the charge-transfer transition is governed chiefly by the ratio of the MO coefficients b/a as given by equation (V-90). In the present case β_0 is equal for both complexes and remains constant independent of the change in solvent polarity. $(W_1 - W_0)$ increases for both complexes; as a result b/a , and therefore μ_{EN} and Abs , should decrease for both. Now, the relative increases in W_1 are the same for both complexes, but, since W_0 remains

constant, the relative increase in $(W_1 - W_0)$ is greatest for complex λ_2 . Therefore μ_{EN} and Abs decrease faster at λ_2 than at λ_1 and $\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)$ should decrease, as observed.

b) Apparent change in ϵ_c due to a change in equilibrium constant. The equilibrium constant ^xK decreases with increasing C_D due to a decrease in complex stability, as measured by the ground state resonance energy R_N . R_N , given by equation (V-92), decreases because the denominator $(W_1 - W_0)$ increases with increasing C_D . As in a) above, β_0^2 remains constant and equal for both complexes and $(W_1 - W_0)$ increases faster, relatively, at λ_2 than at λ_1 . Since R_N was initially smaller for complex λ_2 than for complex λ_1 , and decreases faster for complex λ_2 with increasing C_D , the absolute decrease in R_N may be larger for either complex, depending on the initial magnitudes of R_N and their rates of decrease. A calculation using the parameters of Briegleb et al. [107] (see Table 30) indicates that the absolute decrease in R_N is greatest for the complex absorbing at λ_1 . The difference $R_N(\lambda_1) - R_N(\lambda_2)$ therefore decreases (i.e. becomes less negative) and, according to equation (V-94), the ratio $\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)$ would be expected to increase. Again, this prediction is contrary to the observed behavior.

Summarizing, iii a) predicts a decrease in $\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)$, as is observed, whereas i) and iii b) predict an increase. The question of which factor is more important, iii a) or iii b), can be answered by a calculation of the magnitudes of the effects on $\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)$ caused by, res-

pectively, the decreases in μ_{EN} and x_K . Such a calculation, employing the parameters of Briegleb et al. [107] indicates that the latter factor is most important and that, therefore, $Abs(\lambda_2)/Abs(\lambda_1)$ should increase with increasing C_D or decrease with increasing dielectric constant.

We have still therefore to explain the observed decrease of $Abs(\lambda_2)/Abs(\lambda_1)$ with increasing C_D . It appears impossible to do this convincingly without invoking some contribution to the observed absorbance due to the presence of higher order complexes. It might be expected that these, if present, would absorb to the blue of the 1:1 complexes, and indeed, a blue shift is observed with increasing C_D . However, as discussed above, this can be explained as well on the basis of the general solvent shift and the change in internal energetics of 1:1 complexes. The decrease in $Abs(\lambda_2)/Abs(\lambda_1)$ can be explained satisfactorily on the basis of D_2A complexes being present provided that certain conditions are met. Let the respective equilibrium constants be defined as follows:

$$x_{K_1} = \frac{[DA]_1}{[A](X_D)_{eq.}} \qquad x_{K_1}' = \frac{[D_2A]_1}{[DA]_1(X_D)_{eq.}}$$

$$x_{K_2} = \frac{[DA]_2}{[A](X_D)_{eq.}} \qquad x_{K_2}' = \frac{[D_2A]_2}{[DA](X_D)_{eq.}}$$

The subscripts 1 and 2 here refer to complexes having absorption maxima near λ_1 and λ_2 respectively. The absorbances at λ_1 and λ_2 are then given by

$$\text{Abs}(\lambda_1) = [\text{DA}]_1 \epsilon_1 + [\text{D}_2\text{A}]_1 \epsilon_1' = [\text{DA}]_1 (\epsilon_1 + {}^xK_1' \epsilon_1' (X_D)_{\text{eq}}.)$$

$$\text{Abs}(\lambda_2) = [\text{DA}]_2 \epsilon_2 + [\text{D}_2\text{A}]_2 \epsilon_2' = [\text{DA}]_2 (\epsilon_2 + {}^xK_2' \epsilon_2' (X_D)_{\text{eq}}.)$$

where the primes refer to the appropriate D_2A complex. The ratio $\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)$ can be written

$$\frac{\text{Abs}(\lambda_2)}{\text{Abs}(\lambda_1)} = \frac{{}^xK_2 (\epsilon_2 + {}^xK_2' \epsilon_2' (X_D)_{\text{eq}}.)}{{}^xK_1 (\epsilon_1 + {}^xK_1' \epsilon_1' (X_D)_{\text{eq}}.)}$$

It can be easily shown that $\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)$ will decrease with increasing $(X_D)_{\text{eq}}$. (or C_D), provided that

$$\frac{{}^xK_2' \epsilon_2'}{{}^xK_1' \epsilon_1'} < \frac{\epsilon_2}{\epsilon_1} \quad (\text{V-95})$$

This condition is probably satisfied for the complexes under discussion for the following reasons:

(1) Based on the energetics of complex formation, ${}^xK_1 > {}^xK_2$. By analogy, ${}^xK_1'$ might be expected to be larger than ${}^xK_2'$ and therefore ${}^xK_2'/{}^xK_1' < 1$.

(2) The ratio of the extinction coefficients, ϵ_2'/ϵ_1' may be taken, as a first approximation, as equal to ϵ_2/ϵ_1 .

If these last two approximations hold with sufficient accuracy, condition (V-95) will be satisfied and $\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)$ should decrease, in accord with the observed behavior. This result implies that the formation of D_2A complexes may become significant in solutions with a high concentration of donor.

The preceding discussion of the effect of a change in solvent properties on the extinction coefficient of a 1:1 complex helps to clarify the role of a change in ϵ_c in causing non-linear plots of equations (V-18) and (V-26). It was pointed out earlier that an increase in ϵ_c with increasing concentration of donor could account for the negative curvature observed in these plots. In the case of 1:1 complexes, ϵ_c probably decreases with increasing C_D . (Factors iii a) and b) predict a decrease in ϵ_c while i) predicts an increase. The net effect is probably a decrease because the sensitivity of ^xK to a change in dielectric constant, factor iii b), is very great; a rough calculation of the changes to be expected in ϵ_c due to factors i) and iii b) indicates this to be the case.) The possibility that the non-linearity may be due primarily to an increase in extinction coefficient can therefore be eliminated if only 1:1 complexes are taken into consideration. If D_2A complexes are present, however, the apparent extinction coefficient ϵ_c''' would be expected to increase with increasing C_D , provided that $\epsilon_{D_2A} {}^cK_{D_2A}$ is sufficiently large compared to ϵ_c'' (see equation (V-80)). Since neither the presence of D_2A complexes nor the behavior of ϵ_c''' with increasing C_D can be independently determined, the role of any such complexes in producing the observed non-linearity cannot be definitely confirmed. The fact, however, that the observed decrease in $Abs(\lambda_2)/Abs(\lambda_1)$ with increasing C_D cannot be adequately explained without invoking the

presence of D_2A complexes lends support to the possibility that D_2A species play an important role in solutions with a high concentration of donor.

It should be noted that a change in solvent polarity causes a change in ^xK and should therefore be a factor in producing non-linearity in plots of equations (V-18) and (V-26). It was pointed out earlier that the negative curvature observed in these plots corresponds to an increase in ^xK with increasing concentration of donor. For the complexes under discussion, however, factor iii b) predicts a decrease in ^xK with increasing concentration of donor. It can be concluded, therefore, that the change in ^xK with changing solvent polarity plays only a minor role in producing non-linearity.

Consider next the solvent effects observed with single component solvents. The TCNE-N complex has been studied by several workers [20,102,106,107,110]; a summary of their results is given in Table 31. Since the TCNE-N complex should experience a marked increase in dipole moment upon electronic excitation, the theories of solvent effects upon absorption spectra, for example the theories of McRae [99] and Bakhshiev [100], predict a red shift of the charge-transfer band with increasing solvent polarity. It is apparent, however, from Table 31 that no such correlation exists between the energy of the first charge-transfer band and the dielectric constant of the solvent; on the contrary, a strong blue shift is often

TABLE 31

Effect of Single Component Solvents on the Charge-Transfer Bands of TCNE-N

Solvent	ϵ (20°C)	λ_1 (m μ)	Reference	Abs(λ_2)/Abs(λ_1)	Reference
N-Hexane	1.890	18.7	[110]		
N-Heptane	1.924	18.8	[107]	1.10	[107]
2,2,4-Trimethyl-pentane	1.940	18.6	Present work	1.03	Present work
Cyclohexane	2.023	18.6, 18.6	[102, 107]	1.04	[107]
CCl ₄	2.228	18.2, 18.2, 18.2	[102, 107, 110]	1.01, 1.02	[106, 107]
C ₆ H ₆	2.274	18.4	[102]		
N-Propyl Ether	3.39 (25°C)	19.0	[107]	1.00	[107]
Et ₂ O	4.335	19.2	[107]	1.00	[107]
CHCl ₃	4.806	17.9, 17.9	[102, 107]	0.970	[107]
C ₆ H ₅ Cl	5.621	18.1	[102]		
EtOAc	6.02	20.0	[102]		
CHCl ₂ -CHCl ₂	8.20	17.7	[107]	0.934	[107]
CH ₂ Cl ₂	9.08	18.1, 18.1, 18.2, 18.2	[102, 107, 20, 110]	0.917, 0.903	[107], Present Work
CH ₂ Cl-CH ₂ Cl	10.65	18.3	[107]	0.917	[107]
Cyclohexanone	18.3	~20.8	[102]		
CH ₃ COCH ₃	20.7	~21.3	[102]		
CH ₃ OH	32.63	20.8	[110]		
CH ₃ CN	37.5	20.0	[110]		

observed in polar solvents. The lack of this expected correlation has been noted [101,102,106,107,110,114] for other charge-transfer complexes as well.

A number of explanations have been advanced in an attempt to account for the apparent failure of solvent interaction theory when applied to charge-transfer complexes in polar media. Rosenberg and Hale [110], on the basis of the effect on several TCNE-aromatic complexes of a limited number of solvents (CCl_4 , CH_2Cl_2 , n-hexane, CH_3CN and CH_3OH), proposed a correlation between the red shift and the solvent refractive index. According to this proposal, the solvent polarizability, which is related to refractive index, would make the most important contribution towards stabilization of the excited state. This correlation, however, breaks down just as seriously as does the correlation with dielectric constant when a more varied series of solvents is considered.

Other authors have focused attention on factors which bring about a change in the nature of the complex. Czekalla and Meyer [115] proposed, in the case of the tetrachlorophthalic anhydride-hexamethylbenzene complex, that the blue shifts observed in certain polar solvents could be explained in relation to the corresponding decrease in ΔH . According to this argument the decrease in binding energy should bring about a loosening of the complex (i.e. an increase in $R_{\text{eq.}}$); the Coulombic energy of the dative state should therefore decrease, resulting in a corresponding increase in the energy

of the charge-transfer band. It is important to note, concerning a decrease in ΔH ($\Delta H = W_0 + R_N$), that this decrease must come about principally through a decrease in W_0 , the energy of the van der Waals interaction between D and A. (It was pointed out earlier that if W_0 could be considered to remain constant independent of an increase in solvent polarity, R_N , and hence also ΔH , would be expected to increase.) A decrease in W_0 with increasing solvent polarity implies an increasingly strong interaction between the solvent and complexed A (and/or D), which in turn weakens the interaction between D and A. Alternatively, it may be considered that with increasing solvent polarity the enthalpy of solvation increases faster for the separated components, D and A, than for the complex. In any event, a decrease in ΔH with increasing solvent polarity indicates the presence of a strong specific interaction between the solvent and both the free and complexed components. Data concerning the effect of solvent polarity on ΔH are sparse (see Briegleb [1161]) and show no simple correlation. On the contrary, it appears that the decrease in ΔH is greatest for those solvents which are known to be good π or n type donors (C_6H_6 , substituted benzenes; ethers, ketones), independent of their dielectric constant. This implies that "solvation" effects are most pronounced when the components, and perhaps also the complex, can undergo a charge-transfer interaction with the solvent. If, however, any complexation with the solvent does in fact take place, the ΔH values quoted for these solvents are cast into

doubt, since in measuring χ_K and ΔH any competing equilibria should be explicitly taken into account. In this connection, Carter, Murrell and Rosch [82] have recently pointed out the advantages of explicitly including the molecules of the first solvation shell in the description of the complexation equilibrium.

Davis and Symons [101] attribute the solvent effect to an alteration of charge distribution in the ground state, which, in effect, alters the electronic structure of the complex. Their view is that the degree of charge-transfer in the ground state is small and that therefore polar solvent molecules interact more strongly with local polar centers on the D and A molecules than with the small δ^+ and δ^- charges associated with charge transfer. Since the ground states of uncomplexed D and A molecules should be similarly affected by interaction with the solvent, the absorption spectra of these molecules might be expected to show solvent effects similar to those of the complex. In support of this contention, Davis and Symons obtained a fairly good correlation between the solvent shifts shown by chloranil and those of its hexamethylbenzene complex. Although Davis and Symons couch their explanation in terms of local polar interactions, it is interesting to note that, in the case of the polar blue shifts, the same kind of correlation predicted by them would be expected if charge-transfer complexation occurred between solvent and acceptor. On the one hand, the characteristic absorption of the acceptor would be expected to blue shift

as the strength of the charge-transfer interaction between acceptor and solvent increases; in the case of I_2 as acceptor this effect is well known [1] (see also Briegleb [117]). The charge-transfer absorption of the complex, on the other hand, would be expected to blue shift with increasing solvent-acceptor interaction, due to the accompanying decrease in ΔH of the complex (see above). From another point of view, if formation of a donor-acceptor-solvent complex occurs, the donor-acceptor interaction should become weaker as the acceptor-solvent interaction becomes stronger, thus raising the energy of the donor-acceptor charge-transfer band.

Offen and Abidi [102] discuss the polar blue shifts in terms of the effect of solvation on the valence bond structures describing both the ground and excited states of the complex. They correctly point out that the effect of an increase in solvent polarity should be to lower the energy of the dative structure, and that the enhanced mixing of states W_0 and $W_1 (\sim \frac{1}{W_1 - W_0})$ will result in increased splittings of the ground and excited states (i.e. an increase in $(R_N + R_E)$). They then argue that it can be shown that the increase in $(R_N + R_E)$ is always larger than the decrease in $(W_1 - W_0)$ so that a blue shift should result. This last claim is erroneous. It was previously pointed out that whether a red or a blue shift results is dependent on the initial magnitudes of $(W_1 - W_0)$ and $(R_N + R_E)$. Provided that H_{01} and S remain constant, a red shift will result if $(W_1 - W_0) > (R_N + R_E)$

and a blue shift if $(W_1 - W_0) < (R_N + R_E)$. For most molecular complexes, including those under discussion here, the former condition holds and a red shift is to be expected. Thus, it may be concluded that the considerations employed by Offen and Abidi can account for a blue shift only when particularly strong complexes are involved.

Examination of the data in Table 31 reveals the presence of two opposing trends.

(1) For those solvents (n-hexane, n-heptane, 2,2,4-trimethylpentane, cyclohexane, CCl_4 , CHCl_3 , $\text{CHCl}_2\text{-CHCl}_2$) having relatively low dielectric constants and which are not known to be good π or n type donors, there appears to be a small red shift with increasing dielectric constant.

(2) For those solvents capable of functioning as π or n donors (C_6H_6 , n-propyl ether, Et_2O , $\text{C}_6\text{H}_5\text{Cl}$, EtOAc , cyclohexanone, CH_3COCH_3 , CH_3OH , CH_3CN) or having a dielectric constant of ~ 10 or greater, a trend toward blue shifts is apparent. The magnitudes of the blue shifts observed in these cases, however, bear no relationship to the dielectric constant, thereby indicating that the solvent effects involved are specific in nature.

The red shifts observed in weakly polar solvents are in agreement with both the predictions of solvent shift theory and the considerations of complex energetics (i.e. factors 1) and 3) in the discussion of wavelength shifts). This initial red shift has also been observed, in the case of the TCNE-p-xylene complex, upon transition from the gas phase to

solvents of low dielectric constant [118].

The blue shifts can be explained quite generally on the basis of the considerations given by Czekalla and Meyer; i.e. a decrease in ΔH of complex formation, due to an increase in the difference between the enthalpies of solvation of the components on the one hand, and of the complex on the other. The heats of solvation of donor and acceptor might be expected to be reflected in their solubilities in the various solvents. This appears to hold true in the case of TCNE, where a reasonably good correlation is obtained (see Table 32) between acceptor solubility and the energy of the first charge-transfer band of the TCNE-N complex. Although the solubility of naphthalene varies widely over the series of solvents considered (see Table 33), no correlation with charge-transfer band energy such as is found in Table 32 can be discerned. It thus appears, in the case of TCNE-N, that the most significant solvation interactions are those involving the acceptor. The possibility of strong solvent-donor interactions should not be discounted, however. For example, as previously mentioned, evidence exists for the formation of weak complexes of aromatics with CHCl_3 and CH_2Cl_2 ; other highly chlorinated alkanes might behave similarly.

Looked at from another point of view, the blue shift can be ascribed to a weakening of the D-A charge-transfer interaction as the donor (or acceptor) properties of the solvent increase. This viewpoint emphasizes the increase

TABLE 32

Correlation Between Acceptor Solubility
and Charge-Transfer Band Energy

<u>Solvent</u>	<u>Solubility⁽¹⁾ of TCNE [119]</u>	<u>λ_1(kK)</u>
CCl_4	low	18.2
$\text{CHCl}_2\text{-CHCl}_2$	~ 0.002	17.7
CHCl_3	0.01 (slow)	17.9
CH_2Cl_2	0.1 (heat)	18.1 (18.2)
$\text{CH}_2\text{Cl-CH}_2\text{Cl}$	0.15	18.3
EtOAc	>0.5	20.0
CH_3CN	>0.5	20.0
CH_3OH	high	~ 20.8
CH_3COCH_3	high	~ 21.3

(1) in moles liter⁻¹

in energy of the A-S (or S-D) interaction within an assumed DAS (or SDA) complex, while neglecting formation of any AS (or SD) complexes by uncomplexed A (or D). Although the blue shift must ultimately be due to a weakening of the D-A interaction brought about by an increased interaction between DA and the solvent, the A-S and D-S interactions should be even stronger for the uncomplexed than for the complexed components and therefore should not be ignored. Thus, of these two possible viewpoints, the former is the more general, and is to be preferred.

It can be concluded that the blue shifts observed for TCNE-N are the result of strong specific interactions between

TABLE 33

Comparison of Donor Solubility with Charge-Transfer Band Energy

Solvent	Relative Solubility (Measured Solubility/Ideal Solubility ⁽¹⁾) at						λ_1 (kK)
	20°C	Ref.	25°C	Ref.	30°C	Ref.	
CH ₃ OH	0.0659, 0.0762	[93, 122]	0.0787	[112]			20.8
N-Hexane	0.330, 0.357	[93, 122]	0.387	[122]			18.7
N-Heptane			0.432	[35]			18.8
CH ₃ COCH ₃	0.670, 0.735	[93, 122]	0.739, 0.755	[35, 122]			~21.3
Et ₂ O			0.800	[35]			19.2
CCl ₄	0.752, 0.810, 0.845	[93, 122], [92]	0.787, 0.832, 0.852	[35, 122], [92]			18.2
C ₆ H ₆	0.883, 0.930, 0.945	[93, 122], [123]	0.923, 0.939, 0.955	[35, 122], [123]			18.4
CHCl ₂ -CHCl ₂					1.000	[124]	17.7
C ₆ H ₅ Cl	0.938, 1.023	[93, 122]	1.016	[122]			18.1
CH ₂ Cl-CH ₂ Cl			1.026	[125]	1.026	[125]	18.3
CHCl ₃	1.081	[94]	1.081	[94]			17.9
CH ₂ Cl ₂	>0.867 and <1.158 at 21.8°C (present work)						18.1 (18.2)

(1) Ideal solubilities were computed by means of equation (V-64), taking $\Delta H_f = 4440 \text{ cal. mole}^{-1}$ and $T_M = 80.2^\circ\text{C}$.

the components of the complex and the solvent. Of these, solvent-acceptor charge-transfer complexes probably play the most important role, but hydrogen bonded solvent-donor complexes may also be of significance. Local polar interactions of the kind discussed by Davis and Symons appear to be ineffective since no correlation exists between the blue shift and the solvent dielectric constant.

Before leaving the subject of solvent shifts it should be mentioned that solvent shift theory has been successful in relating the energy of the Stokes shift (i.e. $h\nu$ (absorption) - $h\nu$ (fluorescence)) for molecular complexes to the dielectric constant and refractive index of the solvent, even for those solvents in which the charge-transfer absorption shows a blue shift. This relationship requires a knowledge of the energy of charge-transfer fluorescence in each of the solvents of interest. Unfortunately, such data is available for only one complex, that of tetrachlorophthalic anhydride with hexamethylbenzene. For this case, Czekalla and Meyer [115] (see also Briegleb [126]) found that the solvent shift theory of Lippert [120] gave reasonably good agreement between the predicted and observed Stokes shifts. Bakhshiev [121], applying his own theory to the data of Czekalla and Meyer, obtained a still better correlation in terms of the average energy of the charge-transfer absorption and fluorescence transitions. The success of solvent shift theory in regard to Stokes shifts is apparently due

to the smallness of the anomalous absorption blue shifts in comparison with the relatively large fluorescence shifts. Since it is essentially an ion-pair, the complex in its excited state interacts very strongly with polar solvents; this results in a very large fluorescence red shift. Furthermore, upon excitation the components of the complex probably lose most of their donor or acceptor character, which they partially retain in the ground state. In the excited state, therefore, specific, charge-transfer type interactions between complex and solvent, such as are apparently responsible for the absorption blue shifts, probably either do not exist or are very weak.

The behavior of the ratio $Abs(\lambda_2)/Abs(\lambda_1)$ with increasing dielectric constant of the solvent deserves some comment. This quantity shows an essentially regular decrease in those solvents for which data are available (see Table 31), despite the fact that the energy of the first charge-transfer band behaves quite erratically in the same solvents. On first consideration, this behavior appears to be in accord with that predicted earlier in discussing intensity effects in two-component solvents. The latter prediction was based on the assumption that W_0 remains constant independent of the solvent, in which case R_N , and hence $-\Delta H$, would be expected to increase with increasing solvent dielectric constant. It can be taken as an established fact, however, in those cases where the charge-transfer band shows a blue shift, that ΔH

decreases, due to the effect of strong specific interactions between the components of the complex and the solvent. In view of the fact that ΔH would therefore be expected to vary randomly with increasing dielectric constant, depending on the ability of the solvent to enter into specific interactions, the uniform change in $\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)$ with changing dielectric constant is quite remarkable.

Several conclusions can be drawn from the preceding discussion of solvent effects:

1. The shift in λ_{max} and changes in relative intensities observed with changes in temperature, pressure and solvent composition can be rationalized in terms of the several factors which might theoretically be expected to influence these quantities. The analysis given above makes clear the fact that the structure of any molecular complex changes continuously with changing solvent properties; therefore any method for the determination of K and ϵ_c in which a considerable change in solvent properties occurs will not be capable of giving strictly valid results.

2. The analysis given above was based on the assumption that the bands at λ_1 and λ_2 are the characteristic charge-transfer bands of two separate isomeric 1:1 complexes. The fact that all of the various wavelength and relative intensity changes can be rationalized on this basis lends support to the correctness of this assumption. If only a single complex were responsible for both bands, the changes in relative

intensities would be very difficult to explain since only a change in Franck-Condon factors could be responsible for the observed effects.

3. Since both ϵ_c and ^xK change with changing solvent properties, it might be expected that these changes could be responsible for the curvature observed in plots of equations (V-18) and (V-26). The analysis given above, however, indicates that the expected changes in these quantities would act to produce a curvature opposite to that observed; hence it can be concluded that solvent dependent changes in ϵ_c and ^xK make a minor contribution to the observed curvature. On the other hand, the above analysis indicates that the presence of D_2A complexes may become appreciable at high concentrations of donor; if the absorption spectra of these species meet certain requirements, the apparent extinction coefficient ϵ_c'' would increase with increasing donor concentration and thus contribute to the observed curvature. A similar conclusion regarding the possible importance of D_2A species was reached in Part E-2.

4. The fact that $Abs(\lambda_2)/Abs(\lambda_1)$ decreases uniformly with increasing donor concentration explains the discrepancy previously noted (Part D) between $K^*(\lambda_1)$ and $K^*(\lambda_2)$. The decrease in $Abs(\lambda_2)/Abs(\lambda_1)$ has been attributed, in this case, to the formation of D_2A species.

Section VI. Thermodynamic Constants ΔF° , ΔH° and ΔS° .

Part A. Determination of ΔF° , ΔH° and ΔS°

If the equilibrium constant for a given reaction is known at more than one temperature, the quantities ΔF° , ΔH° and ΔS° can be readily computed from standard thermodynamic relationships. The standard Gibbs free energy at any temperature T is given by

$$-\Delta^{\text{XF}^\circ}(T) = RT \ln^{\text{X}} K_a(T) = RT \ln^{\text{X}} K(T) + RT \ln^{\text{X}} K_Y(T)$$

in which the constants $^{\text{X}}K_a$, $^{\text{X}}K$ and $^{\text{X}}K_Y$ are as previously defined (see equation (V-52)). Although the measured equilibrium constants $^{\text{X}}K^*(T)$ are not ideal solution values (see discussion in V-E), it will be assumed the $^{\text{X}}K_Y(T)$ is approximately unity so that the standard free energies are given approximately by

$$-\Delta^{\text{XF}^\circ}(T) \simeq RT \ln^{\text{X}} K^*(T). \quad (\text{VI-1})$$

Similarly, if the equilibrium constants are expressed in molar concentration units,

$$-\Delta^{\text{CF}^\circ}(T) \simeq RT \ln^{\text{C}} K^{\text{S}}(T). \quad (\text{VI-2})$$

In equation (VI-2), $^{\text{C}}K^*$ has been replaced by $^{\text{C}}K^{\text{S}}$ because the latter quantity obeys the thermodynamic equation $^{\text{C}}K = ^{\text{X}}K V_S$ and because $^{\text{C}}\epsilon_{\text{C}}$ and $^{\text{X}}\epsilon_{\text{C}}^*$ are essentially identical whereas $^{\text{C}}\epsilon_{\text{C}}^*$ and $^{\text{X}}\epsilon_{\text{C}}^*$ differ appreciably (see discussion in Section V, Part E-1); $^{\text{C}}K^{\text{S}}$ is used in place of $^{\text{C}}K^*$ throughout this Section. Values of Δ^{XF° and Δ^{CF° computed via equations (VI-1) and (VI-2) are listed in Table 34.

TABLE 34

Summary of ΔF° Values

Confidence limits are for the 95% confidence level. Units are cal. mole⁻¹. Δ_{MF}° was computed from the values of C_K^6 listed in Table 26.

I. For TCNE-N

<u>t</u>	<u>No. of Points</u>	<u>$\Delta^{\text{X}}F^\circ(\lambda_1)$</u>	<u>$\Delta^{\text{X}}F^\circ(\lambda_2)$</u>	<u>$\Delta_{\text{MF}}^\circ(\lambda_1)$</u>	<u>$\Delta_{\text{MF}}^\circ(\lambda_2)$</u>
30.00	8	-1041 $\pm$ 13	1052 $\pm$ 12	606 $\pm$ 13	595 $\pm$ 12
21.80	8	-1067 $\pm$ 14	-1079 $\pm$ 12	541 $\pm$ 14	529 $\pm$ 12
11.50	7	-1110 $\pm$ 2	-1113 $\pm$ 4	448 $\pm$ 2	446 $\pm$ 4
0.72	8	-1165 $\pm$ 15	-1171 $\pm$ 14	342 $\pm$ 15	336 $\pm$ 14

II. For TCNE-2,6-DMN

30.00	6	-1715 $\pm$ 10	-1733 $\pm$ 8	-68 $\pm$ 10	-86 $\pm$ 8
21.80	6	-1761 $\pm$ 12	-1775 $\pm$ 8	-152 $\pm$ 12	-166 $\pm$ 8
0.68	6	-1845 $\pm$ 14	-1857 $\pm$ 13	-335 $\pm$ 14	-347 $\pm$ 13

III. For TCNE-1-MN

21.80	2	-1436	171

IV. For TCNE-2-MN

21.8	-1485	125

V. For TCNE-1,6-DMN

21.8	-1689	-80

VI. For TCNE-2,3-DMN

21.8	-1823	-214

Standard heats of formation can be determined by means of the van't Hoff equation,

$$\left(\frac{\partial \ln^x K_a}{\partial T} \right)_P = \left(\frac{\partial \ln^c K_a}{\partial T} \right)_P + \left(\frac{\partial \ln V_S}{\partial T} \right)_P = \frac{\Delta H^\circ}{RT^2}$$

Integration, at constant pressure, yields, assuming constancy of ΔH° ,

$$\ln^x K_a = - \frac{\Delta^x H^\circ}{RT} + \text{const.} \quad (\text{VI-3})$$

$$\text{and } \ln^c K_a = - \alpha_S T = - \frac{\Delta^c H^\circ}{RT} + \text{const.} \quad (\text{VI-4})$$

where α_S is the cubic coefficient of thermal expansion for the solvent. Again it is assumed that, to a good approximation, $^x K_a$ and $^c K_a$ can be replaced by the measured values $^x K^*$ and $^c K^s$. $\Delta^x H^\circ$ (or $\Delta^c H^\circ$) is then obtained from the slope of a plot of $\ln^x K^*$ (or $\ln^c K^s - \alpha_S T$) versus $1/T$. Plots according to equations (VI-3) and (VI-4) of the data for TCNE-N and TCNE-2,6-DMN are shown in Figures 38-41; the confidence limits indicated are for a 95% confidence level. Since the confidence limits for the individual data points vary widely, a weighted least squares method (see Appendix I) was used in fitting straight lines to the data. The resulting values of $\Delta^x H^\circ$ and $\Delta^c H^\circ$ are listed in Table 35.

The entropy change at temperature T was calculated according to equations (VI-5) and (VI-6).

$$\Delta^x S^\circ(T) = \frac{\Delta^x H^\circ - \Delta^x F^\circ(T)}{T} \quad (\text{VI-5})$$

Figure 39

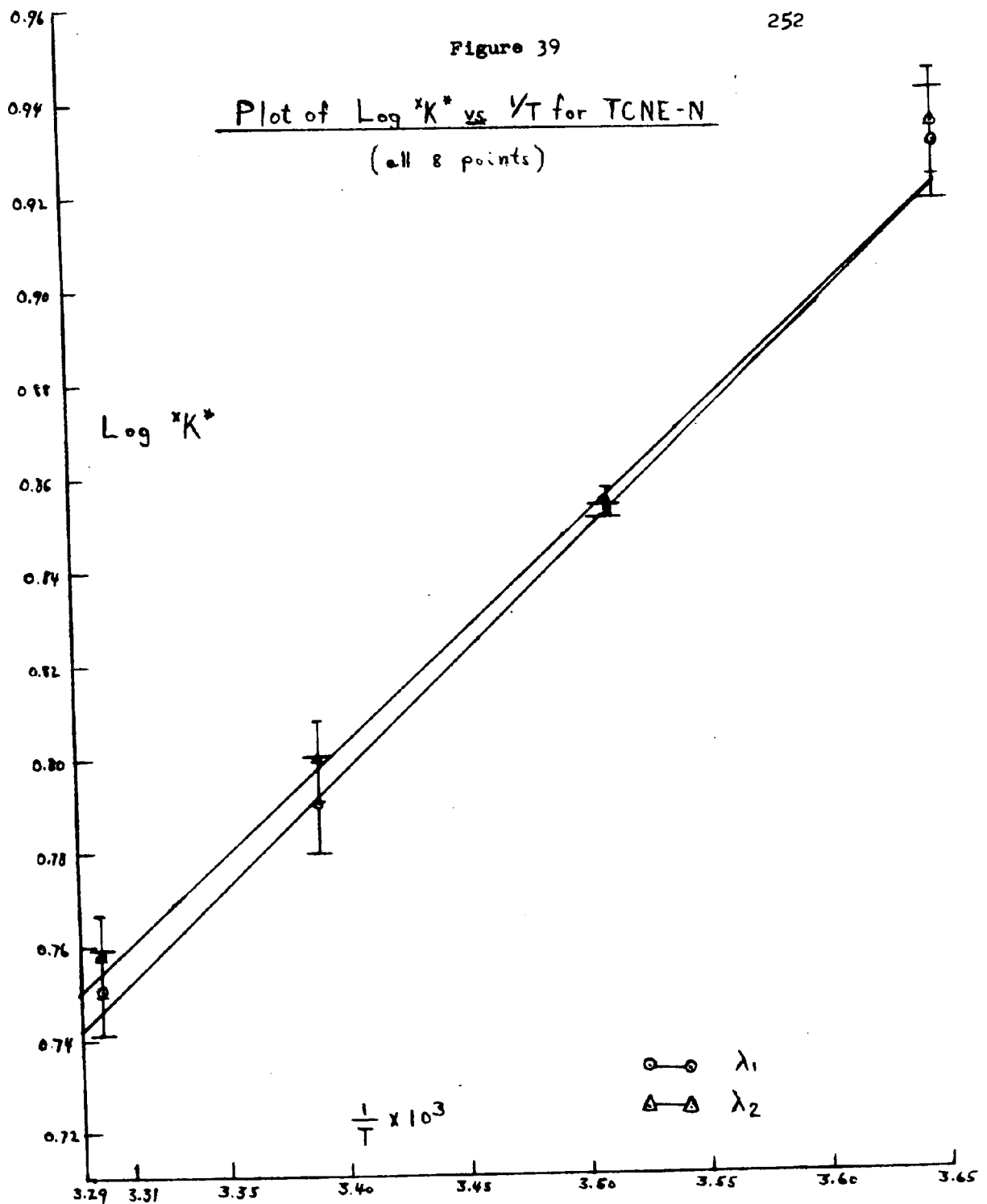


Figure 40

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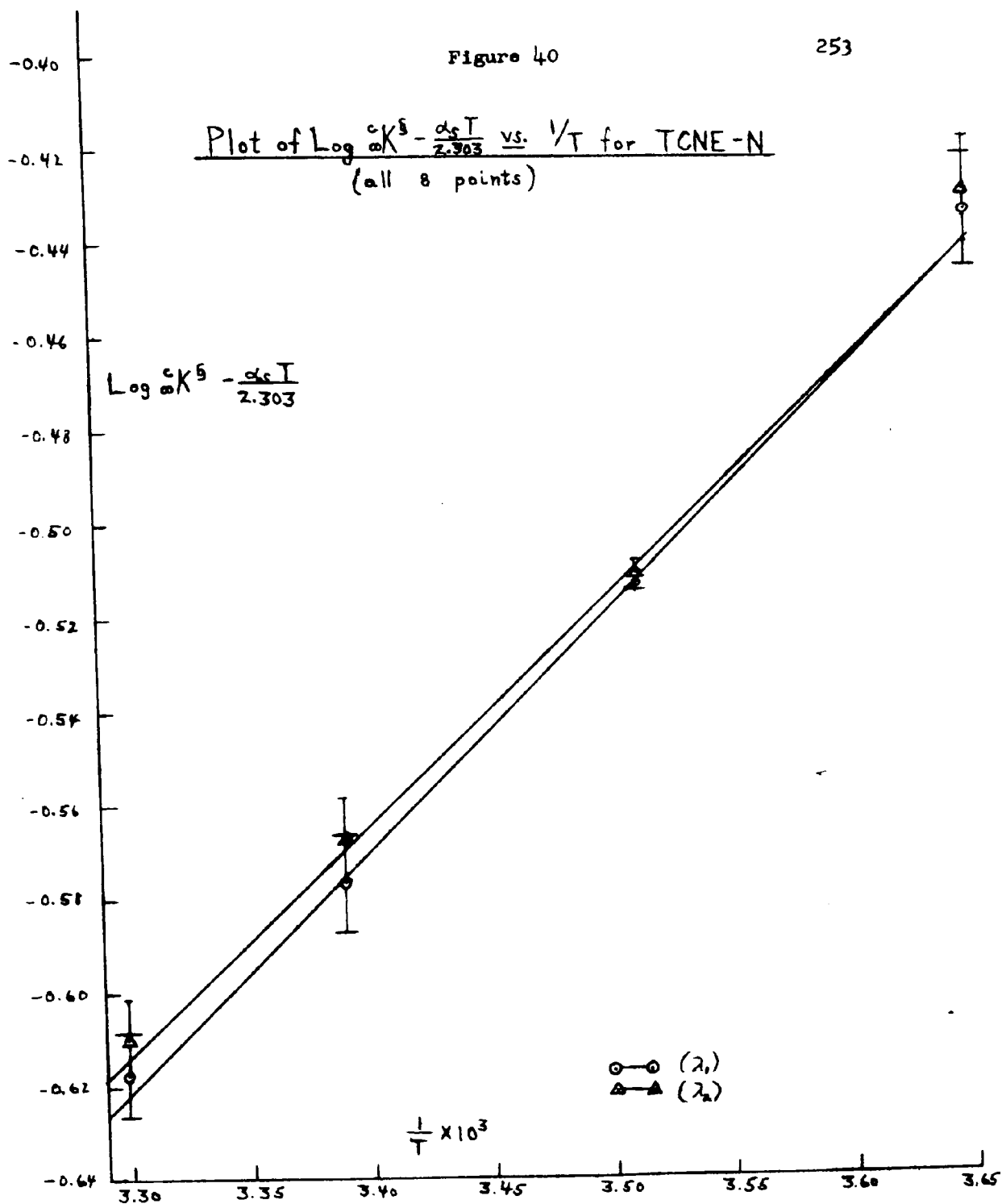
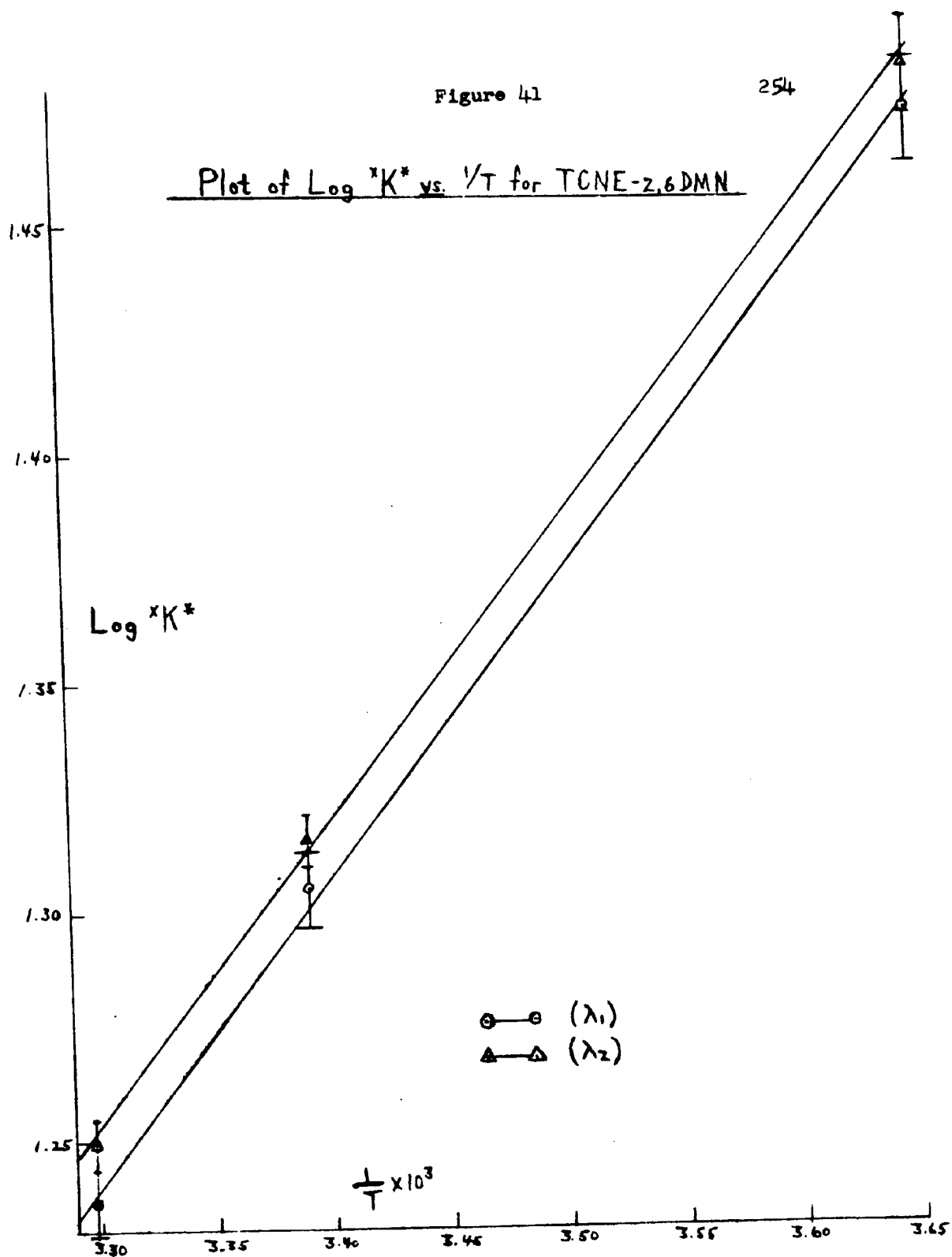


Figure 41

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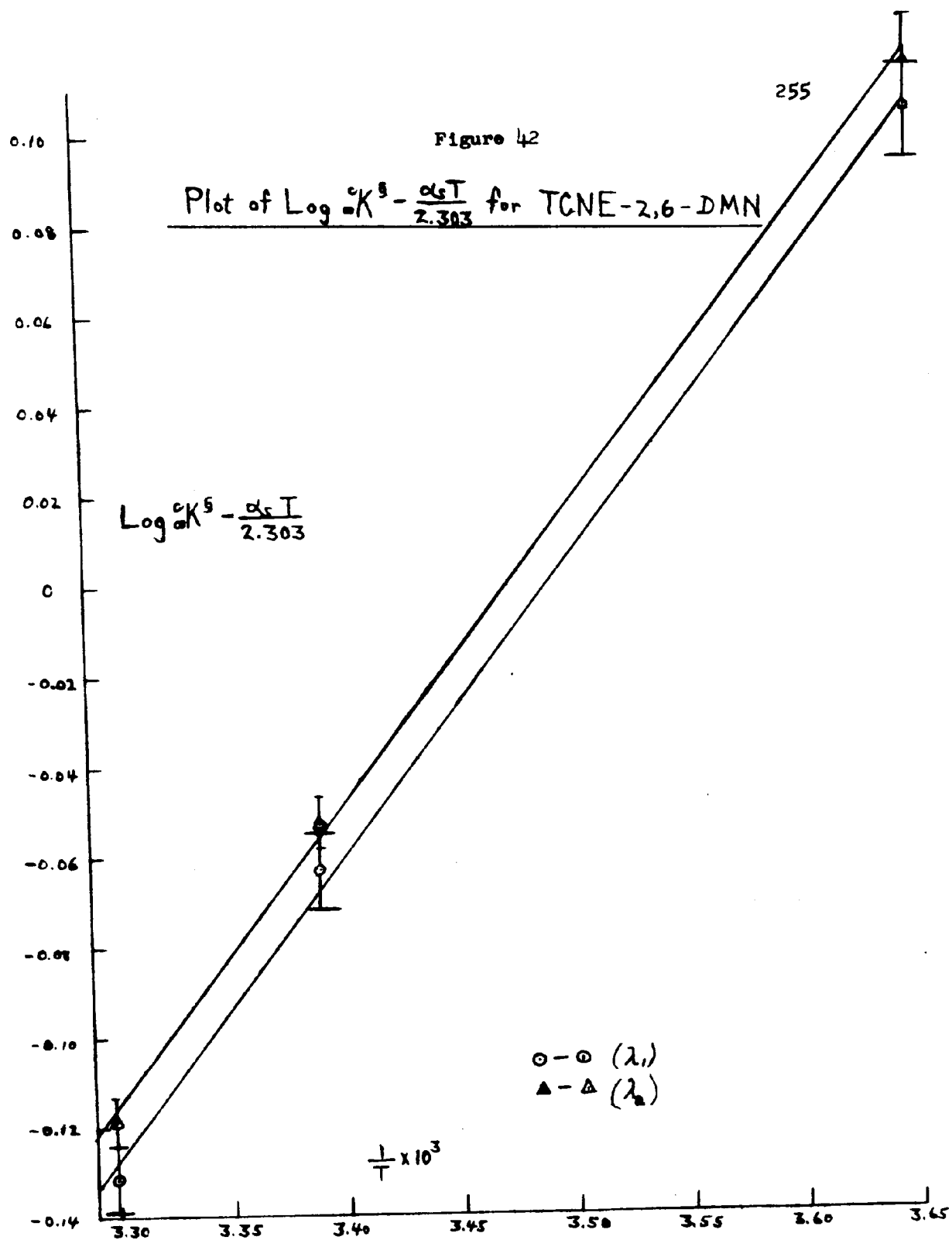


TABLE 35
Summary of ΔH° Values

Units are cal. mole⁻¹

I. For TCNE-N

<u>Quantity</u>	<u>Value</u>	<u>Confidence Level</u>		
		<u>50%</u>	<u>75%</u>	<u>95%</u>
$\Delta^{\text{X}}\text{H}^\circ(\lambda_1)$	-2265	± 3	± 5	± 14
$\Delta^{\text{C}}\text{H}^\circ(\lambda_1)$	-2323	± 4	± 8	± 22
$\Delta^{\text{X}}\text{H}^\circ(\lambda_2)$	-2159	± 15	± 30	± 80
$\Delta^{\text{C}}\text{H}^\circ(\lambda_2)$	-2227	± 18	± 36	± 95
$\Delta^{\text{X}}\text{H}^\circ$ (ave)	-2212			± 33
$\Delta^{\text{C}}\text{H}^\circ$ (ave)	-2275			± 39

II. For TCNE-2,6-DMN

$\Delta^{\text{X}}\text{H}^\circ(\lambda_1)$	-3051	± 59	± 142	± 745
$\Delta^{\text{C}}\text{H}^\circ(\lambda_1)$	-3047	± 63	± 151	± 794
$\Delta^{\text{X}}\text{H}^\circ(\lambda_2)$	-3025	± 48	± 117	± 615
$\Delta^{\text{C}}\text{H}^\circ(\lambda_2)$	-3023	± 49	± 118	± 624
$\Delta^{\text{X}}\text{H}^\circ$ (ave)	-3038			± 149
$\Delta^{\text{C}}\text{H}^\circ$ (ave)	-3035			± 156

$$\Delta_{\infty}^{\text{c}}S^{\circ}(T) = \frac{\Delta_{\infty}^{\text{c}}H^{\circ} - \Delta_{\infty}^{\text{c}}F^{\circ}(T)}{T} \quad (\text{VI-6})$$

The resulting values are listed in Table 36.

Part B. Discussion

It was pointed out in Section V that if several different 1:1 complexes exist in equilibrium, a Benesi-Hildebrand or similar analysis will lead to $^{\text{x}}K'$ and $^{\text{c}}K'$ values which are sums of the individual equilibrium constants involved, and to $^{\text{x}}\epsilon_{\text{c}}'$ and $^{\text{c}}\epsilon_{\text{c}}'$ values which are weighted averages of the individual extinction coefficients. Similarly, Orgel and Mulliken [50] have shown that when several 1:1 complexes are present, a plot of $\log K'$ versus $1/T$ leads to a weighted average value of ΔH° , i.e.

$$\Delta H^{\circ} = \frac{\sum K_i \Delta H_i}{\sum K_i}.$$

Under these conditions a plot of $\log K'$ versus $1/T$ will not be strictly linear unless the ΔH_i° are all equal (and temperature independent), so that non-linearity of such a plot can be taken as indirect evidence of the presence of more than one 1:1 complex.

Since there is evidence that the first two charge-transfer bands of TCNE-naphthalene complexes are due to different orientational isomers (see discussion in V-E), it might be expected that plots of equations (VI-3) and (VI-4) would show some degree of non-linearity. In the case of TCNE-N (Figures 38,39) there is some indication that the

TABLE 36

Summary of ΔS° Values

Confidence limits are for the 95% confidence level. Units are entropy units.

I. For TCNE-N

<u>t</u>	<u>No. of Points</u>	<u>$\Delta^X S^\circ(\lambda_1)$</u>	<u>$\Delta^X S^\circ(\lambda_2)$</u>	<u>$\Delta^C S^\circ(\lambda_1)$</u>	<u>$\Delta^C S^\circ(\lambda_2)$</u>
30.00	8	-4.04 ± 0.09	-3.65 ± 0.30	-9.66 ± 0.12	-9.31 ± 0.35
21.80	8	-4.06 ± 0.09	-3.66 ± 0.31	-9.71 ± 0.12	-9.34 ± 0.36
11.50	7	-4.06 ± 0.06	-3.68 ± 0.29	-9.73 ± 0.08	-9.39 ± 0.35
0.72	8	-4.02 ± 0.11	-3.61 ± 0.35	-9.73 ± 0.14	-9.36 ± 0.40
Average =		-4.04 ± 0.06	-3.65 ± 0.22	-9.71 ± 0.08	-9.35 ± 0.26
Average =		-3.85 ± 0.17		-9.53 ± 0.20	

II. For TCNE-2,6-DMN

30.00	6	-4.41 ± 2.49	-4.26 ± 2.06	-9.83 ± 2.65	-9.69 ± 2.09
21.80	6	-4.37 ± 2.57	-4.24 ± 2.11	-9.82 ± 2.74	-9.69 ± 2.14
0.68	6	-4.40 ± 2.88	-4.27 ± 2.29	-9.90 ± 2.95	-9.77 ± 2.33
Average =		-4.40 ± 0.90	-4.26 ± 0.73	-9.85 ± 0.94	-9.72 ± 0.74
Average =		-4.33 ± 0.49		-9.98 ± 0.51	

plots may be concave upwards, corresponding to an increasingly negative ΔH° at lower temperatures. The weighted least squares line, however, falls within the confidence limits for a 95% confidence level in all cases, so that the apparent curvature cannot be considered to be statistically significant. In the case of TCNE-2,6-DMN complex (Figures 40,41) no apparent curvature can be discerned.

Concerning the small confidence limits associated with $\log x_K^*$ and $\log c_K^s$ for TCNE-N at 11.50°C, it may be recalled that the data used in evaluating these constants seemed to be anomalously "good" (see V-D); to the extent to which the linearity of this data can be considered to be extra-normal, the confidence limits and the values of x_K^* and c_K^s at this temperature should be regarded as suspect. Comparing the ϵ_c values obtained for TCNE-N at 11.50°C with the values obtained at other temperatures (see Table 20), it appears that the former values are somewhat higher than expected; this implies that the corresponding x_K^* and c_K^s values may be somewhat too low. Since an increase in x_K^* and c_K^s at 11.50°C would operate to decrease the apparent curvature of the plots in Figures 38 and 39, this factor, together with the fact that the indicated confidence limits at 11.50°C are probably too small, mitigates the significance of the apparent curvature and argues against the presence of more than one TCNE-N complex.

As a consequence of the small confidence limits for x_K^* and c_K^6 at 11.50°C, the weighted least squares treatment used in fitting a straight line to the data indicates a much smaller uncertainty in ΔH° in the case of TCNE-N than in the case of TCNE-2,6-DMN (see Table 35). This large difference in uncertainties (a factor of 20-40x) is due in part to the fact that the equilibrium constants were measured at four temperatures for TCNE-N compared to only three for TCNE-2,6-DMN; this factor, however, can decrease the uncertainty by only 2-3x, depending on the confidence level under consideration. Since there is reason to suspect that the confidence limits associated with x_K^* and c_K^6 at 11.50°C are too small, the confidence limits for ΔH° , in the case of TCNE-N, should also be regarded as too small, probably by a factor of $\sim 10X$.

From Figures 38 and 39 and from Table 35 it appears that a different value of ΔH° is obtained for each of the first two charge-transfer bands of TCNE-N. In terms of the confidence limits listed in Table 35 the difference between the two ΔH° values is probably real. If, however, the anomalously "good" behavior of x_K^* and c_K^6 at 11.50°C is discounted, the difference between the two ΔH° values becomes of dubious significance. In view of the fact that each of the two charge-transfer bands is believed to be characteristic of a different isomeric 1:1 complex, it is tempting to assume that the two ΔH° 's represent independent

measurements of the heats of formation of the two different complexes. Such an interpretation is wrong. Orgel and Mulliken [50] have emphasized that if several 1:1 complexes are present the measured K value will be the sum of the K values for each of the complexes, regardless of whether one or all of the complexes absorb at the wavelength of measurement. Since the measured K values will therefore be the same at all wavelengths, regardless of the temperature of measurement, a plot of $\log K$ versus $1/T$ will result in the same ΔH° values, regardless of which complex absorbs at the wavelength of measurement. The apparently different ΔH° values obtained for the two charge-transfer bands of TCNE-N therefore cannot be interpreted as characteristic of each of two separate 1:1 complexes.

Despite the theoretical argument that measured values of K should be independent of the wavelength of measurement, the K values obtained in the present study are consistently higher at λ_2 than at λ_1 , both for TCNE-N (Table 20) and TCNE-2,6-DMN (Table 21). To the extent to which the apparent difference in ΔH° values for TCNE-N is significant, it must be attributed to the corresponding differences in the measured K values. The difference in K values, in turn, must be attributed to the essentially uniform decrease of the absorbance ratio $\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)$ throughout the series of test solutions used in the evaluation of K. As pointed out in the preceding discussion (V-E-3), a change in the ratio $\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)$ may in general be due to solvent dependent changes

in the ΔH 's or intrinsic charge-transfer band intensities of the 1:1 complexes involved; however, the decrease in $\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)$ observed for the complexes in the present study could be explained only in terms of higher order complexes (e.g. D_2A) being formed in solutions containing high concentrations of donor. It can be concluded that if the apparent difference in ΔH° 's for TCNE-N is real, it must be a reflection of the fact that higher order complexes exist in the solutions studied. However, since the confidence limits listed for these ΔH° 's are probably much too small, and in view of the fact that the two ΔH° values for TCNE-2,6-DMN are essentially equal, it appears that the difference in ΔH° values for TCNE-N is probably fictitious.

Although no evidence for the existence of two isomeric 1:1 complexes having different ΔH° 's can be derived from plots of $\log K$ versus $1/T$, the difference in ΔH° between two such complexes can be estimated by means of a relationship derived by Briegleb, Czekalla and Reuss [107].

(VI-7)

$$\Delta\Delta H^\circ = \Delta H^\circ(\lambda_1) - \Delta H^\circ(\lambda_2) = \frac{RT_{II}T_{II}}{T_{II}-T_I} \frac{[\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)]_I}{[\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)]_{II}}$$

The subscripts I and II refer to two different temperatures of measurement. In the derivation of equation (VI-7) it is assumed that the absorbances at λ_1 and λ_2 are due solely to one or the other of two possible 1:1 complexes and that the extinction coefficients of the two complexes are independent of temperature. These assumptions are equivalent to assuming that the temperature dependence of the ratio $\text{Abs}(\lambda_2)/$

$\text{Abs}(\lambda_1)$ is governed only by the temperature dependence of the equilibrium constants involved, as given by the van't Hoff equation. It was pointed out in the discussion of temperature effects on charge-transfer band intensities (V-E-3) that the ratio $\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)$ is affected also by temperature dependent changes in the refractive index and dielectric constant of the solvent, which in turn bring about changes in both the intrinsic intensities of the charge-transfer bands and heats of formation of the complexes. These effects, however, are expected to be small in comparison with the primary effect described by equation (VI-7). $\Delta\Delta H^\circ$ values calculated by means of equation (VI-7), for various combinations of temperatures, are listed in Table 37. The values of $[\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)]_I/[\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)]_{II}$ used in these calculations are the averages of the values computed, at various concentrations of donor, from the $\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)$ ratios listed in Table 29. The final $\Delta\Delta H^\circ$ values given for TCNE-N and TCNE-2,6-DMN are weighted averages (with weights roughly proportional to the square of the temperature interval involved) of the values computed for the various combinations of temperatures. The $\Delta\Delta H^\circ$ results given in Table 37 indicate that there is a small but definite difference in the heats of formation of the complexes absorbing at λ_1 and λ_2 , and that complex λ_1 is the more stable of the two. The latter result confirms the earlier prediction (V-E-3) that the complex having the longest wavelength charge-transfer transition should be the

TABLE 37
Summary of $\Delta\Delta H^\circ$ Values

Units are cal. mole⁻¹

I. For TCNE-N

<u>t_I</u>	<u>t_{II}</u>	<u>$\Delta\Delta H^\circ$ (1-2)</u>	<u>wt.</u>	
0.72	30.00	-204	9	- 1836
11.50	30.00	-174	4	- 696
21.80	30.00	-237	1	- 237
0.72	21.80	-188	4	- 752
11.50	21.80	-129	1	- 129
0.72	11.50	-240	<u>1</u>	<u>- 240</u>
			20	- 3890
Average $\Delta\Delta H^\circ$ (1-2) =				- 195

II. For TCNE-2,6-DMN

0.68	30.00	-199	9	- 1791
0.68	21.80	-209	4	- 836
21.80	30.00	-173	<u>1</u>	<u>- 173</u>
			14	- 2800
Average $\Delta\Delta H^\circ$ (1-2) =				- 200

most stable. Furthermore, the smallness of $\Delta\Delta H^\circ$ in comparison with ΔH° explains the fact that no curvature could be discerned in plots of $\log K$ versus $1/T$.

A comparison of the ΔF° , ΔH° , and ΔS° values obtained in the present study with those available from the literature (in the case of TCNE-N) is given in Table 38. Several interesting relationships are apparent:

1. The $-\Delta F^\circ$ and $-\Delta H^\circ$ values are larger for TCNE-2,6-DMN than for TCNE-N (both complexes in CH_2Cl_2), indicating that TCNE-2,6-DMN is the more stable complex. This result is in agreement with the expectation that alkyl-substituted aromatics should be better π -electron donors (i.e. have a lower I_D) than the parent compounds and hence form more stable complexes.

2. $-\Delta H^\circ$ for the TCNE-N complex decreases upon going from CCl_4 to CH_2Cl_2 as solvent. This behavior is in agreement with that expected in the event of a specific solvent effect, as discussed in Section V, E-3. Since CH_2Cl_2 apparently forms a hydrogen-bonded complex with naphthalene, the overall heat of formation of the TCNE-N complex decreases upon going to this solvent.

3. Changes in ΔF° , ΔH° , ΔS° and $\Delta\Delta H^\circ$ roughly parallel each other. A similar trend among ΔF° , ΔH° and ΔS° is apparent in the series of TCNE-aromatic complexes studied by Briegleb, Czekała and Reuss [107].

TABLE 38

Comparison of Thermodynamic Constants with Literature Values

<u>Complex</u>	<u>Solvent</u>	<u>t</u>	<u>x_K</u>	<u>Δ^{XF}°</u>	<u>Δ^{XH}°</u>	<u>Δ^{XS}°</u>	<u>$\Delta\Delta\text{H}^\circ$</u>	<u>Ref.</u>
TCNE-N	CCl ₄	20°C	33.9	-2.05 ⁽¹⁾	-4.06 ⁽¹⁾	-6.85 ⁽²⁾	-0.420 ^(1,3)	[1071]
TCNE-N	CH ₂ Cl ₂	22°C	11.7	-1.46	-2.21			[201]
TCNE-N	CH ₂ Cl ₂	21.8°C	6.23	-1.17	-2.21	-3.85	-0.194	this work
TCNE-2,6-DMN	CH ₂ Cl ₂	21.8°C	20.42	-1.77	-3.04	-4.33	-0.200	this work

(1) Units are kcal mole⁻¹

(2) Units are entropy units

(3) The $\Delta\Delta\text{H}^\circ$ value for TCNE-N in CCl₄ was calculated from a knowledge of the energy separation between λ_1 and λ_2 , assuming that all other parameters ($W_0, H_{01}, S, E_A, e^2/R_{\text{eq.}}$) are the same for both complexes.

Section VII. Origin of the Multiple Charge-Transfer Bands and Nature of the Absorbing Species

The multiple charge-transfer bands observed in the spectra of molecular complexes of TCNE with methylated naphthalenes can be adequately described, in a one-electron approximation, as arising from promotion of an electron from the highest energy, and successively lower energy, occupied π -MO's of the donor to the lowest energy unoccupied π -MO of the acceptor. Geometrical requirements for effective overlap between the unfilled acceptor MO and successive donor MO's imply that the two lowest energy charge-transfer bands should arise from two distinct 1:1 complexes, differing in orientation of the long axes of the donor and acceptor molecules relative to each other within the sandwich-like complex.

Part A. Origin of the Multiple Charge Transfer Bands

Several possible explanations for the appearance of multiple charge-transfer bands suggest themselves. According to equation (I-7) multiple charge-transfer bands may arise because of:

(1) Several different ionization potentials I_D of the donor. This corresponds to ionization of an electron from the highest, and successively lower-lying, occupied π -MO's of the donor.

(2) Several different electron affinities E_A of the acceptor. This corresponds to transfer of the ionized electron to the lowest, and successively higher-lying, π -MO's of the acceptor.

(3) Several different Coulombic energies $-e^2/R_{eq.}$ for the resulting ion-pair. This presupposes the existence of several stable isomeric complexes having different orientations of the two components with respect to each other.

The first of these explanations applies in the case of π, π -complexes involving substituted benzenes as the donor component. It was first shown theoretically by Orgel [21] that since the double degeneracy of the highest energy occupied π -MO of benzene is removed upon substitution, two ionization potentials of slightly different energy should result. The energies of these depend on the kind, number, and placement of the substituents. It was shown by Orgel,

and recently confirmed by Voigt [127], that the splitting observed in the charge-transfer bands of certain substituted benzene complexes is proportional to the difference between the first two ionization potentials of the donor. A similar analysis of the band widths and splitting observed in TCNE-polymethylbenzene complexes was given by Merrifield and Phillips [20].

A second category of molecular complexes exhibiting multiple charge-transfer bands involves the unsubstituted polynuclear hydrocarbons as donors with acceptors such as TCNE and chloranil. In this case the splitting between the charge-transfer bands is much larger than for the substituted benzene complexes and as many as three bands are commonly observed [107]. Briegleb, Czékalla and Reuss [107] showed, on experimental grounds, that the appearance of these multiple bands could be explained only on the basis of more than one ionization potential of the donor. In support of this explanation, they showed that the energy separation between the charge-transfer maxima corresponded to both the calculated and observed energy differences between the highest-lying and next lower-lying π -MO's of the donor. Possibility (2) was eliminated because the form of the charge-transfer spectrum and the energy separation between the band maxima was independent of the acceptor but was characteristic of the complexes of a given donor with different acceptors. If possibility (3) were the correct explanation, the equilibrium constants and heats of formation of the

isomeric complexes would be considerably different; this implies that the temperature dependence (and solvent dependence) of the charge-transfer intensity should be different for each of the multiple bands. The observed differences in temperature dependence, however, led to values of ΔH of at most a few tenths of a kcal mole⁻¹, a value much too small to explain the energy separations between the charge-transfer maxima.

In the case of the TCNE complexes of the methylnaphthalenes, Lepley [23] has shown that the two lowest energy charge-transfer bands can be interpreted as arising from promotion of an electron from either the highest-lying or second highest-lying occupied π -MO of the donor to the lowest energy unoccupied π -MO of the acceptor. This assignment is based on the fact that the wavelength shifts exhibited by the two lowest energy charge-transfer bands of the methylated complexes, compared to the corresponding bands for TCNE-N, can be adequately explained in terms of the changes upon methylation in the orbital energies of the two highest-lying occupied π -MO's of naphthalene. According to the simple first order perturbation treatment used by Lepley [22,23], the change in orbital energy between the methyl derivative and the parent aromatic hydrocarbon is due principally to the inductive effect of the methyl substituent. The change in energy of the i -th orbital is given by

$$-\Delta\epsilon_i = \sum_r C_{ir}^2 h\beta_{AH} \quad (\text{VII-1})$$

where C_{ir} is the Hückel atomic orbital coefficient for carbon atom r in the i -th π -MO of the parent aromatic hydrocarbon and the summation is taken over all positions of substitution; h is a perturbation coefficient which serves simply as a proportionality constant and β_{AH} is the resonance integral for two bonded carbon atoms and is assumed to be constant for all alternant aromatic hydrocarbons. According to equation (VII-1) the perturbation caused by methyl substitution on the energy of the highest-lying occupied π -MO of naphthalene Ψ_5 will be greatest for substitution at a β ring position and relatively much less for substitution at an α position. On the other hand, the energy of the next lower-lying orbital Ψ_4 will not be affected by α substitution but should be strongly affected by β substitution. A comparison between the observed wavelength shifts and the calculated Coulombic perturbation coefficients is presented in Table 39. It is apparent that the agreement between the calculated and observed shifts is much better for the second charge-transfer transition than for the first. The reason for the relatively poor agreement in the case of the first charge-transfer transition may lie either in the admitted crudeness of the particular perturbation treatment used (no account is taken of the hyperconjugative effect of methyl substitution) or in the tacit assumption that the terms on the right hand side of equation (I-7), other than I_D^v , are constant throughout the series of methyl naphthalene complexes. In regard to the first explanation, Streitwieser and Schwager [128]

TABLE 39

Comparison of Shift in Charge-Transfer Band Energy with ΣC_{ir}^2

First Charge-Transfer Band			Second Charge-Transfer Band			Third Charge-Transfer Band		
Substituent Position	$-\Delta h\nu(\lambda_1)$	(1) ΣC_{ir}^2	Substituent Position	$-\Delta h\nu(\lambda_2)$	(1) ΣC_{ir}^2	Substituent Position	ΣC_{ir}^2	Substituent Position
0	(2.22)	(2)	0	(2.90)	(3)	0	---	0
2	0.10	0.069	1	0.07	0	2	0.030	2
2,3	0.19	0.138	1,4	0.09	0	2,3	0.060	2,3
2,6	0.21	0.138	1,5	0.10	0	2,6	0.060	2,6
2,7	0.20	0.138	1,8	0.05	0	2,7	0.060	2,7
1	0.12	0.181	2	0.18	0.167	2,3,5	0.090	2,3,5
2,3,6	0.29	0.207	1,2	0.20	0.167	2,3,6	0.090	2,3,6
1,2	0.20	0.250	1,3	0.21	0.167	1	0.160	1
1,3	0.19	0.250	1,6	0.22	0.167	1,2	0.190	1,2
1,6	0.20	0.250	1,7	0.21	(4)	1,3	0.190	1,3
1,7	0.23	0.250	2,3	0.37	0.333	1,6	0.190	1,6
2,3,5	0.27	0.319	2,6	0.30	0.333	1,7	0.190	1,7
1,4	0.23	0.362	2,7	0.37	0.333	1,4	0.319	1,4
1,5	0.23	0.362	2,3,5	0.38	0.333	1,5	0.319	1,5
1,8	0.26	0.362	2,3,6	0.52	0.500	1,8	0.319	1,8
								1

(1) in electron volts

(2) energy of unsubstituted naphthalene first charge-transfer band

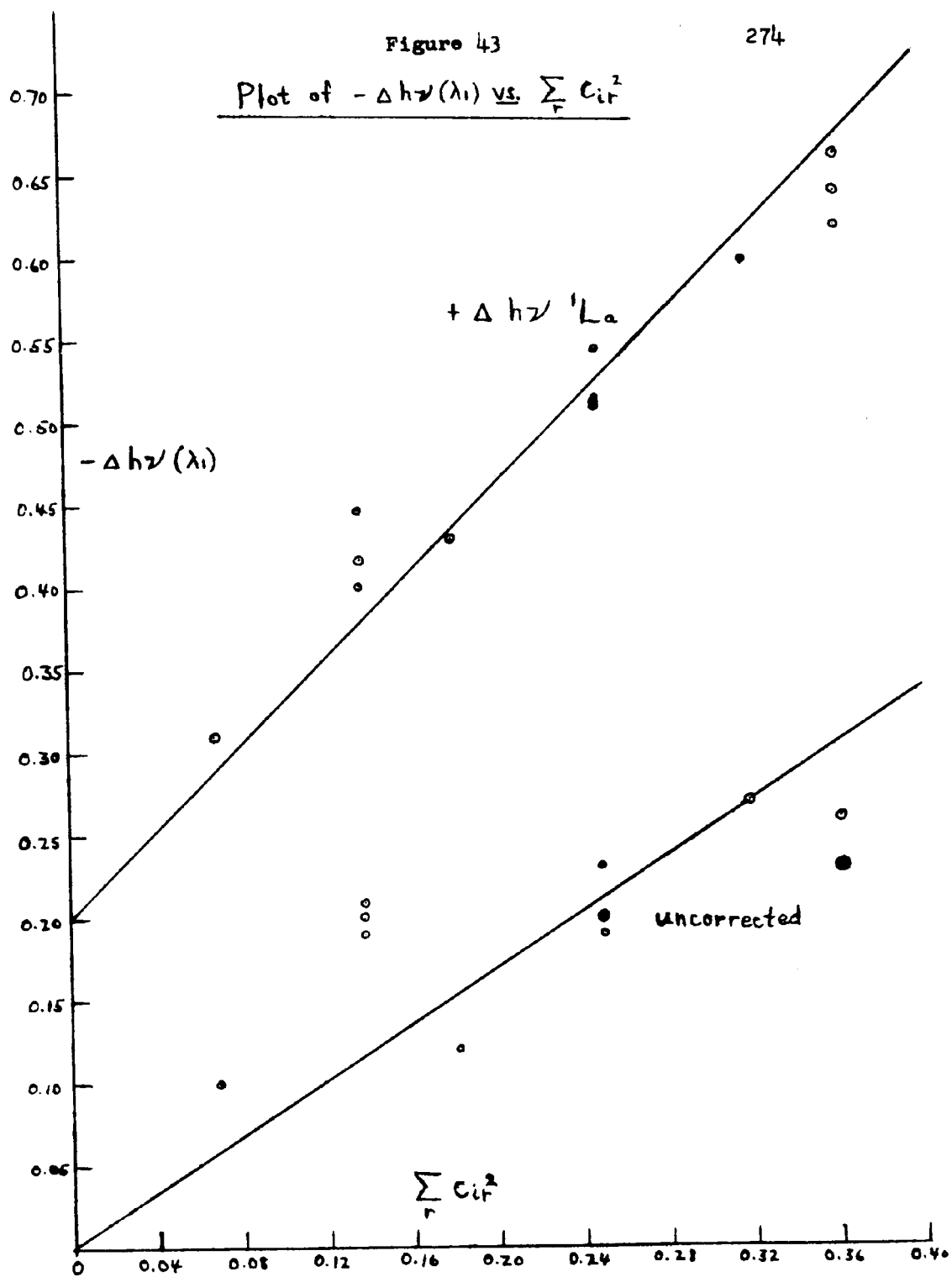
(3) energy of unsubstituted naphthalene second charge-transfer band

(4) present results (uncorrected) in CH_2Cl_2

have shown that the simple first order inductive model used here does not account satisfactorily for the change in polarographic half-wave reduction potentials of the methyl naphthalenes, but that if a correction is made for the hyperconjugative effect a much improved correlation is obtained. As a correction term, Streitwieser and Schwager used the energy shift in the ${}^1L_a$ band of the methylated compound, compared to that of naphthalene; this energy shift has been shown (see, for example Longuet-Higgins and Sowden [129]) to be due, within the approximation of second-order perturbation theory, solely to the second order hyperconjugative effect of the methyl group on the orbital energies of alternant aromatic hydrocarbons. A similar correction applied to Lepley's measured $-\Delta h\nu(\lambda_1)$ values results in a somewhat improved correlation with $\sum_r C_{ir}^2$ (see Figure 43). Unfortunately, it is not possible to estimate the effect of a similar correction on the corresponding correlation for the second charge-transfer band. In any event, it may be concluded that the agreement between $-\Delta h\nu$ and $\sum_r C_{ir}^2$ is sufficiently good, for the first two charge-transfer bands, to support their assignment to electronic promotions involving the highest and second highest occupied π -MO's of the donor.

Figure 43

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Part B. Nature and Conformation of the Absorbing Species

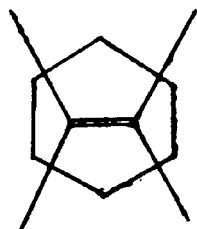
According to the overlap and orientation principle, first stated by Mulliken [3,79], the most stable configuration of donor and acceptor will be that which allows the largest degree of overlap between the donation and acceptation orbitals of the components. Since the two highest energy occupied π -MO's of substituted benzenes have different symmetry properties, it was suggested by Mulliken [79] that the dative structures corresponding to the two lowest ionization potentials of a substituted benzene should favor different orientations of the acceptor molecule; consequently the two charge-transfer bands observed in complexes of the substituted benzenes are likely to originate from different isomeric forms of the complex.

This concept was applied to the TCNE complexes of substituted benzenes by Zweig [129] and Voigt [127], who showed that the short wavelength charge-transfer band of these complexes is most strongly allowed for the conformation in which TCNE and donor have their long axes perpendicular to each other (Figure 44(a)) (the energy of this band should be relatively insensitive to mono- or 1,4-disubstitution). On the other hand, if the components are in a parallel configuration (Figure 44(b)) the short wavelength band becomes symmetry forbidden. Similarly, the long wavelength band (substitution sensitive) is strongly allowed in configuration (b) but symmetry forbidden in configuration (a). Since both bands

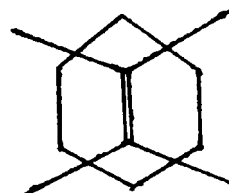
are observed with nearly equal intensity, they must be due either to a single complex having a conformation intermediate between (a) and (b), or to two isomeric complexes represented by (a) and (b) respectively. For either of these two cases, the barrier to internal rotation about an axis passing through the centers of both molecules is probably

Figure 44

Relative Orientations of TCNE
and Donor Long Axes in TCNE-Benzene Complexes



(a)



(b)

quite small--hence for weak complexes in solution at room temperature a model in which free rotation about this axis occurs is probably a good approximation. Whether the observed multiple charge-transfer bands should be considered to arise from one complex or two isomeric complexes depends on the shape and number of minima in the potential energy curve for rotation about this mutually perpendicular axis.

The suggestion that the multiple charge-transfer bands observed in TCNE complexes of polynuclear aromatic hydrocarbons might originate from distinct orientation isomers

was made by Gott and Maisch [97], Kuroda and Akamatu [130] and Lepley [23]. The preferred orientations of donor and acceptor, considering only single charge-transfer states, can be deduced from a consideration of the symmetry properties of the active π -MO's of naphthalene (see Fig. 45) and TCNE (Fig. 46). Maximum overlap between ψ_5^N and ψ_6^{TCNE} is achieved when TCNE is centered over one of the naphthalene rings with its long axis perpendicular to that of naphthalene (Fig. 45(a)), while for maximum overlap of ψ_4^N and ψ_6^{TCNE} the long axis of TCNE is rotated to coincide with that of naphthalene (Fig. 45 (b)). Since the lowest energy charge-transfer transition is symmetry allowed in configuration (a) and forbidden in configuration (b), while the opposite is true for the second charge-transfer transition, it can be concluded that, on the basis of the simplest version of Mulliken's charge-transfer theory, the first two charge-transfer transitions observed in the TCNE-methyl naphthalene complexes probably originate from two distinct configurational isomers. This result provides a theoretical basis for the conclusion reached earlier in this dissertation, that solvent effects on TCNE-N and TCNE-2,6-DMN support the hypothesis that each of the first two charge-transfer bands of these complexes is characteristic of a different 1:1 complex isomer. The results of Bentley and Drickamer [109], cited in Section V, Part E-3, support the assignment of the first two charge-transfer bands to different configurational

Figure 45

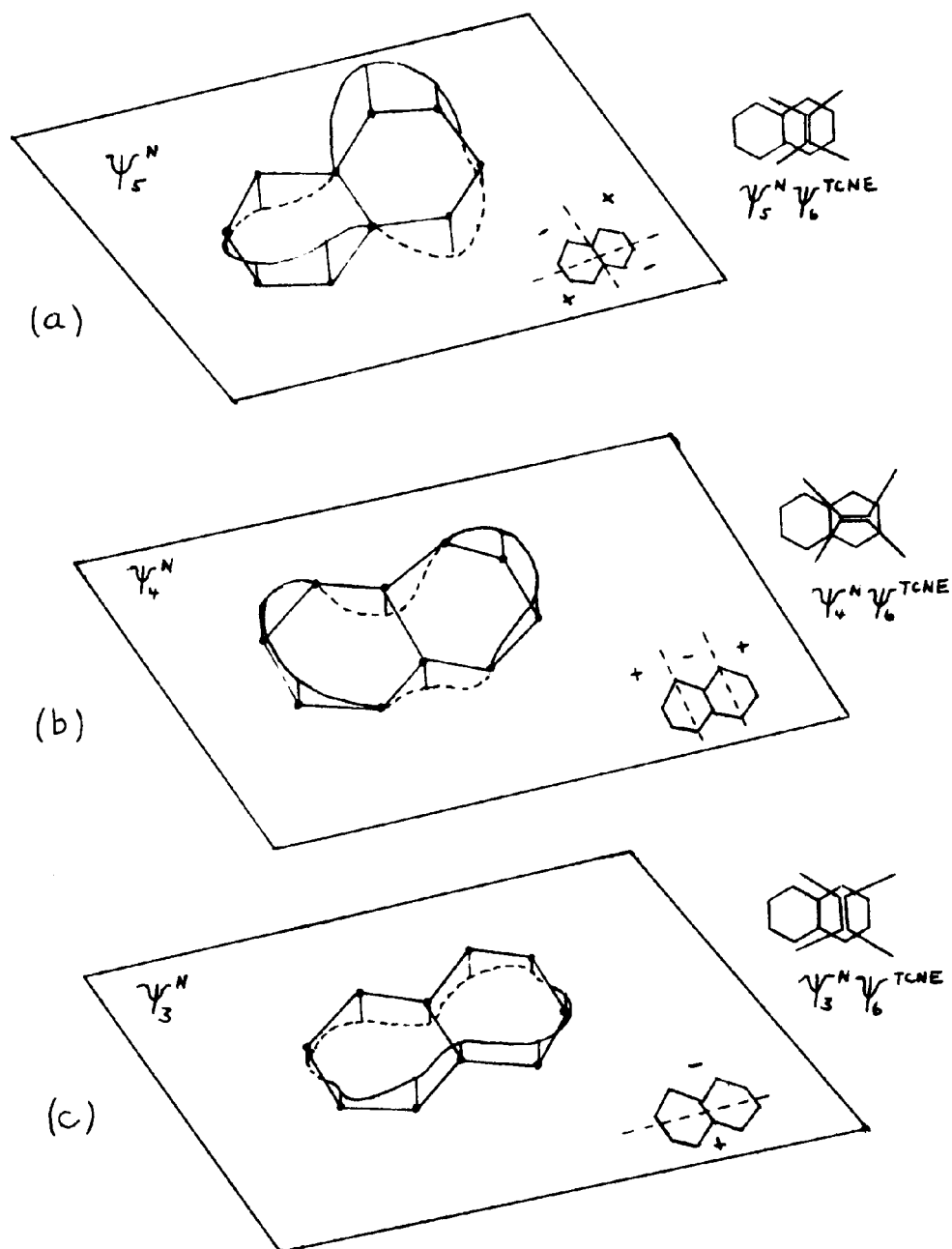
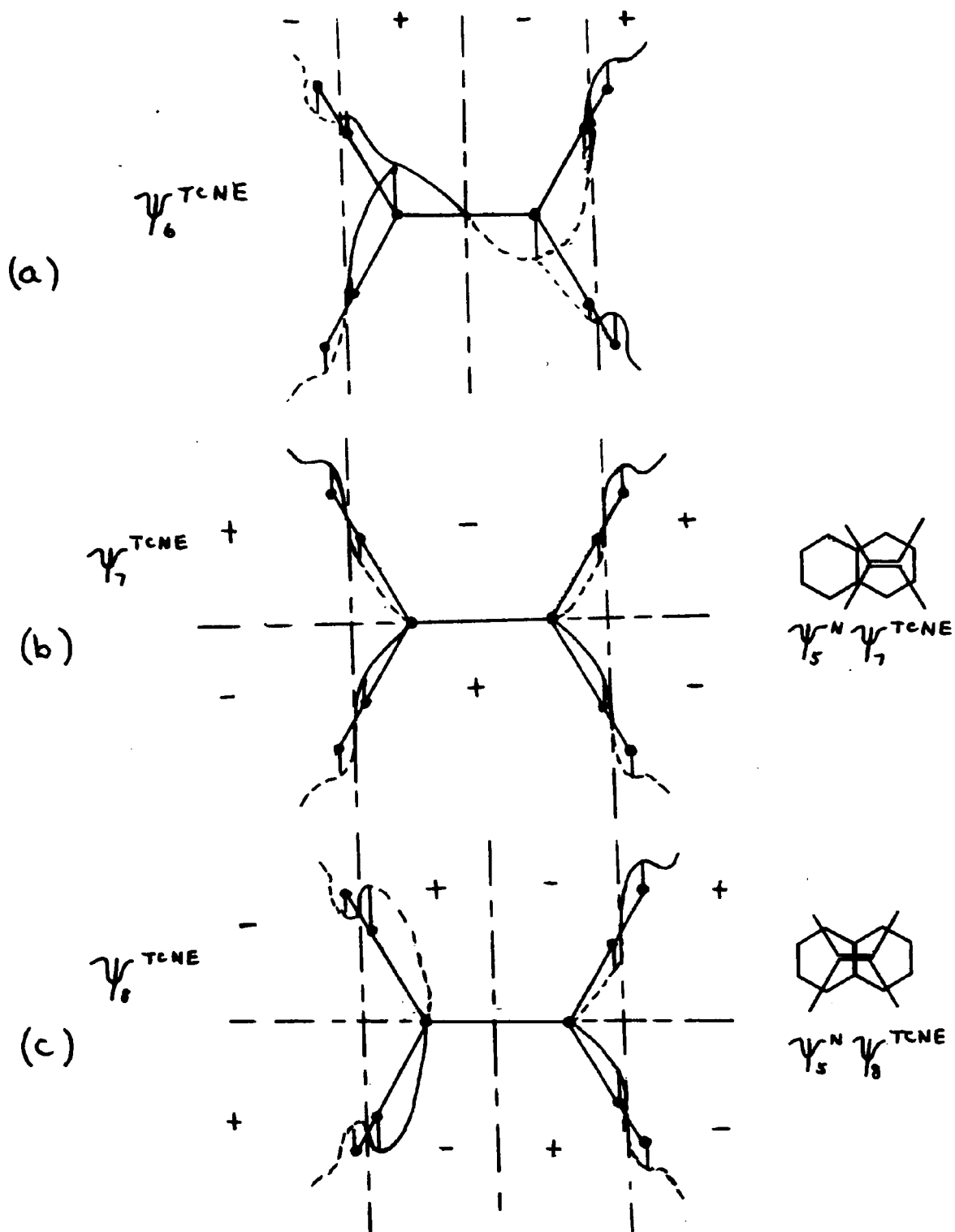
Symmetry Properties of Naphthalene π -MO's

Figure 46

Symmetry Properties of TCNE π -MO's

isomers. Formation of a Diels-Alder adduct between TCNE and naphthalene should be favored for the configuration shown in Figure 45(a), which gives rise to the lowest-energy charge-transfer band. In agreement with this prediction, Bentley and Drickamer found that the lowest energy band of TCNE-N disappeared with greatly increased pressure while the higher energy band, due principally to the configuration shown in Figure 45(b) remained essentially unchanged.

As noted previously, (Section III), several of the methylated naphthalenes show a third distinct charge-transfer band. This behavior is probably characteristic of all of the donors investigated, but is not evident in certain cases because of interference by the characteristic absorption of the donor. In the case of TCNE-N the existence of a third band can be inferred from the appearance of a shoulder on the long-wavelength edge of the characteristic naphthalene absorption when the pressure is increased (see Fig. 1 in the paper by Gott and Maisch [97]); this effect is in accord with the strong pressure red-shift shown by the two lower energy charge-transfer bands of this complex. The fact that the energy of the third charge-transfer band increases in the order $\text{TCNE-1,5-DMN} < \text{TCNE-1,2-DMN} \approx \text{TCNE-1,6-DMN} \approx \text{TCNE-1,7-DMN} < (\text{all remaining complexes studied})$ (cf. Table 5) is in accord with the expected results if this band corresponds to promotion of an electron from Ψ_3 of naphthalene (cf. Table 39). The assignment of this transition is not clear-cut in

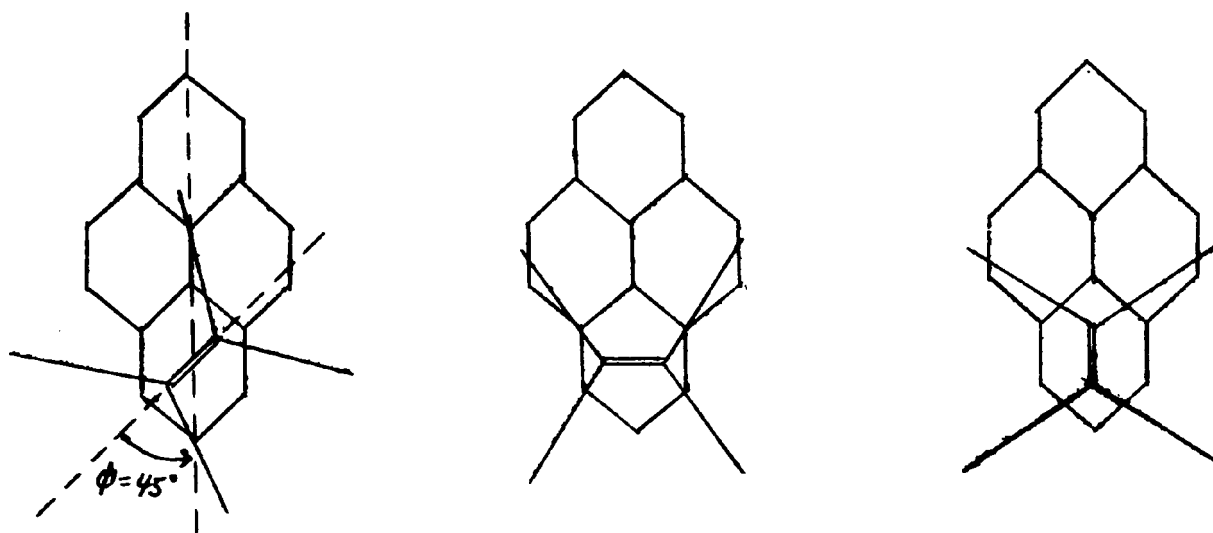
this case since the energy separation between $h\nu_{CT}(\lambda_3)$ and $h\nu_{CT}(\lambda_1)$ is of the order of the energy separation between ψ_6 of TCNE and the degenerate levels ψ_7 and ψ_8 of TCNE (*i.e.* ~ 1.6 ev. [131]; see, however, Penfold and Lipscomb [132]). Thus, $h\nu_{CT}(\lambda_3)$ could possibly correspond to promotion of an electron from ψ_5 of N to ψ_7 (or ψ_8) of TCNE. In this case the energy $h\nu_{CT}(\lambda_3)$ for the series of complexes would be expected to have the same order as for the promotion $\psi_3^N \rightarrow \psi_6^{TCNE}$ (*cf.* Table 39). A consideration of the orbital symmetries involved permits a prediction which, if tested, could resolve these two possibilities. Maximum overlap between ψ_5^N and ψ_7^{TCNE} (or ψ_8^{TCNE}) is achieved when the long axes of both molecules are parallel (see Fig. 46 (b) and (c)); of these, the combination $\psi_5^N \psi_7^{TCNE}$ should be the more stable. If ψ_7^{TCNE} (or ψ_8^{TCNE}) is involved, the structure of the favored complex isomer should be practically identical with that involved in the second charge-transfer band (Figure 45(b)). On the other hand, if ψ_3^N and ψ_6^{TCNE} are involved, the structure of the favored isomer will be practically identical with that involved in the first charge-transfer band (Figure 45(a) and (c)). Assuming, then, that in each case only two distinct isomers are involved, a study of the temperature dependence of absorption at λ_1 , λ_2 and λ_3 should allow a decision between the two possibilities. If the absorption at λ_3 is due to $\psi_3^N \rightarrow \psi_6^{TCNE}$, $Abs(\lambda_3)/Abs(\lambda_1)$ should be approximately temperature independent,

while $\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)$ should vary in accord with the difference in ΔH between the two isomers. On the other hand, if $\psi_5^N \rightarrow \psi_{7,8}^{\text{TCNE}}$ is involved, $\text{Abs}(\lambda_3)/\text{Abs}(\lambda_2)$ should be temperature independent while $\text{Abs}(\lambda_2)/\text{Abs}(\lambda_1)$ should vary.

The discussion presented above has been based on a consideration of single charge-transfer states; thus the overlap of a single donation orbital with a single acceptation orbital leads to the prediction of more than one stable donor-acceptor configuration, depending on which donor (or acceptor) orbitals are taken into consideration. Ideally, the contribution to the total binding energy of the complex of all possible charge-transfer states (a total of 50 for TCNE-N) should be taken into account. Such a treatment, in the case of TCNE-pyrene complex, was given recently by Kuroda and coworkers [131], who considered a total of 32 charge-transfer states for this complex. The configuration of donor and acceptor in the solid state was shown by X-ray analysis [133] to be intermediate between the orientations which would be predicted for the two lowest energy charge transfer states, involving ψ_6^{TCNE} and the highest and second highest occupied orbitals of pyrene, respectively (see Figure 47). Assuming the structure shown in Figure 47(a), calculations considering each of 32 possible charge-transfer states revealed that the states involving overlap of ψ_6^{TCNE} with each of ψ_8 , ψ_7 , ψ_5 and ψ_4 of pyrene all made comparable contributions to the binding energy of the complex. Similar calculations involving variation of the angle ϕ revealed that the potential energy curve

Figure 47

Configuration of Donor and Acceptor
in Solid TCNE-Pyrene Complex



- (a) Observed structure [133]. (b) Predicted structure CT state involving ψ_6^{TCNE} with highest energy filled MO of pyrene (ψ_8^{P}). (c) Predicted structure for CT state involving ψ_6^{TCNE} with ψ_7^{P} .

for rotation about an axis passing through the center of the TCNE molecule was only slightly dependent on ϕ but exhibited two shallow minima (at $\phi \approx 35^\circ, 85^\circ$) separated in energy by only $\sim 0.4 \text{ kcal mole}^{-1}$. It can be concluded from these results that predictions of donor-acceptor configurations based solely on the symmetry properties of the highest (or second highest) occupied MO of the donor and the lowest occupied MO of the acceptor may require modification when all possible charge-transfer states are taken into account. Thus in the case of TCNE-naphthalene complexes, the most

stable configurations may not correspond exactly to the structures predicted in Figure 45. If such is the case, both the first and second charge-transfer transitions will be partially allowed and each stable isomer would then partially contribute to both charge-transfer bands.

APPENDIX I

Least Squares Treatments and Methods of Error EstimationA. Least Squares Treatments

The least squares treatments used in evaluation of K and ϵ_c are the following. We wish to fit a linear equation of the form

$$y_i = a + bx_i$$

where (x_i, y_i) are the coordinates of the line established by the least squares fit. The x_i are assumed to be known exactly while the measured values of y , Y_i , differ from y_i by the residuals δ_i

$$\delta_i = Y_i - y_i = Y_i - (a + bx_i). \quad (A-1)$$

If the sum of squares of the residuals is minimized, a and b are given by

$$a = \frac{\sum Y_i \sum x_i^2 - \sum x_i \sum x_i Y_i}{N \sum x_i^2 - (\sum x_i)^2} = \frac{\bar{Y} \bar{x^2} - \bar{x} \bar{xY}}{\bar{x^2} - (\bar{x})^2} \quad (A-2)$$

$$b = \frac{N \sum x_i Y_i - \sum x_i \sum Y_i}{N \sum x_i^2 - (\sum x_i)^2} = \frac{\bar{xY} - \bar{x} \bar{Y}}{\bar{x^2} - (\bar{x})^2} \quad (A-3)$$

where the sums are over all experimental points i and N is the number of experimental points. This simple method requires that the absolute errors in y be essentially constant.

If, instead, the relative errors in y are constant, the residual equations should be assigned weights w_i given by

$$w_i = (\sigma_i^2)^{-1} = (c^2 Y_i^2)^{-1} \quad (A-4)$$

where σ_i is the standard deviation for the point i and c is the (constant) relative error in y . The average values

appearing in equations (A-2) and (A-3) then become (Wilson [73])

$$\bar{x} = \frac{\sum w_i x_i}{\sum w_i} = \frac{\sum (x_i/y_i)^2}{\sum (1/Y_i)^2} = \frac{\overline{x/Y^2}}{1/Y^2} \quad (\text{A-5})$$

$$\bar{Y} = \frac{\overline{1/Y}}{1/Y^2} \quad (\text{A-6})$$

$$\overline{xY} = \frac{\overline{xy}}{1/Y^2} \quad (\text{A-7})$$

$$\overline{x^2} = \frac{\overline{x^2/Y^2}}{1/Y^2} \quad (\text{A-8})$$

where the single bars signify unweighted averages.

The following weighted least squares treatment was used in the evaluation of ΔH . The equation to be fitted is

$$\log K = a + b (1/T). \quad (\text{A-9})$$

In this case the absolute probable errors in K differ widely and the residual equations must be weighted. Fortunately, the standard deviation of K is given to a good approximation by the square root of the variance in K , S_K , already known from the least squares evaluation of K and ϵ_c . Now, using the fact (Deming [75]) that if

$$Y = \log y$$

$$\text{then } \sigma_y^2 = (0.4343 \sigma_y/y)^2 \quad (\text{A-10})$$

we have for w_i

$$w_i = (\sigma_{\log K}^2)_i^{-1} \cong (S_{\log K}^2)_i^{-1} = (0.4343 S_{K_i}/K_i)^{-2}. \quad (\text{A-11})$$

The slope b is then given by (Bennett and Franklin [76])

$$b = \frac{\sum w_i \sum w_i x_i Y_i - \sum w_i x_i \sum w_i Y_i}{\sum w_i \sum w_i x_i^2 - (\sum w_i x_i)^2} \quad (\text{A-12})$$

B. Methods of Error Estimation

The following relations [76] were used in estimating errors of the various quantities calculated by the method of least squares.

The variance about regression S^2 is given by

$$S^2 = \frac{Q}{N-2} \quad (\text{A-13})$$

where Q is the sum of squares about regression (or sum of squares of residuals) given by

$$Q = \sum \delta_i^2 = \sum (Y_i - y_i)^2 = \sum \{ Y_i - (a + bx_i) \}^2 \quad (\text{A-14})$$

and $(N-2)$ is the number of degrees of freedom (two degrees of freedom have been expended in evaluation of a and b).

In the case of weighted residuals, Q is given by

$$Q = \frac{\sum \delta_i^2 w_i^2}{\sum w_i^2} = \frac{\sum w_i^2 \{ Y_i - (a + bx_i) \}^2}{\sum w_i^2} \quad (\text{A-15})$$

The standard error of estimate S is a measure of the closeness of fit of the data to the calculated least squares line.

The variances of the regression coefficients a and b are given by

$$\text{Var. (a)} = S_a^2 = \frac{S^2 \sum x_i^2}{N \sum x_i^2 - (\sum x_i)^2} = S_b^2 \frac{\sum x_i^2}{N} \quad (\text{A-16})$$

$$\text{Var. (b)} = S_b^2 = \frac{S^2}{\sum (x_i - \bar{x})^2} = \frac{S^2}{\sum x_i^2 - \frac{(\sum x_i)^2}{N}} \quad (\text{A-17})$$

We can now apply the law of propagation of errors (Wilson [77]) to find the variances of K and ϵ_c . Since

$$\sigma^2(\text{for a function } F(x_i)) = \sum \left(\frac{\partial F}{\partial x_i} \right)^2 \sigma x_i^2 \quad (\text{A-18})$$

therefore, for $\epsilon_c = 1/b$, we have

$$S_{\epsilon_c}^2 = \left(\frac{\partial 1/b}{\partial b} \right)^2 S_b^2 = \left(-\frac{1}{b^2} \right)^2 S_b^2 \quad (\text{A-19})$$

In the case of K , where $K = b/a$, we have

$$S_K^2 = \sum \left(\frac{\partial F}{\partial x_i} \right)^2 \sigma x_i^2 = \left(\frac{\partial b/a}{\partial b} \right)^2 S_b^2 + \left(\frac{\partial b/a}{\partial a} \right)^2 S_a^2 \quad (\text{A-20})$$

$$= \frac{1}{a^2} S_b^2 + \frac{b^2}{a^4} S_a^2 = \frac{1}{a^2} [S_b^2 + K_c^2 S_a^2] \quad (\text{A-21})$$

The method of confidence intervals (see for example, Wilson [78]) can now be applied to give an estimate of the upper and lower boundaries for the various quantities (a , b , K , ϵ_c , ΔH) calculated via least squares. These are given by

$$a = \hat{a} \pm t_{N-2, \alpha} S_a \quad (\text{A-22})$$

$$b = \hat{b} \pm t_{N-2, \alpha} S_b \quad (\text{A-23})$$

$$K = \hat{K} \pm t_{N-2, \alpha} S_K \quad (\text{A-24})$$

$$\epsilon_c = \hat{\epsilon}_c \pm t_{N-2, \alpha} S_{\epsilon_c} \quad (\text{A-25})$$

$$\Delta H = -4.5757 (\hat{b} \pm t_{N-2, \alpha} S_b) \quad (\text{A-26})$$

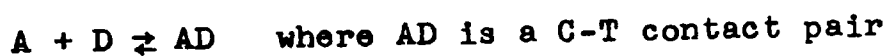
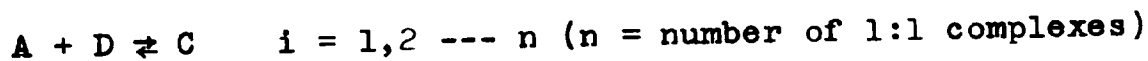
where the symbols marked with a caret denote the values obtained via least squares and $t_{N-2, \alpha}$ is the value of t from Student's t distribution for $N-2$ degrees of freedom and at a confidence level α .

APPENDIX II

Derivation of Equations Applicable to the Presence of Multiple 1:1 Complexes and/or Charge-Transfer Contact Pairs

A. Equation for c_K

Consider the following equilibria



The equilibrium constants in molar concentration units are

$$c_{K_i} = \frac{[C_i]}{[A][D]} = \frac{[C_i]}{(C_A - \sum [C_i])(C_D - \sum [C_i])} \quad (A-27)$$

The concentration of AD pairs is governed by the statistical relation

$$[AD] = c_a [A][D]$$

$$\text{or } c_a = \frac{[AD]}{[A][D]} = \frac{[AD]}{(C_A - \sum [C_i])(C_D - \sum [C_i])} \quad (A-28)$$

where c_a can be regarded simply as a proportionality constant.

With the following definitions

$$c_{K'} \equiv \sum c_{K_i}; \quad [C]' \equiv \sum [C_i]$$

equations (A-27) and (A-28) become

$$c_{K'} = \sum c_{K_i} = \frac{\sum [C_i]}{(C_A - [C]')(C_D - [C]')} = \frac{[C]'}{(C_A - [C]')(C_D - [C]')} \quad (A-29)$$

$$\text{and } c_a = \frac{[AD]}{(C_A - [C]')(C_D - [C]')} \quad (A-30)$$

Comparing equations (A-27), (A-29) and (A-30) we have

$$AD = \frac{[C]'}{c_{K'}} c_a \quad ; \quad [C_i] = \frac{[C]'}{c_{K'}} c_{K_i} \quad (A-31)$$

Now , provided that the components are colorless, the absorbance is given by

$$\text{Abs} = \bar{\epsilon}_{AD} [\text{AD}] + \sum \epsilon_{C_i} [C_i] \quad (\text{A-32})$$

where $\bar{\epsilon}_{AD}$ is a suitable average value of ϵ_{AD} over all configurations. In view of equations (A-31), (A-32) becomes

$$\text{Abs} = \frac{\bar{\epsilon}_{AD} c_a [C]'}{c_{K'}} + \frac{[C]' \sum c_{K_i} \epsilon_{C_i}}{c_{K'}} = \epsilon_C'' [C]' \quad (\text{A-33})$$

Where ϵ_C'' is defined by

$$\epsilon_C'' \equiv \frac{\bar{\epsilon}_{AD} c_a}{c_{K'}} + \frac{\sum c_{K_i} \epsilon_{C_i}}{c_{K'}} .$$

Eliminating $[C]'$ between equations (A-29) and (A-33) and rearranging gives

$$\frac{c_A c_D}{\text{Abs}} = \frac{1}{\epsilon_C''} (c_A + c_D - \frac{\text{Abs}}{\epsilon_C''}) + \frac{1}{c_{K'} \epsilon_C''} \quad (\text{V-18'})$$

which is formally identical with equation (V-18). If there is no contribution from contact charge-transfer absorption, ϵ_C'' can be replaced by ϵ_C' , given by

$$C' \equiv \frac{\sum c_{K_i} \epsilon_{C_i}}{c_{K'}} .$$

B. Equation for x_K

The appropriate equilibrium constants expressed in mole fraction units are

$$x_{K_i} = \frac{(X_{C_i})_{\text{eq.}}}{(X_A)_{\text{eq.}} (X_D)_{\text{eq.}}} \quad \text{and} \quad x_a = \frac{(X_{AD})_{\text{eq.}}}{(X_A)_{\text{eq.}} (X_D)_{\text{eq.}}}$$

Since, in general, $(X_j)_{\text{eq.}} = [j] \bar{V}$, we get

$$x_{K_1} = \frac{[C_1] \ 1/\bar{V}'}{[A] [D]} = \frac{[C_1] \ 1/\bar{V}'}{(C_A - \Sigma [C_1])(C_D - \Sigma [C_1])} = c_{K_1} \ 1/\bar{V}'$$

$$\text{and } x_a = \frac{[AD] \ 1/\bar{V}'}{[A] [D]} = \frac{[AD] \ 1/\bar{V}'}{(C_A - \Sigma [C_1])(C_D - \Sigma [C_1])} = c_a \ 1/\bar{V}'$$

where

$$\begin{aligned} 1/\bar{V}' &\equiv [S] + [A] + [D] + \Sigma [C_1] \\ &= C_S + C_A + C_D - \Sigma [C_1] . \end{aligned}$$

$$\text{Let } x_{K'} = \Sigma x_{K_1} \quad ; \quad [C]' = \Sigma [C_1]$$

$$\text{Then } x_{K'} = \frac{[C]' \ 1/\bar{V}'}{(C_A - [C]')(C_D - [C]')} \quad ; \quad x_a = \frac{[AD] \ 1/\bar{V}'}{(C_A - [C]')(C_D - [C]')} \quad (\text{A-34})$$

$$\text{and } [C_1] = \frac{[C]' \ x_{K_1}}{x_{K'}} = \frac{[C]' \ c_{K_1}}{c_{K'}} \quad ; \quad [AD] = \frac{[C]' \ x_a}{x_{K'}} = \frac{[C]' \ c_a}{c_{K'}} .$$

The absorbance is given by

$$\begin{aligned} \text{Abs} &= \bar{\epsilon}_{AD} [AD] + \Sigma \epsilon_{C_1} [C_1] \\ &= \frac{[C]' \ x_a \ \bar{\epsilon}_{AD}}{x_{K'}} + \frac{[C]' \ \Sigma x_{K_1} \ \epsilon_{C_1}}{x_{K'}} \equiv \epsilon_C'' [C]' \quad (\text{A-35}) \end{aligned}$$

Eliminating $[C]'$ between (A-34) and (A-35) and rearranging gives

$$\frac{C_A C_D}{\text{Abs}} \ \bar{V}' = \frac{\bar{V}'}{\epsilon_C''} (C_A + C_D - \frac{\text{Abs}}{\epsilon_C''}) + \frac{1}{x_{K'} \ \epsilon_C''} \quad (\text{V-26'})$$

which is formally identical with equation (V-26).

APPENDIX III

Derivation of Equations Applicable to Several Cases of Competing EquilibriaA. Complexing Between Solvent and A (or D)

Consider the general case of several 1:1 complexes and/or contact C-T pairs formed between D and A plus formation of an SA (or SD) complex. The equilibria involved are:



with the following concentration equilibrium constants

$$\begin{aligned} c_{K_i} &= \frac{[C_i]}{[D][A]} = \frac{[C_i]}{(C_D - \sum [C_i])(C_A - [C_{SA}] - \sum [C_i])} \\ &= \frac{[C_i]}{(C_D - [C]')(C_A - [C_{SA}] - [C]')} \end{aligned} \quad (A-36)$$

$$c_a = \frac{[AD]}{[D][A]} = \frac{[AD]}{(C_D - [C]')(C_A - [C_{SA}] - [C]')} \quad (A-37)$$

$$c_{K_{SA}} = \frac{[C_{SA}]}{[S][A]} = \frac{[C_{SA}]}{(C_S - [C_{SA}])(C_A - [C_{SA}] - [C]')} \quad (A-38)$$

where $[C]' = \sum [C_i]$.

Then

$$c_{K'} = \sum c_{K_i} = \frac{[C]'}{(C_D - [C]')(C_A - [C_{SA}] - [C]')} \quad (A-39)$$

From (A-38) and (A-39)

$$[C_{SA}] = \frac{c_{K_{SA}}(C_S - [C_{SA}])([C]')}{c_{K'}(C_D - [C]')} \quad (A-40)$$

Combining (A-39) and (A-40) and rearranging gives

$$\frac{1}{c_{K'}} = \frac{1}{1+c_{KSA}(C_S-[C_{SA}])} \left[\frac{C_A C_D}{[C]} - C_D - C_A + [C]' \right]. \quad (A-41)$$

Assuming A, D, A, and SA do not absorb,

$$\text{Abs} = \bar{\epsilon}_{AD}[AD] + \sum \epsilon_{C_i}[C_i].$$

Since, from equations (A-36), (A-37) and (A-39)

$$[C_i] = \frac{[C]' c_{K_i}}{c_{K'}}; [AD] = \frac{[C]' c_a}{c_{K'}},$$

$$\text{Abs} = \frac{\bar{\epsilon}_{AD} c_a [C]'}{c_{K'}} + \frac{[C]'}{c_{K'}} \sum \epsilon_{C_i} c_{K_i} = \epsilon_c'' [C]'$$

where

$$\epsilon_c'' = \frac{\bar{\epsilon}_{AD} c_a}{c_{K'}} + \frac{\sum \epsilon_{C_i} c_{K_i}}{c_{K'}}.$$

Equation (A-41) now becomes

$$\frac{1}{c_{K'}} = \frac{1}{1+c_{KSA}(C_S-[C_{SA}])} \left[\frac{C_A C_D}{\text{Abs}} \epsilon_c'' - C_A - C_D + \frac{\text{Abs}}{\epsilon_c''} \right]. \quad (V-67)$$

In terms of mole fraction equilibrium constants,

$$x_{K_i} = \frac{(X_{C_i})_{\text{eq.}}}{(X_D)_{\text{eq.}} (X_A)_{\text{eq.}}} = \frac{[C_i]^{1/\bar{V}''}}{[D][A]} = c_{K_i}^{1/\bar{V}''}$$

where

$$1/\bar{V}'' = [S] + [D] + [A] + [C_{SA}] + \sum [C_i]$$

$$= C_S + C_D + C_A - [C_{SA}] - [C]'.$$

Similarly,

$$x_{K'} = \frac{[C]'^{1/\bar{V}''}}{[D][A]} = c_{K'}^{1/\bar{V}''}$$

$$x_{KSA} = \frac{[C_{SA}]^{1/\bar{V}''}}{[S][A]} = c_{KSA}^{1/\bar{V}''}$$

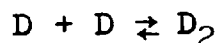
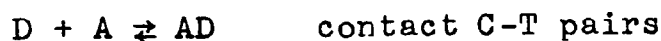
$$x_a = \frac{[AD]1/\sqrt{V}''}{[D][A]} = c_a 1/\sqrt{V}'' .$$

Then, directly from equation (V-67) we get

$$\frac{1}{x_{K'}} = \frac{1}{1/\sqrt{V}'' + x_{K_{SA}}(C_S - [C_{SA}])} \left[\frac{C_A C_D}{Abs} \epsilon_c'' - C_A - C_D + \frac{Abs}{\epsilon_c''} \right]. \quad (V-68)$$

B. Self-Complex Formation Between Molecules of D (or A)

Consider the general case of several 1:1 complexes and/or contact C-T pairs formed between D and A plus formation of a DD (or AA) complex. The equilibria involved are:



Then, letting $\Sigma[C_i] = [C]'$, the molar concentration equilibrium constants involved are:

$$\begin{aligned} c_{K_i} &= \frac{[C_i]}{[D][A]} = \frac{[C_i]}{(C_A - \Sigma[C_i])(C_D - 2[D_2] - \Sigma[C_i])} \\ &= \frac{[C_i]}{(C_A - [C]')(C_D - 2[D_2] - [C]')} \end{aligned} \quad (A-42)$$

$$c_a = \frac{[AD]}{[D][A]} = \frac{[AD]}{(C_A - [C]')(C_D - 2[D_2] - [C]')} \quad (A-43)$$

$$c_{K_{D_2}} = \frac{[D_2]}{[D]^2} = \frac{[D_2]}{(C_D - 2[D_2] - [C]')^2} \quad (A-44)$$

$$c_{K'} = \Sigma c_{K_i} = \frac{[C]'}{(C_A - [C]')(C_D - 2[D_2] - [C]')} \quad (A-45)$$

From (A-44) and (A-45)

$$[D_2] = \frac{c_{K_{D_2}}([C]')^2}{(c_{K'})^2(C_A - [C]')^2} \quad (A-46)$$

Inversion of (A-45) and substitution for $[D_2]$ from (A-46)

yields

$$\frac{1}{c_{K'}} = \left[\frac{c_A c_D}{[C]'} - c_D - c_A + [C]' \right] - \frac{2^c K_{D_2} [C]'}{(c_{K'})^2 (c_A - [C]')}$$

which rearranges to

$$\frac{1}{c_{K'}} = \frac{1}{1 + \frac{2^c K_{D_2} [C]'}{c_{K'} (c_A - [C]')}} \left[\frac{c_A c_D}{[C]'} - c_D - c_A + [C]' \right]. \quad (A-47)$$

Elimination of $\frac{[C]'}{c_{K'} (c_A - [C]')}$ between (A-47) and (A-45) then gives

$$\frac{1}{c_{K'}} = \frac{1}{1 + 2^c K_{D_2} (c_D - [C]' - 2[D_2])} \left[\frac{c_A c_D}{[C]'} - c_D - c_A + [C]' \right]. \quad (A-48)$$

Assuming A, D, S and D_2 do not absorb,

$$\text{Abs} = \bar{\epsilon}_{AD} [AD] + \sum \epsilon_{C_i} [C_i]. \quad (A-49)$$

Now, from equations (A-42), (A-43) and (A-45)

$$C_i = \frac{[C]' c_{K_i}}{c_{K'}}; [AD] = \frac{[C]' c_a}{c_{K'}}$$

so that (A-49) becomes

$$\text{Abs} = \frac{[C]'}{c_{K'}} [\bar{\epsilon}_{AD} c_a + \sum \epsilon_{C_i} c_{K_i}] = \epsilon_c'' [C]'$$

where ϵ_c'' is defined by

$$\epsilon_c'' \equiv \frac{1}{c_{K'}} [\bar{\epsilon}_{AD} c_a + \sum \epsilon_{C_i} c_{K_i}].$$

Equation (A-48) can now be written

$$\frac{1}{c_{K'}} = \frac{1}{1 + 2^c K_{D_2} (c_D - [C]' - 2[D_2])} \left[\frac{c_A c_D}{\text{Abs}} \epsilon_c'' - c_A - c_D + \frac{\text{Abs}}{\epsilon_c''} \right]. \quad (V-72)$$

In terms of mole fraction equilibrium constants,

$$x_{K_i} = \frac{(X_{C_i})_{eq.}}{(X_D)_{eq.} (X_A)_{eq.}} = \frac{[C_i] 1/\bar{V}'''}{[D][A]} = c_{K_i} 1/\bar{V}'''$$

$$\begin{aligned} \text{where } 1/\bar{V}''' &= [S] + [D] + [A] + [D_2] + \sum [C_i] \\ &= C_S + C_D + C_A - [D_2] - [C]' . \end{aligned}$$

Similarly,

$$x_{K'} = \frac{[C]' 1/\bar{V}'''}{[D][A]} = c_{K'} 1/\bar{V}'''$$

$$x_{K_{D_2}} = \frac{[D_2] 1/\bar{V}'''}{[D]^2} = c_{K_{D_2}} 1/\bar{V}'''$$

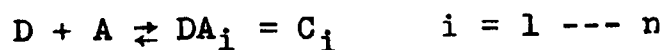
$$x_a = \frac{[AD] 1/\bar{V}'''}{[D][A]} = c_a 1/\bar{V}''' .$$

Then, directly from equation (V-72) we get

$$\frac{1}{x_{K'}} = \frac{1}{1/\bar{V}''' + 2x_{K_{D_2}}(C_D - [C]' - 2[D_2])} \left[\frac{C_D C_A}{Abs} \epsilon_c'' - C_A - C_D + \frac{Abs}{\epsilon_c''} \right] . \quad (V-73)$$

C. Formation of Higher Order Complexes Between D and A

Consider the general case of several 1:1 complexes and/or contact C-T pairs formed between D and A plus formation of a complex D_2A . The equilibria involved are:



Then, letting $\sum [C_i] = [C]'$, the molar concentration equilibrium constants are:

$$c_{K_1} = \frac{[C_1]}{[A][D]} = \frac{[C_1]}{(C_A - \sum [C_1] - [D_2A])(C_D - \sum [C_1] - 2[D_2A])}$$

$$= \frac{[C_1]}{(C_A - [C]' - [D_2A])(C_D - [C]' - 2[D_2A])} \quad (A-50)$$

$$c_{K'} = \sum c_{K_1} = \frac{[C]'}{(C_A - [C]' - [D_2A])(C_D - [C]' - 2[D_2A])} \quad (A-51)$$

$$\bar{c}_a = \frac{[AD]}{[A][D]} = \frac{[AD]}{(C_A - [C]' - [D_2A])(C_D - [C]' - 2[D_2A])} \quad (A-52)$$

$$c_{K_{D_2A}} = \frac{[D_2A]}{\sum [D_2A][D]} = \frac{[D_2A]}{[C]'(C_D - [C]' - 2[D_2A])} \quad (A-53)$$

$$c_{K'D_2A} = \frac{[D_2A]}{[A][D]^2} \quad (A-54)$$

From (A-51) and (A-53)

$$\frac{[D_2A]}{[C]'} = \frac{c_{K_{D_2A}}[C]'}{c_{K'}(C_A - [C]' - [D_2A])} \quad (A-55)$$

Inverting (A-51) and expanding gives (A-56)

$$\frac{1}{c_{K'}} = \left[\frac{C_A C_D}{[C]'} - C_A - C_D + [C]' \right] - \frac{[D_2A]}{[C]'} \left[2(C_A - [C]' - [D_2A]) + (C_D - [C]') \right].$$

Eliminating $\frac{[D_2A]}{[C]'}$ between (A-55) and (A-56) gives (A-57)

$$\frac{1}{c_{K'}} = \frac{1}{1 + c_{K_{D_2A}}[C]'} \left[2 + \frac{(C_D - [C]')}{(C_A - [C]' - [D_2A])} \right] \left[\frac{C_A C_D}{[C]'} - C_A - C_D + [C]' \right].$$

If A, D and S do not absorb

$$\text{Abs} = \bar{\epsilon}_{AD} [AD] + \sum \epsilon_{C_1} [C_1] + \epsilon_{D_2A} [D_2A]. \quad (A-58)$$

Now, from equations (A-50), (A-51) and (A-52)

$$[C_i] = \frac{[C]'^c K_i}{c_{K'}}; [AD] = \frac{[C]'^c c_a}{c_{K'}}$$

so that (A-58) becomes

$$\text{Abs} = \frac{\bar{\epsilon}_{AD}^c c_a [C]'}{c_{K'}} + \frac{[C]'}{c_{K'}} \sum \epsilon_{C_i}^c K_i + \epsilon_{D_2A} [D_2A] = \epsilon_c''' [C]'$$

$$\text{where } \epsilon_c''' \equiv \frac{\bar{\epsilon}_{AD}^c c_a}{c_{K'}} + \frac{\sum \epsilon_{C_i}^c K_i}{c_{K'}} + \epsilon_{D_2A} \frac{D_2A}{[C]'} \quad (\text{A-59})$$

From equations (A-51) and (A-54)

$$\frac{[D_2A]}{[C]'} = \frac{c_{K'} D_2A}{c_{K'}} [D]$$

so that (A-59) becomes

$$\epsilon_c''' = \frac{1}{c_{K'}} \left[\bar{\epsilon}_{AD}^c c_a + \sum \epsilon_{C_i}^c K_i + \epsilon_{D_2A}^c K_i' D_2A [D] \right].$$

Note that ϵ_c''' is not a true constant as is ϵ_c'' , but is a function of $[D]$. Equation (A-57) now becomes

$$\frac{1}{c_{K'}} = \frac{\left[\frac{C_A C_D}{\text{Abs}} \epsilon_c''' - C_A - C_D + \frac{\text{Abs}}{\epsilon_c'''} \right]}{1 + c_{K'} D_2A [C]'} \left[2 + \frac{(C_D - [C]')}{(C_A - [C]' - [D_2A])} \right] \quad (\text{V-77})$$

In terms of mole fraction equilibrium constants,

$$x_{K_i} = \frac{(X_{C_i})_{\text{eq.}}}{(X_A)_{\text{eq.}} (X_D)_{\text{eq.}}} = \frac{[C_i] 1/\bar{V}''''}{[A][D]} = c_{K_i} 1/\bar{V}''''$$

$$\begin{aligned} \text{where } 1/\bar{V}'''' &= [S] + [D] + [A] + [D_2A] + \sum [C_i] \\ &= C_S + C_D + C_A - 2 [D_2A] - [C]'. \end{aligned}$$

Similarly,

$$x_{K'} = \frac{[C]'1/\bar{V}'''}{[A][D]} = c_{K'} 1/\bar{V}'''$$

$$x_a = \frac{[AD]1/\bar{V}'''}{[A][D]} = c_a 1/\bar{V}'''$$

$$x_{K_{D_2A}} = \frac{[D_2A]1/\bar{V}'''}{[DA][D]} = c_{K_{D_2A}} 1/\bar{V}'''$$

$$x_{K'_{D_2A}} = \frac{[D_2A](1/\bar{V}''')^2}{[A][D]^2} = c_{K'_{D_2A}}(1/\bar{V}''')^2$$

Equation (V-77) now becomes

$$\frac{1}{c_{K'}} = \frac{\left[\frac{C_A C_D}{Abs} \epsilon_c''' - C_A - C_D + \frac{Abs}{\epsilon_c'''} \right]}{1/\bar{V}''' + x_{K_{D_2A}}[C]' \left[2 + \frac{(C_D - [C]')}{(C_A - [C]' - [D_2A])} \right]} \quad (V-78)$$

REFERENCES

1. H. A. Benesi and J. H. Hildebrand, J. Am. Chem. Soc. 71, 2703 (1949).
2. R. S. Mulliken, J. Am. Chem. Soc. 72, 600 (1950).
3. R. S. Mulliken, J. Am. Chem. Soc. 74, 811 (1952).
4. G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe", Springer Verlag, Berlin, 1961.
5. L. J. Andrews, Chem. Revs. 54, 713 (1954).
6. R. S. Mulliken, J. Phys. Chem. 56, 801 (1952).
7. R. S. Mulliken, J. de Chimie Physique 61, 20 (1964).
8. S. P. McGlynn, Chem. Revs. 58, 1113 (1958).
9. J. N. Murrell, Quarterly Revs. (London) 15, 191 (1961).
10. L. E. Orgel, Quarterly Revs. (London) 8, 422 (1954).
11. S. F. Mason, Quarterly Revs. (London) 15, 287 (1961).
12. G. Briegleb and J. Czekalla, Angew. Chem. 72, 401 (1960).
13. A. Szent-Györgyi, "Introduction to a Submolecular Biology", Academic Press, New York, 1960.
14. S. P. McGlynn, Radiation Research Suppl. 2, 300 (1960).
15. D. Booth, Sci. Progr. 48, 435 (1960).
16. L. J. Andrews and R. M. Keefer, Advances Inorg. Chem. and Radiochem. 3, 91 (1961).
17. O. Hassel and C. Rømming, Quarterly Revs. (London) 16, 1 (1962).
18. R. S. Mulliken and W. B. Person, Ann. Rev. Phys. Chem. 13, 107 (1962).
19. G. Briegleb, Angew. Chem. Internat. Edit. 3, 617 (1964).
20. R. E. Merrifield and W. D. Phillips, J. Am. Chem. Soc. 80, 2778 (1958).
21. L. E. Orgel, J. Chem. Phys. 23, 1352 (1955).

22. A. R. Lepley, J. Am. Chem. Soc. 86, 2545 (1964).
23. A. R. Lepley, Tetrahedron Letters 39-40, 2823 (1964).
24. H. McConnell, J. S. Ham and J. R. Platt, J. Chem. Phys. 21, 66 (1953).
25. A. Streitwieser Jr., "Molecular Orbital Theory for Organic Chemists", John Wiley and Sons, Inc., New York, 1961.
26. W. J. Middleton, E. L. Little, D. D. Coffman and V. A. Engelhardt, J. Am. Chem. Soc. 80, 2795 (1958).
27. B. C. McKusick and G. F. Biehn, Chem. and Eng. News 38, 114 (1960).
28. "Azeotrope Data", Advances in Chemistry Series, Vol. No. 6, American Chemical Society, 1952.
29. Technical Bulletin on Chloromethanes, Solvay Process Division of Allied Chemical and Dye Corporation.
30. R. W. Kreinest, Division Manager, Matheson, Coleman and Bell, personal communication.
31. S. P. McGlynn, R. Sunseri and N. Christodouleas, J. Chem. Phys. 37, 1818 (1962).
32. T. L. Cairns, R. A. Carboni, D. D. Coffman, V. A. Engelhardt, R. E. Heckert, E. L. Little, E. G. McGeer, B. C. McKusick, W. J. Middleton, R. M. Scribner, C. W. Theobald and H. E. Winberg, J. Am. Chem. Soc. 80, 2775 (1958).
33. A. Bader, Chief Chemist, Aldrich Chemical Company, Inc., personal communication.
34. "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds", American Petroleum Institute Project 44, best values as of Dec. 31, 1952.
35. R. R. Dreisbach, "Physical Properties of Chemical Compounds", Vol. 1, Advances in Chemistry Series, No. 15, American Chemical Society, 1955.
36. Instruction Manual 305, "The Beckman Model DU Spectrophotometer", Beckman Instruments Inc., Fullerton, Cal.
37. K. S. Gibson, "Spectrophotometry", U. S. Dept. of Commerce, National Bureau of Standards Circular 484, Sept. 15, 1949.

38. W. Slavin and T. J. Porro, "Measurement of Photometric Accuracy in U.V.-Vis. Spectrophotometry", a paper delivered at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March, 1960.
39. J. M. Vandenberg, J. Opt. Soc. Am. 44, 641 (1954).
40. J. M. Vandenberg, J. Opt. Soc. Am. 50, 24 (1960).
41. L. Cahn, J. Opt. Soc. Am. 45, 953 (1955).
42. P. Job, Ann. Chim, Paris 9, 113 (1928).
43. W. C. Vosburgh and G. R. Cooper, J. Am. Chem. Soc. 63, 437 (1941).
44. Instruction Manual, Beckman DK2-A, Beckman Instruments Inc., Fullerton, Cal.
45. G. H. Schenk and M. Ozolins, Anal. Chem. 33, 1562 (1961).
46. R. Vars, L. A. Tripp and L. W. Pickett, J. Phys. Chem. 66, 1754 (1962).
47. M. J. S. Dewar and A. R. Lepley, J. Am. Chem. Soc. 84, 395 (1962).
48. A. Zweig, J. Phys. Chem. 67, 506 (1963).
49. G. N. Lewis and M. Kasha, J. Am. Chem. Soc. 66, 2100 (1944).
50. L. E. Orgel and R. S. Mulliken, J. Am. Chem. Soc. 79, 4839 (1957).
51. R. Anderson and J. M. Prausnitz, J. Chem. Phys. 39, 1225 (1963).
52. H. Kuroda, M. Kobayashi, M. Kinoshita and S. Takemoto, J. Chem. Phys. 36, 457 (1962).
53. R. L. Scott, Rec. trav. chim. 75, 787 (1956).
54. J. A. A. Ketelaar, C. Van de Stolpe, A. Goudsmit and W. Dzcubas, Rec. trav. chim. 71, 1104 (1952).
55. R. E. Buckles and J. F. Mills, J. Am. Chem. Soc. 75, 552 (1953).
56. R. Foster, D. Ll. Hammick and A. A. Wardley, J. Chem. Soc. 3817 (1953).
57. G. Kortum and G. Weber, Z. Elektrochem. 64, 642 (1960).

58. S. Nagakura, J. Am. Chem. Soc. 76, 3070 (1954).
59. R. Foster, J. Chem. Soc. 5098 (1957).
60. N. J. Rose and R. S. Drago, J. Am. Chem. Soc. 81, 6138 (1959).
61. R. S. Drago and N. J. Rose, J. Am. Chem. Soc. 81, 6141 (1959).
62. M. Tamres, J. Phys. Chem. 65, 654 (1961).
63. R. M. Keefer and L. J. Andrews, J. Am. Chem. Soc. 74, 1891 (1952).
64. S. D. Ross, M. Finkelstein and W. Leach, J. Am. Chem. Soc. 76, 69 (1954).
65. S. D. Ross and M. M. Labes, J. Am. Chem. Soc. 79, 76 (1957).
66. R. P. Lang, J. Am. Chem. Soc. 84, 1185 (1962).
67. M. Tamres and Sr. M. Brandon, J. Am. Chem. Soc. 82, 2134 (1960).
68. W. Liptay, Z. Elektrochem, 65, 375 (1961).
69. W. Liptay, Chapter 12 in "Elektronen-Donator-Acceptor-Komplexe" by G. Briegleb, Springer Verlag, Berlin, 1961.
70. H. J. G. Hayman, J. Chem. Phys. 37, 2290 (1962).
71. J. B. Scarborough, "Numerical Mathematic Analysis", 2nd. Ed., The Johns Hopkins Press, Baltimore, 1950, Art. 145.
72. N. Ogimachi, L. J. Andrews and R. M. Keefer, J. Am. Chem. Soc. 77, 4202 (1955).
73. E. B. Wilson, Jr., "An Introduction to Scientific Research", McGraw-Hill Book Co., Inc., New York, 1952, Sec. 8.13.
74. J. B. Scarborough, op. cit., Art. 148.
75. W. Edwards Deming, "Some Notes on Least Squares", The Graduate School, The Department of Agriculture, Washington, D.C., 1938, p. 30.
76. C. A. Bennett and N. L. Franklin, "Statistical Analysis in Chemistry and the Chemical Industry," John Wiley and Sons, Inc., New York, 1954, p. 244.

77. E. B. Wilson, Jr., op. cit., Sec. 9.11
78. E. B. Wilson, Jr., op. cit., Sec. 9.2.
79. R. S. Mulliken, Rec. trav. chim. 75, 845 (1956).
80. N. Smith, Ph.D. Thesis, University of Chicago, Chicago, Ill.
81. J. N. Murrell, J. Am. Chem. Soc. 81, 5037 (1959).
82. S. Carter, J. N. Murrell and E. J. Rosch, J. Chem. Soc. 2048 (1965).
83. R. M. Keefer and L. J. Andrews, J. Am. Chem. Soc. 74, 4500 (1952).
84. R. M. Keefer and L. J. Andrews, J. Am. Chem. Soc. 77, 2164 (1955).
85. R. M. Keefer and L. J. Andrews, J. Am. Chem. Soc. 72, 5170 (1950).
86. D. F. Evans, J. Chem. Phys. 23, 1424, 1426 (1955).
87. H. Murakami, Bull. Chem. Soc. Japan 26, 441 (1953).
88. J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules", John Wiley and Sons, Inc., New York, 1963, Art. 6.4.
89. K. G. Denbigh, "The Principles of Chemical Equilibrium", Cambridge University Press, Cambridge, 1955, Sec. 9.4.
90. K. G. Denbigh, op. cit., Sec. 8.13.
91. A. Bogojawlenski, Chem. Zent. 9II, 945 (1905).
92. E. Schroeder, Z. Phys. Chem. 11, 456 (1893).
93. G. Scatchard, Chem. Revs. 8, 329 (1931).
94. C. L. Speyers, Am. J. Sci. [4] 14, 294 (1902).
95. C. E. Looney and J. R. Downing, J. Am. Chem. Soc. 80, 2840 (1958).
96. L. W. Reeves and W. G. Schneider, Can. J. Chem. 35, 251 (1957).
97. J. R. Gott and W. G. Maisch, J. Chem. Phys. 39, 2229 (1963).

98. S. Basu, *Advances in Quantum Chem.* 1, 145 (1964).
99. E. G. McRae, *J. Phys. Chem.* 61, 562 (1957).
100. N. G. Bakhshiev, *Optics and Spectroscopy* 10, 379 (1961); 16, 446 (1964); 19, 196 (1965).
101. K. C. M. Davis and M. C. R. Symons, *J. Chem. Soc.* 2079 (1965).
102. H. W. Offen and M. S. F. A. Abidi, *J. Chem. Phys.* 44, 4642 (1966).
103. N. Q. Chako, *J. Chem. Phys.* 2, 644 (1934).
104. G. Briegleb, J. Czekalla and G. Reuss, *Z. Physik. Chem. N.F.* 30, 333 (1961).
105. G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer Verlag, Berlin, 1961, pp. 22, 25.
106. G. Briegleb, *op. cit.* pp. 48-54.
107. G. Briegleb, J. Czekalla and G. Reuss, *Z. Physik. Chem. N.F.* 30, 316 (1961).
108. H. W. Offen and A. H. Kadhim, *J. Chem. Phys.* 45, 269 (1966).
109. W. H. Bentley and H. G. Drickamer, *J. Chem. Phys.* 42, 1573 (1965).
110. H. M. Rosenberg and D. Hale, *J. Chem. Phys.* 69, 2490 (1965).
111. G. Briegleb and J. Czekalla, *Z. Elektrochem.* 58, 249 (1954).
112. W. D. Phillips, J. C. Rowell and S. I. Weissman, *J. Chem. Phys.* 33, 626 (1960).
113. F. E. Stewart, M. Eisner and W. R. Carper, *J. Chem. Phys.* 44, 2866 (1966).
114. R. Foster and T. J. Thomson, *Trans. Faraday Soc.* 58, 860 (1962).
115. J. Czekalla and K. O. Meyer, *Z. Physik. Chem. N. F.* 27, 185 (1961).
116. G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer Verlag, Berlin, 1961, pp. 114-120.

117. G. Briegleb, op. cit. pp. 54 ff.
118. M. Kroll and M. L. Ginter, J. Phys. Chem. 69, 3671 (1965).
119. G. H. Schenk, M. Santiago and P. Wines, Anal. Chem. 35, 167 (1963).
120. E. Lippert, Z. Naturforsch. 10a, 541 (1955); Z. Elektrochem. 61, 962 (1957).
121. N. G. Bakhshiev, Optics and Spectroscopy 20, 542 (1966).
122. H. L. Ward, J. Phys. Chem. 30, 1316 (1926).
123. P. Schlöpf and R. Flacks, Helv. Chim. Acta 10, 381 (1927).
124. E. Cohen, W. A. T. de Meester and A. L. Moesveld, Z. Physik. Chem. 114, 321 (1924-25).
125. A. A. Sunier and C. Rosenblum, J. Phys. Chem. 32, 1049 (1928).
126. G. Briegleb, op. cit. p. 20.
127. E. M. Voigt, J. Am. Chem. Soc. 86, 3611 (1964).
128. A. Streitwieser Jr. and I. Schwager, J. Phys. Chem. 66, 2316 (1962).
129. A. Zweig, Tetrahedron Letters No. 2 89 (1964).
130. H. Kuroda and H. Akamatu, J. Chem. Phys. 40, 3748 (1964).
131. H. Kuroda, I. Ikemoto and H. Akamatu, Bull. Chem. Soc. Japan 39, 1842 (1966).
132. R. R. Penfold and W. N. Lipscomb, Acta Cryst. 14, 589 (1961).
133. H. Kuroda, I. Ikemoto, and H. Akamatu, Bull. Chem. Soc. Japan 39, 547 (1966).

VITA

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