exhibited statistically somewhat low analytical results. The reason was probably attributed to incomplete conversion of organic halogens to halogen ions and to losses occuring during the transfer of the absorption liquid to the beaker, although the conversion rate and loss are quite reproducible. Analysts are strongly advised to standardize the concentration of silver nitrate solution against the standard organic halogen compounds such as *p*-chlorobenzoic acid. A list of representative analyses involving different types of organic halogen compounds is shown in Table IV where the over-all distribution of the analytical errors has been evaluated as  $\sigma = 0.15$  (%) which is quite acceptable for microanalysis.

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# Preparation, Analysis, and Comparative Study of Silver Perchlorate Complexes with Methylbenzenes

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A convenient method for the preparation of crystals of silver perchlorate complexes with o-, p-, and m-xylene, and with mesitylene is described. A spectrophotometric method for the analysis of the crystals and determination of the ratios of the components of the molecular complexes is presented. p-Xylene and mesitylene appear to form molecular complexes of one composition only (2 p-xylene:1 silver perchlorate, and 1 mesitylene form both the 1:1 and 2:1 aromatic: silver complexes.

THE EXISTENCE of molecular complexes between hydrocarbons with donor properties and inorganic acceptor type compounds is well documented by now (1, 2). These complexes can sometimes be isolated as solids of definite composition (usually of simple molecular ratios). In other instances the interaction products are sufficiently unstable so that their formation can be recognized only through changes in the physical properties of solutions of their components. The donor properties responsible for the formation of molecular aromatic complexes are usually due to the aromatic  $\pi$ -electron systems. Acceptor ability of inorganic compounds in such complexes usually necessitates the availability of unfilled (mostly d) orbitals. The complexes thus formed are of considerable theoretical and experimental interest (3, 4) and include, as a particular case, the so-called charge transfer complexes. The ability of silver (either as nitrate or as perchlorate) to form such complexes was noted long ago, and has been the subject of several studies (e.g., refs. 3-9).

Because of the extreme instability of the crystals of such complexes and the lack of preparative details in the literature, it was thought useful to work out a convenient laboratory

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- (5) G. Peyronel, G. Belmondi, and J. M. Vezzosi, J. Inorg. Nucl. Chem., 8, 577 (1958).
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- (9) R. J. Prosen and K. N. Trueblood, Acta Crystallogr., 9, 741 (1956).

technique for preparing crystals of silver perchlorate-aromatic complexes, as well as reliable methods of analysis of the crystals, and then use these for comparative study of the composition of crystalline molecular complexes of silver perchlorate with a series of methylbenzenes.

Daasch (10) described a method for preparing such crystals by gradual removal of the excess organic solvent in a vacuum desiccator. In several cases, this is not practical owing to the long period required to evaporate solvents with relatively low vapor pressure (e.g., mesitylene). Peyronel *et al.* (5) prepared the solid benzene-silver perchlorate complex by adding ligroin to a saturated solution of silver perchlorate in benzene. This method has two main disadvantages:

It is not possible to grow well-defined and large crystals necessary for X-ray work and it is very difficult to dry the fine crystals that contain ligroin.

The analysis of such crystals is usually based on silver determination.

# EXPERIMENTAL

Spectrophotometric measurements were carried out at 22 °C using a Cary 14 instrument with matched 1-cm quartz cells.

The solvents used were *p*-xylene (B.D.H., A.R.), *m*-xylene (Fluka, C.P.), *o*-xylene (Fluka, A.R.), toluene (Merck, A.R.) and mesitylene (B.D.H., C.P.). All reagents were used without further purification. AgClO<sub>4</sub> (B.D.H., L.R.) was dried by heating for 24 hr at 200 °C and was kept in a desiccator over  $P_2O_5$  [see also ref. (11)].

The details for the preparation of the crystals are given in Figure 1 and described in the caption. To summarize, the anhydrous silver perchlorate is dissolved in the appropriate aromatic hydrocarbon and the concentrated (nearly saturated) solutions are evaporated by passing dry nitrogen over them. With a flow rate of nitrogen of about 500 to 700 ml per second, the time of crystallization varies from 3 to 20 days, at a temperature of 25 °C. Because of the extreme sensitivity of the crystals to atmospheric moisture, their removal from the mother liquor is performed by placing vessel A (see Figure 1) in a dry box flushed with dry nitrogen. Tube I is then detached, the mother liquor decanted, and the crystals are gently removed by tapping the upper end of I on black hard filter paper.

<sup>(10)</sup> L. W. Daasch, Spectrochim. Acta, 9, 726 (1959).

<sup>(11)</sup> L. El-Sayed and R. O. Ragsdale, J. Inorg. Nucl. Chem., 30, 651 (1968).



Figure 1.  $G_1$  is a washing bottle containing concentrated sulfuric acid.  $G_2$  contains glass wool to trap  $H_2SO_4$  droplets.  $T_1$  is immersed in liquid nitrogen to trap traces of unwanted gases or vapors.  $T_2$  is a trap serving to control the temperature of the current of gas. A is the crystallization vessel. I consists of a detachable glass tube, stopcocks, S, and a capillary, C, which together with glass tube D containing anhydrous CaCl<sub>2</sub>, serves to prevent atmospheric moisture from entering into I



Figure 2. Absorbance of various concentrations of methylbenzenes in concentrated sulfuric acid in the range 194 to 220 m $\mu$ 

- 2  $\mu$ g/ml *p*-xylene 1.
- $1 \ \mu g/ml \ o$ -xylene 2. 3.
- $2 \mu g/ml m$ -xylene 4. 2  $\mu$ g/ml mesitylene
- 5. 1.5  $\mu$ g/ml toluene



# ANALYTICAL

A spectrophotometric method was developed for the analysis of the crystals. As a check, silver was also determined volumetrically.

The volumetric method used was essentially Volhard's titration. The amounts of silver perchlorate ( $N_s$  moles) and of organic solvent ( $N_{a}$  moles) in the crystals (total weight  $W_{2}$ grams) are given by:

$$N_s = \frac{W_o}{A}, \quad N_o = \frac{W_2 - W_o(M_s/A)}{M_o}$$

where  $W_{o}$  is the weight of silver in the sample determined by titration as above,  $M_o$  and  $M_s$  are the molecular weights of the complexing organic solvent and silver perchlorate, respectively, and A is the atomic weight of silver.

The spectrophotometric method developed involves the independent determination of each of the two components in the complex.

Silver perchlorate was determined by the dithizone method (12) according to which silver reacts quantitatively with a slight excess of dithizone in 0.5N sulfuric acid to form the primary dithizonate Ag(HDz) which dissolves in carbon tetrachloride giving a yellow solution, the absorption spectrum band of which has a maximum at 462 m $\mu$ . It was more convenient to determine the silver in a 3.6N H<sub>2</sub>SO<sub>4</sub> solution instead of the 0.5N solution that has been proposed, as the





Figure 3. Absorbance of various concentrations of methylbenzenes in concentrated sulfuric acid in the range 210 to 250  $m\mu$ 

- 10  $\mu$ g/ml *p*-xylene 10  $\mu$ g/ml o-xylene 2. 8 µg/ml m-xylene 3. 10  $\mu$ g/ml mesitylene 4.
- 5. 10  $\mu$ g/ml toluene

crystal is initially dissolved in concentrated H<sub>2</sub>SO<sub>4</sub> (see the following description of the analytical procedure).

For the determination of the organic component, a spectrophotometric method was developed using concentrated sulfuric acid as the solvent. The method is based on the fact (13) that aromatic compounds form complexes with concentrated sulfuric acid. The spectrum of the mesitylene-sulfuric acid complex was recorded by Nagakura and coworkers (14) while investigating the progressive blue shifts observed in the UV and visible spectra of various mixtures of acetone with concentrated sulfuric acid, but nothing has been mentioned as to the possible use of this for analytical purposes. We developed an analytical method based on the above as follows: Concentrated sulfuric acid solutions (98% by weight) containing about 1 mg of aromatic compound per 1 ml of solution were prepared by dissolving accurately weighed samples of toluene, o-, p-, and m-xylene, and mesitylene in known volumes of concentrated sulfuric acid.

Solutions of 0.5 to 40  $\mu$ g of aromatic compound per ml of solution were prepared by diluting the original solutions. Absorbance measurements were performed immediately after the preparation of the solutions. Figures 2, 3, and 4 represent diagrams of absorption spectra of various concentrations of methylbenzenes in concentrated sulfuric acid in the UV range. These calibration curves make it possible to determine the concentrations of methylbenzenes even when mixed together, in an unknown sample, as long as there is no interference from the other species present in the sample.

The analytical procedure for the molecular complex crystals is then as follows:

A small part of a crystal (lower limit about 0.05 mg) is

<sup>(13)</sup> R. J. Gillespie and J. A. Leisten, Quart. Rev., 8, 40 (1954).

<sup>(14)</sup> S. Nagakura, A. Minegishi, and K. Stanfield, J. Amer. Chem. Soc., 79, 1033 (1957).



Figure 4. Absorbance of various concentrations of methyl benzenes in concentrated sulfuric acid in the range 250 to 300 m $\mu$ 

- 1. 50  $\mu$ g/ml *p*-xylene
- 2. 50  $\mu$ g/ml *o*-xylene
- 3. 50  $\mu$ g/ml *m*-xylene
- 4. 30  $\mu$ g/ml mesitylene
- 5. 50  $\mu$ g/ml toluene

quickly transferred to a glass-stoppered flask containing concentrated sulfuric acid. The exposure to atmospheric moisture must not exceed 1 minute. The solution is then vigorously stirred in the stoppered flask for about 10 minutes. After the crystal is completely dissolved, an aliquot of the solution is transferred to a glass container and diluted tenfold with distilled water (the final sulfuric acid concentration is about 3.6N). The solution is then cooled, transferred to a separating funnel and shaken with a dilute solution of dithizone in CCl<sub>4</sub>. The optical density of the extracted silverdithizone complex Ag(HDz) in the CCl<sub>4</sub> solution is then measured in the visible range ( $\lambda_{max} = 462 \text{ m}\mu$ ) and the silver content determined. The optical density of the concentrated sulfuric acid solution of the sample after shaking is measured in the UV range (200 to 300 m $\mu$ ) and gives the content of the aromatic material. Since each of the aromatic species has its specific absorption band (see Figures 2-4), it is possible to identify each aromatic substance as well as to determine it quantitatively.

The main advantages of the spectrophotometric method are



Figure 5. Absorbance of mesitylene and *p*-xylene in isooctane

1. 330  $\mu$ g/ml mesitylene 2. 152  $\mu$ g/ml *p*-xylene

2. 152  $\mu$ g/m *p*-xylen

identification of all components of the complex, independent determination of each component in the complex, and easy analysis of even micro quantities of crystals. Thus, the method is better than organic microanalysis which usually determines only the percentage of hydrogen (and carbon) in the complex and is less reproducible.

# **RESULTS AND DISCUSSION**

Table I shows the data of the absorption spectra of methylbenzenes in concentrated sulfuric acid. The absorption bands of the spectra as measured in the UV range are represented by their maximum wavelengths and the corresponding molar extinction coefficients.

On comparing the spectra of methylbenzenes in concentrated sulfuric acid (see Table I) with the spectra of methylbenzenes in isooctane as recorded by us and by Tunnicliff and coworkers (15), quite different spectra are obtained, with a much higher value of extinction coefficients (compare Figures

(15) D. D. Tunnicliff, R. R. Brattain, and L. R. Zumwalt, ANAL CHEM., **21**, 890 (1949).

Table I. Absorption Data of Methylbenzenes in Concentrated Sulfuric Acid								
Compound	$\lambda_{\max}$ in m $\mu$	Abs <sup><i>a</i></sup> of 1 $\mu$ g per ml in log ( $I_o/I$ )	Beer's law range, µg/ml	£	$\lambda_{max}$ in m $\mu$	Abs. <sup>a</sup> of 1 $\mu$ g per ml in log ( $I_o/I$ )	Beer's law range, µg/ml	¢
p-Xylene	197.0	0.360	1-3	38000	222.0	0.062	1-20	6600
o-Xylene	198.5	0.390	0.5-4	41400	229.5	0.085	2-15	9000
<i>m</i> -Xylene	199.5	0.425	1-4	45100	230.5	0.090	1-20	9550
Mesitylene	201.5	0.490	0.5-4	58800	234.5	0.089	2-40	10700
Toluene	<195.0				226.0			
<i>p</i> -Xylene	279.5	0.018	6-50	1820	286.0	0.015	6-50	1520
o-Xylene	271.0	0.013	10-50	1380	278.0	0.014	10-50	1480
<i>m</i> -Xylene	272.0	0.014	10-50	1480	279.5	0.013	10-50	1380
Mesitylene	279.0	0.019	2-50	2280	286.5	0.020	2-50	2400
Toluene	273.0				279.5			
<sup>a</sup> Abs = Absorbar	ice							



Figure 6. Absorbance of *m*- and *o*-xylene in isooctane

1. 223  $\mu$ g/ml *m*-xylene

2. 326  $\mu$ g/ml *o*-xylene

2-4 with Figures 5 and 6), suggesting the formation of new species. The spectra obtained for pure methylbenzenes in sulfuric acid are identical with those for the molecular complexes of methylbenzenes-silver perchlorate in concentrated sulfuric acid, *i.e.*, the complexes, as expected, are immediately decomposed by the acid.

It is supposed (13, 16–18), that the aromatic hydrocarbon forms in the acidic medium a protonated activated complex (a carbonium ion complex) of the type [Ar H]<sup>+</sup> where Ar = benzene, toluene, o-xylene, p-xylene, m-xylene, or mesitylene. The existence of the proposed protonated complex is supported by the fact that it is stable only in very concentrated sulfuric acid (about 98% by weight). Thus, we found that the addition of even small quantities of water to the medium destroys the complex, a fact which is easily detected by the absence of absorption spectra in the UV range. Rapid (less than a few hours) sulfonation of the hydrocarbon is not likely to occur in the sulfuric acid medium at room temperature, as concentrated sulfuric acid contains only very small amounts of the acting sulfonating agents (SO<sub>3</sub>) or HSO<sub>3</sub><sup>-</sup>. Also the protonated hydrocarbon tends to decrease the tendency of sulfonation (13).

- (16) J. E. Leffler, "The Reactive Intermediates of Organic Chemistry," Interscience, New York, 1956, pp 140-3.
  (17) L. J. Andrews and R. M. Keefer, "Molecular Complexes in
- (17) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964, pp 152-4.
- (18) W. I. Aalborsberg, G. J. Hoigbruk, E. L. Mackor, and W. P. Weyland, J. Chem. Soc., 1959, 3049.

## Table II. Results of Analysis of Crystals of p-Xylene-Silver Perchlorate Complex

<i>A</i> Sample	<i>B</i> Sample	C Method of	D No. of moles of	<i>E</i> No. of moles of	Ratio of	Ratio expressed	Molecular structure as determined by	
No.	wt, mg	determination	silver perchlorate	<i>p</i> -xylene	E/D	in whole no.	Peyronel	Amma
1	70.0	Volumetric	$1.78 \times 10^{-4}$	$3.12 \times 10^{-4}$	1.75	2:1	2:1ª	2:1
2	20.5	Volumetric	$5.00 \times 10^{-5}$	9.6 $\times 10^{-5}$	1.92	2:1		
2	Small part of a crystal	Spectrophoto- metric	$5.95 \times 10^{-6}$	$11.8 \times 10^{-6}$	1.98	2:1		
3	Small part of a crystal	Spectrophoto- metric	$5.48 \times 10^{-6}$	$10.4 \times 10^{-6}$	1.90	2:1		
3	Small part of a crystal	Spectrophoto- metric	$8.9 \times 10^{-6}$	$15.6 \times 10^{-6}$	1.75	2:1		

<sup>a</sup> Crystals were formed by direct crystallization.

#### Table III. Results of Analysis of Crystals of o-Xylene-Silver Perchlorate Complex

<i>A</i> Sample	<i>B</i> Sample	C Method of	D No. of moles of	<i>E</i> No. of moles of	Ratio of	Ratio expressed in whole no.	Molecular structure as determined by	
No.	wt, in mg	determination	silver perchlorate	o-xylene	E/D		Peyronel	Amma
1	279	Volumetric	6.7 $\times 10^{-4}$	$13.2 \times 10^{-4}$	1. <b>97</b>	2:1	$2:1^{a,b}$	2:1
2	72.5	Volumetric	$2.30 \times 10^{-4}$	$2.34 \times 10^{-4}$	1.02	1:1		
2	Small part of a crystal	Spectrophoto- metric	$1.11 \times 10^{-5}$	$1.13 \times 10^{-5}$	1.02	1:1		
3	100.3	Volumetric	$3.10 \times 10^{-4}$	$3.39 \times 10^{-4}$	1.09	1:1		
3	Small part of a crystal	Spectrophoto- metric	$3.9 \times 10^{-6}$	$4.42 \times 10^{-6}$	1.13	1:1		
1	Small part of a crystal	Spectrophoto- metric	$4.55 \times 10^{-6}$	$7.70 \times 10^{-6}$	1.70	2:1		
3	Small part of a crystal	Spectrophoto- metric	$7.90 \times 10^{-6}$	$7.95 \times 10^{-6}$	1.01	1:1		
3	6.534	Microanalysis of hydrogen	$2.27 \times 10^{-5}$	$1.72 \times 10^{-5}$	0.76	1:1		
3	5.007	Microanalysis of hydrogen	$1.76 \times 10^{-5}$	1.36 × 10⁻⁵	0.77	1:1		

<sup>a</sup> Crystals were formed by direct crystallization.

<sup>b</sup> Crystals were formed by addition of ligroin to saturated solution of silver perchlorate in the aromatic hydrocarbon.

# Table IV. Results of Analysis of Crystals of m-Xylene-Silver Perchlorate Complex

A	<i>B</i> Sample wt in mg	<i>C</i> Method of determination	D No. of moles of silver perchlorate	Ε	Ratio of <i>E/D</i>	Ratio expressed	Molect as det	ular struct	cture I by
Sample No.				No. of moles of <i>m</i> -xylene		in whole no.	Peyronel	Torre- Mori	Amma
1	203.7	Volumetric	5.0 $\times 10^{-4}$	$9.4 \times 10^{-4}$	1.88	2:1	$2:1^{a}$	1:1	2:1
2	739	Volumetric	$1.75 \times 10^{-3}$	$3.54 \times 10^{-3}$	2.02	2:1	$1:1^{a}$		
2	Small part of a crystal	Spectrophoto- metric	$1.17 \times 10^{-5}$	$2.41 \times 10^{-5}$	2.06	2:1	1:10		
3	Small part of a crystal	Spectrophoto- metric	$7.88 \times 10^{-6}$	$8.90 \times 10^{-6}$	1.13	1:1			
3	Small part of a crystal	Spectrophoto- metric	$7.61 \times 10^{-6}$	$8.40 \times 10^{-6}$	1.10	1:1			
4	Small part of a crystal	Spectrophoto- metric	$2.36 \times 10^{-6}$	$2.82 \times 10^{-6}$	1.18	1:1			

<sup>a</sup> Crystals were formed by direct crystallization.

<sup>b</sup> Crystals were formed by addition of ligroin to a saturated solution of silver perchlorate in the aromatic hydrocarbon.

A Sample No.	<i>B</i> Sample wt in mg	<i>C</i> Method of determination	D No. of moles of silver perchlorate	<i>E</i> No. of moles of mesitylene	Ratio of $E/D$	Ratio expressed in whole no	Molecular st as determin	ructure ructure and by
1	A small part of a crystal	Spectrophoto-	$7.0 \times 10^{-7}$	$8.2 \times 10^{-7}$	1.18	1:1	1:1ª	1:1
1	A small part of a crystal	Spectrophoto- metric	$3.26 \times 10^{-6}$	$3.12 \times 10^{-6}$	0.98	1:1		
2	A small part of a crystal	Spectrophoto- metric	$3.60 \times 10^{-6}$	$3.52 \times 10^{-6}$	0.98	1:1		
3	A small part of a crystal	Spectrophoto- metric	$5.85 \times 10^{-6}$	$5.31 \times 10^{-6}$	0,91	1:1		
3	10.86	Microanalysis of carbon	$3.56 \times 10^{-5}$	$2.86 \times 10^{-5}$	0.81	1:1		
3	10.86	Microanalysis of hydrogen	$3.73 \times 10^{-5}$	$3.11 \times 10^{-5}$	0.83	1:1		
4	A small part of a crystal	Spectrophoto- metric	$7.25 \times 10^{-6}$	$8.8 \times 10^{-6}$	1.13	1:1		
4	A small part of a crystal	Spectrophoto- metric	$9.65 \times 10^{-6}$	$9.24 \times 10^{-6}$	0.96	1:1		
4	6.719	Microanalysis of carbon	$2.46 \times 10^{-5}$	$1.35 \times 10^{-5}$	0.55	1:1		
4	6.719	Microanalysis of hydrogen	$2.19 \times 10^{-5}$	$1.82 \times 10^{-5}$	0.83	1:1		
5	A small part of a crystal	Spectrophoto- metric	$1.20 \times 10^{-6}$	$1.12 \times 10^{-6}$	0.93	1:1		
<sup>a</sup> Molecu	ular complex forme	d in solution.						

## Table V. Results of Analysis of Crystals of Mesitylene-Silver Perchlorate Complex

Since silver perchlorate dissolved in concentrated sulfuric acid absorbs only slightly in the UV range, it is possible to identify the aromatic substance when a crystal of the complex is dissolved in the acid. Table I shows that it is also possible to identify in this way the various aromatic components of a mixture.

Tables II–V show the results of the volumetric, spectrophotometric, and organic microanalysis of various crystal samples. It can be seen that the results of the three independent analytical methods are in satisfactory agreement. The Tables also include a comparison with the work of Peyronel (5), Torre-Mori (7), and Amma (19).

As can be seen from the Tables, our results show that *p*-xylene and mesitylene seem to form molecular complexes of one composition only, *i.e.*, 2 *p*-xylene:1 silver perchlorate and 1 mesitylene:1 silver perchlorate, while *o*-xylene and *m*-xylene form two kinds of molecular complexes, namely, 1

(19) E. L. Amma, private communication, and J. Amer. Chem. Soc., 91, 5745 (1969). *o*-xylene:1 silver perchlorate and 2 *o*-xylene:1 silver perchlorate and analogously for *m*-xylene.

The question arises why o- and m-xylene form two kinds of complexes while p-xylene and mesitylene form only one kind. Two differences between the two pairs of methylbenzenes may be part of the explanation:

First, it should be noted that *p*-xylene and mesitylene are not polar while *o*- and *m*-xylene are. This should increase the interaction between these last and the silver, and perhaps confer stability on complexes which cannot be stabilized in the case of the first pair because of lack of polarity.

The second point is connected with the fact that the silver is probably not in the axis of the ring but rather over one of the bonds or one of the carbons (3, 20). In *p*-xylene and mesitylene, all ring carbons are either attached to or adjacent to a methyl group. In the *o*- and *m*-xylene there are nonadjacent carbons, with reduced steric interactions, thus, again

(20) D. F. R. Gilson and C. A. McDowell, J. Chem. Phys., 39, 1825 (1963). giving these molecules more flexibility in complex formation. However, as mesitylene is more heavily substituted than p-xylene, this may contribute to its being able to accommodate only one silver perchlorate molecule as opposed to two for p-xylene.

The above observations are, of course, somewhat speculative, but it is interesting to observe that they can also explain other related phenomena such as the solubility of silver perchlorate in such aromatic solvents (21). Of course, the answer to the puzzle could be simply experimental, *i.e.*, that we have not hit upon the correct experimental conditions for obtaining the other complexes of *p*-xylene and mesitylene.

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# Computation of Equilibrium Constants for Multicomponent Systems from Spectrophotometric Data

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A general method is described for the evaluation of equilibrium constants and their errors for multicomponent systems from spectrophotometric data. Factor analysis is used to estimate the number of independently varying components and for data reduction. Molar absorptivities of individual components are also calculated and spectra interpolated from these values can be plotted. In addition to the absorbance data, only the stoichiometric coefficients and initial estimates of equilibrium constants are required as input data for this program. The formation constants for the bismuth-chloride system are determined by this method.

APPROXIMATE METHODS are widely used to evaluate equilibrium constants from absorbance data. Data recorded at only one or a few selected wavelengths are often employed to simplify the calculations. To treat very complex systems in which numerous equilibria prevail, it is feasible to use spectral data at many wavelengths. The most far-reaching procedure in this respect is perhaps the program described by Nagano and Metzler (1). Their program was specifically written for certain pyridoxal equilibria but could be easily extended to other equilibrium systems by writing appropriate subprograms. For this reason, the program is not sufficiently flexible to lend itself well to the solution of problems in which a rapid decision about the stoichiometric coefficients of the assumed equilibria must be made on the basis of the previous calculations.

This report describes a general method by which a digital computer calculates the equilibrium constants and their errors from absorbance data at several wavelengths and the assumed stoichiometric coefficients and plots the spectra of individual components. Matrix algebra is used for data reduction and least squares calculations.

#### MATRIX ANALYSIS OF SPECTROPHOTOMETRIC DATA

Matrix algebra is ideally applicable to the treatment of spectrophotometric data. Sternberg, Stillo, and Schwendeman (2) have used a least squares method in matrix form for the analysis of complex mixtures when the spectra of indi-

vidual components are known. Several authors (3-6) have shown that the rank of a matrix of absorbance measurements is related to the number of independently varying components in the system. Reeves (7) has used factor analysis to separate medium effects from concentration effects in dye solutions.

The generalized form of Lambert-Beer's law for unit path length can be represented by the matrix equation

$$A = EC \tag{1}$$

where A is the  $n_w \times n_s$  absorbance matrix, E is the  $n_w \times n_c$ matrix of molar absorptivities, and C is the  $n_c \times n_s$  concentration matrix. Here  $n_w$  denotes the number of wavelengths,  $n_s$  the number of solutions whose spectra have been recorded, and  $n_c$  the number of components which absorb in the chosen spectral range.

The rank of the matrix A is obtained from the equation

 $\operatorname{rank}(A) = \min \left\{ \operatorname{rank}(E), \operatorname{rank}(C) \right\} \leq \min \left\{ n_w, n_c, n_s \right\}$ 

If we now experimentally arrange that  $n_w > n_c$  and  $n_s > n_c$ , we obtain

$$\operatorname{rank}(A) \le n_c \tag{2}$$

The inequality applies only when either

 $\operatorname{rank}(E) < n_c \tag{3}$ 

or

$$\operatorname{rank}(C) < n_c \tag{4}$$

The first case is clearly possible only when one of the spectra of the individual components is linearly dependent on the other  $n_c - 1$  spectra. For example, in some dimerization reactions the spectrum of the dimer is often very well approximated by the spectrum in which the absorbances are multiplied by two.

The second case is possible if the concentration of one of the components is linear function of the concentrations of the other components

$$c_{ij} = \sum_{\nu \neq i} \lambda_{\nu} c_{\nu j}, \quad j = 1, \ldots, n_s$$

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