RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

August 1974

Translated from *Uspekhi Khimii*, **43**, 1337-1358 (1974)

U.D.C. 541.122 : 543.422.6 : 547.386

Ultraviolet Spectroscopic Determination of the Stabilities of Weak Organic Complexes

E.G.Polle

The methods described in the literature for the determination of the stability constants K and extinction coefficients ϵ of weak organic electron-donating and electron-accepting complexes are discussed. It is shown that the majority of the methods based on a combination of the Bouguer-Beer-Lambert law and the law of mass action and involving the use of an excess of one component suffer from the same disadvantages as the parent spectrophotometric method—the Benesi-Hildebrand method (the inconsistency between K and ϵ, the appearance of negative values of K, the dependence of K on the wavelength used, the dependence of K and ϵ on the relative amounts of the donor and acceptor, etc.). The reliability criteria of Pearson and Deranleau are discussed and their limitations are demonstrated. It is suggested that the absolute values of K and ϵ obtained spectrophotometrically are of interest only from a comparison of complex formation in series of organic compounds with similar structures and that all measurements should as far as possible be made under identical conditions. The review covers studies published up to the middle of 1973.
The bibliography includes 177 references.

CONTENTS

I. Introduction 631
II. Spectrophotometric methods for the determination of the stability constants of weak organic complexes 632
III. The difficulties arising in the determination of K and ϵ 634
IV. The reliability of the literature values of K and ϵ 638

I. INTRODUCTION

Numerous reviews[1-6], dealing mainly with the stable inorganic and organic-inorganic complexes, have been devoted to studies on the stabilities of complexes in solution. There have also been a fair number of publications on weak organic electron donor–acceptor complexes[7-17], but attention has been concentrated on the properties of the complexes and not on the calculation of the stability constants. The group of complexes under consideration ($K \leq 20$ litre mole^{-1}) exhibit a specific absorption in the electronic spectrum. Even very weak complexes frequently give rise to an appreciable deviation from additivity of optical densities in the spectrum of a mixture of the reacting molecules. The reasons for this phenomenon are being widely discussed—it may be due to a charge-transfer band, or to a singlet–triplet absorption by the donor, or to the resolution of latent bands of the acceptors, etc.—and in the present review they will not be considered. However, the appearance of a new absorption following interaction has led to a very frequent application of spectrophotometric methods. On the other hand, there is not in the literature even one critical study of the entire series

of methods used to investigate weak molecular complexes. Such an examination is particularly necessary, since the determination of the stability constants was not the main aim of the majority of investigators; one may say that, for organic chemists dealing with syntheses, the constant K provides a comparison of the complex-forming capacities of new substances with those investigated previously, etc. A method widely described in the literature, usually the Benesi–Hildebrand method [18] (or its modifications) which is very easy and clear-cut, is employed.

The aim of the present review is to demonstrate the limitations of the spectrophotometric methods for the determination of K and ϵ and the necessity for much caution in the assessment of the results.

II. SPECTROPHOTOMETRIC METHODS FOR THE DETERMINATION OF THE STABILITY CONSTANTS OF WEAK ORGANIC COMPLEXES

Spectrophotometric methods for the investigation of the stability of organic complexes have been known for a long time (see, for example, Halban and Zimpelmann [19] and Michaelis and Granick [20]), but the methods became widely used only from the beginning of the 1950s. This was stimulated by Mulliken's theoretical studies [21–24], partly based on the experimental data of Benesi and Hildebrand [18,25]. The basic postulates used in the analysis of complex-forming systems by the Benesi–Hildebrand (B–H) method [18] can be formulated as follows: (a) the system is in a state of equilibrium; (b) the optical density of the solution is due to a molecular compound; (c) only one complex is formed in solution; (d) the absorption by the complex obeys the Bouguer–Beer–Lambert law.

For the reaction

$$A + nB \rightleftarrows AB_n \ , \qquad (1)$$

we have

$$K = C_{AB_n}/C_A \cdot C_B^n \ , \qquad (2)$$

where A and B are the components, K is the stability constant, C_{AB_n} the concentration of the complex at equilibrium, $C_A = a - C_{AB_n}$, and $C_B^n = (b - C_{AB_n})^n$, a and b being the initial acceptor and donor concentrations and C_A and C_B the equilibrium concentrations.

According to the Bouguer–Beer–Lambert law, one can write for the complex

$$D = C_{AB_n}\varepsilon_{AB_n}l \ , \qquad (3)$$

where D is the optical density of the solution, ϵ_{AB_n} the molar extinction coefficient of the complex, and l the optical pathlength.

On combining Eqns. (2) and (3), Benesi and Hildebrand arrived at the expression

$$al/D = (1/K \cdot \varepsilon_{AB_n})(1/b^n) + 1/\varepsilon_{AB_n} \ . \qquad (4)$$

The plot of al/D against $1/b^n$ is linear, $1/\epsilon_{AB_n}$ being the slope and $1/\epsilon_{AB_n}K$ the intercept. Three possibilities arise for this linear plot: (a) the intercept is positive, i.e. ϵ_{AB_n} and K are positive and non-zero; (b) the intercept is zero, i.e. $\epsilon_{AB_n} = \infty$ and $K = 0$; (c) the intercept is negative, i.e. $\epsilon_{AB_n} < 0$ and $K < 0$.

As an illustration we shall consider the *m*-dinitrobenzene (DNB)–*o*-bromoaniline and *m*-dinitrobenzene–2-methylnaphthalene systems [26] (Figs. 1 and 2). In both systems different straight lines are obtained at different donor concentrations. In the presence of a 60–124 and 124–200-fold excess of *o*-bromoaniline the first system gives rise to straight lines *a* and *b* respectively in Fig. 1. In the presence of a 40–120- and 120–320-fold excess of 2-methylnaphthalene the second system gives rise to straight lines *a* and *b* respectively in Fig. 2.

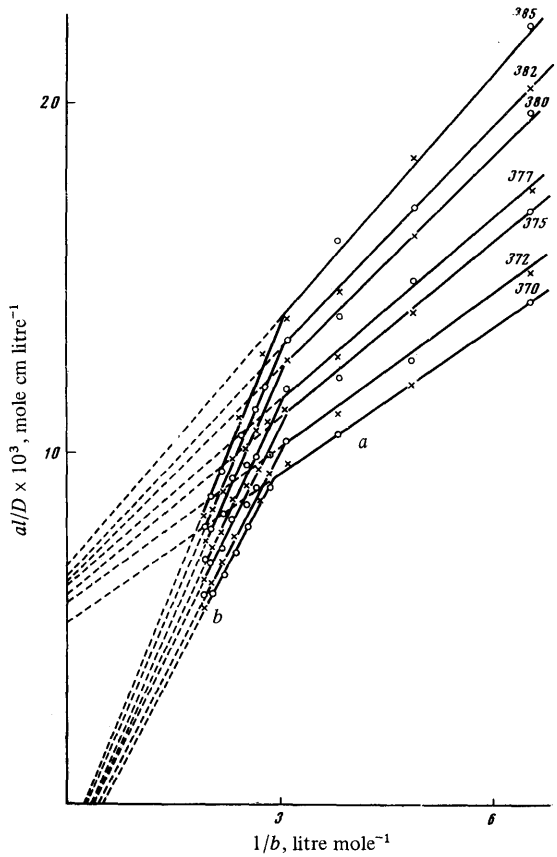


Figure 1. Application of the Benesi–Hildebrand method to the *m*-dinitrobenzene–*o*-bromoaniline system [26] in methanol; the numerals against the plots represent wavelengths (nm).

The Benesi–Hildebrand method is most commonly used at present [25,27] and the investigators do not always treat the results critically. The equation of Ketelaar et al. [58], which differs from the Benesi–Hildebrand expression by taking into account the absorption by the acceptor, is more accurate for the calculation of K and ϵ_{AB}:

$$1/(\varepsilon_a - \varepsilon_A) = 1/K \cdot b \ (\varepsilon_{AB} - \varepsilon_A) + 1/(\varepsilon_{AB} - \varepsilon_A) \ , \qquad (5)$$

where $\epsilon_a = D/la$. The plot of $1/(\epsilon_a - \epsilon_A)$ against $1/b$ is linear and permits the determinations of K and ϵ_{AB}. [59–62] Landauer and McConnell [63] derived an expression for the estimation of K_1 and K_2 for 1 : 1 and 1 : 2 complexes present

simultaneously in solution[51,60,64-73]. An effective extinction coefficient is introduced: $\bar{\epsilon} = D/al$, where D is the total optical density of the solution. If $l = 1$, then

$$D = a\bar{\epsilon} = \varepsilon_A \; C_A + \varepsilon_{AB} \; C_{AB} + \varepsilon_{AB_2} \; C_{AB_2} \; , \qquad (6)$$

since

$$a = C_A + C_{AB} + C_{AB_2}$$

or

$$a = C_A(1 + K_1 b + K_2 b^2) \; . \qquad (7)$$

Putting

$$Q = b/(\bar{\epsilon} - \epsilon_A) \qquad (8)$$

and using Eqns. (6) and (7), we obtain

$$Q = \frac{1 + K_1 b + K_2 b^2}{(\varepsilon_{AB} - \varepsilon_A) K_1 + (\varepsilon_{AB_2} - \varepsilon_A) K_2 b} \; . \qquad (9)$$

It is assumed that $C_{AB} \gg C_{AB_2}$ and therefore to a first approximation one can neglect the term containing K_2, i.e.

$$Q = (1 + K_1 b)/(\varepsilon_{AB} - \varepsilon_A) K_1 \; . \qquad (10)$$

Q varies linearly with b and K_1 and ϵ_{AB} can be obtained from the plot. Knowing them, it is possible to estimate K_2 and ϵ_{AB_2}:

$$(1 + K_1 b)/Q = (\varepsilon_{AB} - \varepsilon_A) K_1 + (\varepsilon_{AB_2} - \varepsilon_A) K_2 b \; .$$

After substitution of Q from Eqn. (8) and a slight rearrangement, Eqn. (10) becomes

$$al/(D - \varepsilon_A l) = 1/(\varepsilon_{AB} - \varepsilon_A) K_1 b + 1/(\varepsilon_{AB} - \varepsilon_A) \; . \qquad (11)$$

When $\epsilon_A = 0$, Eqn. (11) transforms into Eqn. (4), i.e. when the acceptor does not absorb the method reduces to the Benesi–Hildebrand method and differs from the latter by the arrangement of the parameters.

Using Eqns. (1)–(3), Foster and coworkers[74-76] arrived at the expression

$$D/b^n = Kal\varepsilon_{AB_n} - KD \; . \qquad (12)$$

When the relation between L/b^n and L is linear, it is possible to find K and ϵ_{AB_n}. Three cases arise in the application of the method[55,60-69,72,77-85]: (*a*) the slope is negative, i.e. K and ϵ_{AB_n} are positive and non-zero; (*b*) the slope is zero, i.e. $K = 0$ and $\epsilon_{AB_n} = \infty$; (*c*) the slope is positive, i.e. $K < 0$ and $\epsilon_{AB_n} < 0$.

Scott[86] modified the Benesi–Hildebrand method and suggested that $x_B al/D$ be plotted against x_B, where x_B is the mole fraction of the donor. This permits the investigation of the initial slope at very low concentrations since the plot is extrapolated through the region of decreasing concentrations to the intercept[55,87].

Rose and Drago[88,89] demonstrated the applicability of the following relation to systems comprising a Lewis base and molecular iodine:

$$K^{-1} = (D - D_A)/(\varepsilon_{AB} - \varepsilon_A) - a - b + ab(\varepsilon_{AB} - \varepsilon_A)/(D - D_A). \qquad (13)$$

Eqn. (13) is valid for an optical path length of 1 cm. The presence of two unknowns necessitates the calculation of K and ϵ_{AB} for two solutions with different ratios of a and b. If the experimental conditions are such that $(D - D_A)/(\epsilon_{AB} - \epsilon_A) - a$ is negligibly small compared with $ab(\epsilon_{AB} - \epsilon_A)/(D - D_A) - b$, then Eqn. (13) assumes the form of Eqn. (5). When the bands do not overlap at the chosen wavelength, D_A and ϵ_A are zero and Eqn. (13) reduces to

$$K^{-1} = D/\varepsilon_{AB} - a - b + ab \; \varepsilon_{AB}/D \; . \qquad (14)$$

If $L/\epsilon_{AB} - a$ is negligibly small, Eqn. (14) readily transforms into Eqn. (4), i.e. the Benesi–Hildebrand and Ketelaar equations are special cases of Eqn. (13), which is widely used in practice[54,90-94]. Kortüm and Weber[95] introduced the modulus of extinction $m = \epsilon_A C_A + \epsilon_B C_B + \epsilon_{AB} C_{AB}$ for the calculation of the stability. For reaction (1), we have

$$(m - \varepsilon_A a - \varepsilon_B \; b)/a - b = (\varepsilon_{AB} - \varepsilon_A - \varepsilon_B)[K_1 - K_1^2(a + b)] \; , \qquad (15)$$

it is suggested that Eqn. (15) be used for 1 : 1 complexes. The authors propose the following relation for the determination of the parameters of 1 : 1 and 1 : 2 complexes when they are present simultaneously:

$$m/ab = \varepsilon_{AB} \; K_1[1 - K_1(a + b) + K_1^2 ab - 2K_1 K_2 ab - K_1 K_2 b^2] + \\ + \varepsilon_{AB_2} \; K_1 K_2[b - 2K_1 ab - K_2 b] \; .$$

The present author investigated twenty systems by this method[96]. The results differ little from those calculated using the literature data[18,63,74].

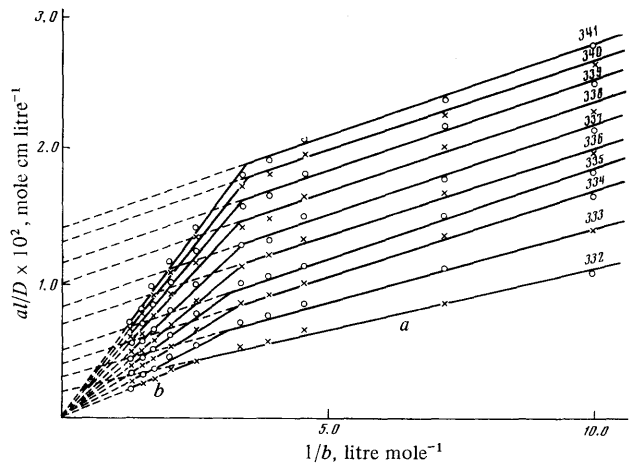


Figure 2. Application of the Benesi–Hildebrand method in the *m*-dinitrobenzene–2-methylnaphthalene system[26] in cyclohexane; the numbers against the plots represent wavelengths (nm).

Liptay[97] was the first to propose a method requiring a computer treatment and applicable for any concentration ratio of the components[98].

Lang[99] and Chandra[100-102] proposed modifications of the Benesi–Hildebrand method. Cilento and Sanioto[103] used a method on dilution. The working equation is

$$V^n = K\varepsilon_{AB} \; l \; m_A m_B^n/VD - Km_B^n \; ,$$

where V is the volume of the solution, D its optical density, and m_A and m_B are the numbers of moles of A and B. The plot of V^n against $1/VD$ should be linear. The intercept is $-Km_B^n$ and the slope is $K\epsilon_{AB} l m_A m_B^n$. Data for different wavelengths should yield the same intercept but different slopes.

Lavrushkin et al.[104] proposed two equations permitting a graphical determination of K and ϵ_{AB} when $b \gg a$:

$$a/(D-D_A) = 1/(\varepsilon_{AB}-\varepsilon_A) + 1/Kab(\varepsilon_{AB}-\varepsilon_A) ,$$
$$(D-D_A)/a = \varepsilon_{AB}-\varepsilon_A-(D-D_A)/Kab \quad .$$

Dewar and Thompson[105] put forward a system of four equations to be used for computer calculations whereby it is possible to find K, ϵ_{AB}, and C_{AB} (l = 1 cm):

$$C_{AB} = \{Ka+Kb+1-\sqrt{[K(a-b)+2Ka+2Kb+1]}\}/2K , \quad (16)$$
$$D_{AB} = \varepsilon_{AB} \quad C_{AB} = D-\varepsilon_A(a-C_{AB})-\varepsilon_B(b-C_{AB})\ldots , \quad (17)$$
$$ab/D_{AB} = 1/K\cdot\varepsilon_{AB}+(a+b-C_{AB})/\varepsilon_{AB}\ldots , \quad (18)$$
$$ab/D_{AB}(a+b-C_{AB}) = 1/K\cdot\varepsilon_{AB}(a+b-C_{AB})+1/\varepsilon_{AB}\ldots \quad (19)$$

The method of solution is as follows: using an arbitrary value of K, Eqn.(16) is solved for C_{AB}, D_{AB} is subtracted from Eqn.(17), and $1/\epsilon_{AB}$ and $1/K\epsilon_{AB}$ are found from Eqns.(18) and (19) respectively. The latter two values are used to find a new value of K.

Complex formation is not always accompanied by an increase of the optical density; the reverse process, i.e. an absorption by the reaction mixture less than the additive value, is commonly observed in the spectrum of the mixture of interacting components. Gol'tsev et al.[106] modified the method of Foster et al.[74] K can be obtained by plotting $(D_A-D)/b^n$ against D_A-D. The slope of this relation is numerically equal to K.

Hammond[107,108] simplified the method of Cilento and Sanioto[103] by introducing the dilution coefficient n into the equation and obtained the relation

$$1/nD = n/Ka^2\varepsilon_{AB}+1/\varepsilon_{AB}\cdot a+1/\varepsilon_{AB}\cdot b \quad . \quad (20)$$

Hence we have the working equation

$$d\lg D/d\lg n = -\{1+1/[1+(Ka+Kb)/n]\} \quad . \quad (21)$$

Eqns.(20) and (21) are valid when $a \gg b$ or $b \gg a$, which permits the neglect of $(1/\epsilon_{AB})b$ or $(1/\epsilon_{AB})a$ respectively, or when $a = b$.

Mamedov and Aleskerova[109] proposed a method which hardly differs from Nagakura's procedure[110,111]. Here

$$K = [a(D_0-D_1)+a'(D-D_0)]/a\cdot a'(D_1-D) , \quad (22)$$

where D_0, D, and D_1 are the optical densities of solutions in which the concentrations of the molecules of A are zero, a, and a' respectively. Eqn.(22) can be used when $C_{AB} \ll a$ and when D_A is negligibly small at the wavelengths used to determine the stability constant.

Gol'dshtein and Gur'yanova[112] developed a procedure called the "method for eliminating one of the unknowns" and suitable for the evaluation of K from spectroscopic (ultraviolet, infrared, Raman, and NMR), dielectric, calorimetric, etc. data for complexes of any stoichiometry. The method has been analysed in detail[113] and therefore is not quoted here. We shall only describe the general procedure. One unknown is eliminated from the general equation with two unknowns ϵ and K. This is achieved by taking logarithms in the general equation for K and by subsequent differentiation of the resulting expression. This yields a quadratic equation with one unknown. The method is suitable for a computer treatment and gives good results when not less than ten experimental points are used.

Meallier et al.[114] demonstrated the application of the following relations to the dioxane (A)–aniline (B) complex in hexane:

$$a/(\bar{\varepsilon}-\varepsilon_0) = [1/(\varepsilon_1-\varepsilon_0)]\,1/K+a/(\varepsilon_1-\varepsilon_0)+b(\varepsilon_1-\varepsilon_0)+b(\bar{\varepsilon}-\varepsilon_0)/(\varepsilon_1-\varepsilon_0)^2 , \quad (23)$$

where ϵ_0 and ϵ_1 are the molar extinction coefficients of aniline in hexane and dioxane respectively and $\bar{\epsilon} = D/bl$ is the formal extinction coefficient of aniline in the dioxane–hexane mixture. When $a \gg b$, Eqn.(23) becomes

$$a/(\bar{\varepsilon}-\varepsilon_0) = [1/(\varepsilon_1-\varepsilon_0)]\,1/K+a/(\varepsilon_1-\varepsilon_0) ,$$

whence

$$K = (\bar{\varepsilon}-\varepsilon_0)/a(\varepsilon_1-\bar{\varepsilon}) \quad .$$

An equation describing a hyperbolic curve and suitable for 1 : 1 complexes has been put forward[26,115]:

$$y^2+Kxy-y[Ka(\varepsilon_{AB}-\varepsilon_A-\varepsilon_B^*)+\varepsilon_B^*]-x\varepsilon_B^*K = 0 , \quad (24)$$

where $x = D$, $y = D/b$, and ϵ_B^* is the extinction coefficient of the donor in solution in the acceptor. The plot of D/b against D should yield a hyperbola or one of its branches [cf. Eqn.(12)]:

$$K = -\tan 2\alpha,$$

where α is the angle of rotation of the coordinate axes relative to the axis of the hyperbola. Fig. 3 illustrates the application of the method for a system which cannot be treated by the Benesi–Hildebrand method[18] and the method of Foster et al.[74] (Fig. 1): $K_1 = 0.69$ litre mole^{-1}.

Eqn.(24) can only be used effectively in a computer treatment using the method of least squares, since a manual graphical plot gives errors of the order of 20–30%.

Using the method of differential spectroscopy, Kampar and Neiland[116] put forward the relation

$$cl/\Delta D = 1/\varepsilon_{AB}+[(1-KC_{AB})/2K\ \varepsilon_{AB}]\cdot 1/c , \quad (25)$$

where $c = a = b$ and $\Delta D = \epsilon_{AB}C_{AB}\times 2l$ is the difference between the optical densities of the test and reference systems. Since in the majority of cases $KC_{AB} \ll 1$, it is assumed that $KC_{AB} = 0$ and Eqn.(25) represents the linear correlation between the function $cl/\Delta D$ and the argument $1/c$. When the linearity fails, the authors suggest an expression permitting a more accurate determination of K and ϵ_{AB}:

$$cl/\Delta D = 1/2\varepsilon_{AB}+[(1+\sqrt{4Kc+1})/4K\cdot\varepsilon_{AB}]1/c \quad .$$

The method can be used to determine K and ϵ_{AB} in those cases where both components and the complex absorb in the same region. The authors proposed their method for complexes of the ion–ion type, but it can also be used to investigate complexes of other types. However, it undoubtedly suffers from some of the disadvantages of the Benesi–Hildebrand method.

Apart from the equations discussed above, many expressions have been proposed for the determination of K and ϵ, differing from those quoted mainly by their form or by a different arrangement of the initial parameters[65,98,117–133].

Thus all the expressions employed to calculate K and ϵ were derived by combining the mass action and Bouguer–Beer–Lambert Laws and the majority presupposed the employment of an overwhelming excess of one of the components. For this reason, the fundamental defects of the Benesi–Hildebrand method are characteristic of all spectroscopic methods for determining K and ϵ for weak molecular complexes[134,135].

III. THE DIFFICULTIES ARISING IN THE DETERMINATION OF K AND ϵ

The main difficulties are the inconsistency of K and ϵ for weak molecular complexes, i.e. low values of K and very high values of ϵ are determined experimentally.

Orgel and Mulliken[136] were the first to attempt to elucidate this behaviour. They put forward the concept of contact charge transfer, according to which complexes with zero stability and appreciable absorbance can exist, i.e. the absorption by the complex arises in the course of random collisions. To illustrate their concept, the authors employed complexes of molecular iodine with saturated and aromatic hydrocarbons treated by the Benesi–Hildebrand method. The slight curvature obtained in the plot of $\ln K$ against $1/T$ was used by Orgel and Mulliken as evident proof that several geometrical isomers are present. It was shown that the iodine–n-heptane system forms only contact pairs and this is why the Benesi–Hildebrand line intersects the ordinate at the origin. Taking into account the "contact", Eqn.(4) becomes

$$al/D = 1/Kb\epsilon_{\text{eff}} + 1/\epsilon_{\text{eff}} ,$$

where $\epsilon_{\text{eff}} = \epsilon_{AB} + \alpha C_{AB}/K$, α being a coefficient characterising the number of molecules of B near the molecules of A.

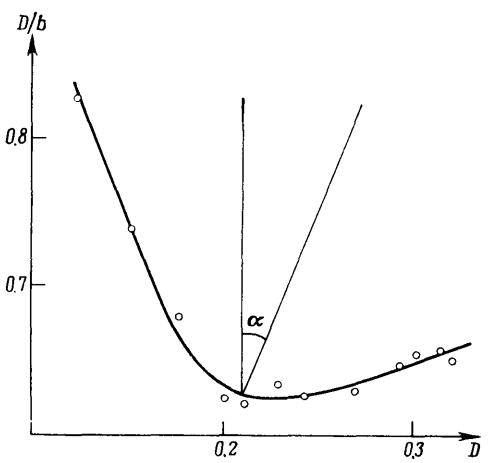


Figure 3. The *m*-dinitrobenzene–*o*-bromoaniline system[26] in methanol; $\lambda = 380$ nm; $l = 1$ cm.

Prue[137] derived an equation for the stability constants of 1 : 1 contact charge-transfer complexes of electron-donating and electron-accepting molecules: $K = 4\pi r^2 \Delta r N$, where r and $r + \Delta r$ are the distances between the centres of the molecules for which the presence of complexes is revealed in the charge-transfer spectra. When $r = 5$ Å and $\Delta r = 0.94$ Å, we have $K \simeq 0.2$ litre mole^{-1}. It was shown that values of K smaller than this and estimated from charge-transfer spectra do not constitute evidence for any kind of attractive forces between the donor and acceptor molecules in the ground state apart from the usual dispersion forces.

It should be noted that the estimation of r and $r + \Delta r$ in real systems is very complicated.

Murrell[138], who considered the inconsistency between K and ϵ, suggested that in a series of related complexes the relative behaviour of the intensity of the charge-transfer band and of the stability of the complex depends on the energy difference between the most stable configuration and the configuration contributing most to the intensity.

Many investigators attribute the inconsistency between K and ϵ to the effect of the solvent[86,124,139–148].

In an analysis of the concept of contact charge transfer, Carter et al.[142] concluded that it is unsatisfactory for two reasons: (a) the small thermodynamic justification of the hypothesis of two types of complexes one of which obeys the law of mass action and the other does not; (b) failure to take into account the role of the solvent in the theory despite the fact that in the case of weak complexes the donor competes with the solvent for a site around the acceptor.

Bearing in mind the competition between complex formation and solvation, there is no need to introduce two types of complexes and the behaviour of weak complexes can be accounted for by the same theory as that of strong complexes[142–144]:

$$AS_n + BS_m \rightleftarrows ABS_p + qS ,$$

where $q = n + m - p$, i.e. the donor, acceptor, and the complex are surrounded by a solvation shell:

$$K = C_{AB} x_S q / C_{AS_n} C_{BS_m} ,$$

where x_S is the mole fraction of the free solvent determined from the total number of moles of A, B, and S (bound and free). K is determined in the same way as in the Benesi–Hildebrand method:

$$al/D = (x_S q/K \cdot \varepsilon_{AB})(1/b) + 1/\varepsilon_{AB} .$$

The authors conclude that the Benesi–Hildebrand analysis underestimates K by an amount $q(m + 1)/G_0$ (G_0 is the total concentration of the solvent and $b = 0$) and overestimates ϵ_{AB} by an amount K/K_{B-H}. For stable complexes, $K \gg q(m + 1)/G_0$ and the Benesi–Hildebrand method gives good results.

The method proposed cannot be widely employed, since it is by no means easy to determine the numbers of solvent molecules with which the donor and acceptor are combined.

Semiempirical methods for the assessment of the influence of solvents have been proposed[124,145]. Hunter et al.[146], who examined four-component systems, demonstrated a method permitting the separation of the role of the solvent for moderately strong complexes of the type of chloranil–hexamethylbenzene (HMB)–n-heptane–carbon tetrachloride. The fundamental equation is

$$1/\varepsilon_A = 1/\ Y \cdot \varepsilon_{AB} + 1/K_{AB} \cdot Y\ \varepsilon_{AB}\ \ X\ b\ . \qquad (26)$$

Eqn.(26) differs from Eqn.(4) only by the presence of the terms X and Y, ϵ_A being the formal extinction coefficient of the acceptor calculated by dividing the total optical density of the solution by a and l.

$$X = 1 - (C_2 + C_3 + \ldots)b,\ Y = 1 - (C_2' + C_3' + \ldots)/a ,$$

where C_2, C_3, etc. are the concentrations of complexes of the solvent with the donor and C_2', C_3', etc. are the concentrations of complexes of the solvent with the acceptor. The method is based on the same postulates as the Benesi–Hildebrand method, i.e. $C_{AB} \ll b$. X and Y are expressed in terms of the concentrations of the four components present in the system:

$$X = (1 + T)^{-1},\ Y = [1 + S/(1 + K_{AB}\ \ b\ \ X)]^{-1} ,$$

where

$$T = \sum_{n=2}^{n} K_n(x) x_l^{n-1},\ S = \sum_{m=2}^{m} K_m(x) x_h^{m-1} ,$$

in which K_m is the stability constant of the chloranil–(n-heptane)$_{m-1}$ complex, K_n is the stability constant of the hexamethylbenzene–$(CCl_4)_{n-1}$ complex, and x_h and x_l

are the mole fractions of n-heptane and carbon tetrachloride respectively.

In the experimental test of the method, the concentration ratio of n-heptane and carbon tetrachloride was varied but K and ϵ remained constant in all cases. The fact that the K are much higher than for the complexes in pure carbon tetrachloride [149] (although the hexamethylbenzene–carbon tetrachloride complex is very weak) indicates the influence of carbon tetrachloride on the complex formation process.

It has been shown [146] that, even for very strong complexes, the interaction of the components with the solvent is comparable to the complex formation proper. The authors suggest that the formation of competing complexes with the solvent is the most likely explanation of the inconsistency between K and ϵ.

The simultaneous employment of different concentration scales (litre mole^{-1} in the determination of K_{AB} and the reciprocal of the mole fraction in the determination of K_{As} and K_{Bs}) hinders the application of the method [142].

Scott [147] considered the determination of the stability constants of weak complexes from the standpoint of a quasichemical calculation for a cell with donor, acceptor, and inert solvent molecules. Using Guggenheim's theory [150], the author showed that the stability constants calculated by methods of the Benesi–Hildebrand type are imaginary. A disadvantage of the proposed method is that it is based on the concept of contact charge transfer. Moreover, the author considers the possibility of the existence of contact complexes with $\epsilon = 0$ and $K > 0$.

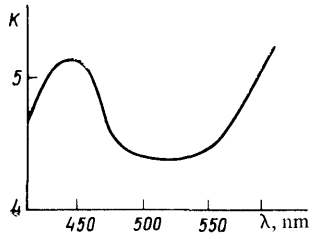


Figure 4. Variation of K with wavelength [32] in the tetracyanoethylene–naphthalene system in carbon tetrachloride at 25°C.

To predict the effect of solvents on the equilibrium, Christian et al. [148] employed a non-polar analogue model (NAM) in which a non-polar analogue of the polar solute is used in the calculation of the properties of the solutions. The chosen NAM molecule must have the same molecular volume and the same energy of interaction with the surrounding solvent as the polar solute. It was shown that NAM can be used under a wide range of conditions.

Kuntz et al. [36] attribute the inconsistency between K and ϵ to an incorrect choice of the concentration scale. They considered reaction (1) in the presence of an inert solvent S, i.e. they assumed that there is no competition between the donor and the solvent. This resulted in relations between different concentration scales:

$$(K_x)_{B-H} = K_c/v_S + (v_B - v_S)/v_S;\ (\epsilon_x)_{B-H} = K_c\epsilon_{AB}/(v_B - v_S + K_c);$$
$$(K_m)_{B-H} = \rho_S(K_c + v_B);\ (\epsilon_m)_{B-H} = \epsilon_{AB}\ K_c/(K_c + v_B)\ ,$$

where x is the concentration expressed in terms of mole fractions, m the molality, c the molarity, ρ the density, and v the molar volume. It is concluded that reasonable values of K_C, v_B, and v_S can give rise to zero or negative values of K_X when the Benesi–Hildebrand method is used. However, the form of the Benesi–Hildebrand linear plot cannot be used to conclude that one or other concentration scale is preferable; an experimental study with the aid of two inert solvents is necessary. For complexes of the aromatic amine–aromatic nitro-compound type, the concentration is best expressed on the molar scale.

General equations for the interaction with solvents relating different concentration scales have been published [143].

The problem of the inconsistency between K and ϵ can also be approached in a different way. On the basis of solvation theory, one should observe constant products $K\epsilon$, obtained by the Benesi–Hildebrand or similar methods, over a wide range of donor and acceptor concentrations. This was in fact done in a study of the *NN*-dimethylaniline–1,3,5-trinitrobenzene (TNB) in chloroform. K varied from 0.62 to 1.18 litre mole^{-1} and ϵ from 1800 to 954. Ross and Labes [151] explained this result by postulating the existence of 1 : 2 and 2 : 1 complexes in the system. Foster and coworkers [152,153] suggested that the observed extinction coefficient is a function of the concentration of the component present in excess, usually the donor: $\epsilon = \epsilon_0(1 + \alpha b)$, where ϵ_0 is the extinction coefficient at infinite dilution. Application of this expression showed that appreciable variation in K_{B-H} and ϵ_{B-H} may occur for very small values of α; ϵ is overestimated and K underestimated. On the other hand, the product $K\epsilon$ remains unchanged. It is nowadays frequently recommended that $K\epsilon$ and not K be used to determine the thermodynamic parameters [12,154].

A remarkable phenomenon has been noted by a number of workers [29,32,34,53,66–69,105,121,144,155–163]—the dependence of K on wavelength. This has been interpreted in different ways. Thus Johnson and Bowen [32] (Fig. 4) believe that this relation cannot be explained by the presence of isomeric 1 : 1 charge-transfer complexes and (or) contact absorption. They postulate the existence of stable charge-transfer complexes with at least two different stoichiometric compositions.

The study of complexes of aromatic nitro-compounds with alkylbenzenes in carbon tetrachlorides [156] demonstrated a dependence of K on the wavelength for all the systems studied. For example, K for the *p*-dinitrobenzene–1,3,5-trinitrobenzene complex decreases from 2.24 to 0.62 litre mole^{-1} when λ is raised from 325 to 390 nm. Jurinski and de Maine [156] suggest that the results cannot be accounted for by the existence of any isomeric 1 : 1 complexes or higher-order complexes.

Carter [144] extended the Benesi–Hildebrand method to the case of the simultaneous presence of 1:1 and 1 : 2 complexes:

$$al/D = (1/K_1 \cdot \varepsilon_1)(1/b) + (K_1 - \varepsilon_2 K_2/\varepsilon_1)/K_1\varepsilon_1\ .$$

When the condition $b \gg a$ is maintained, the observed $K = K_1 - (\epsilon_2/\epsilon_1)K_2$ and the slope yields $K_1\epsilon_1$, which was in fact observed on the assumption that 1 : 2 complexes exist. Hence follows the conclusion that the presence of 1 : 2 complexes should lead to a dependence of K on λ. Christie and Selinger [160] analysed the experimental data and conclusions of Johnson and Bowen [32] and showed that the dependence of K on λ need not be explained by the presence of isomeric complexes, but could simply be a result of the algebraic addition of the optical densities of the donor, acceptor, and the complex.

A clear example of the dependence of the observed K on λ and on the ratio of the donor and acceptor concentrations is illustrated in Table 1. The method[105] described above was used.

Table 1.

λ, nm	[TCNE] = 1.8×10^{-3} M [HMB] = (1.2–4.1) × 10^{-3} M	[TCNE] = 1.4×10^{-4} M [HMB] = 0.222–0.333 M	λ, nm	[TCNE] = 1.8×10^{-3} M [HMB] = (1.2–4.1) × 10^{-3} M	[TCNE] = 1.4×10^{-4} M [HMB] = 0.222–0.333 M
450	47.4	19.1	560	26.6	19.1
460	46.9	19.4	570	28.8	19.2
470	39.3	20.1	580	27.6	19.1
480	39.0	20.2	590	26.1	19.2
490	36.7	20.4	600	27.2	19.6
500	33.3	20.1	610	28.4	20.1
510	32.0	20.3	620	24.7	21.1
520	27.7	20.2	630	27.5	22.2
530	31.6	19.7	640	25.5	26.5
540	30.7	19.6	650	23.2	28.6
550	29.7	19.3			

Note. TCNE = tetracyanoethylene, HMB = hexamethylbenzene.

It is remarkable that the values of K obtained for more concentrated solutions vary little with the wavelength and the direction of their variation is the opposite to that observed at low concentrations. If the relation between K and λ is due to the appearance of complexes with a higher stoichiometry[32,144], the opposite behaviour should have been observed, i.e. the changes should have been greater at higher concentrations, since there is a greater probability of the formation of higher-order complexes.

The dependence of K and ϵ on the ratio of the donor and acceptor concentrations has been observed and discussed frequently[13,53,56,105,164]. Using the Benesi–Hildebrand method, Inoue and Kato[53] put forward two series of K values for the *NN*-dimethylaniline–nitrobenzene system in cyclohexane. When a donor concentration less than 0.3 M was used, $K_{ev} = 0.22$ litre mole^{-1}; at donor concentration greater than 0.3 M, $K_{ev} = 0.083$ litre mole^{-1}. The nitrobenzene concentration was 0.0162 M. Generally speaking, the Benesi–Hildebrand lines have the form analogous to that illustrated in Figs. 1 and 2 with the sole difference that the intercept is positive for both donor concentration ranges.

All three types of intercept (positive, zero, and negative) in the application of the Benesi–Hildebrand method were demonstrated for real systems by Davis and Farmer[34]. A negative intercept of the Benesi–Hildebrand method [Eqn. (4)] corresponds to a positive slope of Foster's method [Eqn. (12)]. We shall refer to the slope as anomalous, since it yields values of K and ϵ lacking physical significance.

The first attempt to account for the anomaly was undertaken by Fofonova[165] in connection with the interpretation of the results of Syrneva and Fofonova[77]. When the singlet–singlet band of the acceptor, displaced to one side under the influence of intermolecular interaction, is superimposed on the singlet–triplet band of the donor, the following observations may be made. If in the spectral region studied the intensities of both bands are of the same order of magnitude (the singlet–triplet band is located on the wing of the singlet band), then the intensities of both bands increase simultaneously with increase of the concentration of one of the components. Under these conditions, the experimental straight lines of the Benesi–Hildebrand method and the method of Foster et al. will have anomalous slopes and the characteristics of the complex cannot be determined.

It is possible to examine the cause of the anomaly from a different standpoint. Consider the commonest cases arising in the study of the absorption spectra of complex-forming systems (we are considering systems with a positive deviation of the optical density from additivity).

1. The complex AB absorbs in the region where A and B are absolutely transparent. The solvent is put in the reference cuvette, $b \gg a$, and K is calculated from Eqns. (4) or (12). For any numerical values of ϵ_{AB}, the straight lines should have the normal slope.

2. A also absorbs in the region of absorption by the complex, the reference cuvette contains a solution of A at a concentration a, and $b \gg a$. The spectrophotometric data are analysed in terms of Eqns. (5) and (27):

$$D/b^n = -KD + Kal(\varepsilon_{AB} - \varepsilon_A) \quad . \tag{27}$$

Since $\epsilon_{AB} > \epsilon_A$ (positive deviation from additivity), the straight lines described by Eqns. (5) and (27) will always have the normal slope regardless of the value of ϵ_A. Thus the intrinsic absorption by the component A does not alter the form of the straight line, but does affect the value of K. Calculation without allowing for ϵ_A yields values of ϵ_{AB} which are too low by an amount equal to ϵ_A.

3. The deviation from additivity in the mixture of components is observed only in the regions where A and B absorb.

On the basis of the Bouguer–Beer–Lambert law, the optical density of the solution (1 : 1 complex) can be written as follows:

$$D = l[(a - C_{AB})\varepsilon_A + (b - C_{AB})\varepsilon_B^* + C_{AB} \cdot \varepsilon_{AB} - a\varepsilon_A] \quad , \tag{28}$$

where ϵ_B^* is the extinction coefficient of the donor in solution in the acceptor (one must not confuse this with ϵ_B — the extinction coefficient of the donor in the pure solvent).

An expression for the concentration of the complex can be obtained from Eqn. (28).

$$C_{AB} = (D - bl\varepsilon_B^*)/l(\varepsilon_{AB} - \varepsilon_A - \varepsilon_B^*) \quad . \tag{29}$$

Next we have

$$(D - bl\varepsilon_B^*)/l(\varepsilon_{AB} - \varepsilon_A - \varepsilon_B^*) = Kab/(1 + Kb) \quad , \tag{30}$$

where the right-hand side of the equation is an expression obtained from the law of mass action subject to the condition $b \gg a$. The replacement of $(b - c)$ by b does not give rise to a large error.

When $l = 1$, Eqn. (30) can be written as:

$$D - \varepsilon_B^* b + KbD - Kb^2\varepsilon_B^* = Ka(\varepsilon_{AB} - \varepsilon_A - \varepsilon_B^*) \quad . \tag{31}$$

After elementary transformations, we obtain from Eqn. (31)

$$D/b + KD = Ka(\varepsilon_{AB} - \varepsilon_A - \varepsilon_B^*) + \varepsilon_B^* + Kb\varepsilon_B^* \quad . \tag{32}$$

When the notation $D/b = y$, $D = x$, and $b = x/y$ is introduced, Eqn. (32) can be rewritten in the form of the fundamental equation (24). If $\epsilon_{AB} = \epsilon_A + \epsilon_B^*$, the hyperbola defined by Eqn. (24) splits into two straight lines:

$$\begin{cases} y_1 = \varepsilon_B^* \\ y_2 = -Kx \end{cases} \quad . \tag{33}$$

The coordinates of the focus of the hyperbola are

$$\begin{cases} y = \varepsilon_B^* \\ x = -\varepsilon_B^*/K \end{cases} \quad . \tag{34}$$

When $\epsilon^*_B = 0$, Eqn.(24) becomes

$$y^2 + Kxy - yKa(\varepsilon_{AB} - \varepsilon_A) = 0 \ . \qquad (35)$$

Eqn.(35) describes a degenerate hyperbola, which splits into two intersecting straight lines:

$$\begin{cases} y_1 = 0 \\ y_2 = -Kx + Ka(\varepsilon_{AB} - \varepsilon_A) \ . \end{cases} \qquad (36)$$

Fig. 5 illustrates two limiting cases of Eqn.(24): $\epsilon^*_B = 0$ and $\epsilon_{AB} = \epsilon_A + \epsilon^*_B$. The A'B'C' lines corresponds to two intersecting asymptotic lines defined by Eqns.(33): the section $y_0 = \epsilon^*_B$ and the section $x_0 = -\epsilon^*_B/K$. The ABC line describes two intersecting straight lines defined by Eqn.(36), the line AB representing the linear plot of Foster's method [Eqn.(12)]. When $\epsilon^*_B = 0$, the line BC coincides with the abscissa axis and, when $\epsilon^*_B > 0$, it lies above the axis and is responsible for the appearance of anomalous slopes in the graph.

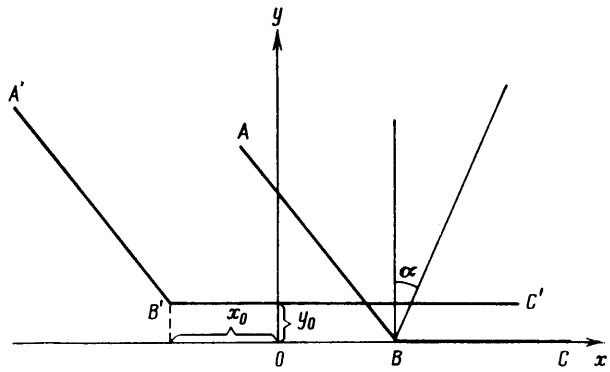


Figure 5. The limiting cases of the equation of the hyperbola [26].

Thus the slopes of the straight lines are influenced by the ratio ϵ^*_B/K. The higher its value (i.e. the higher the value of ϵ^*_B and the lower the value of K) the greater the probability of obtaining lines with an anomalous slope and neither a change in the donor concentration nor in the other experimental conditions yields straight lines with a normal slope. Hence the appearance of anomalous straight lines for weak complexes and the absence of "anomalies" for strong complexes with $K \gg \epsilon^*_B$ becomes understandable. For high values of ϵ^*_B/K, methods taking into account the absorption by the donor [88,112] will not help either, since there is no possibility of an experimental determination of ϵ^*_B. For low values of ϵ^*_B/K and high values of $\epsilon_{AB} - \epsilon_A - \epsilon^*_B$ in a study covering a fairly wide range of donor concentrations, we obtain hyperbolic plots of D/b against D and the stability constant is determined in terms of the tangent of the angle of rotation of the coordinate axes, in accordance with Eqn.(24).

IV. THE RELIABILITY OF THE LITERATURE VALUES OF K AND ϵ

The need to determine K and ϵ, the fundamental characteristics of complex-forming systems, has given rise to publications where the conditions under which the usual methods are applicable are discussed.

Thus Hammond [167,168] examined the influence of experimental errors on K and ϵ obtained when four terms of the Benesi–Hildebrand equation [Eqn.(4)] are used.

$$ab/D = 1/K\varepsilon_{AB} + b/\varepsilon_{AB} \ ; \ (a)\ b/D = 1/K \cdot \varepsilon_{AB}\ a + b/\varepsilon_{AB}\ a \ ; \ (b)$$
$$a/D = (1/K \cdot \varepsilon_{AB})(1/b) + 1/\varepsilon_{AB} \ ; \ (c)\ 1/D = (1/K \cdot \varepsilon_{AB}\ a)(1/b) + 1/\varepsilon_{AB}\ a \ (d)$$

The scatter of the points around the straight lines has different effects on K. Thus Eqns.(a) and (b) give rise to a significant scatter for low values of K and Eqn.(c) and (d) give rise to a large scatter for high values of K. This means that, for the same value of a, b, and D, Eqns.(a) and (b) are most suitable when $K < 1$ litre mole^{-1}. Eqn.(d) is suggested for the case where the scatter of the points is caused only by errors in the determination of b and D (a = const.). It has been shown that, when the error in the measurement of D is 1%, the relative error in the determination of K increases from 11% (K = 1 litre mole^{-1}) to 83% (K = 0.10 litre mole^{-1}). The errors in the determination of ϵ are approximately the same; 9 and 81% respectively. The optimal conditions in the determination of K by the Benesi–Hildebrand method are obtained when $5 < K < \epsilon/12$.

In an analysis of the methods described [18,58,86,88], Pearson [163] concluded that reliable stability constants are obtained only when the equilibrium concentration of the complex is of the same order of magnitude as the equilibrium concentration of the dilute component. If the donor and acceptor form 1:1 compounds only, then $D_{AB} = \epsilon_{AB}lC_{AB} = \epsilon_{AB}lKC_AC_B$. When $b \gg a$, we have $C_B \simeq b$ and $C_A \simeq a - C_{AB}$.

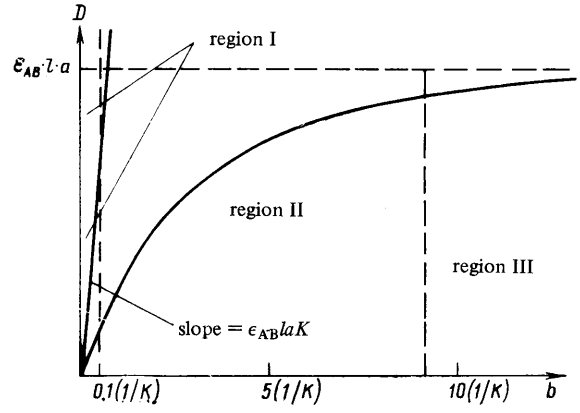


Figure 6. Variation of the absorption of the complex as a function of increasing donor concentration [169].

If a slight excess of the donor is used, the concentration of the complex in solution will be very small, so that $C_A \simeq a$. In this case $D_{AB} = \epsilon_{AB}lKab$ and the absorption by the complex increases linearly with increase of the initial concentration of the donor. On the other hand, in

the presence of a large excess of the donor the entire acceptor is in the complex and the addition of more donor does not alter the optical density.

Fig. 6 shows that the plot of the absorption by the complexes against donor concentration can be divided into three regions. In region I, where the donor concentration is low, the absorption increases linearly. For large values of b, the absorption remains unaltered. Between these two extremes, there is region II where the absorption does not increase linearly with increase of b. It is suggested that measurements should be made in the intermediate concentration range. This range has been determined approximately:

$$0.1a < C_{AB} < 0.9a \text{ or } 0.1(1/K) < b < 9.0(1/K) . \quad (37)$$

From this it follows that a zero slope in the methods of Foster et al.[74] and Scott[86] or a zero Benesi–Hildebrand intercept[18] can be obtained for any complexes, including strong complexes—this depends on the ratio of the donor and acceptor.

Deranleau[168,170] uses the term "saturation fraction" s:

$$s \equiv C_{AB}/a = Kb/(1 + Kb) . \quad (38)$$

The saturation fraction varies in the range $0 \leqslant s \leqslant 1$. For region II (Fig. 6) with $b = 0.1(1/K)$ and $9(1/K)$ the saturation fraction is respectively 0.09 and 0.9; the half-saturation point ($s = 0.5$) occurs when $b = 1/K$. For $b \gg a$, C_{AB} is neglected in Eqn. (38) and an error is introduced into the calculation:

$$(K^1 - K)/K = -sa/b , \quad (39)$$

where K^1 is an approximate value of the constant and K the value calculated from the exact equation.

This error cannot exceed a/b and is always negative[116] whatever the value of s, i.e. K calculated with this approximation is always greater than the correct value. If the errors in a and b are insignificant compared to the error in s, the relative error in K is in practice determined explicitly:

$$\Delta K/K \geqslant \Delta s[1/s^2 - 1/(1-s)^2] .$$

The error in ϵ_{AB} is given by the equation

$$\Delta\epsilon_{AB}/\epsilon_{AB} \geqslant \Delta s\sqrt{2/s} . \quad (40)$$

Eqns. (39)–(40) give the minimum values, but their derivation in a practical experiment is difficult. The relative errors defined by Eqns. (39) and (40) have been plotted as a function of s in Fig. 7. The most accurate values of ϵ_{AB} are obtained when the concentration of the complex is a maximum ($s = 1$), but an adequate accuracy can be achieved above a saturation fraction of 0.2. The correct values of K are obtained when s varies from 0.2 to 0.8. Beyond the limits of this range, the values investigated become indefinite and the error reaches 100% and more.

Deranleau believes that only by measuring 75% of the saturation curve can one asses with certainty the validity of the composition and the parameters of the complex being analysed. Generally speaking, the author reaches this conclusion for weak complexes, but notes that the proposed criterion is suitable for any instance of complex formation.

Table 2 illustrates[134] the employment of the reliability criteria of Pearson[168] and Deranleau[166]. Analysis of the data presented shows that systems with $K > 1$ satisfy Pearson's requirement (37). We shall consider the values of s for the tabulated systems. Complexes of 2-methylnaphthalene with nitro-compounds satisfy Deranleau's criterion, i.e. the measurements are in the region where the errors in K and ϵ_{AB} are minimal. For nitrobenzene–benzene ($K = 0.094$ litre mole^{-1}) and 1,3,5-trinitrobenzene–benzene ($K = 0.184$ litre mole^{-1}) complexes, the optical density measurements do not fall within the region of reliability as defined by Pearson and Deranleau. In measurements on the nitrobenzene–benzene system the donor (benzene) concentration was varied in the range 0.68–1 M, which correspond to the variation of the saturation fraction from 0.06 to 0.09, whereas according to Deranleau's reliability criterion, the benzene concentration should vary in the range from 1.5 to 40 M and according to Pearson's criterion from 1 to 90 M. For complexes with $K < 1$ litre mole^{-1}, it is difficult to reach in practice even the lower limit of reliability, let alone achieve the measurement of 75% of the saturation curve.

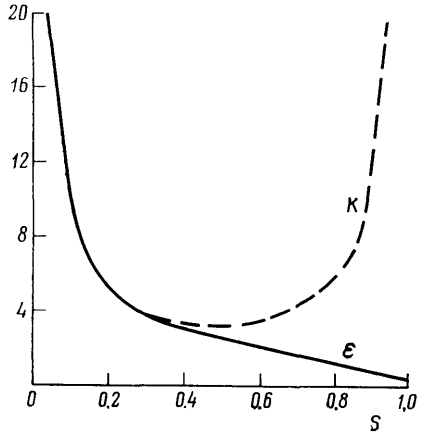


Figure 7. The relative percentage errors $100\,\Delta K/K$ and $100\,\Delta\epsilon/\epsilon$ as a function of s.[166]

The reliability criteria proved to be the most favourable for complexes with stability constants in the range 2–10 litre mole^{-1}. Thus for $K = 2$, 3, 5, and 10 litre mole^{-1}, the concentration ranges are respectively 0.12–2.0, 0.06–1.33, 0.05–0.8, and 0.025–0.40 M. These values are quite realistic for donors and the saturation fraction can be used as a criterion of the reliability of the results for complexes with stability constants in the above range. For complexes with stability constants of the order of 20 litre mole^{-1} and above, other difficulties arise in the choice of concentrations. According to both Pearson and Deranleau, the required donor concentration is so low that it is difficult to select an acceptor concentration satisfying the condition $b \gg a$.

The assessment of the reliability of the results by the Deranleau and Pearson methods is complicated by the fact that, not knowing the stability constant, it is impossible to predict the choice of the concentrations of the component present in excess for a correct determination of the parameters of the complex but, having determined the constant (possibly incorrectly), we will know whether the right concentration range has been used. This uncertainty in the values of K makes it difficult to employ the above reliability criteria.

The criteria have been used[40,54,164], but they have also been criticised. Heric[171] concluded that under certain conditions Pearson's criterion leads to incorrect findings.

Using the principles of mathematical statistics, the author suggests the investigation of groups of points on the Benesi–Hildebrand straight line and not all the points at once. One group includes points differing by not more than two standard deviations from the average Benesi–Hildebrand line fitted by least squares and the other includes the remaining points. Next these groups are divided into subgroups containing points differing along the ordinate by not more than two standard deviations. Similar subgroups are set up also with respect to the abscissae. Next the application of a special statistical table makes it possible, according to the author, to obtain more reliable results than those achieved with the aid of Pearson's criteria.

Table 2. The limits of reliability according to Pearson and Deranleau.

System	$-\Delta K/K$		s		b (after Pearson)	
	min.	max.	min.	max.	min.	max.
m-DNB-2-methylnaphthalene	$0.4\cdot10^{-5}$	$0.22\cdot10^{-3}$	0.08	0.44	$0.37/K$	$0.87/K$
o-DNB-2-methylnaphthalene	$0.5\cdot10^{-4}$	$0.5\cdot10^{-3}$	0.40	0.80	$1.04/K$	$5.2/K$
p-DNB-2-methylnaphthalene	$0.14\cdot10^{-4}$	$0.4\cdot10^{-3}$	0.04	0.32	$0.16/K$	$0.68/K$
1,3,5-TNB-2-methylnaphthalene	$0.25\cdot10^{-4}$	$0.24\cdot10^{-3}$	0.40	0.77	$0.66/K$	$3.32/K$
NB–2-methylnaphthalene	$0.8\cdot10^{-4}$	$0.13\cdot10^{-2}$	0.16	0.52	$0.20/K$	$1.14/K$
NB–benzene	$0.13\cdot10^{-3}$	$0.24\cdot10^{-3}$	0.06	0.09	$0.066/K$	$0.094/K$
1,3,5-TNB–benzene	$0.25\cdot10^{-4}$	$0.21\cdot10^{-3}$	0.05	0.17	$0.062/K$	$0.184/K$

The errors in the determination of K and ϵ have been analysed in studies [172,173] other than those discussed above.

---o0o---

To summarise, one can point out the causes of the anomalies discussed above (the inconsistency between K and ϵ, zero and negative values of K when the complexes absorb strongly, the dependence of K on wavelength, etc.).

1. The calculated stability constants are concentration constants, since the activity coefficients are in most cases totally unknown. This is probably the reason for the dependence of K on the ratio of the donor and acceptor concentrations. There is no doubt that an incorrectly chosen concentration scale also has an effect.

2. The possible failure of the Bouguer–Beer–Lambert Law for the complexes under investigation. If the law holds, then in the presence of a large excess of the donor a linear relation should be observed between the optical density of the complex and the initial acceptor concentration [174].

3. Effect of the solvent, i.e. competition of the solvent with the components in the formation of association complexes. Absolutely inert solvents are known not to exist; moreover, the choice of the inert solvent is affected by the solubilities of the reactants. If the equilibrium constants for the reactions between A and S and between B and S are negligibly small compared with K for the reaction between A and B, the solvent is assumed to be neutral and can be used in the investigation.

4. The absorption by the donor in the acceptor solution, which is usually assumed in practice to be equal to its absorption in the pure solvent. It was shown above that the higher the value of ϵ^*_B/K the greater the probability of a curvature in the Foster, Benesi–Hildebrand, and other plots.

5. The existence of complexes with a higher stoichiometry. As a rule conclusions concerning the existence of 1 : 2, 1 : 3, etc. complexes are speculative or based on Foster, Benesi–Hildebrand, and other plots. To obtain a linear relation between L/b^n and L (Foster's method) when there is a curvature for $n = 1$, one substitutes $n = 2$, 3, etc. until a straight line is obtained. It was shown in Section III that the deviation of Foster's plot from linearity is due to ϵ^*_B; when this is taken into account, the parameters of the 1 : 1 complex can be calculated. An independent determination of the compositions of weak complexes is extremely difficult, but in many cases the application of Job's and Bent and French's methods [171,175] gives good results.

6. The error of the calculations of K and ϵ_{AB}. The few reports where graphs from which K and ϵ were calculated are published [34,40,41,43,62] show that on average not more than five points are used for 2–3 wavelengths. We may recall the non-equivalence of the points corresponding to high and low donor concentrations when methods of the Benesi–Hildebrand type are used. For example, for six consecutive additions the value for the most dilute solution (the least accurate value) will have a statistical weight approximately equal to the statistical weight for the four values corresponding to more concentrated solutions [166]. Experience shows that in such cases the line is drawn on the basis of the two least accurate values (the most dilute solutions). This reduces the probability of detecting the curvature in the graph. The application of the method of least squares without a preliminary analysis of the relation conceals the error in the determination of K and ϵ. When a small number of experimental points are used, no reliability criteria can be of assistance. In the determination of K it is necessary to employ not less than 10–15 points over the longest possible concentration range and the investigation should be carried out over the entire wavelength range where the complex absorbs. The variation of K with the wavelength can be used for an unambiguous determination of the electron-donating component of the donor–acceptor complex [56]. Thus, in publishing K and ϵ values, it is essential to indicate the concentration ranges, the number of experimental points, and the wavelength range in which the study was made.

The employment of published literature values of K and ϵ requires a certain amount of caution. The values of K obtained for a series of donors with a single acceptor and under identical conditions and conversely are valuable. We then obtain an unambiguous answer to the question of the relative stabilities of the complexes and can infer the structure of the association complexes formed. It is interesting to use the relative stabilities K/K_S, [176,177] where K_S is the stability constant of a reference acceptor for a series of donor or of a reference donor for a series of acceptors.

The objective nature of spectrophotometric results can be confirmed by a comparison with the results of fundamentally different techniques (dielectric constant measurements, calorimetry, NMR spectroscopy, etc.).

REFERENCES

1. A. K. Babko, "Fiziko-khimicheskii Analiz Kompleksnykh Soedinenii v Rastvorakh" (Physicochemical Analysis of Complexes in Solution), Izd. Akad. Nauk Ukrain. SSR, Kiev, 1955, p. 81.

2. K. B. Yatsimirskii and V. P. Vasil'ev, "Konstanty Nestoikosti Kompleksnykh Soedinenii" (Instability Constants of Complexes), Izd. Akad. Nauk SSSR, Kiev, 1955.
3. L. Sůcha, Chem. Listy, **54**, 344 (1960).
4. V. B. Kolychev and V. I. Paramonov, in "Spektroskopicheskie Metody v Khimii Kompleksnykh Soedinenii" (Spectroscopic Methods in the Chemistry of Complex Compounds), Izd. Khimiya, Moscow–Leningrad, 1964, p. 30.
5. G. L. Shlefer, "Kompleksoobrazovanie v Rastvorakh" (Complex Formation in Solution), Izd. Khimiya, Moscow–Leningrad, 1964.
6. F. J. Rossotti and H. S. Rossotti, "Determination of Stability Constants and Other Equilibrium Constants in Solution" (Translated into Russian), Izd. Mir, Moscow, 1965.
7. A. N. Terenin, Uspekhi Khim., **24**, 121 (1955).
8. S. P. McGlynn, Chem. Rev., **58**, 1113 (1958).
9. G. Briegleb, "Electronen–Donator–Acceptor Komplexe", Springer, Berlin, 1961.
10. V. P. Parinin, Uspekhi Khim., **31**, 822 (1962) [Russ. Chem. Rev., No. 7 (1962)].
11. R. S. Mulliken and W. B. Person, Ann. Rev. Phys. Chem., **13**, 107 (1962).
12. L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry" (Translated into Russian), Izd. Mir, Moscow, 1967.
13. J. Rose, "Molecular Complexes", Pergamon Press, Oxford, 1967.
14. V. A. Kargin (Editor), "Organicheskie Poluprovodniki" (Organic Semiconductors), Izd. Nauka, Moscow, 1968, p. 331.
15. E. M. Kosower, in "Novye Problemy Fizicheskoi Organicheskoi Khimii" (New Problems in Physical Organic Chemistry) (Translated into Russian), Izd. Mir, Moscow, 1969, p. 36.
16. R. S. Mulliken and W. B. Person, "Molecular Complexes", Wiley Interscience Publ., New York, 1969.
17. R. Foster, "Organic Charge-transfer Complexes", Acad. Press, London, 1969.
18. H. A. Benesi and H. J. Hildebrand, J. Amer. Chem. Soc., **71**, 2703 (1949).
19. H. Halban and E. Zimpelmann, Z. phys. Chem., **117**, 461 (1925).
20. Z. Michaelis and S. Granick, J. Amer. Chem. Soc., **66**, 1023 (1944).
21. R. S. Mulliken, J. Amer. Chem. Soc., **72**, 600 (1950).
22. R. S. Mulliken, J. Chem. Phys., **19**, 514 (1951).
23. R. S. Mulliken, J. Amer. Chem. Soc., **74**, 811 (1952).
24. R. S. Mulliken, J. Phys. Chem., **56**, 801 (1952).
25. H. A. Benesi and H. J. Hildebrand, J. Amer. Chem. Soc., **70**, 2302 (1948).
26. N. N. Polle, Candidate's Thesis, Institute of Chemistry, the Urals Scientific Centre, USSR Academy of Sciences, Sverdlovsk, 1972.
27. G. Briegleb and J. Czekalla, Z. Elektrochem., **59**, 184 (1955).
28. G. Briegleb, J. Czekalla, and G. Reuss, Z. phys. Chem. (Frankfurt), **30**, 333 (1961).
29. H. Hayman, J. Chem. Phys., **37**, 2290 (1962).
30. R. Lang, J. Amer. Chem. Soc., **84**, 1185 (1962).
31. P. Hammond, J. Chem. Soc., 471 (1964).
32. G. Johnson and R. Bowen, J. Amer. Chem. Soc., **87**, 1655 (1965).
33. A. Cŏoper, C. Crowne, and P. Farrell, Trans. Faraday Soc., **62**, 2725 (1966).
34. K. Davis and M. Farmer, J. Chem. Soc. (B), 28(1967).
35. A. Ewald, Trans. Faraday Soc., **64**, 733 (1968).
36. J. Kuntz, F. Gasparro, M. Johnston, and R. Taylor, J. Amer. Chem. Soc., **90**, 4778 (1968).
37. A. B. Tronov and N. N. Polle, "Trudy Altaiskogo Politekhnicheskogo Instituta, Khimiya i Khimicheskaya Tekhnologiya" (Transactions of the Altai Polytechnic Institute, Chemistry and Chemical Engineering), Barnaul, 1968, p. 49.
38. N. N. Polle and E. G. Polle, Zhur. Obshch. Khim., **39**, 1619 (1969).
39. S. B. Gol'shtein, S. D. Stavrova, and S. F. Medvedev, Dokl. Akad. Nauk SSSR, **187**, 93 (1969).
40. Yu. A. Serguchev and E. A. Shilov, Teor. Eksper. Khim., **6**, 680 (1970).
41. V. A. Trofimov, O. N. Chupakhin, and Z. V. Pushkareva, Dokl. Akad. Nauk SSSR, **191**, 1302 (1970).
42. R. Chan and S. Liao, Canad. J. Chem., **48**, 299 (1970).
43. I. P. Chikhacheva and S. D. Stavrova, Uch. Zap. Moskov. Inst. Tonkoi Khim. Tekhnol., **1**, 60 (1971).
44. B. V. Tronov and A. Goncarov, Scienca Rev. (Beograd), **22**, 17 (1971).
45. T. Urbanski, Wiad. Chem., **25**, 405 (1971).
46. R. Foster and I. Matheson, Spectrochim. Acta, **A27**, 1171 (1971).
47. G. Cauquis, O. Chalvet, and G. Thibaud, Bull. Soc. chim. France, 1015 (1971).
48. D. Armitage, T. Beament, K. Davis, D. Hall, and K. Morcem, Trans. Faraday Soc., **67**, 2548 (1971).
49. V. P. Pozdnyakov and V. A. Gorodyskii, Zhur. Fiz. Khim., **46**, 561 (1972) [Russ. J. Phys. Chem., No. 3 (1972)].
50. R. S. Tsekhanskii, Izv. Vys. Ucheb. Zaved., Khim. i Khim. Tekhnol., **15**, 1493 (1972).
51. B. A. Radbil', Zhur. Prikl. Spektrosk., **17**, 907 (1972).
52. E. A. Krulikovskaya and S. V. Dozmorov, Zhur. Obshch. Khim., **42**, 2248 (1972).
53. H. Inoue and G. Kato, Tetrahedron, **28**, 527 (1972).
54. E. Ong and M. Sambhi, J. Phys. Chem., **76**, 2102 (1972).
55. M. Barigand, J. Orszagh, and J. Tondeur, Bull. Soc. chim. France, part 1, 48 (1973).
56. R. M. Fofonova, Symposium, "Spektroskopiya, Metody i Primeneniya" (Spectroscopy. Methods and Applications), Izd. Nauka, Moscow, 1973, p. 247.
57. D. Simov, L. Kamenev, and S. Stoyanov, Khim. Geterotsikl. Soed., 497 (1973).
58. J. Ketelaar, C. Stolpe, A. Gaugsmit, and W. Dzcubas, Rec. Trav. chim., **71**, 1104 (1952).
59. A. Brier, Rec. Trav. chim., **75**, 866 (1956).
60. G. L. Ryzhova and G. N. Mishustina, Trudy Tomsk. Univ., **192**, 182 (1968).
61. A. Graczyk and J. Konarski, Biul. WAT J. Dabrowskiego, **21**, No. 3, 73 (1972).
62. R. Srivastava and P. Srivastava, Bull. Acad. polon. Sci., Ser. Sci., chim., geol., geog., **20**, 759 (1972).
63. J. Landauer and H. McConnell, J. Amer. Chem. Soc., **74**, 1221 (1952).
64. D. Lawrey and H. McConnell, J. Amer. Chem. Soc., **74**, 6175 (1952).
65. N. Thakur and C. Kanekar, Current Sci. (India), **35**, No. 4, 93 (1966).
66. B. V. Tronov and E. G. Polle, Zhur. Obshch. Khim., **36**, 1411 (1966).
67. B. V. Tronov and E. G. Polle, Zhur. Obshch. Khim., **37**, 2444 (1967).

68. B.V. Tronov and E.G. Polle, Zhur. Obshch. Khim., 38, 470 (1968).
69. E.G. Polle, L.M. Sitnikova, and B.V. Tronov, Zhur. Obshch. Khim., 38, 1864 (1968).
70. A.B. Tronov, "Trudy 1-i Nauchnoi Konferentsii Tomskogo Otdeleniya VKhO im. B.I. Mendeleeva" (Proceedings of the First Scientific Conference of the Tomsk Division of the All-Union Mendeleev Chemical Society), Izd. Tomsk. Univ., Tomsk, 1969, p. 151.
71. B.V. Tronov and I.M. Yakovleva, "Trudy 1-i Nauchnoi Konferentsii Tomskogo Otdeleniya VKhO im. B.I. Mendeleeva" (Proceedings of the First Scientific Conference of the Tomsk Division of the All-Union Mendeleev Chemical Society), Izd. Tomsk. Univ., Tomsk, 1969, p. 175.
72. G.P. Naletova, N.V. Schastlivtseva, and A.A. Galechek, Zhur. Fiz. Khim., 45, 1484 (1971) [Russ. J. Phys. Chem., No. 6 (1971)].
73. G.L. Ryzhova and A.M. Pogaleeva, Zhur. Fiz. Khim., 47, 1104 (1973) [Russ. J. Phys. Chem., No. 5 (1973)].
74. R. Foster, D. Hammick, and A. Wardley, J. Chem. Soc., 3817 (1953).
75. R. Foster and D. Hammick, J. Chem. Soc., 2685 (1954).
76. R. Foster, J. Chem. Soc., 1075 (1960).
77. N.V. Syrneva and R.M. Fofonova, Izv. Vys. Ucheb. Zaved, Fiz., No. 2, 46 (1964).
78. N.N. Polle and E.G. Polle, Zhur. Obshch. Khim., 39, 1847 (1969).
79. P. Emslie, R. Foster, J. Horman, J. Morris, and D. Twiselton, J. Chem. Soc. (B), 1161 (1969).
80. V.N. Nagareva, N.N. Polle, and E.G. Polle, Zhur. Obshch. Khim., 40, 2320 (1970).
81. I.M. Korenman and A.A. Gorokhov, Zhur. Obshch. Khim., 41, 948 (1971).
82. B.V. Tronov, A.E. Goncharov, and A.B. Tronov, Zhur. Obshch. Khim., 41, 280 (1971).
83. A.Ya. Deich, V.S. Lomakina, N.N. Polle, and E.G. Polle, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 42 (1973).
84. V.N. Nagareva, E.G. Polle, A.Ya. Deich, and M.S. Zakharov, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 368 (1973).
85. B.N. Nagareva, E.G. Polle, M.Z. Fakhretdinova, and M.S. Zakharov, Zhur. Fiz. Khim., 47, 2387 (1973) [Russ. J. Phys. Chem., No. 9 (1973)].
86. R. Scott, Rec. Trav. chim., 75, 787 (1956).
87. I. Sharma, Z. phys. Chem. (Leipzig), 249, 408 (1972).
88. N. Rose and H. Drago, J. Amer. Chem. Soc., 81, 6138 (1959).
89. R. Drago and N. Rose, J. Amer. Chem. Soc., 81, 6141 (1959).
90. T. Tasinski, T. Misiak, and T. Skarzynska, Roczniki Chem., 39, 1485 (1965).
91. R. Drago, T. Bolles, and R. Niedzielski, J. Amer. Chem. Soc., 88, 2717 (1966).
92. T. Jasinski and Z. Kokot, Roczniki Chem., 41, 139 (1967).
93. T. Widernig, K.T. Skarzynska, and T. Jasinski, Roczniki Chem., 45, 1767 (1971).
94. I. Dupont, I. D'Hondt, and T. Zeegers-Huyskens, Bull. Soc. chim. belge., 80, 369 (1971).
95. G. Kortüm and G. Weber, Z. Elektrochem., 64, 642 (1960).
96. E.G. Polle, Candidate's Thesis, Tomsk University, Tomsk, 1967, p. 49.
97. W. Liptay, Z. Elektrochem., 65, 375 (1961).
98. A. Ewald and J. Scudder, J. Phys. Chem., 76, 249 (1972).
99. V. Krishna and B. Bhowmik, J. Amer. Chem. Soc., 90, 1700 (1968).
100. A. Chandra and D. Banerjee, J. Phys. Chem., 66, 952 (1962).
101. A. Chandra and D. Mukherjee, Trans. Faraday Soc., 60, 62 (1964).
102. D. Mukherjee and A. Chandra, J. Phys. Chem., 68, 477 (1964).
103. G. Cilento and D. Sanioto, Z. phys. Chem. (Leipzig), 223, 333 (1963).
104. V.F. Lavrushkin, V.N. Tolmachev, L.A. Sinyagovskaya, and N.D. Trusevich, Zhur. Obshch. Khim., 35, 1534 (1965).
105. M. Dewar and C. Thompson, Tetrahedron, Suppl. 7, 97 (1966).
106. V.D. Gol'tsev, A.P. Izakenaite, L.V. Zinov'eva, N.D. Strel'nikova, and B.V. Tronov, Symposium, "Primenenie Molekulyarnoi Spektroskopii v Khimii" (Chemical Application of Molecular Spectroscopy), Izd. Nauka, Moscow, 1966, p. 183.
107. P. Hammond, J. Phys. Chem., 72, 2272 (1968).
108. P. Hammond and L. Burkardt, J. Phys. Chem., 74, 639 (1970).
109. F.D. Mamedov and S.M. Aleskerova, Dokl. Akad. Nauk Azerb. SSR, 26, 24 (1970).
110. S. Nagakura, J. Amer. Chem. Soc., 76, 3070 (1954).
111. S. Nagakura, J. Amer. Chem. Soc., 80, 520 (1958).
112. I.P. Gol'dshtein and E.N. Gur'yanova, Teor. Eksper. Khim., 7, 542 (1970).
113. E.N. Gur'yanova, I.P. Gol'dshtein, and I.P. Romm, "Donorno-Aktseptornaya Svyaz'" (The Donor–Acceptor Bond), Izd. Khimiya, Moscow, 1973.
114. P. Meallier, J. Randeau, and B. Pouyet, Spectrochim. Acta, 27, 2243 (1971).
115. N.N. Polle and E.G. Polle, Trudy Tyumensk. Ind. Inst., Khim. i Khim. Tekhnol., 229 (1972).
116. V.E. Kampar and O.Ya. Neiland, Zhur. Org. Khim., 8, 225 (1972).
117. M. Frank and R. Oswald, J. Amer. Chem. Soc., 69, 1321 (1947).
118. G. Schwarzenbach and J. Heller, Helv. Chim. Acta, 34, 1876 (1951).
119. R. Keefer and L. Andrews, J. Amer. Chem. Soc., 74, 1891 (1952).
120. R. Foster, J. Chem. Soc., 5098 (1957).
121. C. Thompson and P.A.D. de Maine, J. Amer. Chem. Soc., 85, 3096 (1963).
122. C. Thompson and P.A.D. de Maine, J. Phys. Chem., 69, 2766 (1965).
123. B. Ghosh and S. Basu, Trans. Faraday Soc., 61, 2097 (1965).
124. Pham Van Huong and J. Lascombe, J. Chim. Phys., 63, 892 (1966).
125. B. Chakrabarti and S. Basu, J. Chim. Phys., 64, 950 (1967).
126. R.W. Ramette, J. Chem. Educ., 44, 647 (1967).
127. I. Moriguchi and N. Kaneniwa, Chem. Pharm. Bull. (Tokyo), 17, 2173 (1969).
128. I. Moriguchi, S. Fushimi, and N. Kaneniwa, Chem. Pharm. Bull. (Tokyo), 19, 2132 (1971).
129. M. Barigand, J. Orszagh, and J. Tondeur, Bull. Soc. chim. France, 4864 (1972).
130. K. Davis, Photoelectr. Spectrom. Group Bull., 603 (1972).
131. V.A. Khadeev, Zhur. Anal. Khim., 27, 2090 (1972).

132. W. Lüblers and R. Wodick, Naturwiss., 59, 362 (1972).
133. B. Budesinsky, Anal. Chim. Acta, 62, 95 (1972).
134. N. N. Polle and E. G. Polle, Trudy Tyumensk. Ind. Inst., Khim. i Khim., Tekhnol., 202 (1972).
135. E. G. Polle, in "II Vsesoyuznoe Soveshchanie po Kompleksam s Perenosom Zaryada i Ion-radikal'nym Solyam" (The Second All-Union Conference on Charge-transfer Complexes and Radical-ion Salts), Izd. Zinatne, Riga, 1973, p. 3.
136. L. E. Orgel and R. S. Mulliken, J. Amer. Chem. Soc., 79, 4839 (1957).
137. J. Prue, J. Chem. Soc., 7534 (1965).
138. J. Murrell, J. Amer. Chem. Soc., 81, 5037 (1959).
139. I. Corkill, R. Foster, and D. Hammick, J. Chem. Soc., 1202 (1955).
140. R. Merrifield and W. Phillips, J. Amer. Chem. Soc., 80, 2779 (1958).
141. M. Tamres, J. Phys. Chem., 65, 654 (1961).
142. S. Carter, J. Murrell, and E. Rosch, J. Chem. Soc., 2048 (1965).
143. P. Trotter and M. Hanna, J. Amer. Chem. Soc., 88, 3724 (1966).
144. S. Carter, J. Chem. Soc. (A), 404 (1968).
145. I. Grundness and C. Sherrill, J. Amer. Chem. Soc., 90, 2239 (1968).
146. T. Hunter, N. Cutress, K. Mitchinson, G. Rowley, and M. Stillman, Spectrochim. Acta, A27, 1207 (1971).
147. R. L. Scott, J. Phys. Chem., 75, 3843 (1971).
148. S. Christian, R. Frech, and K. Yeo, J. Phys. Chem., 77, 813 (1973).
149. T. Hunter and D. Norfolk, Spectrochim. Acta, 25A, 193 (1969).
150. E. Guggenheim, Trans. Faraday Soc., 56, 1159 (1960).
151. S. Ross and M. Labes, J. Amer. Chem. Soc., 79, 76 (1957).
152. P. Emslie, R. Foster, C. Fyfe, and J. Horman, Tetrahedron, 21, 2843 (1965).
153. P. Emslie and R. Foster, Tetrahedron, 21, 2851 (1965).
154. R. Foster and I. Matheson, Spectrochim. Acta, 27A, 1171 (1971).
155. P. A. D. de Maine, M. Maine, and C. Froese, J. Mol. Spectroscopy, 8, 373 (1962).
156. N. Jurinski and P. A. D. de Maine, J. Amer. Chem. Soc., 86, 3217 (1964).
157. R. Foster and J. Horman, J. Chem. Soc. (B), 171 (1966).
158. H. Kuroda, T. Amano, I. Ikemoto, and H. Akamatu, J. Amer. Chem. Soc., 89, 6056 (1967).
159. T. Matsuo and O. Hiquchi, Bull. Chem. Soc. Japan, 41, 518 (1968).
160. J. Christie and B. Selinger, Spectrosc. Letters, 1, 55 (1968).
161. R. Arnaud and J. Bonnier, J. Chim. phys., 66, 954 (1969).
162. H. Craenen, T. Verhoeven, and T. Bour, Tetrahedron, 27, 1615 (1971).
163. R. Foster, Ind. Chim. belge, 37, 547 (1972).
164. M. Hanna and D. Rose, J. Amer. Chem. Soc., 94, 2601 (1972).
165. R. M. Fofonova, Symposium, "Primenenie Molekulyarnoi Spektroskopii v Khimii" (Chemical Applications of Molecular Spectroscopy), Izd. Nauka, Moscow, 1966, p. 83.
166. D. Deranleau, J. Amer. Chem. Soc., 91, 4044 (1969).
167. P. Hammond, J. Chem. Soc., 471 (1964).
168. P. Hammond, J. Chem. Soc., 479 (1964).
169. W. B. Person, J. Amer. Chem. Soc., 87, 167 (1965).
170. D. Deranleau, J. Amer. Chem. Soc., 91, 4050 (1969).
171. E. Heric, J. Phys. Chem., 73, 3496 (1969).
172. K. Conrew, D. Johnson, and R. Bowen, J. Amer. Chem. Soc., 86, 1025 (1964).
173. T. Maier and R. Drago, Inorg. Chem., 11, 1861 (1972).
174. D. Holder and C. Thompson, J. Tenn. Acad. Sci., 46, 115 (1971).
175. H. Bent and C. French, J. Amer. Chem. Soc., 63, 569 (1941).
176. M. Charton, J. Organ. Chem., 33, 3878 (1968).
177. See Ref. 12, p. 109.

Tyumen Industrial Institute