atoms. The calculations in Table III are clearly imperfect since predicted values of $\rho_1{}^C$ are all low by comparison with the experimental proton coupling constant of 5.0 gauss which corresponds to $\rho_1{}^C \approx 0.2$. Nevertheless, we note with interest that if the spin densities in column B, Table III, are used together with the Stone–Maki[9] estimate of $(S^N + 2Q_{NC}{}^N)$, 30.9 gauss, then the magnitude of the experimental nitrogen coupling constant can be reproduced by choosing $Q_{CN}{}^N$ as -4.1 gauss.

$\Delta^{2,2'}$-*Biisobenzimidazolylidene Anion.* For the first two azine anions discussed, it was possible to examine the coupling constants of the analogous hydrocarbon anion radicals. That is not the case for the anion of compound III since the corresponding hydrocarbon, 2,2′-biisoindene, has not been synthesized.

Results of a HMO calculation of spin densities in the $\Delta^{2,2'}$-biisobenzimidazolylidene anion are shown in Figure 6.[27] The experimental proton coupling constants were assigned to the molecular positions shown in Figure 6 solely on the basis of the HMO calculations. The close agreement between the larger proton coupling constant, 1.40 gauss, and the value of 1.46 gauss which is predicted from eq. 2 and the calculated spin density (Figure 6) must be regarded as fortuitous.

Because the interior CNC angle in this anion radical is expected to be somewhat smaller than the angle of *ca.* 120° in the benzenoid azine radicals, the spin polarization parameters in eq. 4 will be changed. Thus a direct comparison of the nitrogen coupling constant in the anion radical of III with other nitrogen coupling constants is not possible.

(27) Calculation done with $\alpha_N = \alpha_C + 0.75\beta_{CC}$.

Computation of Association Constants from Spectrophotometric Data. II. Multiple Equilibria

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It is shown that the criterion of linearity of Benesi–Hildebrand plots for indicating the presence of only stable 1:1 charge-transfer complexes and/or "contact" absorptions is not a valid one. Synthetic data were calculated for systems involving the formation of stable AD and A_2D, and also AD and AD_2 charge-transfer complexes. Widely different values of K_1, K_2, and of the molar absorptivities of the complexes were used in calculating these data. In no case, however, did the resulting Benesi–Hildebrand plots reveal significant variations from linearity such that the presence of the second stable charge-transfer complex would be suspected. It was found that the Benesi–Hildebrand method gave values of K which exhibited a systematic variation with wave length. The system tetracyanoethylene–naphthalene–carbon tetrachloride was carefully examined, and a systematic variation of K with wave length was observed. The results cannot be explained by isomeric, stable 1:1 charge-transfer complexes and/or "contact" absorptions. It is necessary to postulate the existence of stable charge-transfer complexes of at least two different stoichiometries. Temperature dependencies of ΔH and total oscillator strengths can yield no useful information for such systems. The present work indicates the necessity to examine the variation of K with wave length in order to pass upon the presence or absence of equilibria other than 1:1 stable isomeric charge-transfer complexes and/or "contact" absorptions.

Spectrophotometric methods have been employed in the determination of a great variety of association constants. These constants have been determined by graphical procedures. A relationship between absorbances and association constants was first reported by Benesi and Hildebrand.[2] If an initial concentration of an acceptor molecule, $[A_0]$, is mixed in an inert solvent with a donor molecule of original concentration $[D_0]$, an interaction occurs to form a charge-transfer complex: $A + D \rightleftarrows C$. The equilibrium constant for this association is given by

$$K = \frac{C}{(A_0 - C)(D_0 - C)} \tag{1}$$

where italic letters A, C, and D refer to concentrations of A, C, and D. The absorbance is given by application of the Beer–Lambert law

$$O.D./b = \epsilon_a(A_0 - C) + \epsilon_d(D_0 - C) + \epsilon_c C \tag{2}$$

where $O.D.$ = optical density (absorbance), b = path length in cm., and ϵ_i = molar absorptivities.

(1) (a) Portion of a dissertation presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy in chemistry at Kansas State University; (b) National Science Foundation Research Participation for College Teachers Fellow.

(2) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, 71, 2703 (1949).

Table I. Synthetic Data and Deviations from Linear B–H Plots for AD + A$_2$D

| Case no.	D_0, M	ϵ_c	ϵ_i	O.D.	Δ-O.D.	ϵ_i	O.D.	Δ-O.D.	ϵ_i	O.D.	Δ-O.D.
1	0.01	1000	0	0.143	0.000	1000	0.143	0.000	100,000	0.145	0.000
(K_1, 5.0; K_2, 0.5)	0.02			0.272	0.000		0.272	0.000		0.276	0.000
	0.04			0.499	0.000		0.500	0.000		0.506	0.000
	0.08			0.856	0.000		0.857	0.000		0.866	0.000
	0.16			1.333	0.000		1.333	0.000		1.344	0.000
2	0.01	1000	0	0.143	0.000	1000	0.143	0.000	100,000	0.163	0.000
(K_1, 5.0; K_2, 5.0)	0.02			0.272	0.000		0.273	0.000		0.309	0.000
	0.04			0.499	0.000		0.500	0.000		0.562	0.000
	0.08			0.856	0.000		0.857	0.000		0.948	0.000
	0.16			1.333	0.000		1.333	0.000		1.444	−0.001
3	0.01	5000	0	0.075	0.000	5000	0.075	0.000	100,000	0.077	0.000
(K_1, 0.5; K_2, 5.0)	0.02			0.148	0.000		0.149	0.000		0.153	0.000
	0.04			0.294	0.000		0.294	0.000		0.303	0.000
	0.08			0.577	0.000		0.578	0.000		0.593	0.000
	0.16			1.111	0.000		1.112	0.000		1.142	0.000
4	0.01	8000	0	0.119	0.000	8000	0.121	0.000	100,000	0.142	0.000
(K_1, 0.5; K_2, 50.0)	0.02			0.238	0.000		0.241	0.000		0.282	0.000
	0.04			0.470	0.000		0.477	0.000		0.557	0.000
	0.08			0.922	0.000		0.935	0.000		1.088	0.000
	0.16			1.774	0.000		1.798	0.000		2.081	0.000

In the Benesi–Hildebrand (B–H) method the experimental conditions are chosen such that $D_0 \gg A_0$ and the simplifying approximation, $D_0 - C \approx D_0$ may be used. Elimination of C between eq. 1 and 2 gives

$$\frac{A_0}{\text{O.D.}/b - \epsilon_a A_0 - \epsilon_d D_0} = \frac{1}{K D_0 (\epsilon_c - \epsilon_a)} + \frac{1}{\epsilon_c - \epsilon_a} \quad (3)$$

which is the equation of a straight line when the left-hand side of the equation is plotted against $1/D_0$. The desired parameters may be obtained by the relationships

$$K = \frac{\text{intercept}}{\text{slope}} \qquad \epsilon_c = \frac{1}{\text{intercept}} + \epsilon_a$$

It has been widely accepted that the linearity of such plots provides evidence for the presence of only a 1:1 stable charge-transfer complex and that no competing equilibria of other stoichiometries exist.[3–6] Moreover Orgel and Mulliken have shown that if "isomeric" 1:1 stable charge-transfer complexes (i.e., differing in geometrical configuration) are formed, the B–H plots will still be linear.[7]

$$C_2 \underset{}{\overset{K_2}{\rightleftharpoons}} A + D \underset{}{\overset{K_1}{\rightleftharpoons}} C_1$$
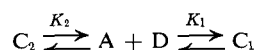
In this case, the association constant determined, K_d assuming a single 1:1 complex, will be given by

$$K_d = \sum_i K_i \quad (4)$$

and the molar absorptivities determined, ϵ_{cd}, will be weighted averages.

$$\epsilon_{cd} = \sum_i K_i \epsilon_{ci} / \sum_i K_i \quad (5)$$

"Moreover, these results should be independent of the wave length in the analysis, no matter whether it belongs to the absorption spectrum of one complex or another or to the superposed absorption of more than one complex."[7]

It should be noted that eq. 4 and 5 may be derived without employing the approximation that $D_0 - C \approx D_0$, as

$$K_d = \sum_i K_i = \frac{\sum_i C_i}{(A_0 - \sum_i C_i)(D_0 - \sum_i C_i)} \quad (6)$$

$$\text{O.D.}/b = \epsilon_a(A_0 - \sum_i C_i) +$$
$$\epsilon_d(D_0 - \sum_i C_i) + \frac{\sum_i K_i \epsilon_{ci}}{\sum_i K_i} \sum_i C_i \quad (7)$$

It can be shown that "contact" absorption may occur during random encounters whenever a donor and an acceptor are sufficiently close to one another, even if no stable complex is formed.[7,8] The concentration of these DA contacts is given by

$$DA = \alpha A D \quad (8)$$

where α is the average number of contact (i.e., next-neighbor) sites for a D molecule around any A molecule under conditions of loose thermal contact.

For a system exhibiting both "contact" and 1:1 stable charge-transfer complex absorptions, the K determined will be the same as determined if *no contact absorptions occurred.*

It is now shown that multiple equilibria, involving the formation of both a 1:1 stable complex and a 2:1 stable complex may also yield linear B–H plots.

$$A + D \underset{}{\overset{K_1}{\rightleftharpoons}} C$$
$$A + C \underset{}{\overset{K_2}{\rightleftharpoons}} J$$
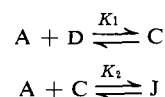
The association constants are given as

$$K_1 = \frac{C}{(A_0 - C - 2J)(D_0 - C - J)} \quad (9)$$

$$K_2 = \frac{J}{(A_0 - C - 2J)C} \quad (10)$$

(3) R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **72**, 4677 (1950).
(4) R. M. Keefer and L. J. Andrews, *ibid.*, **73**, 462 (1951).
(5) R. E. Merrifield and W. D. Phillips, *ibid.*, **80**, 2778 (1958).
(6) E. M. Voigt, *ibid.*, **86**, 3611 (1964).
(7) L. E. Orgel and R. S. Mulliken, *ibid.*, **79**, 4839 (1957).
(8) R. S. Mulliken, *Rec. trav. chim.*, **75**, 845 (1956).

Table II. B-H Treatment of Synthetic Case, AD + A₂D

K_1	K_2	ϵ_c	ϵ_j	K_d	ϵ_{cd}	ϵ_j	K_d	ϵ_{cd}	ϵ_j	K_d	ϵ_{cd}
5.0	0.5	1000	0	4.989	1000.8	1000	4.989	1000.8	100,000	5.063	1000.9
5.0	5.0	1000	0	4.997	999.0	1000	5.005	999.0	100,000	5.682	1010.7
0.5	5.0	5000	0	0.5013	4986.5	5000	0.5020	4986.5	100,000	0.5159	4990.5
0.5	50.0	8000	0	0.5141	7780.0	8000	0.5217	7781.6	100,000	0.5959	7969.7

Table III. Synthetic Data and Deviations from Linear B-H plots for AD + AD₂

Case no.	D_0, M	ϵ_c	ϵ_j	O.D.	Δ-O.D.	ϵ_j	O.D.	Δ-O.D.	ϵ_j	O.D.	Δ-O.D.
1	0.01	1000	0	0.143	0.000	500	0.143	0.000	10,000	0.150	0.000
(K_1, 5.0; K_2, 0.5)	0.02			0.272	0.000		0.273	0.000		0.299	0.000
	0.04			0.496	0.002		0.502	0.001		0.596	0.001
	0.08			0.845	0.002		0.863	0.001		1.184	0.001
	0.16			1.303	−0.017		1.347	−0.009		2.338	−0.023
2	0.01	800	0	0.114	−0.001	400	0.117	0.000	10,000	0.121	0.000
(K_1, 5.0; K_2, 5.0)	0.02			0.213	0.003		0.225	0.002		0.241	0.002
	0.04			0.375	0.012		0.418	0.007		0.474	0.009
	0.08			0.604	0.011		0.733	0.005		0.918	0.003
	0.16			0.870	−0.084		1.174	−0.073		1.728	−0.155
3	0.01	4000	0	0.060	0.000	400	0.060	0.000	3,000	(K_d and ϵ_{cd} are	
(K_1, 0.5; K_2, 5.0)	0.02			0.119	0.000		0.120	0.000		negative)	
	0.04			0.233	0.001		0.238	0.001			
	0.08			0.453	0.001		0.472	0.001			
	0.16			0.857	−0.018		0.924	−0.018			
4	0.01	5000	0	0.075	0.000	250	0.077	0.000	2,500	(K_d and ϵ_{cd} are	
(K_1, 0.5; K_2, 50.0)	0.02			0.145	0.002		0.152	0.002		negative)	
	0.04			0.273	0.010		0.302	0.009			
	0.08			0.489	−0.011		0.591	0.008			
	0.16			0.807	−0.110		1.136	−0.160			

Table IV. B-H Treatment of Synthetic Case, AD + AD₂

K_1	K_2	ϵ_c	ϵ_j	K_d	ϵ_{cd}	ϵ_j	K_d	ϵ_{cd}	ϵ_j	K_d	ϵ_{cd}
5.0	0.5	1000	0	5.276	949.2	500	4.884	1023.7	10,000	0.1670	29,949.1
5.0	5.0	800	0	7.943	518.4	400	4.129	983.5	10,000	0.8307	4,908.7
0.5	5.0	4000	0	0.7753	258.7	400	0.2579	7774.9	3,000	Neg.	Neg.
0.5	50.0	5000	0	3.326	774.9	250	0.5296	4848.6	2,500	Neg.	Neg.

Elimination of J between (9) and (10) gives

$$(1 - 4\alpha)K_2C^3 + (1 - 2D_0K_2 - 4\alpha)C^2 - \{A_0 +$$
$$\lfloor D_0 + K_1^{-1} + K_2A_0(A_0 - 2D_0)\}C + A_0D_0 = 0 \quad (11)$$

where $\alpha = K_2/K_1$ and $K_1^{-1} = 1/K_1$. The expression for the absorbance is

$$O.D./b = \epsilon_a(A_0 - C - 2J) +$$
$$\epsilon_d(D_0 - C - J) + \epsilon_cC + \epsilon_jJ \quad (12)$$

Using eq. 10–12, absorbance data were calculated for various hypothetical combinations of K_1, K_2, ϵ_c, and ϵ_j. These synthetic data are given in Table I. (In each case $\epsilon_a = \epsilon_d = 0$, $A_0 = 0.0003\ M$, $b = 10$ cm.)

The data in Table I were treated according to the B-H approach for a 1:1 equilibrium by the least-squares criterion (regression on the left-hand side of eq. 3). The deviations of the data from linear plots were determined from eq. 3 by assuming that these were due to "errors" in absorbances. The deviations are given in Table I (columns labeled ΔO.D.).

The values of K_d and ϵ_{cd} (determined by the B-H approach) are given in Table II.

Equations similar to eq. 9–12 were developed for the formation of a 1:1 complex and a 1:2 complex.

$$A + D \xrightleftharpoons{K_1} C$$

$$C + D \xrightleftharpoons{K_2} J$$
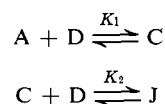
Synthetic data were calculated and treated as before. The results are given in Tables III and IV. (Again $\epsilon_a = \epsilon_d = 0$, $b = 10$ cm., $A_0 = 0.0003\ M$.)

In addition, the tetracyanoethylene (TCNE)–naphthalene–carbon tetrachloride system was studied in the visible range from 420 to 610 mμ. Absorbances for each of nine concentrations were measured at 52 wave lengths.

Using the assumption that only a 1:1 complex was formed in this system, values of K were determined at each wave length. However these values varied over a rather large range. Figure 1 shows the variation of K_d with wave length. Figure 2 shows the spectra of three of the concentrations.

Because of the dependence of K_d upon wave length, a meaningful value of K cannot be reported. However, Table V gives average values of K_d for several portions of the spectrum (corresponding to the two points of maximum absorbance and the point of minimum absorbance) and the average value of K_d for all 52 wave lengths studied in the 420–610 mμ region. The standard deviations of these values are also given.
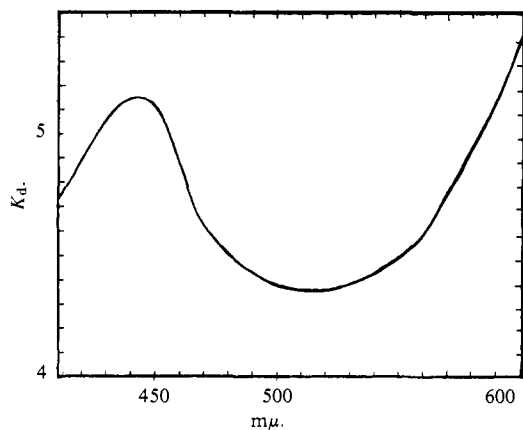
Figure 1. TCNE–naphthalene–carbon tetrachloride system at 25°. Variation of K_d with wave length.

Figure 2. TCNE–naphthalene–carbon tetrachloride system at 25° [TCNE] = 3.419 × 10^{-4} M; [naphthalene] = 0.01011, 0.06530, 0.1125 M.

(These are not given as "error limits." The actual value of K may be quite removed from the determined value, K_d.) Literature value, K = 3.27 (20°) at O.D. maximum in CCl_4.[9]

Table V. TCNE–Naphthalene–Carbon Tetrachloride System at 25°

Wave length range, $m\mu$	No. of wave lengths	K_d (mean)	Std. dev.
542–560	10	4.44	±0.05
420–436	9	4.86	±0.10
465–490	5	4.67	±0.25
420–610	52	4.68	±0.85

Experimental

The synthetic data presented in Tables I and III were calculated by a computer program employing eq. 10–12. Equation 11, a cubic in C, was solved to 14 decimals by Newton's method. These values of C were employed in eq. 10 to calculate J. The values of C and J were then used in eq. 12 to calculate absorbance data accurately to eight decimals. The computer was an IBM 1410, PR 155. Copies of the program SYNDATA may be obtained from the authors for either A_2D or AD_2 formation.

The computer program fit these data to a straight line by the method of least squares, based on eq. 3. The slope and intercept obtained, along with the values of A_0 and D_0, were then used to calculate new absorbances. The columns labeled ΔO.D. in Tables I and III are equal to the input absorbances minus the recalculated absorbances.

The TCNE employed was Eastman White Label and was recrystallized from chlorobenzene, vacuum distilled, and sublimed in a nitrogen atmosphere. Two liters of a 0.00068385 M stock solution were prepared in a drybox using Matheson Coleman and Bell Spectroquality carbon tetrachloride which had previously been purged with dry nitrogen.

The naphthalene used was Baker and Adamson material and was recrystallized three times from methanol, dried over $CaCl_2$, and sublimed.

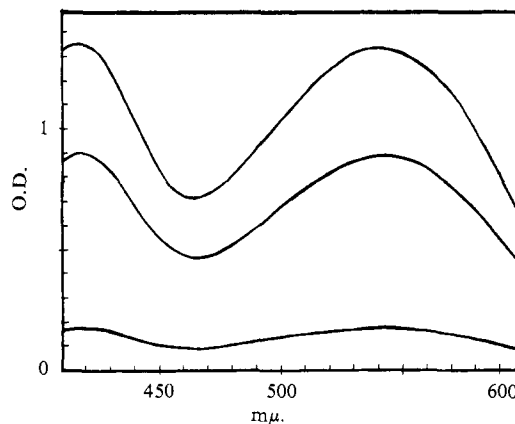(9) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961, p. 129.

The naphthalene–TCNE solutions were prepared in 50.00-ml. volumetric flasks by adding 25.00 ml. of the stock TCNE solution (at 25.0 ± 0.1°) to the volumetric flasks containing weighed amounts of naphthalene. The solutions were diluted to volume at 25.0 ± 0.1°. It is estimated the concentrations of the solutions were accurate to ±1.0%.

The spectra were obtained on a Cary Model 11 recording spectrophotometer (solvent reference). A 10-cm. cylindrical cell was employed. The cell compartment was thermostated at 25.0 ± 0.1°. The spectrophotometer was equipped with a 0–1 slidewire; and readings were taken directly from the pointer to eliminate errors owing to the lack of dimensional stability of the chart paper. The absorbances read in this manner are reproducible to ±0.003 absorbance units.

The data were processed by a computer program B-HDATA. The molar absorptivities of TCNE and of naphthalene were small and were not included in the calculations.

Discussion

Two Complexes of the Stoichiometry AD and A_2D. The results given in Table I were unexpected. Linear B–H plots have always been considered as evidence for the existence of only 1:1 complexes and/or "contact" absorptions.[3-7,9] However, for all cases given in Table I, ΔO.D. (the deviation from a linear plot) is less than the accuracy to which absorbances may be measured.

The deviations from a straight line are much less than the contribution to the spectra by the second complex $(\epsilon_j J)$. For example, in case 2 (where ϵ_j = 100,000, ϵ_c = 1000) the percentage of the absorbance owing to the second complex is 7.69%, but the deviation from a linear plot is only 0.86%. The contribution of the second complex to the total amount of the complexes is 0.83%, more nearly in line with the observed deviation. The amount of the second complex will always be necessarily small, compared to the first complex. Applying the approximation that $(D_0 - C) \approx D_0$ to eq. 9 and 10 gives, after suitable manipulation

$$J = \frac{C^2 K_2}{D_0 K_1} \tag{13}$$

Since C must always be less than A_0 and $D_0 \gg A_0$, J will be small compared to C. For example, in case number 4 given in Table I ($K_1 = 0.5$ and $K_2 = 50.0$), when $D_0 = 0.08\ M$, the ratio of $C:J$ is 694:1.

In cases where the B–H method may not be applied (*i.e.*, $D_0 \approx A_0$) a 2:1 complex of the stoichiometry A_2D would be easier to detect. (If $K_1 = 0.1$, $K_2 = 10.0$, $A_0 = 0.005\ M$, and $D_0 = 0.01\ M$, the ratio of $C:J$ is 20:1.)

Since a linear B–H plot has been shown not to be a valid criterion for the existence of only a 1:1 complex, an attempt was made to find a better one. The results in Table II suggest one such criterion: the constancy of K_d with wave length. However, even in the most favorable cases studied, the change in K_d with varying $\epsilon_c:\epsilon_j$ ratios (corresponding to widely separated wave lengths) was only 15%. Thus together with the "extreme sensitivity of K to errors in input data,"[10] it is possible that random experimental errors may completely obscure any systematic variation of K_d with wave length.

It must be stressed that any attempt to calculate K_1 and K_2 for systems such as those in Table I will meet with failure if only one wave length at a time is considered. Since the variations from linearity in these plots are vanishingly small, the only information available for the calculation of K_1 and K_2 in these systems is the variation of K_d with wave length.

There are numerous examples in the literature where data have been obtained at the wave length of maximum absorbance and association constants and molar absorptivities determined from these data.[9,11] It is very likely, and has been reported on occasion,[12] that the values of K_d are functions of wave length. Thompson and de Maine[13] have concluded from their study of the 1,3,5-trinitrobenzene–naphthalene system in carbon tetrachloride, that, in the region of 335 to 400 mμ, since the values of K_d vary over the "small" ranges of 5.09 to 5.23 (at 20°) and 3.28 to 3.58 (at 45°), only 1:1 complex(es) is (are) being formed.

Two Complexes of the Stoichiometry AD and AD$_2$. The results given in Table III better fit the concept of nonlinear plots for multiple equilibria. However the deviations are still rather small. For all cases, the average deviation from a linear plot is less than 0.016 absorbance unit; the standard deviation is 0.039 absorbance unit. If a computer program is used with a "reject–restore" mechanism,[14] five data points out of the 50 listed in Table III would probably be rejected, and the standard deviation would drop to less than 0.007 absorbance unit.

Normal experimental procedure involves varying the concentration of donor over a 10:1 range. A much wider range would be desirable,[9] but a 15:1 range in absorbances is all that can be conveniently measured. The first four concentrations in each group listed in

(10) K. Conrow, G. D. Johnson, and R. E. Bowen, *J. Am. Chem. Soc.*, **86**, 1025 (1964).
(11) W. E. Wentworth, G. W. Drake, W. Hirsch, and E. Chen, *J. Chem. Educ.*, **41**, 373 (1964).
(12) N. B. Jurinski and P. A. D. de Maine, *J. Am. Chem. Soc.*, **86**, 3217 (1964).
(13) C. C. Thompson, Jr., and P. A. D. de Maine, *ibid.*, **85**, 3096 (1963).
(14) P. A. D. de Maine and R. D. Seawright, "Digital Computer Programs for Physical Chemistry," Vol. 1, The Macmillan Co., New York, N. Y., 1963.
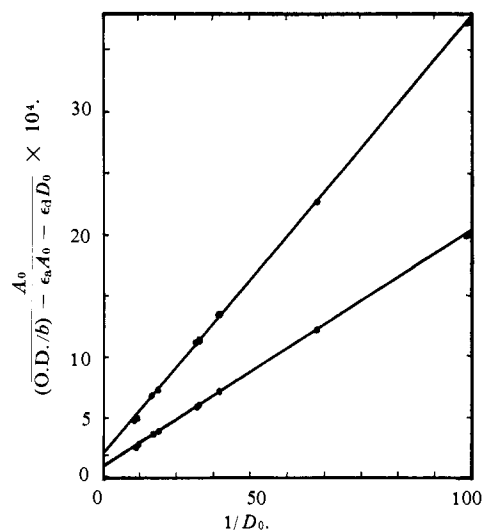
Figure 3. Benesi–Hildebrand plots for the TCNE–naphthalene–carbon tetrachloride system (25°) at 470 and 552 mμ.

Table III correspond to an 8:1 range of donor concentrations. If only this concentration range were studied, the deviations from linear plots would be within experimental error.

These facts, coupled with the inaccuracy of graphical procedures, would in most cases give "linear" plots. In constructing a B–H graph, the y-axis is set equal to the left-hand side of eq. 3. In case 4 (Table III, $\epsilon_j = 0$) the range of the y-axis is 0.00400 to 0.00037, corresponding to absorbances of 0.075 and 0.807, respectively. If the y-axis were made 200 units long and could be read accurately to ± 0.5 unit, an error of only 0.001 absorbance unit at the lower value (0.075) would produce a point not lying on the line. On the other hand, an error of 0.022 absorbance unit at the higher value (0.807) would be necessary to produce a point not lying on the line. This points out the much greater effect of small errors in absorbance at low absorbances in the B–H approach.

Table IV shows larger variations of K_d with varying $\epsilon_c:\epsilon_j$ ratios compared to the AD + A$_2$D case (Table II).

The TCNE–Naphthalene System. Figure 1 shows the marked variation of K_d with wave length. This variation cannot be accounted for by the presence of stable isomeric 1:1 charge-transfer complexes and/or "contact" absorptions. Theory predicts that in these cases K_d will be given by eq. 4 and will be independent of the wave length employed in the analysis. Thus, the observed dependence of K_d on wave length can only be explained by postulating the presence of multiple equilibria of at least two different stoichiometries.

Merrifield and Phillips stated that since TCNE–naphthalene in methylene chloride yields linear B–H plots ". . .complexes other than the simple 1:1, therefore, need not be considered."[5] They did not state the wave length at which K was determined or the range of donor concentrations employed.

With the experimental conditions employed in this laboratory ($A_0 = 0.0003\ M$, $D_0 = 0.01$ to $0.11\ M$, and $\lambda = 420$–610 mμ) the B–H plots were "nearly" linear. Figure 3 gives two representative B–H plots for the TCNE–naphthalene system.

Table VI.

System	Linear B–H plots	K independent of wave length	ΔH independent of temp.	Total oscillator strength independent of temp.
1:1 CT[a] complex	Yes	Yes	Yes	Yes
1:1 CT complex + contact	Yes	Yes	Yes	No
1:1 CT complex + isomeric 1:1 CT complex	Yes	Yes	No[c]	No
1:1 CT complex + higher order CT complex	Yes[b]	No[c]	No[c]	No
1:1 CT complex, isomeric 1:1 + higher order CT complex	Yes[b]	No[c]	No[c]	No

[a] Charge transfer = CT. [b] Theoretical deviation is often too small to be detected. [c] Although the expected deviation may be too small to be detected.

Orgel and Mulliken[7] point out that two good criteria for the presence of a single complex are the constancy of ΔH and total oscillator strength with temperature. The criterion of linear B–H plots as proof of the absence of higher order stable charge-transfer complexes has been discussed earlier in this paper. Table VI summarizes the results which would be obtained with various possible systems in regard to the various suggested criteria.

Since the TCNE–naphthalene system yields "nearly" linear B–H plots, the principal absorbing species must be a 1:1 stable charge-transfer complex. In addition to a 1:1 stable charge-transfer complex and a higher order charge-transfer complex, it is possible that isomeric 1:1 complexes as well as contact absorptions are occurring in the TCNE–naphthalene system.

The temperature dependence of ΔH and total oscillator strength can only confirm the presence of more than one equilibrium but can give no information concerning the nature of the additional equilibria. In the case of additional higher order equilibria, the determined values of ΔH and total oscillator strength will be meaningless. Thus, to determine the presence of higher order complexes, the variation of K with wave length must be determined.

Application of High-Temperature Mass Spectrometry to the Determination of the Enthalpy–Composition Function of Nonstoichiometric Binary Compounds[1]

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The application of high temperature, Knudsen-cell mass spectrometry to the determination of the enthalpy–composition function is shown for nonstoichiometric compounds that have a range of composition and vaporize by decomposition into a volatile component and a solid solution of the same phase. In principle, the temperature dependence of the partial pressure of the volatile component is measured for a constant composition of the solid and a partial enthalpy value derived. The enthalpy–composition function for the whole homogeneity range is obtained accordingly by measurements for different compositions. The approach is demonstrated for praseodymium monophosphide. The partial molal enthalpy of P_2 decomposition, $\overline{\Delta H}_T[P_2]$, for the reaction $(2/x)PrP_y(s) = (2/x)PrP_{y-x}(s) + P_2(g)$ was found to increase with decreasing P/Pr atomic ratio from 79.5 to 120.5 kcal. over the composition range measured. The suitability and limitations of the proposed method are discussed.

I. Introduction

The experimental findings of partial thermodynamic properties of compounds with high melting points and wide homogeneity ranges are rather sparse. This is in particular true for the partial enthalpies. Direct experimental measurements at temperatures above 1000° have been performed for a limited number of cases where experimental conditions were favorable for the method used. E.m.f. measurements involving galvanic cells have been used up to 1400° but become very dependent upon the availability of a suitable ionic conductor if applied above 1000° and upon the true reversibility of the cell reactions. Therefore, little use of this method has been possible for accurate determination of the temperature coefficient of the e.m.f. and thus the corresponding partial enthalpy. The direct measurement of integral enthalpies for different compositions of solid solutions using calorimetric methods has been applied up to 1400°. However, high temperature calorimetry above 1000° causes many delicate problems and is so far limited to certain alloy systems. Measurement of vapor pres-