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THE DETERMINATION OF HETERO-ASSOCIATION CONSTANTS BY A NEW VAPOR DENSITY METHOD

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THE DETERMINATION OF HETERO-ASSOCIATION CONSTANTS BY A NEW VAPOR DENSITY METHOD

APPROVED BY

Sherril D. Christian

Harold E. Affsprung

Arthur Bernhart

J. C. Colbert

H H Rowley

DISSERTATION COMMITTEE

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

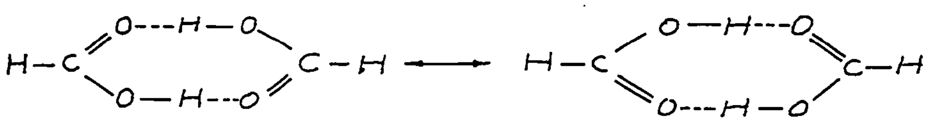
THE DETERMINATION OF HETERO-ASSOCIATION CONSTANTS BY A NEW VAPOR DENSITY METHOD

CHAPTER I

INTRODUCTION

In recent years, it has become well known that an atom of hydrogen may be attracted by two electronegative atoms instead of one. That is, in addition to a relatively strong primary bond, a hydrogen atom may be involved in a weaker, largely electrostatic hydrogen bond. The hydrogen bond plays a very conspicuous role in human life, for it is responsible in part for the adherence of dirt to our skin, the structure of proteins, the action of glues and adhesives, the rigidity of many synthetic polymers, such as polyamides, and many other biological phenomena.

The hydrogen bond was first mentioned by Moore and Winmil,[1] then by Pfeiffer.[2] The importance of the hydrogen bond and its extensive occurrence was recognized by Latimer and Rodebush,[3] who used this concept to discuss the highly associated liquids such as water and hydrogen fluoride, with their abnormally high dielectric constant, the small extent of ionization of ammonium hydroxide, and the formation of double molecules by acetic acid. They proposed that hydrogen should be regarded as divalent, and that there was resonance of a covalent character between two structures. In formic acid for example, the resonance forms could be written



After the development of the quantun-mechanical theory of valence, it was recognized that a hydrogen atom with only one stable orbital can not form more than one pure covalent bond, thus ruling out the divalent idea of Latimer and Rodebush. Also their assumption that resonance stabilizes the structure is ruled out by the fact that resonance does not provide significant stabilization energy unless the proton is midway between the two oxygens.[4] There is ample structural evidence that the hydrogen is not located half way between the two electronegative elements in most hydrogen bonds.[5,6,7,8,9]

At the present, it is generally supposed[10] that there are three distinct contributions to the total energy of the hydrogen bond and that all three are of the same order of magnitude. First, the electrostatic energy is due to the attraction between the 'bare' proton, with its extremely small atomic radius, and a covalently bonded electronegative atom. Following the ionic concept of the hydrogen bond, it might be expected that the strength of the bond should increase with increase in the electronegativity scale, we might expect that fluorine, oxygen, nitrogen, and chlorine would possess this ability to an extent decreasing in this order. It is found empirically that fluorine forms very strong hydrogen bond, oxygen weaker ones, and nitrogen still weaker ones. Although it has practically the same electronegativity as nitrogen,chlorine shows relatively little tendency to form hydrogen bonds, and this may be attributed to its large size (relative to nitrogen) which causes its electrostatic interaction to be weaker than that of nitrogen. The second contribution to hydrogen bond energy is the delocalization energy. There is ample evidence that the effect of hydrogen bonding on the intensity of IR absorption corresponding to the -O····H- or -N····H- stretch is many fold in excess of that explainable by the electrostatic model.[11,12,13,] The absence of correlation between hydrogen bond strength and dipole moment of the base[6,14] has led to the introduction of the concept of the delocalization energy. It assumed that in the formation of a hydrogen bond in the -O-H...O- case, for example, both the hydrogen electrons and the far oxygen electrons in -O-H...O- are at least partly delocalized. Third, there is repulsive energy of interaction between the two electronegative atoms. Both the electrostatic and delocalization force would tend to shorten the total length of the hydrogen bond. It is therefore evident that there must be some repulsive force which predominates when the atoms approach too closely together. It is probable that a fourth contribution i.e. the dispersion energy, should also be considered. This effect may be attributed to the high polarizability of unshared pairs of electrons, as for example those on both oxygens in water. Estimated energy contributions to a hydrogen bond in ice are listed below

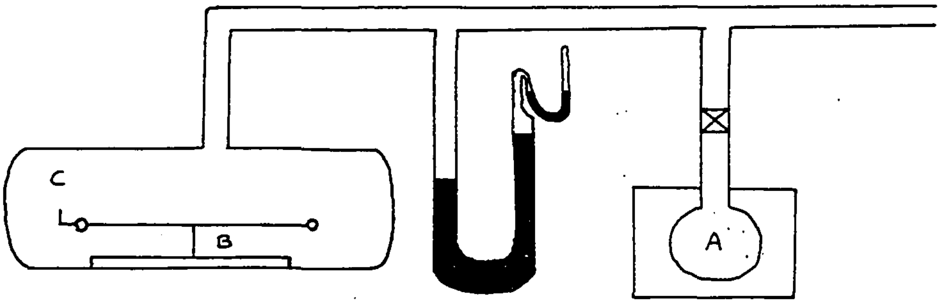
Type of energy	kcal/mole
Electrostatic	+6
Delocalization	+8
Repulsive	-8.4
Dispersion	+3
Total (theoretical)	+8.6
Experimental value	+6.1

Hydrogen bonding occurs in all three phases of matter, but it is less important at high temperatures and less common in the gas phase. Up to the present, relatively few studies have been made of the hydrogen bond in the vapor phase. Most of these studies of vapor phase hydrogen bonding have involved the determination of self-association constants of the lower organic acids (C_1 -C_7) and of the halogen substituted acids. Until now, the hetero-hydrogen bond in the vapor phase has been studied only by Christian and Hansen,[15] who investigated trifluoroacetic acid-acetic acid system and propionic acid-pentafluoropropionic acid system at 25°C. In view of the simplicity of vapor reactions, as opposed to reactions on condensed phases, it is desirable that further studies be made of hydrogen bonding in the vapor phase.

Vapor density measurement is one of several methods for studying hydrogen bonding in the vapor phase. The ideal gas law states that $PV = \frac{W}{M} RT$ .... (1) where P is the total pressure measured, V is the total volume of the system, W is the total amount of sample in the vapor phase, M is the molecular weight of the sample, T is the operating temperature of the system, R is the gas constant. The vapor density of an ideal gas is $\frac{W}{V} = \frac{PM}{RT}$, and if M, T, V are constant, P is proportional to W for a specific species at a definite temperature and volume. However, if polymerization occurs, M, the molecular weight, will gradually increase from the value of monomer to the maximum value of the polymer. The measured pressure is thus lower than that calculated by equation (1) where M is assumed to be the monomer value. Hence from vapor density and vapor pressure measurements, qualitative and quantitative information will be obtained for a compound undergoing hydrogen bond formation in the vapor phase.

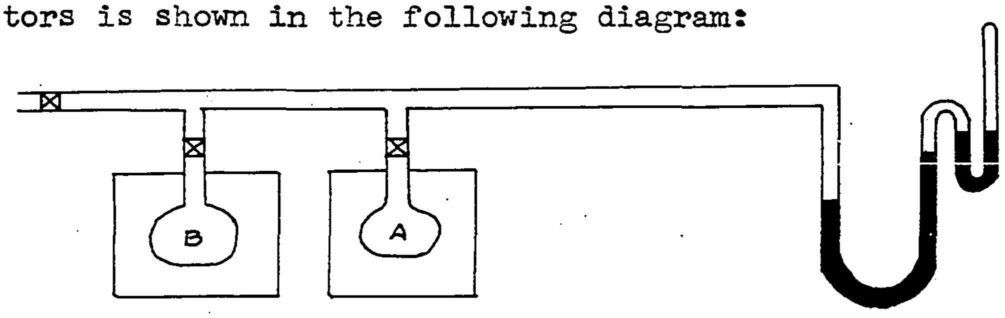
A. S. Coolidge[16] first studied the vapor density of formic acid. Following this, F. H. MacDoguall,[17] L. H. Simmon,[18] H. I. Ritter,[18] E. W. Johnson,[19] L. K. Nash,[19] M. D. Taylor,[20] J. Bruton,[21] R. E. Lundin,[22] F. E. Harris[22] and M. Templeman[23] reported on the self-association of several of the organic acids.

The type of apparatus which the preceding workers used in vapor density measurement are described briefly below. The apparatus used by Johnson and Nash is the silica vapor density balance.



A is the sample bulb, cooled in a dry ice bath, B is the silica balance, C is the pointer, and the whole system is calibrated with ideal vapors of known density.

The type of apparatus used by most of the other investigators is shown in the following diagram:



A is the sample bulb, cooled with a dry ice bath, B is the condensation bulb. The sample is vaporized from the bulb A to the system under the vacuum, the pressure is read, then vapor is condensed and collected in the bulb B and titrated with standard alkali.

Besides vapor density measurements, there are several other methods used in studying hydrogen bonds in the vapor phase. R. N. Badger[24], R. C. Herman[25], G. N. Barrow[26], R. E. Kagarise[27], have studied self-association with IR spectra. L. G. Bonner and L. S. K. Smith[28] with Raman spectra. R. N. Fuson, E. A. Jones and I. R. Lawson[29] have used both IR and

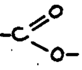
Raman spectra. I. E. Coop, N. R. Davidson and L. E. Sutton[30] have applied dielectric polarization measurements and J. Karl and L. Brockway[6] have used electron diffraction.

The dimerization constants and other thermodynamic data for some acids which have been studied are listed in Table 1.

Table 1[17]

Equilibrium Constants and Thermodynamic Functions for the Dimerization of Carboxylic Acids

ACID	$K^{160°C}$ $(atm)^{-1}$	$-\Delta H^{100°C}$ (kcal)	$-\Delta F^{100°C}$ (kcal)	$-\Delta S^{100°C}$ (e.u,)
Trifluoroacetic Acid	0.135	14,050	415	36.8
Formic Acid	0.182	14,110	686	36.0
Acetic Acid	0.557	15,270	1570	36.7
Propionic Acid	0.495	15,175	1594	36.4
Butyric Acid	0.625	13,900	-	-
Heptanoic Acid	0.607	13,400	-	-
Trimethylacetic Acid	0.910	14,030	-	-

From the results reported for different acids with the various methods, a general idea can be obtained of the homo-hydrogen bond strength in a series of acids with varying chain length and substituents. The chain length and branching of the group attached to the carboxylic group has no appreciable effect on the heat of dimerization. Both oxygen on  $-C{\genfrac{}{}{0pt}{}{\nearrow O}{\searrow O-}}$ group are subjected to the inductive effect of strongly electronegative substituents. Thus, the reduction of the negative charge on oxygen tend to reduce the strength of a hydrogen bond in which this oxygen acts as the electron donor. However, the reduction of the effective negative charge on the hydroxyl oxygen will also increase the polarity of the hydroxyl group and increase the effective positive charge of the hydrogen atom. Hence in the homo-associated dimer, the weakened basicity of the carbonyl oxygen appears to be largely compensated by an increase in the polarity of the hydroxyl group with which it interacts.

At present, relatively little is known about hetero-hydrogen bonding. It should be interesting and worthwhile to study the hetero-hydrogen bond in the vapor phase using systems in which few associated species are present. In studies of the vapor phase, more direct information about hydrogen bonding can be obtained, since there are no solvent effects involved as there are in all solution studies. The solvent effect has not been sucessfully accounted for and leads to great complications in treating experimental results.

In this research a new grease-free vapor density apparatus has been invented and applied to the study of hetero-hydrogen bonding in the vapor phase. Four binary systems, involving mixed vapors of water, dioxane, ethylenediamine, acetic acid and trifluoroacetic acid are reported. Both hetero- and homo-association constants have been reported for these systems.

CHAPTER II

OBJECTIVES

The primary objectives of this research were:

1. To develop an accurate and reasonably fast method for determination of the vapor density and vapor pressure of mixtures of volatile organic substances in the vapor phase. In dealing with organic liquids, two difficulties arise: first, these liquids are readily absorbed by stopcock grease; second, these liquids are very hygroscopic. It was desired to build an apparatus in which no grease is involved and to develop a technique for adding accurately known quantities of dry samples.

2. To determine the most probable formulas of the associated species which are present in the vapor phase of the following vapor mixtures:

(1) trifluoroacetic acid-acetic acid
(2) ethylenediamine-water
(3) trifluoroacetic acid-water
(4) trifluoroacetic acid-dioxane

and to determine the value of their corresponding equilibrium constants.

3. To attempt to infer probable structures of the complex species existing in the vapor phase for the above-mentioned systems.

CHAPTER III

MATERIALS

The trifluoroacetic acid and p-dioxane used in this research were obtained from the Matheson Coleman & Bell Company, Norwood, Ohio. Ethylenediamine was obtained from Eastman Organic Chemicals Company, Rochester, N. Y. and acetic acid from Baker and Adamson General Chemical Company, New York, N. Y. All the reagent were either analytical reagents or C. P. reagents. Water was obtained from the distilled water supply at the chemistry laboratory at the University of Oklahoma. All the compounds except water were further purified by double distillation through a 30 plate Oldershaw column at reflux ratios in excess of 10-1. The organic compounds were shaken well with anhydrous P_2O_5 before distillation. After purification, acetic acid and ethylenediamine were stored in an H-shaped tube containing anhydrous P_2O_5 in one side of the tube. Dioxane was stored in a beaker in a desiccator containing anhydrous P_2O_5. The boiling point ranges of the central fractions used in this work, corrected to 760 mm, were:

Substance	Boiling Point (°C)
trifluoroacetic acid	72.3 - 72.5
acetic acid	118.0 - 118.3
ethylenediamine	116.1 - 116.4
p-dioxane	101.4 - 101.6

All boiling points are within ± 0.3°C of the best avaliable literature values.

CHAPTER IV

EXPERIMENTAL INVESTIGATION

The new grease-free vapor density measurement apparatus has been described by Christian, Affsprung, and Lin.[31] In this work, a few modifications of the original apparatus have been made. The apparatus is shown in Figure 1.

A is a 3-liter round bottom flask. B is a fine or medium sintered-glass disc sealed with mercury above. C is a $ 25/15 ball-joint, the outer part of which is ring-sealed to the flask. This ball-joint is sealed with mercury in the tube D. The disc tube can easily be removed from the system for cleaning or replacement. E is a $ 7/25 ball-joint. Its outer part is ring-sealed to the inside of the 25 mm galss tube F and the inner part is sealed to a 6 mm glass rod G, whose end just fits inside a rubber tube P. This rubber tube is used to move the rod up and down through the tube G for opening and closing the ball-joint E. O is a teflon-plug stopcock. H is a mercury leveling bulb used to seal the ball-joint E. I is a manometer. J is the temperature control and stirring system, K is the thermometer and L is the constant-temperature water bath. The whole system can be evacuated through M, by draining all the mercury into the leveling bulb and raising the rod G to open the ball-joint E. After evacuation, the rod G is lowered to close the ball-joint E and the joint is sealed with mercury.

The known pressure of a given vapor is first introduced into system through the sintered-glass disc B, using a Roger Gilmont 2 ml micrometer buret. Then, samples of a second vapor are added into the system step by step by introducing known volumes of the liquid with the same buret. After each addition, the tip of the buret is immersed in the mercury just above the disc in tube D using a clamp on the frame. It should be noted that it is difficult to accurately add a low molecular weight vapor, such as water, to the apparatus, since a small increment of a low molecular weight liquid will produce a large change in the pressure of the vapor. Consequently, in systems which involve water, it is desirable to add a sample of water first, to measure the pressure and then to add accurately known volumes of the second compound.

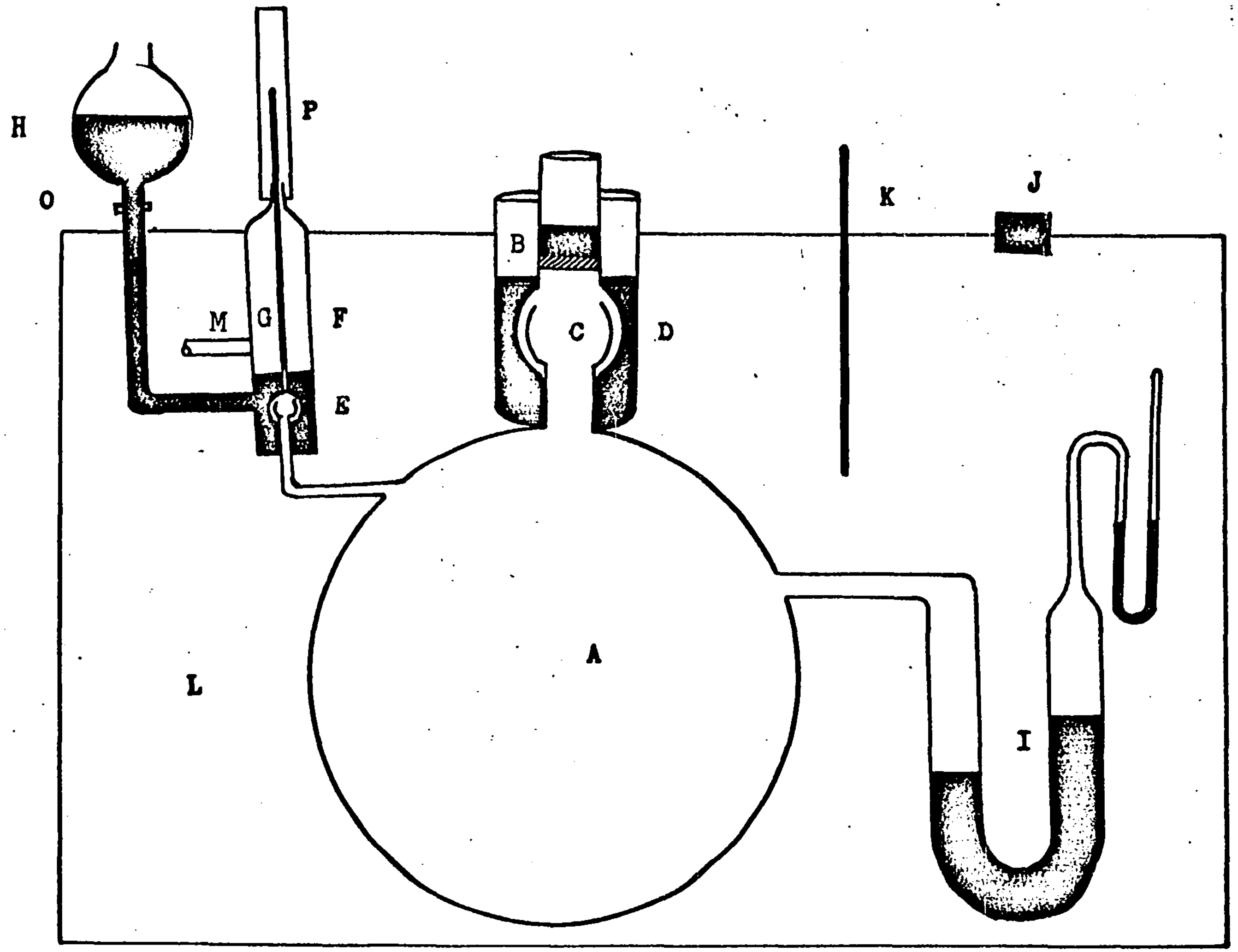


Fig. 1.-----Vapor Density Apparatus

CHAPTER V

EXPERIMENTAL RESULT

The following four systems were studied:

1. trifluoroacetic acid-acetic acid
2. ethylenediamine-water
3. trifluoroacetic acid-water
4. trifluoroacetic acid-dioxane

The systems 1, 2, and 4 were studied at 20°C, but system 3 was studied at 40°C, since at 20°C the saturated vapor pressure of the system was too low to permit accurate measurements.

The experimental and calculated total vapor pressure data for trifluoroacetic acid-acetic acid system, ethylenediamine-water system, trifluoroacetic acid-water system and trifluoroacetic acid-dioxane system are given in Tables 2 through 30. Figures 3 through 6 are the total vapor pressure plots. The solid lines are calculated by methods described in Chapter VI and all the points are experimental.

The symbol π used in plots, tables and equations is defined by the equation

$$\pi = \frac{\rho vRT}{M V} = C_f RT$$

where v is the volume of liquid added to the vapor density apparatus, ρ is the density of liquid added, M is the formula weight of liquid added, T is the operating temperature, V is the total volume of the vapor density system and C_f is the formal concentration of a given compound in vapor density apparatus. π is given the name "formal pressure" by analogy to the term "formal concentration" commonly used in solution studies. Both π and the total pressure P_T, are expressed in mm of Hg units. The abbreviation EDA is used for ethylenediamine, TFA for trifluoroacetic acid, HAc for acetic acid, and E for the standard deviation of experimental pressures from computed pressures.

The only experimental points which were used for the calculation of association constants were those for which the pressure was less than that at the starred point in each Table. These were known to be unsaturated, whereas the following points were in regions in which condensation may have occurred. In the trifluoroacetic acid-acetic acid system, the runs in Table 3 and 9 are excluded from the calculation of association constants, because of the large discrepancy between these values and other results. If the two runs are included in calculating association constants, the resulting standard deviation is 0.164 mm, whereas it is only 0.099 mm if the two runs are excluded.

Table 2

Total Vapor Pressure of Trifluoroacetic Acid-Acetic Acid System at 20°C with Initial Acetic Acid Pressure of 1.11 mm

v_{TFA} (ml)	π_{HAc} (mm)	π_{TFA} (mm)	P_T^{exp} (mm)	P_T^{cal} (mm)
0.05	1.75	3.94	3.40	3.47
0.10	1.75	7,87	5.86	5.90
0.15	1.75	11.80	8.20	8.21
0.20	1.75	15.74	10.56	10.47
0.25	1.75	19.67	12.81	12.69
* 0.30	1.75	23.61	15.11	-
0.40	1.75	31.48	19.51	-
0.45	1.75	35.40	21.83	-

Table 3

Total Vapor Pressure of Trifluoroacetic Acid-Acetic Acid System at 20°C with Initial Acetic Acid Pressure of 2.61 mm

	v_{TFA} (ml)	π_{HAc} (mm)	π_{TFA} (mm)	P_T^{exp} (mm)	P_T^{cal} (mm)
*	0.05	4.46	3.94	4.78	-
	0.10	4.46	7.87	7.49	-
	0.15	4.46	11.80	9.96	-
	0.20	4.46	15.74	12.35	-
	0.25	4.46	19.67	14.59	-
	0.30	4.46	23.61	16.81	-
	0.35	4.46	27.54	19.10	-
	0.40	4.46	31.48	21.26	-

Table 4

Total Vapor Pressure of Trifluoroacetic Acid-Acetic Acid System at 20°C with Initial Acetic Acid Pressure of 3.22 mm

v_{TFA} (ml)	π_{HAc} (mm)	π_{TFA} (mm)	P_T^{exp} (mm)	P_T^{cal} (mm)
0.05	5.56	3.94	5.58	5.25
0.10	5.56	7.87	7.62	7.53
0.15	5.56	11.80	9.98	9.88
0.20	5.56	15.74	12.36	12.16
0.25	5.56	19.67	14.58	14.40
* 0.30	5.56	23.61	16.87	-
0.35	5.56	27.54	19.00	-
0.40	5.56	31.48	21.24	-
0.45	5.56	35.40	23.52	-

Table 5

Total Vapor Pressure of Trifluoroacetic Acid-Acetic Acid System at 20°C with Initial Acetic Acid Pressure of 3.79 mm

v_{TFA} (ml)	π_{HAc} (mm)	π_{TFA} (mm)	P_T^{exp} (mm)	P_T^{cal} (mm)
0.05	6.61	3.94	5.73	5.79
0.10	6.61	7.87	8.00	8.00
0.15	6.61	11.80	10.32	10.33
0.20	6.61	15.74	12.63	12.62
0.25	6.61	19.67	14.86	14.87
* 0.30	6.61	23.61	17.09	-
0.35	6.61	27.54	19.29	-
0.40	6.61	31.48	21.62	-

Table 6

Total Vapor Pressure of Trifluoroacetic Acid-Acetic Acid System at 20°C with Initial Acetic Acid Pressure of 4.20 mm

v_{TFA} (ml)	π_{HAc} (mm)	π_{TFA} (mm)	P_T^{exp} (mm)	P_T^{cal} (mm)
0.05	7.36	3.94	6.19	6.19
0.10	7.36	7.87	8.35	8.35
0.15	7.36	11.80	10.66	10.66
0.20	7.36	15.74	13.04	12.96
0.25	7.36	19.67	15.36	15.21
* 0.30	7.36	23.61	17.64	-
0.35	7.36	27.54	19.89	-
0.40	7.36	31.48	22.26	-

Table 7

Total Vapor Pressure of Trifluoroacetic Acid-Acetic Acid System at 20°C with Initial Acetic Acid Pressure of 6.48 mm

v_{TFA} (ml)	π_{HAc} (mm)	π_{TFA} (mm)	P_T^{exp} (mm)	P_T^{cal} (mm)
0.05	11.65	3.94	8.30	8.45
0.10	11.65	7.87	10.29	10.49
0.15	11.65	11.80	12.48	12.63
0.20	11.65	15.74	14.90	14.88
0.25	11.65	19.67	17.25	17.13
* 0.30	11.65	23.61	19.53	-
0.35	11.65	27.54	21.79	-
0.40	11.65	31.48	24.05	-

Table 8

Total Vapor Pressure of Trifluoroacetic Acid-Acetic Acid System at 20°C with Initial Acetic Acid Pressure of 6.49 mm

v_{TFA} (ml)	π_{HAc} (mm)	π_{TFA} (mm)	P_T^{exp} (mm)	P_T^{cal} (mm)
0.05	11.65	3.94	8.34	8.45
0.10	11.65	7.87	10.34	10.49
0.15	11.65	11.80	12.59	12.63
0.20	11.65	15.74	14.78	14.88
0.25	11.65	19.67	17.16	17.13
* 0.30	11.65	23.61	19.38	-
0.35	11.65	27.54	21.58	-
0.40	11.65	31.48	23.66	-

Table 9

Total Vapor Pressure of Trifluoroacetic Acid-Acetic Acid System at 20°C with Initial Acetic Acid Pressure of 5.16 mm

	v_{TFA} (ml)	π_{HAc} (mm)	π_{TFA} (mm)	P_T^{exp} (mm)	P_T^{cal} (mm)
*	0.05	9.15	3.94	7.49	-
	0.10	9.15	7.87	9.65	-
	0.15	9.15	11.80	12.38	-
	0.20	9.15	15.79	14.38	-
	0.25	9.15	19.67	16.78	-
	0.30	9.15	23.61	19.00	-
	0.40	9.15	31.48	21.16	-

Table 10

Total Vapor Pressure of Ethylenediamine-Water System at 20°C with Initial Water Pressure of 1.64 mm

	v_{EDA} (ml)	π_{H_2O} (mm)	π_{EDA} (mm)	P_T^{exp} (mm)	P_T^{cal} (mm)
	0.01	1.64	0.89	2.17	2.18
	0.02	1.64	1.79	2.72	2.64
	0.03	1.64	2.68	3.23	3.17
	0.04	1.64	3.57	3.72	3.77
	0.05	1.64	4.46	4.25	4.39
*	0.06	1.64	5.36	4.72	-
	0.07	1.64	6,24	5.18	-
	0.08	1.64	7.13	5.70	-

Table 11

Total Vapor Pressure of Ethylenediamine-Water System at 20°C with Initial Water Pressure of 0.56 mm

v_{EDA} (ml)	π_{H_2O} (mm)	π_{EDA} (mm)	P_T^{exp} (mm)	P_T^{cal} (mm)
0.01	0.56	0.89	1.28	1.34
0.02	0.56	1.79	2.01	2.08
0.03	0.56	2.68	2.80	2.81
0.04	0.56	3.57	3.57	3.54
0.05	0.56	4.46	4.30	4.26
0.06	0.56	5.36	5.06	4.99
0.07	0.56	6.24	5.63	5.69
* 0.08	0.56	7.13	6.21	-
0.09	0.56	8.03	6.74	-
0.10	0.56	8.92	7.22	-
0.11	0.56	9.82	7.51	-

Table 12

Total Vapor Pressure of Ethylenediamine-Water System at 20°C with Initial Water Pressure of 0.84 mm

v_{EDA} (ml)	π_{H_2O} (mm)	π_{EDA} (mm)	P_T^{exp} (mm)	P_T^{cal} (mm)
0.01	0.84	0.89	1.42	1.56
0.02	0.84	1.79	2.18	2.23
0.03	0.84	2.68	2.97	2.91
0.04	0.84	3.57	3.77	3.61
0.05	0.84	4.46	4.44	4.31
0.06	0.84	5.36	5.08	5.03
0.07	0.84	6.24	5.68	5.71
* 0.08	0.84	7.13	6.28	-
0.09	0.84	8.03	6.76	-
0.10	0.84	8.92	7.29	-

Table 13

Total Vapor Pressure of Ethylenediamine-Water System at 20°C with Initial Water Pressure of 1.55 mm

v_{EDA} (ml)	π_{H_2O} (mm)	π_{EDA} (mm)	P_T^{exp} (mm)	P_T^{cal} (mm)
0.02	1.55	1.79	2.59	2.60
0.03	1.55	2.68	3.28	3.14
0.05	1.55	4.46	4.36	4.39
* 0.07	1.55	6.24	5.37	-
0.09	1.55	8.03	6.06	-
0.11	1.55	9.82	6.78	-

Table 14

Total Vapor Pressure of Ethylenediamine-Water System at 20°C with Initial Water Pressure of 2.07 mm

	v_{EDA} (ml)	π_{H_2O} (mm)	π_{EDA} (mm)	P_T^{exp} (mm)	P_T^{cal} (mm)
	0.01	2.07	0.89	2.37	2.52
	0.02	2.07	1.79	2.85	2.89
	0.03	2.07	2.68	3.39	3.33
	0.04	2.07	3.57	3.87	3.86
	0.05	2.07	4.46	4.31	4.45
*	0.06	2.07	5.36	4.77	-
	0.07	2.07	6.24	5.09	-
	0.08	2.07	7.13	5.40	-
	0.09	2.07	8.03	5.81	-
	0.10	2.07	8.92	6.21	-
	0.11	2.07	9.82	6.43	-
	0.12	2.07	10.70	6.58	-

Table 15

Total Vapor Pressure of Trifluoroacetic Acid-Water at 20°C with Initial Water Pressure of 0.97 mm

v_{TFA} (ml)	π_{H_2O} (mm)	π_{TFA} (mm)	P_T^{exp} (mm)	P_T^{cal} (mm)
0.05	0.97	3.94	3.86	3.74
0.15	0.97	11.80	8.64	8.40
0.20	0.97	15.74	11.01	10.64
* 0.30	0.97	23.61	15.53	-
0.40	0.97	31.48	20.07	-
0.50	0.97	39.35	24.42	-

Table 16

Total Vapor Pressure of Trifluoroacetic Acid-Water System at 20°C with Initial Water Pressure of 1.93mm

	v_{TFA} (ml)	π_{H_2O} (mm)	π_{TFA} (mm)	P_T^{exp} (mm)	P_T^{cal} (mm)
	0.05	1.93	3.94	4.58	4.61
	0.10	1.93	7.87	6.85	6.97
	0.15	1.93	11.80	9.05	9.23
	0.20	1.93	15.74	11.10	11.46
*	0.25	1.93	19.67	13.21	-
	0.30	1.93	23.61	15.34	-
	0.40	1.93	31.48	19.37	-
	0.50	1.93	39.35	23.42	-

Table 17

Total Vapor Pressure of Trifluoroacetic Acid-Water System at 20°C with Initial Water Pressure of 2.65 mm

v_{TFA} (ml)	π_{H_2O} (mm)	π_{TFA} (mm)	P_T^{exp} (mm)	P_T^{cal} (mm)
0.05	2.65	3.94	5.21	5.26
0.10	2.65	7.87	7.60	7.59
0.15	2.65	11.80	9.88	9.84
* 0.20	2.65	15.74	12.30	-
0.25	2.65	19.67	14.37	-
0.30	2.65	23.61	16.78	-
0.40	2.65	31.48	21.04	-
0.50	2.65	39.35	24.15	-

Table 18

Total Vapor Pressure of Trifluoroacetic Acid-Water System at 20°C with Initial Water Pressure of 2.89 mm

	v_{TFA} (ml)	π_{H_2O} (mm)	π_{TFA} (mm)	P_T^{exp} (mm)	P_T^{cal} (mm)
	0.05	2.89	3.94	5.60	5.48
	0.10	2.89	7.87	7.92	7.79
	0.15	2.89	11.80	10.01	10.03
*	0.20	2.89	15.74	12.29	-
	0.25	2.89	19.67	14.28	-
	0.30	2.89	23.61	16.53	-
	0.40	2.89	31.48	20.74	-
	0.50	2.89	39.35	24.90	-

Table 19

Total Vapor Pressure of Trifluoroacetic Acid-Water System at 20°C with Initial Water Pressure of 3.43 mm

	v_{TFA} (ml)	π_{H_2O} (mm)	π_{TFA} (mm)	P_T^{exp} (mm)	P_T^{cal} (mm)
	0.05	3.43	3.94	6.04	5.95
	0.10	3.43	7.87	8.36	8.24
	0.15	3.43	11.80	10.50	10.47
*	0.20	3.43	15.74	12.60	-
	0.25	3.43	19.67	14.85	-
	0.30	3.43	23.61	16.98	-
	0.40	3.43	31.48	21.13	-
	0.50	3.43	39.35	25.05	-

Table 20

Total Vapor Pressure of Trifluoroacetic Acid-Water System at 20°C with Initial Water Pressure of 3.86 mm

v_{TFA} (ml)	π_{H_2O} (mm)	π_{TFA} (mm)	P_T^{exp} (mm)	P_T^{cal} (mm)
0.05	3.86	3.94	6.30	6.32
0.10	3.86	7.87	8.47	8.59
0.15	3.86	11.80	10.65	10.81
* 0.20	3.86	15.74	12.77	-
0.25	3.86	19.67	14.66	-
0.30	3.86	23.61	16.69	-
0.40	3.86	31.48	20.54	-
0.50	3.86	39.35	24.36	-

Table 21

Total Vapor Pressure of Trifluoroacetic Acid-Water System at 20°C with Initial Water Pressure of 5.29 mm

v_{TFA} (ml)	π_{H_2O} (mm)	π_{TFA} (mm)	P_T^{exp} (mm)	P_T^{cal} (mm)
0.05	5.29	3.94	7.70	7.53
0.10	5.29	7.87	9.75	9.73
* 0.15	5.29	11.80	11.58	-
0.20	5.29	15.74	13.53	-
0.25	5.29	19.67	15.20	-
0.30	5.29	23,61	16.91	-
0.40	5.29	31.48	20.24	-
0.50	5.29	39.35	23.70	-

Table 22

Total Vapor Pressure of Trifluoroacetic Acid-Water System at 20°C with Initial Water Pressure of 6.26 mm

V_{TFA} (ml)	π_{H_2O} (mm)	π_{TFA} (mm)	P_T^{exp} (mm)	P_T^{cal} (mm)
* 0.05	6.26	3.94	8.39	8.39
0.10	6.26	7.87	10.23	10.46
* 0.15	6.26	11.80	11.79	-
0.20	6.26	15.74	13.37	-
0.25	6.26	19.67	15.00	-
0.30	6.26	23.61	16.53	-
0.40	6.26	31.48	19.81	-
0.50	6.26	39.35	23.11	-

Table 23

Total Vapor Pressure of Trifluoroacetic Acid-Dioxane System at 40°C with Initial Trifluoroacetic Acid Pressure of 2.17 mm

$V_{dioxane}$ (ml)	π_{TFA} (mm)	$\pi_{dioxane}$ (mm)	P_T^{exp} (mm)	P_T^{cal} (mm)
0.02	2.50	1.51	3.53	3.48
0.04	2.50	3.02	4.83	4.82
0.05	2.50	3.78	5.56	5.51
0.07	2.50	5.29	6.89	6.89
★ 0.09	2.50	6.80	8.28	-
0.12	2.50	9.07	10.42	-

Table 24

Total Vapor Pressure of Trifluoroacetic Acid-Dioxane System at 40°C with Initial Trifluoroacetic Acid Pressure of 2.45 mm

$V_{dioxane}$ (ml)	π_{TFA} (mm)	$\pi_{dioxane}$ (mm)	P_T^{exp} (mm)	P_T^{cal} (mm)
0.02	2.88	1.51	3.73	3.75
0.04	2.88	3.02	5.08	5.08
0.06	2.88	4.53	6.41	6.44
0.07	2.88	5.29	7.16	7.12
0.08	2.88	6.04	7.84	7.81
* 0.10	2.88	7.55	9.34	-
0.12	2.88	9.07	10.69	-

Table 25

Total Vapor Pressure of Trifluoroacetic Acid-Dioxane System at 40 °C with Initial Trifluoroacetic Acid Pressure of 3.70 mm

$v_{dioxane}$ (ml)	π_{TFA} (mm)	$\pi_{dioxane}$ (mm)	P_T^{exp} (mm)	P_T^{cal} (mm)
0.02	4.56	1.51	4.95	4.93
0.04	4.56	3.02	6.14	6.19
0.06	4.56	4.53	7.43	7.48
* 0.08	4.56	6.04	8.74	-
0.10	4.56	7.55	9.90	-

Table 26

Total Vapor Pressure of Trifluoroacetic Acid-Dioxane System at 40°C with Initial Trifluoroacetic Acid Pressure of 3.87 mm

$v_{dioxane}$ (ml)	π_{TFA} (mm)	$\pi_{dioxane}$ (mm)	P_T^{exp} (mm)	P_T^{cal} (mm)
0.02	4.80	1.51	5.04	5.09
0.03	4.80	2.27	5.71	5.72
0.04	4.80	3.02	6.36	6.35
* 0.06	4.80	4.53	7.51	-
0.08	4.80	6.04	8.62	-

Table 27

Total Vapor Pressure of Trifluoroacetic Acid-Dioxane System at 40°C with Initial Trifluoroacetic Acid Pressure of 3.14 mm

$v_{dioxane}$ (ml)	π_{TFA} (mm)	$\pi_{dioxane}$ (mm)	P_T^{exp} (mm)	P_T^{cal} (mm)
0.01	3.80	0.76	3.70	3.77
0.03	3.80	2.27	4.90	5.05
0.04	3.80	3.02	5.67	5.69
0.06	3.80	4.53	7.01	7.01
0,08	3.80	6.04	8.32	8.35

Table 28

Total Vapor Pressure of Trifluoroacetic Acid-Dioxane System at 40°C with Initial Trifluoroacetic Acid Pressure of 2.73 mm

$v_{dioxane}$ (ml)	π_{TFA} (mm)	$\pi_{dioxane}$ (mm)	P_T^{exp} (mm)	P_T^{cal} (mm)
0.01	3.24	0.76	3.33	3.36
0.02	3.24	1.51	4.04	4.05
0.04	3.24	3.02	5.30	5.32
0.06	3.24	4.53	6.65	6.66
0.08	3.24	6.04	8.05	8.02
* 0.09	3.24	6.80	8.69	-

Table 29

Total Vapor Pressure of Trifluoroacetic Acid-Dioxane System at 40°C with Initial Trifluoroacetic Acid Pressure of 3.68 mm

$V_{dioxane}$ (ml)	π_{TFA} (mm)	$\pi_{dioxane}$ (mm)	P_T^{exp} (mm)	P_T^{cal} (mm)
0.01	4.55	0.76	4.31	4.31
0.03	4.55	2.27	5.60	5.55
0.04	4.55	3.02	6.17	6.19
0.05	4.55	3.78	6.85	6.83
0.06	4.55	4.53	7.52	7.48
* 0.07	4.55	5.28	8.17	-
0.08	4.55	6.80	9.40	-

Table 30

Total Vapor Pressure of Trifluoroacetic Acid-Dioxane System at 40°C with Initial Trifluoroacetic Acid Pressure of 4.82 mm

v_{dioxane} (ml)	π_{TFA} (mm)	π_{dioxane} (mm)	P_T^{exp} (mm)	P_T^{cal} (mm)
0.01	6.14	0.76	5.47	5.41
0.02	6.14	1.51	6.09	6.00
0.03	6.14	2.27	6.73	6.60
* 0.05	6.14	3.78	7.96	-
0.06	6.14	4.53	8.20	-
0.07	6.14	5.29	8.49	-
0.08	6.14	6.04	8.69	-

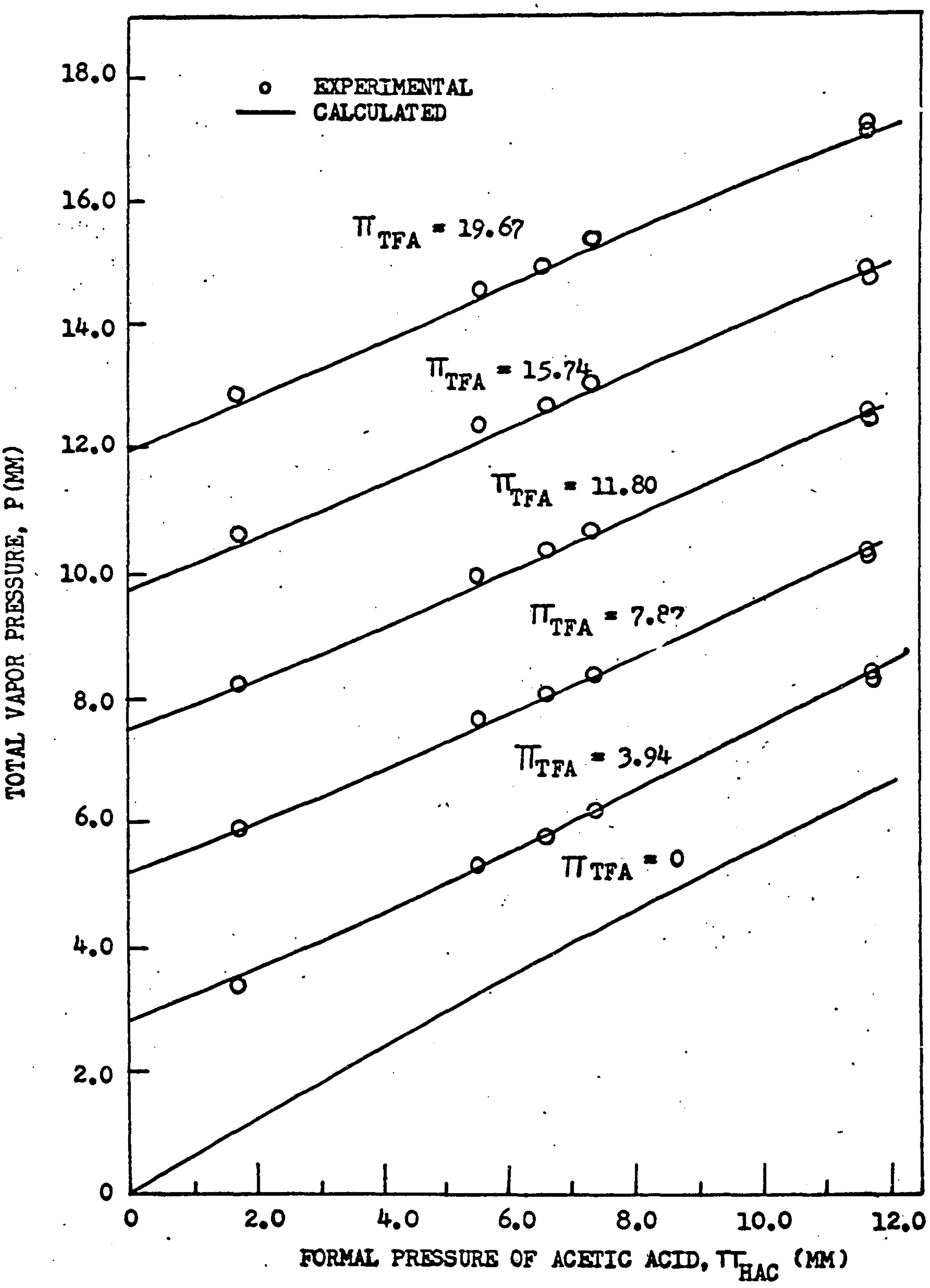


Fig. 2.— Total Vapor Pressure of Trifluoroacetic Acid-Acetic Acid System at 20°C

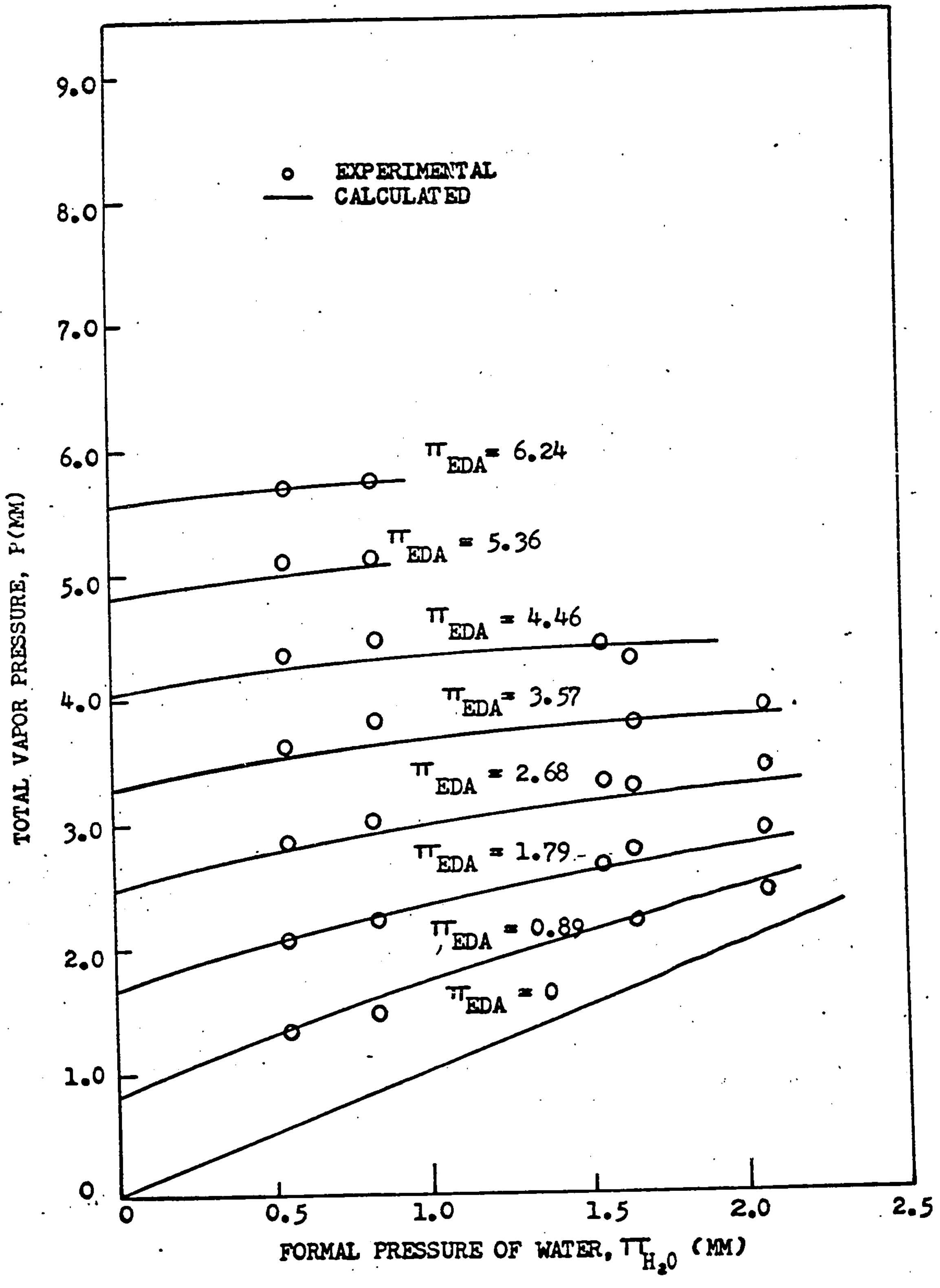


Fig. 3.— Total Vapor Pressure of Ethylenediamine-Water System at 20°C

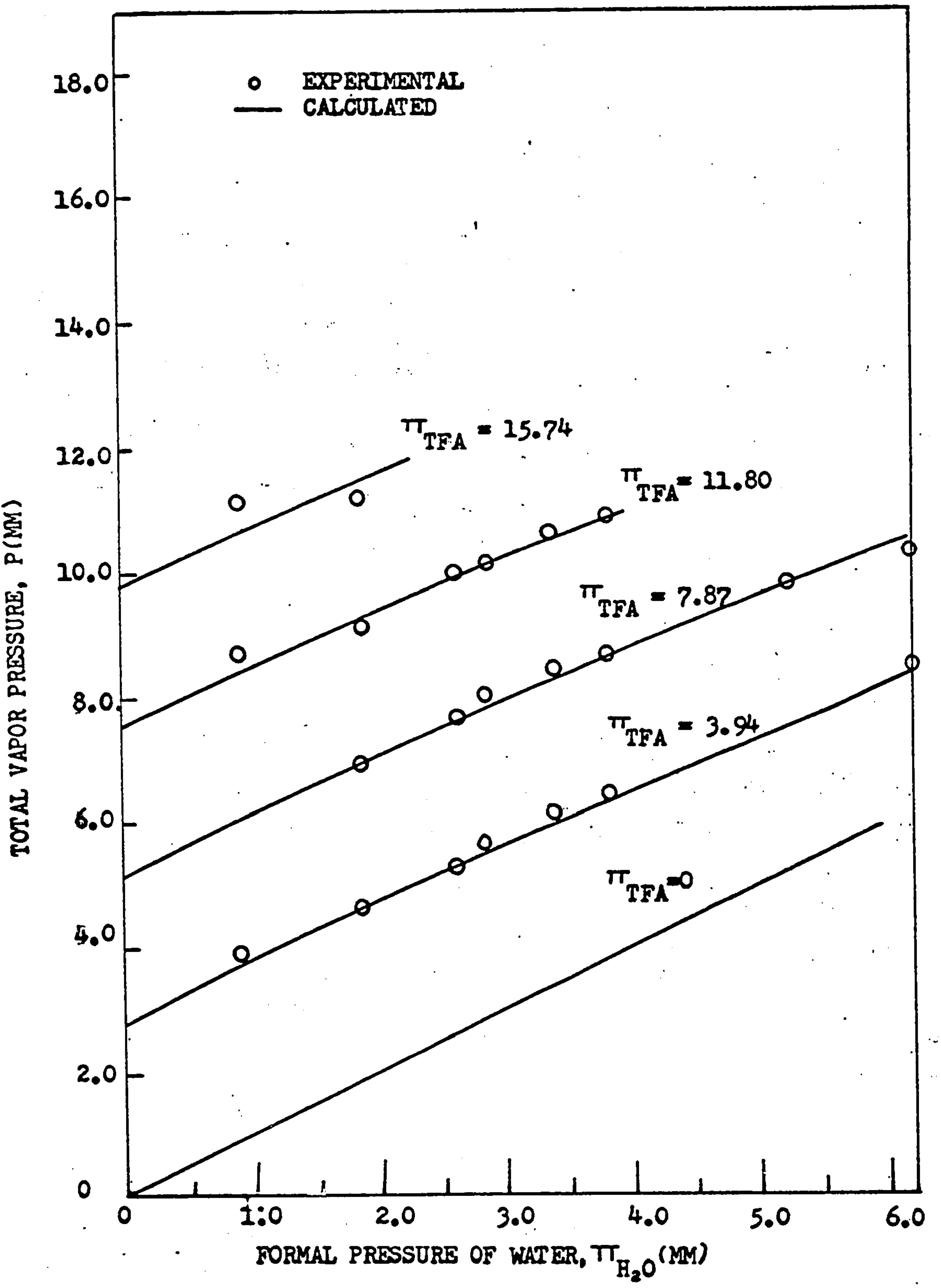


Fig. 4. --- Total Vapor Pressure of Trifluoroacetic Acid-Water System at 20°C

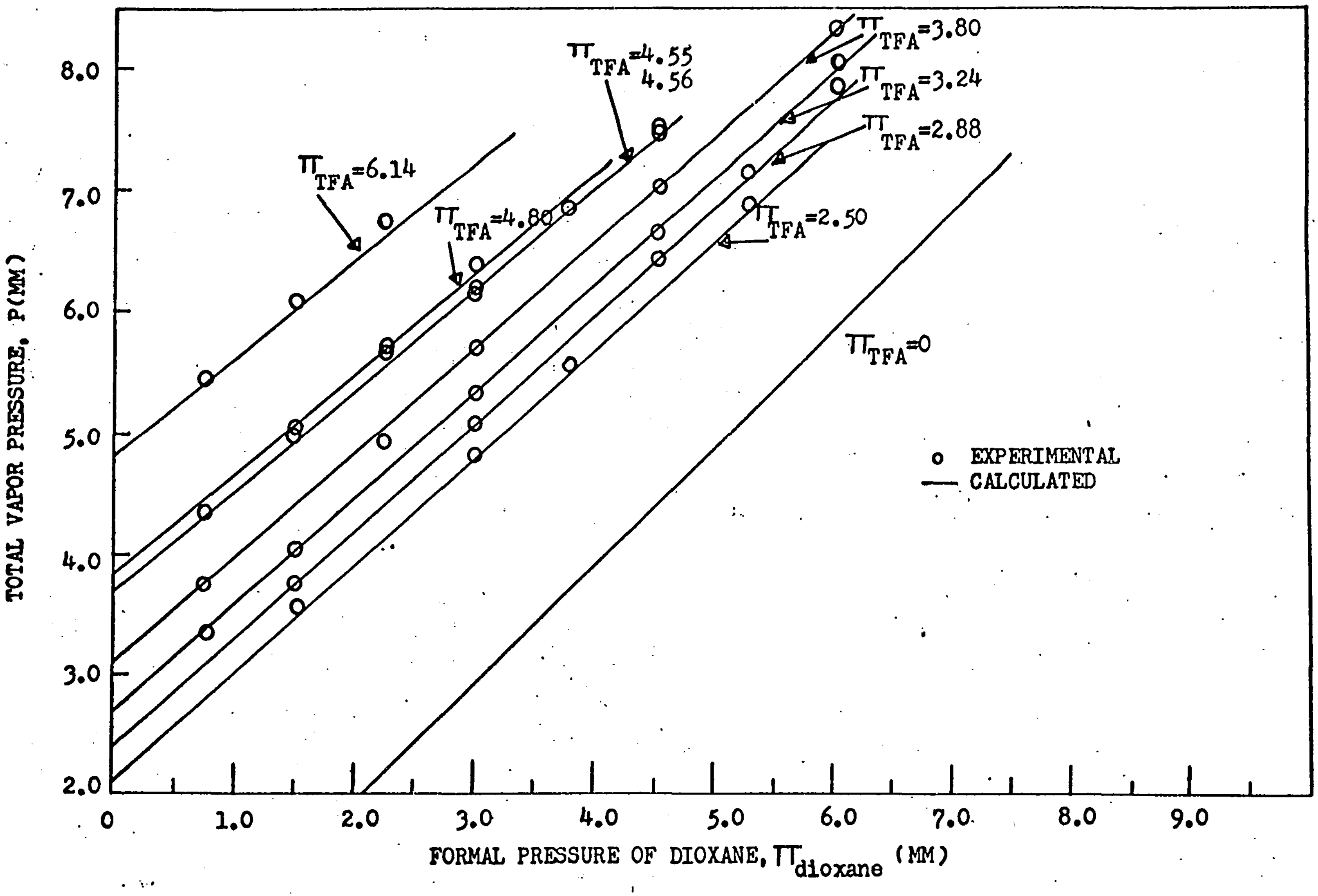


Fig. 5.---- Total Vapor Pressure of Trifluoroacetic Acid-Dioxane System at 40°C

CHAPTER VI

METHOD OF CALCULATION

In this research the IBM 1410 computer was used in calculating theoretical values of the total vapor pressure of the mixture in the vapor phase, based on experimental values of π_1 and π_2 and an assumed set of assoication constants. The dimerization constants of pure acetic acid at 20°C were obtained by the method described in Appendix C. Dimerization constants of trifluoroacetic acid and ethylenediamine at 20°C were obtained using experimental methods described in this research. The dimerization constant of trifluoroacetic acid at 40°C was calculated by interpolating values of the dimerization constant at various temperatures obtained by Dr. Affsprung[32] and in this research.

In each system, the value of each equilibrium constant reported is that which leads to the smallest standard deviation; i.e. the constant is obtained by plotting the standard deviation versus assumed values of the equilibrium constant. In the cases where 2 constants are varied, contour lines for the standard deviation are plotted as functions of the K values.

The detailed IBM 1410 computer program, which was developed by Dr. S. D. Christian, is attached in Appendix B.

Figures 6 through 13 illustrate the variation of standard deviation with the equilibrium constant plots.

A summary of the results for the four systems is given in Table 31.

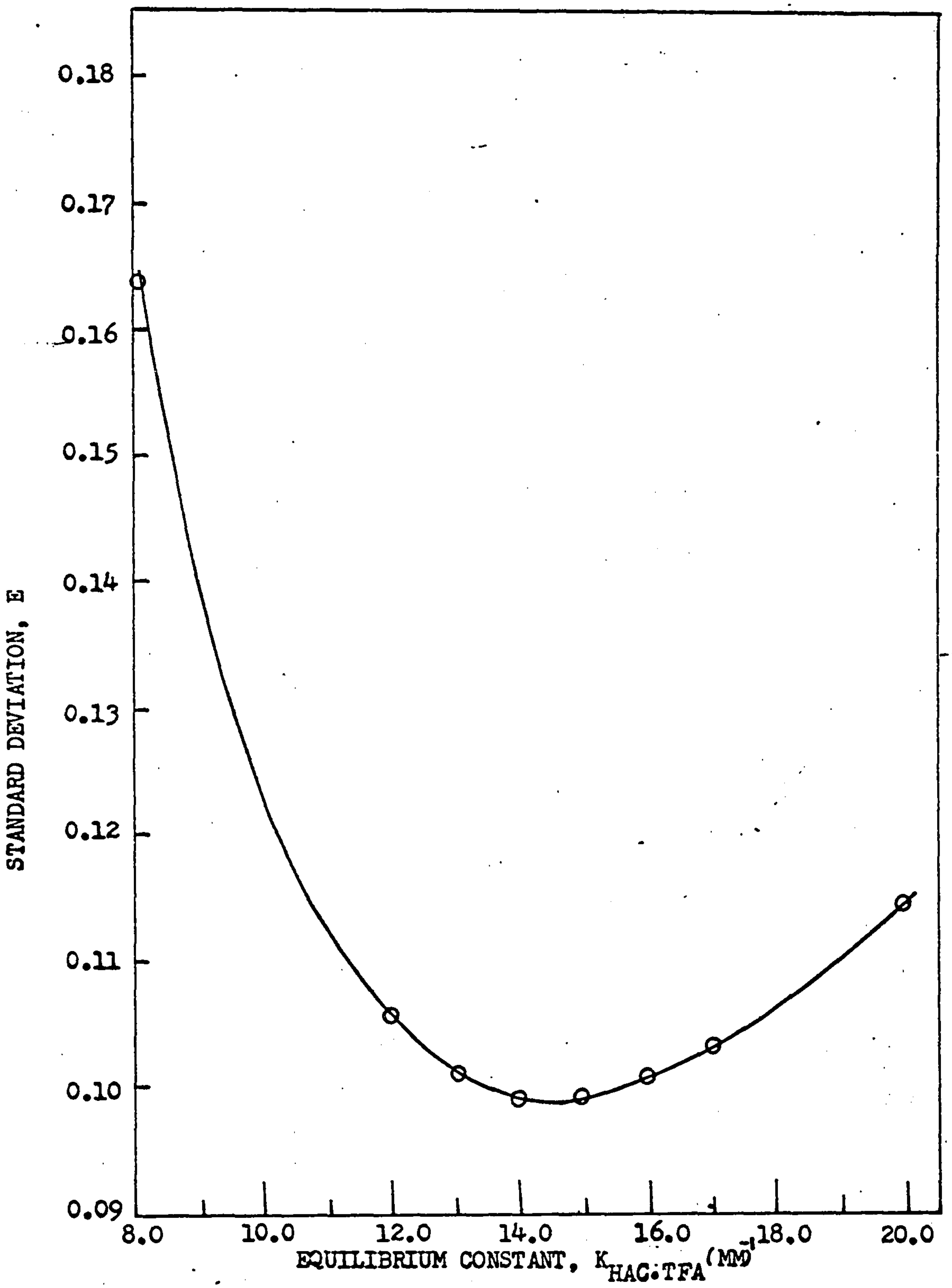


Fig 6.--- Variation of Standard Deviation with Value of Equilibrium Constant of one-one Complex in Trifluoroacetic Acid-Acetic Acid System at 20°C

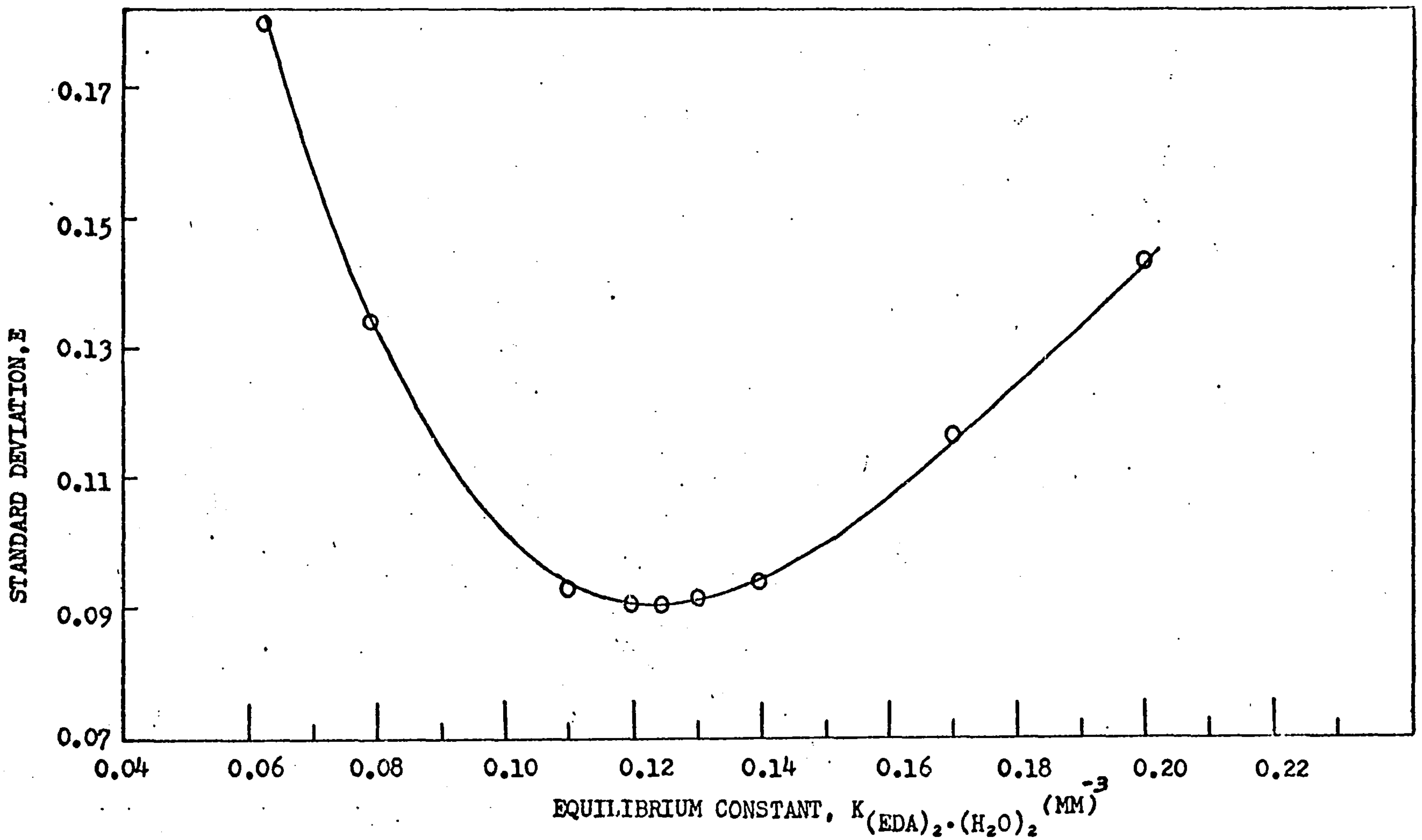


Fig. 7. ---- Variation of the Standard Deviation with Value of Equilibrium Constant of Two-Two Complex in Ethylenediamine-Water System at 20.°C

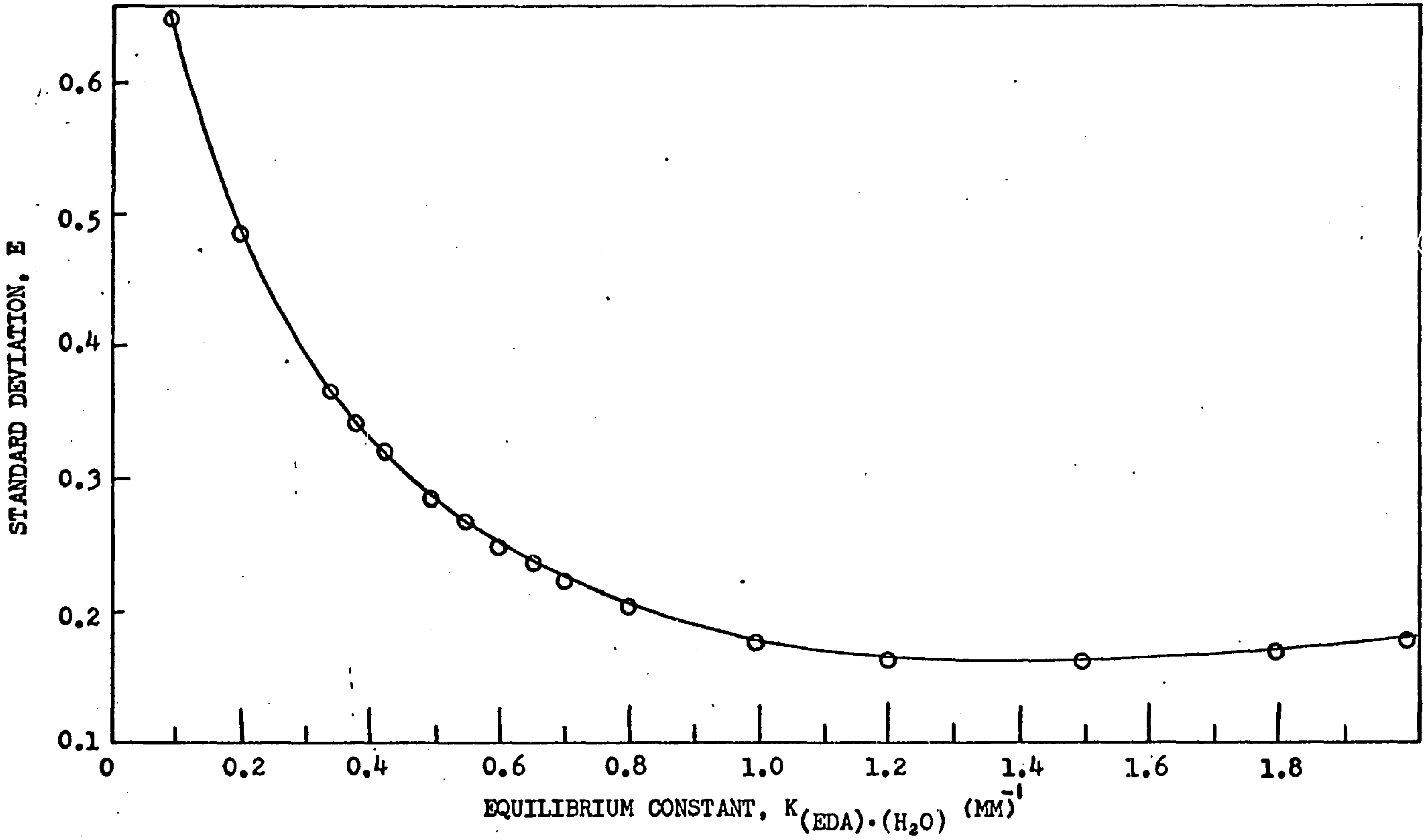


Fig. 8.---- Variation of Standard Deviation with Value of Equilibrium Constant of One-One Complex in Ethylenediamine-Water System at 20°C

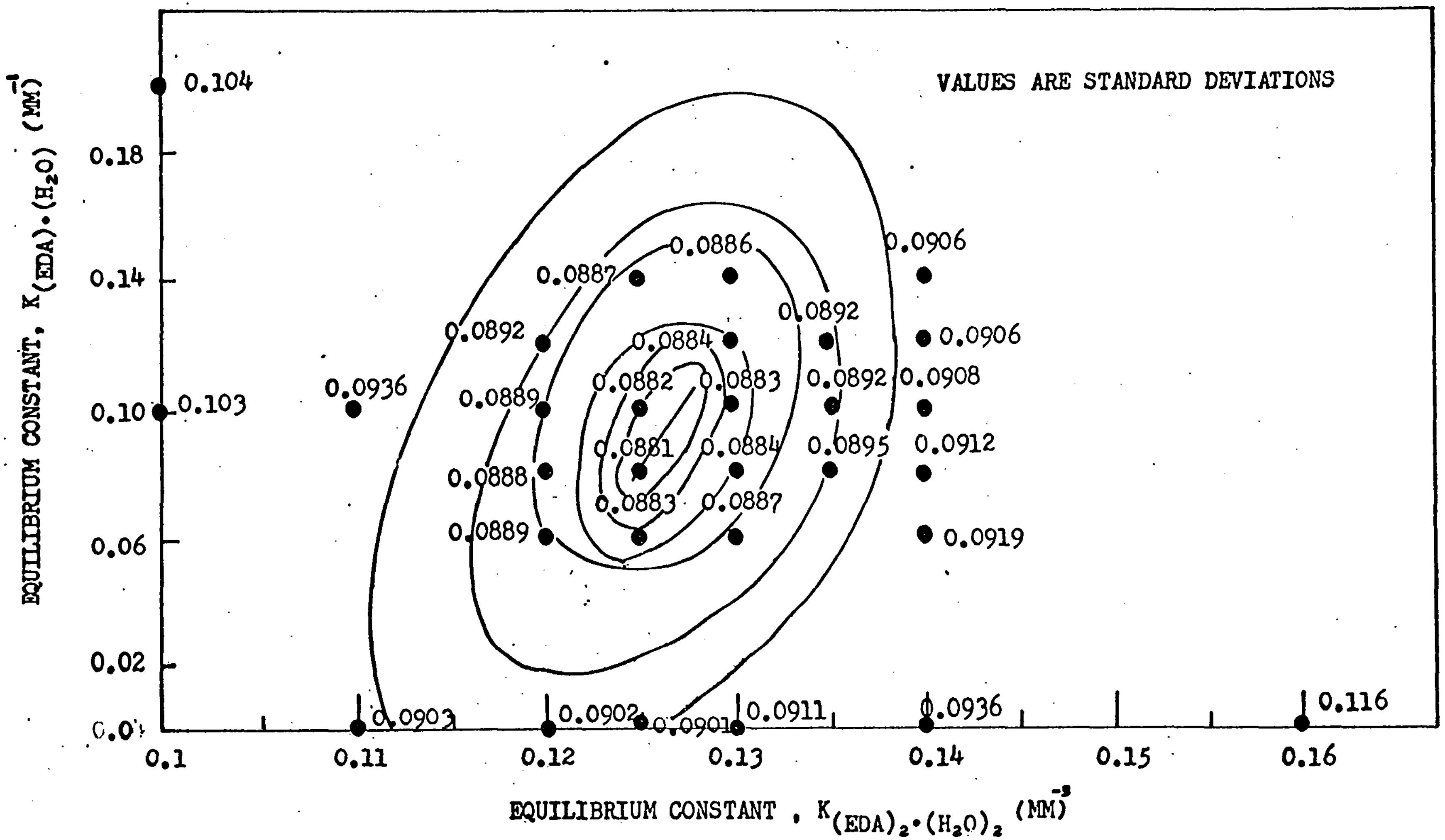


Fig. 9.----Variation of Standard Deviation with Value of Two Equilibrium Constants of Two-Two Complex and One-One Complex in Ethylenediamine-Water System at 20°C

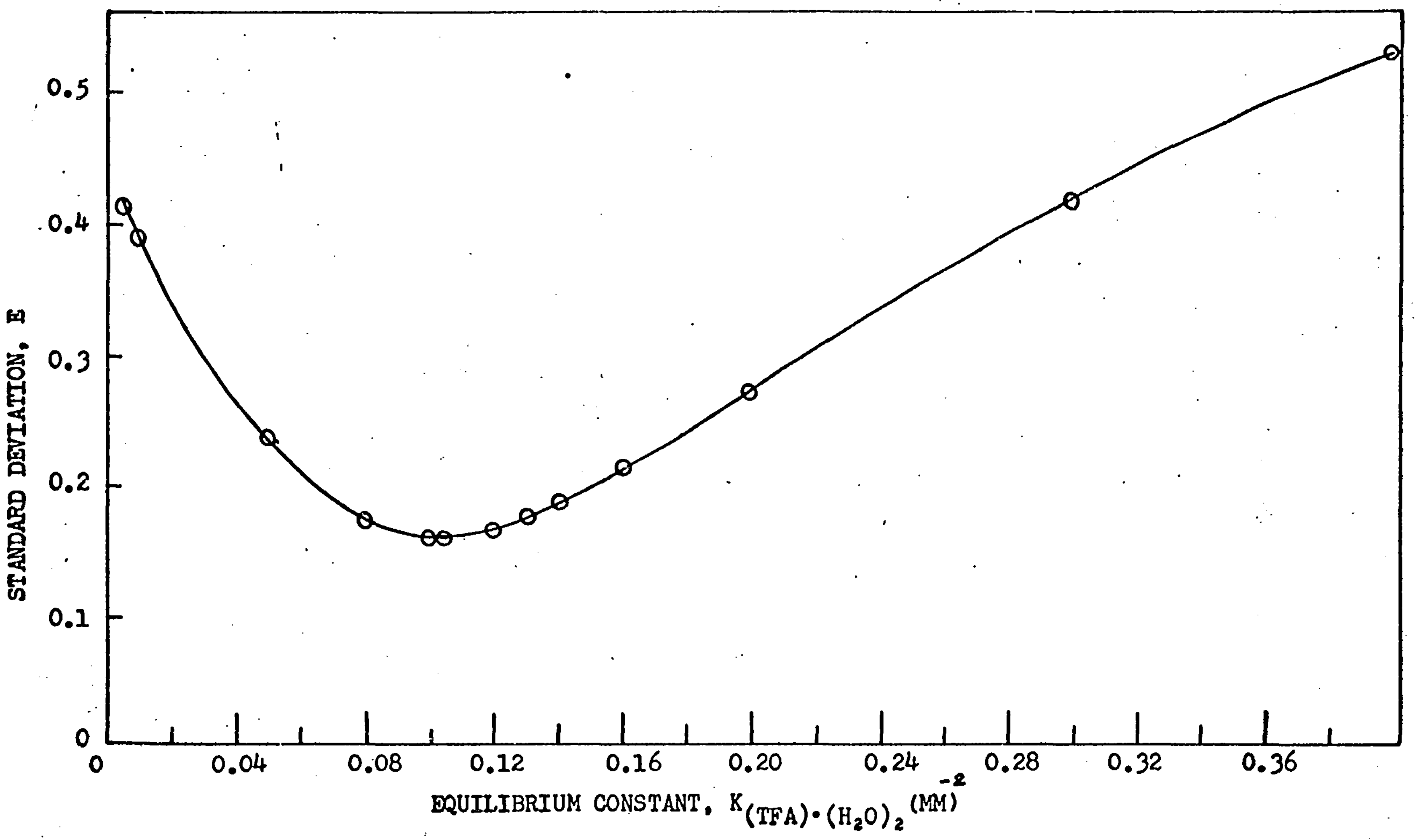


Fig. 10.----Variation of Standard Deviation with Value of Equilibrium Constant of One-Two Complex in Trifluoroacetic Acid-Water System at 20°C

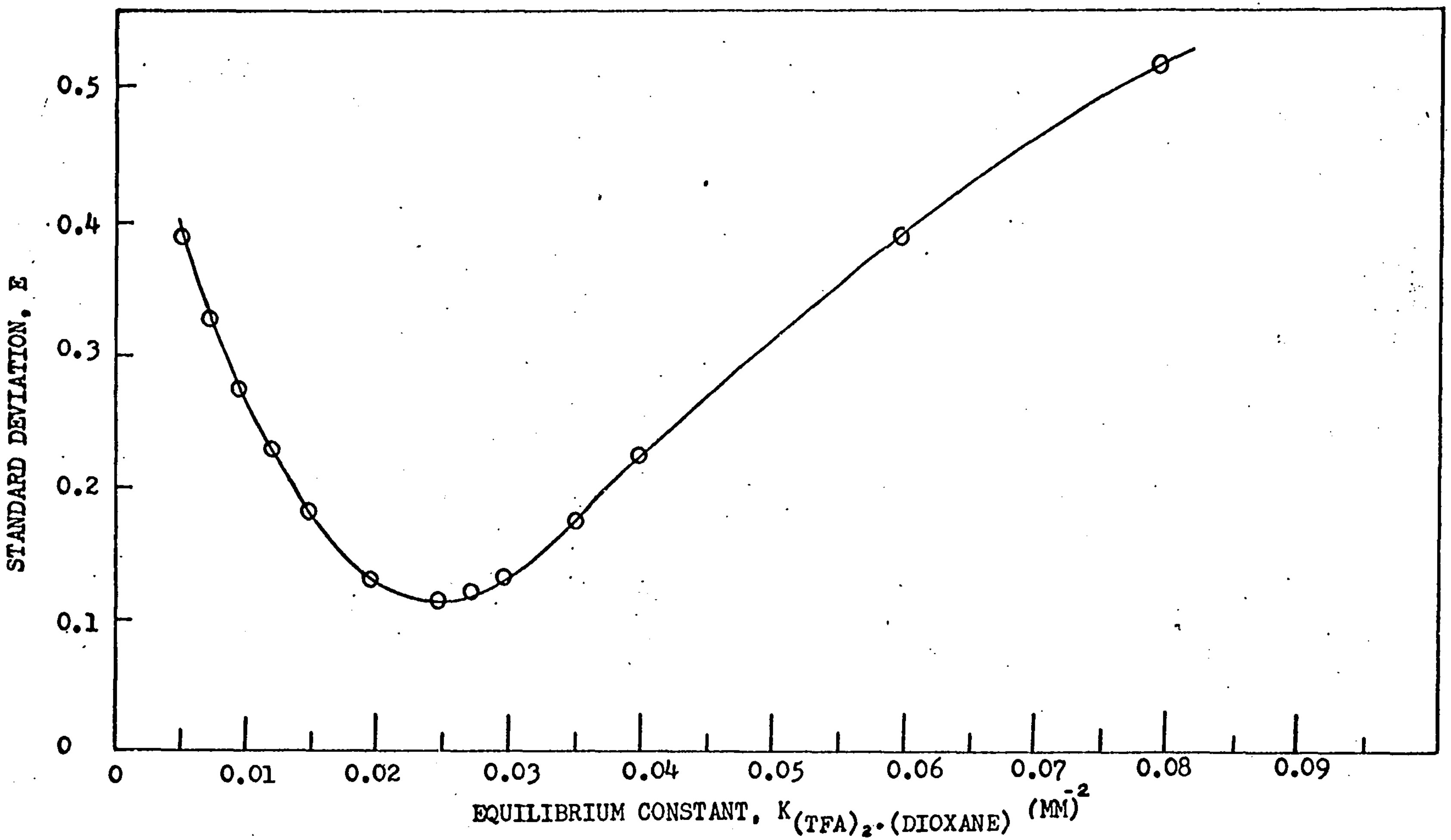


Fig. 11.--- Variation of Standard Deviation with Value of Equilibrium Constant of Two-One Complex in Trifluoroacetic Acid-Dioxane System at 40°C

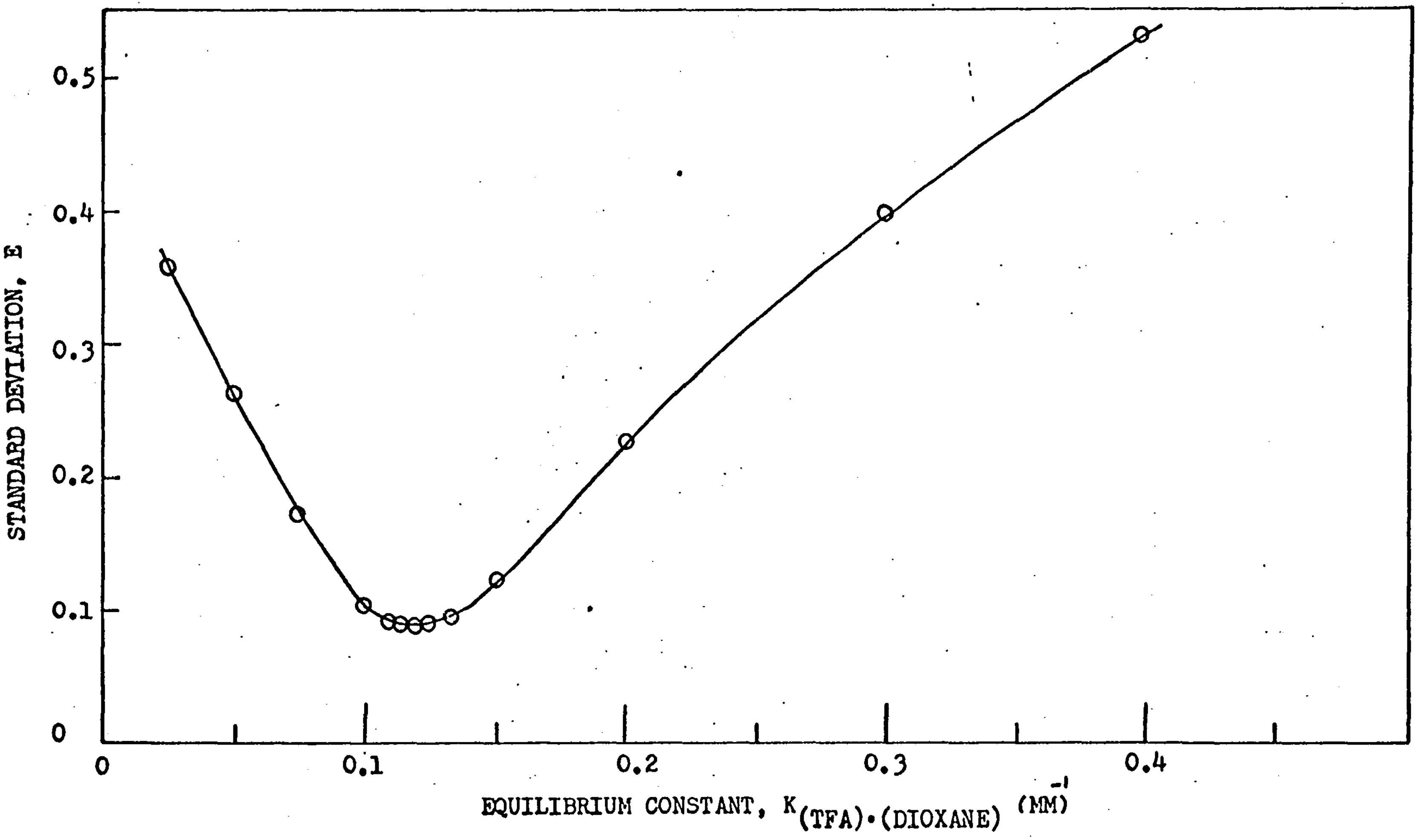


Fig. 12. --- Variation of Standard Deviation with Value of Equilibrium Constant of One-One Complex in Trifluoroacetic Acid-Dioxane System at 40°C

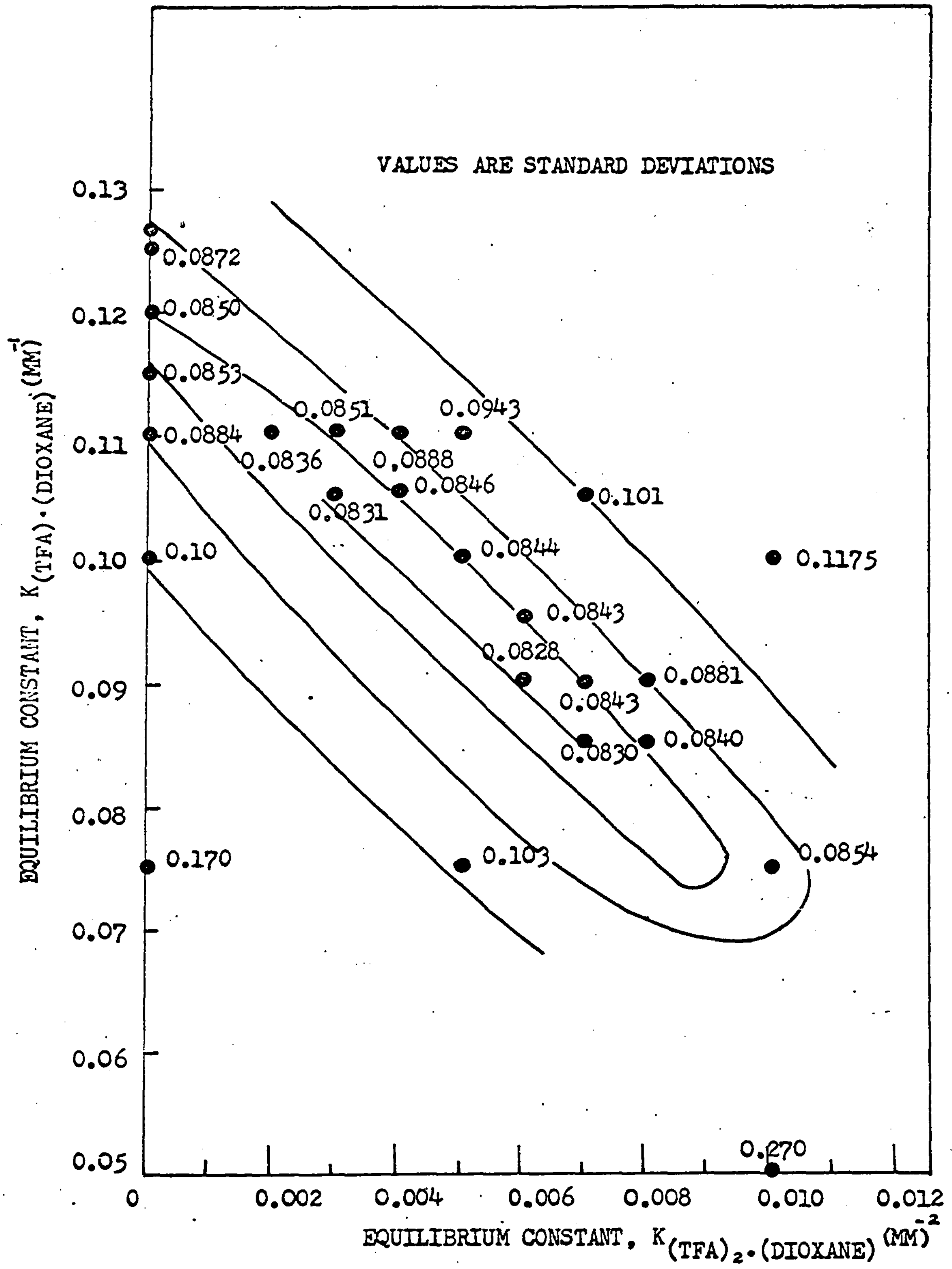


Fig. 13.--- Variation of Standard Deviation with Value of Two Equilibrium Constants of One-One Complex and Two-One Complex in Trifluoroacetic Acid-Dioxane System at 40°C

Table 31

Summary of Results for Trifluoroacetic Acid-Acetic Acid, Ethylenediamine-Water, Trifluoroacetic Acid-Water, and Trifluoroacetic Acid-Dioxane Systems

SYSTEMS	ASSUMED REACTIONS	EQUILIBRIUM CONSTANTS (mm units)	STANDARD DEVIATION (mm)
Trifluoroacetic Acid-Acetic Acid (at 20°C)	$2HAc = (HAc)_2$	3.15	0.099
	$2TFA = (TFA)_2$	0.456	
	$TFA + HAc = TFA.HAc$	14.00	
Ethylenediamine-Water (at 20°C)	$2EDA = (EDA)_2$	0.030	0.088
	$EDA + H_2O = EDA \cdot H_2O$	0.080	
	$2EDA + 2H_2O = (EDA)_2 \cdot (H_2O)_2$	0.125	
Trifluoroacetic Acid-Water (at 20°C)	$2TFA = (TFA)_2$	0.456	0.161
	$TFA + 2H_2O = (TFA).(H_2O)_2$	0.010	
Trifluoroacetic Acid-Dioxane (at 20°C)	$2TFA = (TFA)_2$	0.107	0.083
	TFA + dioxane = TFA.dioxane	0.090	
	TFA.dioxane + TFA = $(TFA)_2$.dioxane	0.006	

CHAPTER VII

DISCUSSION AND CONCLUSION

1. DISCUSSION OF ERRORS

The least precise measurment in this study was that of the volume of the liquid samples. Samples were added through the sintered-glass disc using a 2 ml micrometer buret with the tip of buret touching the disc. The expected error in pressure, per given volume of liquid added, varies inversely with the molecular weight of the vapors of species added. Thus, while water could not be added with precision with the buret, compounds having vapor molecular weight greater than about 60 could be manipulated with considerable accuracy. The buret was calibrated with liquids which gave ideal vapors such as carbon tetrachloride, benzene and cyclohexane. The average error in the total volume of sample added was about ± 0.0015 ml. The error in reading the manometer was about ± 0.01 mm Hg. The pressure was in each case corrected for the variation of the density of the mercury with the temperature. The error in the bath temperature was about ± 0.1 °C.

For each of the systems an estimate was made of the error in pressure, P, which would arise due to the supposed error in volume of the sample added. The method of estimation is illustrated for the TFA-HAc system. In this system the following equations were involved in calculating the error in the total calculated pressures.

$$\pi_{TFA} = \frac{\rho vRT}{MV} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$\pi_{TFA} = P_{TFA} + 2K_{(TFA)_2} P_{TFA} + K_{TFA \cdot HAc} P_{TFA} P_{HAc} \quad \ldots\ldots (2)$$

$$\pi_{HAc} = P_{HAc} + 2K_{(HAc)_2} P_{HAc} + K_{TFA \cdot HAc} P_{TFA} P_{HAc} \quad \ldots\ldots (3)$$

$$P_{total} = P_{TFA} + P_{HAc} + K_{(TFA)_2} P_{TFA} + K_{(HAc)_2} P_{HAc} + K_{TFA \cdot HAc} P_{TFA} P_{HAc} \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

where P_{TFA} and P_{HAc} are the monomer pressures of the TFA and HAc respectively; $K_{(TFA)_2}$ and $K_{(HAc)_2}$ are the dimerization constants for pure TFA and HAC, respectively. $K_{TFA \cdot HAc}$ is the equilibrium constant for the one to one complex.

Differentiating equations (1), (2) and (4), we have

$$d\pi_{TFA} = \frac{\rho R}{MV} (vdT + Tdv) \quad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

$$\begin{aligned} d\pi_{TFA} &= dP_{TFA} + 4K_{(TFA)_2} P_{TFA} dP_{TFA} + K_{TFA \cdot HAc} P_{HAc} dP_{TFA} \\ &= dP_{TFA} (1 + 4K_{(TFA)_2} P_{TFA} + K_{TFA \cdot HAc} P_{HAc}) \quad \ldots\ldots (6) \end{aligned}$$

$$\begin{aligned} dP &= dP_{TFA} + 2K_{(TFA)_2} P_{TFA} dP_{TFA} + K_{TFA \cdot HAc} P_{HAc} dP_{TFA} \\ &= dP_{TFA} (1 + 2K_{(TFA)_2} P_{TFA} + K_{TFA \cdot HAc} P_{HAc}) \quad \ldots\ldots\ldots (7) \end{aligned}$$

From equations (5), (6), and (7), we have, approximately, for a typical data point,

$$\Delta P = \frac{\rho R}{MV}(T\Delta v + v\Delta T)\ \frac{(1 + 2K_{(TFA)_2}P_{TFA} + K_{TFA \cdot HAc}P_{HAc})}{(1 + 4K_{(TFA)_2}P_{TFA} + K_{TFA \cdot HAc}P_{HAc})}$$

$$= \frac{1.48 \times 62300}{114 \times 3030}\left[293 \times (\pm 0.0015) + 0.2 \times (\pm 0.1)\right] \times$$

$$\left[\frac{(1 + 2 \times 0.46 \times 1.5 + 14 \times 0.5)}{(1 + 4 \times 0.46 \times 1.5 + 0.5)}\right]$$

$$= [\pm 0.12 + (\pm 0.005)] \times 0.87 \qquad \ldots\ldots\ldots\ldots \quad (8)$$

$$= \pm 0.11 \text{ mm}$$

The errors of three other systems were calculated by the same procedure and were, for typical data points,

$$P_{TFA-H_2O} = [\pm 0.12 + (\pm 0.008)] \times 0.70$$
$$= \pm 0.09 \text{ mm}$$

$$P_{EDA-H_2O} = [\pm 0.134 + (\pm 0.012)] \times 0.91$$
$$= \pm 0.12 \text{ mm}$$

$$P_{TFA-dioxane} = [\pm 0.11 + (\pm 0.0016)] \times 1.0$$
$$= \pm 0.11 \text{ mm}$$

In equation (8), the value of ± 0.12 may be identified as the contribution due to inaccuracy in the sample volume (Δv), while ±0.005 is due to the error in temperature (ΔT), and 0.87 is the proportionality constant. It is seen that the major error arises from the error in Δv. The calculated error is consistent with the actual error obtained for all the systems expect the TFA-H_2O system, which has a slightly higher value of standard deviation in pressure than predicted.

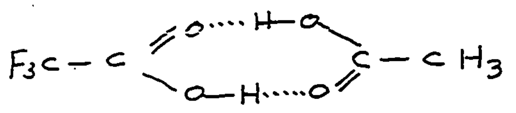
2. TRIFLUOROACETIC ACID-ACETIC ACID SYSTEM

The hetero-hydrogen bonded species is believed to be the one to one complex. Vapor dinsity data could best be fitted by assuming a value of 14.0 mm^{-1} for the equilibrium constant for the reaction

$$CF_3COOH + CH_3COOH = CF_3COOH \cdot CH_3COOH$$

The homo-dimerization constant for trifluoroacetic acid and of acetic acid were taken to be 0.456 mm^{-1}, and 3.15 mm^{-1}, respectively, at 20°C. This indicates that the cross dimer TFA•HAc is very much favored over either of the homo-dimers. One might predict that the hetero-dimerization constant would be greater than the geometric mean of the homo-dimerization constant by a factor of two, since the symmetry number of the hetero-dimer is unity and the symmetry number of each of the homo-dimers is 2.[33] However, the fact that the hetero-dimerization constant has been found to be several times greater than this predicted value has not been satisfactorily explained.

The structure of this complex is very likely the cyclic form:



The results reported here support the work of Hansen and Christian,[15] who reported that the hetero-dimer formed in preference to homo-dimer in the vapor phase systems acetic acid-trifluoroacetic acid, propionic acid-pentafluoropropionic acid and n-butyric-heptafluoro-n-butyric acid.

Also Affsprung, Christian and Melnick[34] noted this effect in studying the hetero-dimerization of acetic acid and trichloroacetic acid in carbon tetrachloride solution. Kohler et.al.[35] have determined calorimetrically that the reaction

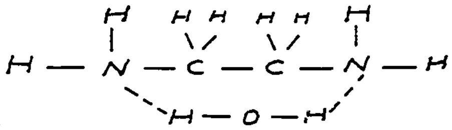
$$1/2\ (CH_3COOH) + 1/2\ (CF_3COOH) = CH_3COOH \cdot CF_3COOH$$

occurs exothermically in dilute solution in CCl_4 and that the mixing of liquid acetic acid and liquid trifluoroacetic acid is strongly exothermic.

3. ETHYLENEDIAMINE-WATER SYSTEM

The hetero-hydrogen bonding species are postulated to be the one to one complex and the two to two complex. The equilibrium constant for the complex $EDA \cdot H_2O$ was calculated to be 0.08 mm^{-1} and for the complex $(EDA)_2 \cdot (H_2O)_2$, 0.125 mm^{-3}. The dimerization constant of pure EDA was found to be approximately 0.03 mm^{-1} at 20°C.

The one to one complex structure may be the following

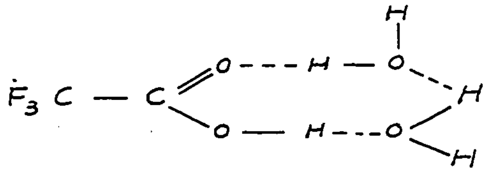


where two basic nitrogens in EDA bond with the two hydrogens of water to form a 7-membered cyclic ring.

It is difficult to propose a single most plausible structure for the complex $(EDA)_2 \cdot (H_2O)_2$. Perhaps a cyclic dimer of EDA is "cemented together" by two water molecules attached through hydrogens to the basic nitrogens.

4. TRIFLUOROACETIC ACID-WATER SYSTEM

The hetero-hydrogen bonded species is most probably the complex $(TFA)\cdot(H_2O)_2$, for which the equilibrium constant was calculated to be 0.010 $mm.^{-2}$ The structure assumed for this species is the cyclic 8-membered ring.

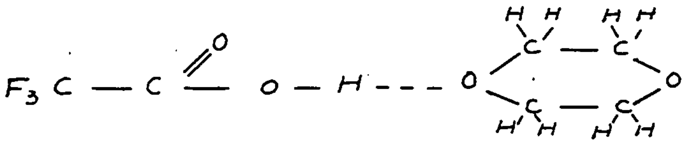


This structure has three hydrogen bonds of which the bond between the acid hydrogen and the water oxygen is probably the strongest. Since water does not self-associate appreciably at this temperature, the formation of a hydrated species with two water molecules must be a result of the great acidity of TFA. It is noteworthy that acetic acid does not appear to hydrate in the vapor phase under similar conditions of pressure and temperature.

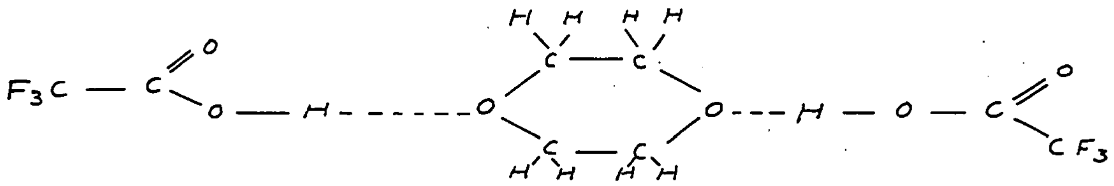
5. TRIFLUOROACETIC ACID-DIOXANE SYSTEM

The hetero-hydrogen bonded species are apparently the one to one complex and a complex involving one dioxane and two TFA molecules. The calculated best values of the equilibrium constants were 0.09 mm^{-1} for the one to one complex and 0.006 mm^{-2} for the one to two complex.

The hydrate structures assumed to be most likely are:



and



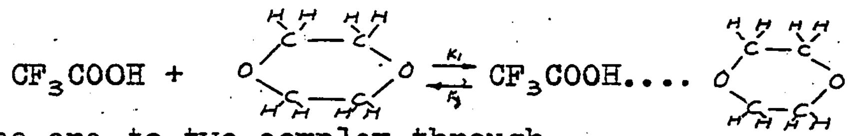
A relation between the two equilibrium constants K_{11} and K_{12}, where K_{11} is the equilibrium constant for the reaction

$$CF_3COOH + \text{dioxane} = CF_3COOH{\cdot}\text{dioxane}$$

and K_{12} is the equilibrium constant for the reaction

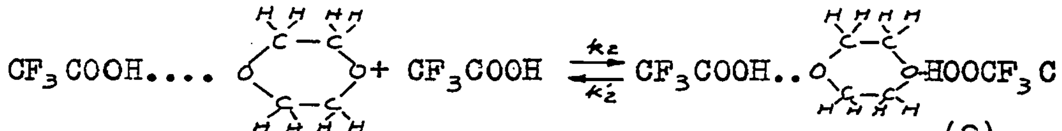
$$2CF_3COOH + \text{dioxane} = (CF_3COOH)_2{\cdot}\text{dioxane}$$

can be predicted theoretically, assuming that the two sites for hydrogen bond formation are equivalent and that there is no influence of one of the hydrogen bonds on the formation of a second hydrogen bond. It may be assumed that the one to one complex forms through



....(1)

and the one to two complex through



....(2)

where k_i is the rate constant for the forward reaction, and k'_i is the rate constant for the reverse reaction. The equilibrium constant in each case is

$$K_i = \frac{k_i}{k'_i}$$

also

$$K_{12} = \frac{P_{(TFA)_2.(dioxane)}}{P_{TFA} \times P_{dioxane}} = K_1 \times K_2 \qquad ..... (3)$$

Since in the forward reaction of equation (1), there are two sites for TFA to attach, while in reaction (2), only one site is available, we might assume that

$$k_1 = 2k_2 \qquad .... (4)$$

Similarly for the reverse reactions of (1) and (2), we predict

$$k'_2 = 2k'_1 \qquad .... (5)$$

Dividing (4) by (5), we have

$$\frac{k_1}{k'_1} = 4 \frac{k_2}{k'_2} \qquad \text{or } K_1 = 4K_2$$

Substituting this relation into (3), one obtains

$$K_{12} = \frac{K_{11}^2}{4}$$

It may be noted in Figure 13 that the contour curves for the error function for this system are such that K_{12} cannot be accurately determined. In fact, assuming that $K_{12} = K_{11}^2/4$ as predicted above, the calculated constants become $K_{11} = 0.103\ mm^{-1}$ and $K_{12} = 0.0026\ mm^{-2}$, and the error function is changed only from 0.0828 to 0.0831. It seems plausible that the sequential hydration scheme is the correct one for this system.

6. SUMMARY

Vapor density data have been reported and analyzed for four binary systems: trifluoroacetic acid-acetic acid, ethylenediamine-water, trifluoroacetic acid-water and trifluoroacetic acid-dioxane. In all these systems, there is definite indication of the formation of hetero-hydrogen bonds. Homo- and hetero- association constants have been reported for these systems. In this study, an attempt was made to determine which hetero-species exist by determining which set of assumed species led to the smallest standard deviation for each system. It would not be possible to conclude with certainty that the species reported are the correct species. It can only be said that these species are the most plausible, based on the data available. Since each system has been studied at only one temperature, the strength of the hydrogen bonds can not be calculated. However, this research represents basic work in a new area which should be followed by a more detailed study of the hetero-hydrogen bonding in these four systems and other systems as well. From the results of this study, it appears that systems in which vapor phase association occurs are likely to be those in which the formation of cyclic hydrogen-bonded species is possible. Since the number of the systems in which extensive hydrogen bond formation occurs in the vapor phase is much less than the number which exhibits hydrogen bond formation in solution, it will be desirable in the future to investigate the vapor phase behavior of numerous systems in which the possibility of the formation of cyclic hydrogen bonds exists.

7. EXTENSION OF THE METHOD

The reliability of the vapor density apparatus invented in the course of this research has been verified.[26] It has proved to be much simpler and more rapid than conventional methods and the reproducibility of results compares favorably with earlier methods. The method is idealy suited for the study of hetero-association.

The mercury seal vacuum unit E in Figure 1 can be replaced by a teflon vacuum stopcock, thus making the operation even simpler. Flasks of capacity greater than 3 liters may be used to increase the accuracy of the measurements to the point where even low molecular weight vapors, such as water, may be added with accuracy.

One of the side applications of this apparatus which has been developed during this research is the calculation of the vapor phase dimerization constant from pressure-temperature data alone. The detailed report of this method is included as Appendix C, which is a pre-print of an article to appear in the Journal of the Chemical Society.

The heat of association of the reactions investigated can be obtained by operating at several different temperatures. It should be especially interesting to study the behavior of vapor phase hydrates using this technique.

Using this apparatus the vapor pressure of a pure liquid or the dew point pressure of a mixture may be determined. It has been demonstrated that the dew point curve for a binary system may be utilized in the calculation of the activities and activity coefficient.[36, 37]

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APPENDIX A

S. D. Christian,
H. E. Affsprung and **C. Lin**
University of Oklahoma
Norman

Vapor Density Apparatus

Vapor density experiments, as performed in the undergraduate physical chemistry laboratory, are frequently inaccurate and time-consuming. The requirements that a known mass of vapor be contained in a known volume at known temperature and pressure, in the absence of stopcock grease, are quite demanding on the skill of the student and the quality of the apparatus.

We have devised a vapor density method, suitable for instructional or research use, that is both rapid and capable of considerable accuracy. The method has been tested on several vapors of known molecular weight.

Apparatus and Method

The apparatus is sketched in Figure 1. In preparing for a run, the 1-liter flask *F* is evacuated through tube *B* while the mercury in the tube is maintained at a level slightly below the sintered-glass disc *A*. The mercury level may be adjusted by manipulating the Teflon-plug stopcock *C* (not greased) and the three-way stopcock *D*, thereby either forcing mercury into or out of the reservoir *E*. When the pressure in *F* has been reduced to a sufficiently low value (as indicated by the closed-end manometer *M*), the mercury level in *B* is raised to a height about 1 cm above the disc *A*. Stopcock *C* is securely closed, air is allowed into tube *B* and the standard taper cap *G* is removed.

A run may now be made by introducing a known volume of a volatile liquid through the disc *A*, using a graduated volumetric pipet.[1] After the addition of each increment of liquid, the pressure and temperature are measured. With liquids such as benzene, cyclohexane and carbon tetrachloride, a total volume of several tenths of a ml may be introduced at room temperature before saturation is reached. Upon completion of a set of measurements, the mercury level in *B* is lowered, and flask *F* is again evacuated. For non-associating vapors, it is not necessary to evacuate the system to zero pressure, since a correction can be made for the pressure of residual gases or vapors in the system at the start of the experiment.

Results

The results of a series of runs on benzene, carbon tetrachloride and cyclohexane vapors are shown in Figure 2. The total pressure increment, Δp, resulting

---

[1] This is accomplished by filling the pipet to a given mark, wiping the tip to remove adhering liquid, and inserting the tip of the pipet through the mercury until it contacts the disc. Since the pressure inside the flask *F* is less than the pressure in the pipet, liquid will be sucked through the disc. When a sufficient volume has been added, the pipet is withdrawn and the final liquid level is noted. Occasionally a small amount of liquid mercury enters the pipet as it is withdrawn—this must be drained before the final liquid level is measured. A 0.1 ml graduated pipet was used in all the experiments described here.

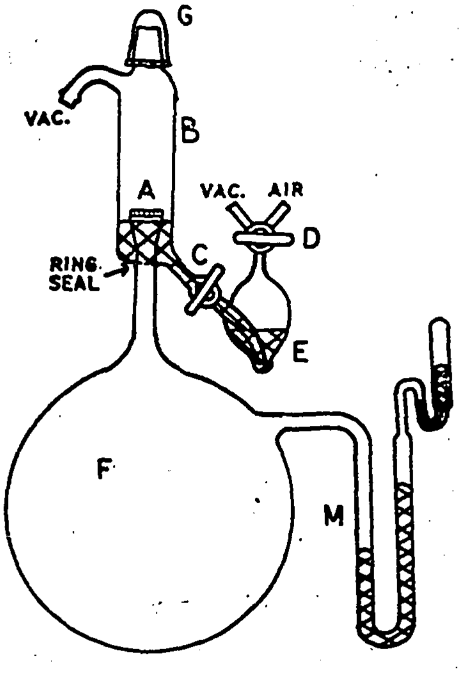

Figure 1. Vapor density apparatus.

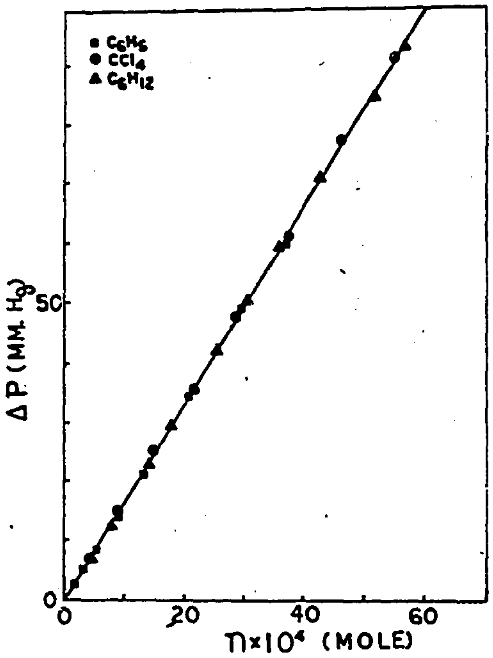

Figure 2. Benzene, carbon tetrachloride, and cyclohexane vapors at 23.6 ± 0.2° C. Line represents least squares fit of data.

[Reprinted from Journal of Chemical Education, Vol. 40, Page 323, June, 1963.]

from the cumulative addition of n moles of liquid at 23.6 ± 0.2°C is plotted versus n. From the plot it can be seen that nearly the same curve is defined by data for each of the liquids. By a least squares method, values of the slope m in the equation

$$n = m\Delta p \tag{1}$$

were calculated for each vapor, as well as σ, the standard deviation in n, assuming all the error to reside in the n values. Also calculated were the values of m and the standard deviation in n for all points considered collectively. These constants and the values of the system volume, V, calculated from the ideal gas equation, are reported in Table 1. Examination of the table reveals that the standard deviation in n is nearly the same for all points collectively as for each system by itself. The slopes, m, lie in the range $m = 0.6035 \times 10^{-4} \pm 0.003 \times 10^{-4}$ mole mm Hg^{-1}, which corresponds to a net uncertainty in the system volume of about ±6 ml. The standard deviation in n corresponds to a standard deviation in the volume of liquid added through the pipet of about 0.002 ml.

Table 1. Curve Parameters for Equation (1)

System	$m \times 10^4$ (mole mm Hg^{-1})	$\sigma \times 10^4$ (mole)	V (ml)
Benzene	0.6060	0.12	1122
Carbon tetrachloride	0.6008	0.22	1112
Cyclohexane	0.6028	0.14	1117
All systems together	0.3035	0.19	1116

It should be noted that the system volume actually varies slightly as the mercury level in the manometer changes, and a correction for this can be made if necessary. However, if several vapors are to be studied over a common range of pressure, it is adequate to calibrate the system using vapors of known molecular weight in the same pressure range.

Discussion

Several advantages of this apparatus recommend it for use in studying vapors at pressures less than one atmosphere. First, no greased parts need be used in the entire apparatus. Second, liquid mixtures of known composition may be investigated as easily as pure liquid compounds. Third, it is possible to thermostat the entire apparatus below the sintered-glass disc A. This is particularly important in studies of the vapor densities of associating compounds, as for example carboxylic acids. In such experiments it is desirable to vary the temperature while a known mass of vapor is present in the system. Further, calibration is simple—a sample of a known liquid is first introduced and measured, whereupon an unknown sample may be added immediately without evacuating the system.

Provided the system is adequately thermostated, vapor pressures of pure liquids or dew-point pressures of mixtures may be determined. Successive increments of the liquid or liquid mixture are added as before until condensation occurs. The vapor pressure or dew-point pressure is identified as the pressure at which a break occurs in the Δp versus n curve. It has been demonstrated that the dew-point curve for a binary system may be utilized in the calculation of activities and activity coefficients[2,3]; hence the present apparatus might be applied in studying liquid-vapor equilibria.

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APPENDIX B

IBM 1410 PROGRAM FOR COMPUTING THE TOTAL PRESSURES, PARTIAL PRESSURES(p_1,p_2) AND ERROR FUNCTIONS FROM FORMAL PRESSURES (π_1, π_2) FOR THE SPECIES IN THE VAPOR PHASE MIXTURE

BY

S.D. Christian
Department of Chemistry, University of Oklahoma

1. THEORY

$$P_T = \sum_{i=1}^{3}\sum_{j=1}^{3} K_{i-1,j-1}\, p_1^{(i-1)} p_2^{(j-1)}$$

$$\pi_1 = \sum_{i=1}^{3}\sum_{j=1}^{3} (i-1)K_{i-1,j-1}\, p_1^{(i-1)} p_2^{(j-1)}$$

$$\pi_2 = \sum_{i=1}^{3}\sum_{j=1}^{3} (j-1)K_{i-1,j-1}\, p_1^{(i-1)} p_2^{(j-1)}$$

The program will take a set of $K_{i-1,j-1}$ (equilibrium constants) and using data points P_T, π_1, π_2, calculated $p_1$and p_2 for each data set, by simultaneous solution of $\pi_1 = \pi_1(K_{i-1,j-1}, p_1, p_2)$ and $\pi_2 = \pi_2\ (K_{i-1,j-1}\ p_1, p_2)$. Then it will calculate:

$$\text{Standard deviation} = \sqrt{\frac{\sum(P_T^{\text{exp}} - P_T^{\text{cal}})^2}{(\text{No. of points} - \text{No. of parameters})}}$$

2. INPUT

CARD 1................II JJ IPTS IPAR

All numbers are integers of type I3. Both II and JJ must have the value 3. IPTS is the number of sets of points (π_1, π_2, P_T) and IPAR is the total number of $K_{i-1,j-1}$ parameters used in the fit; e.g. if II = 3, JJ = 3, IPTS = 27, and IPAR = 4, Card 1 would read

003003027004

column 1..... 12

CARD 2 ....DELT1	DELT2	FACT	$DELT_3$	CODE
column 1-10	11-20	21-30	31-40	41-50

DELT1, a F10.0 number, is the allowable error in the function $(\pi_1^{exp} - \pi_1^{cal})^2 + (\pi_2^{exp} - \pi_2^{cal})^2$ used in computing p_1 and p_2. This function should have the value zero for correct values of p_1 and p_2, and DELT1 has been chosen as 0.0000001 in this research.

FACT is a F10.0 number used todetermine the maximum number of iteration cycles to be used in calculating p_1 and p_2. If FACT = x, the number of cycles will be 10/x. FACT was chosen as 2.0 in this work.

DELT2, DELT3 and CODE are arbitrary F10.0 constants which may be used as code numbers. If CODE>FACT, the calculated p_1, p_2 and P_T values and the experimental π_1, π_2 and P_T values will be printed after each calculation of p_1 and p_2 for a given data point.

CARD 3 ....Data are entered on cards 3 to 3 + IPTS - 1, inclusive F10.0 numbers. The approximate p_1 and p_2 values entered need not be very accurate.

P_T	π_1	π_2	p_1 (approx)	p_2 (approx)
•	•	•	•	•
•	•	•	•	•
•	•	•	•	•

The next 3 cards have K values (note $K_{00} = 0$, $K_{10} = 1$, $K_{01} = 1$), and if a given $K_{i-1,j-1}$ is not used in the fitting process, it is entered as zero.

CARD 3 + IPTS	K_{00}	K_{01}	K_{02}	K_{03}
	K_{10}	K_{11}	K_{12}	K_{13}
CARD 3 + IPTS + 2	K_{20}	K_{21}	K_{22}	K_{23}

CARD 3 + IPTS + 3 .... The next 3 cards can be a set of K's different from the above set and the program will stop when all the cards have read and data processed.

OUTPUT

If CODE>FACT, the printer will print IPTS lines with the values

DELT1	DELT2	FACT	DELT3	CODE	
P_1	P_2	π_1	π_2	P_T	P_T
(cal)	(cal)	(exp)	(exp)	(exp)	(cal)
•	•	•	•	•	•
•	•	•	•	•	•
•	•	•	•	•	•

For each set of data points, the standard deviation will be printed

$$\text{Standard Deviation} = \sqrt{\frac{(P_T^{exp} - P_T^{cal})^2}{\text{No. of points} - \text{No. of parameter}}}$$

Following this all the K's will be printed along with CODE

K_{00}	K_{01}	K_{02}	K_{03}	CODE
K_{10}	K_{11}	K_{12}	K_{13}	CODE
K_{2}	K_{21}	K_{22}	K_{23}	CODE

When all this had been printed, the program is repeated using the next set of K's as input, if CODE$<$100.00, or going back to the beginning to read in an entire set of input constants and data if CODE$>$100.00. Program will stop on a read statement when all data have been used.

```
            IDENTED-00103 S D CHRISTIAN
     40KFORTRANRUN
            BOP
C       CURVE FIT FOR VAPOR DENSITY DATA
        DIMENSION PX(100), PI1X(100), PI2X(100),
       1P1(100), P2(100), C(7,7)
     19 READ 1, II, JJ, IPTS, IPAR
     20 READ 2, DELT1, DELT2, FACT, DELT3, CODE
        PRINT 2, DELT1, DELT2, FACT, DELT3, CODE
     21 DO 22 I=1, IPTS
     22 READ 2, PX(I), PI1X(I), PI2X(I), P1(I), P2(I)
     23 DO 24 I=1, II
     24 READ 2, C(I,1), C(I,2), C(I,3), C(I,4), C(I,5)
     25 IP = 0
     26 PERR=0
    216 IP=IP+1
        CYCLE=0.0
    219 KK=1
        GO TO 410
    220 ERR1=ERR
    221 P1OLD=P1(IP)
        P2OLD=P2(IP)
    222 P1(IP)=P1(IP)+((PI1X(IP)-PI1)*PI22-
       1(PI2X(IP)-PI2)*PI12)/(PI11*PI22-
       2PI12*PI21)
        P2(IP)=P2(IP)+((PI2X(IP)-PI2)*PI11-
       1(PI1X(IP)-PI1)*PI21)/(PI11*PI22-
       2PI12*PI21)
        P1(IP)=(P1(IP)**2)**0.5
        P2(IP)=(P2(IP)**2)**0.5
    223 KK=2
        GO TO 410
    232 IF (ERR-DELT1)234,234,233
    233 CYCLE=CYCLE+FACT
        PRINT 7, ERR
        IF(CYCLE-10.0) 219,219,234
    234 PERR=PERR+(PX(IP)-P)**2
        PRINT 6, P1(IP),P2(IP), PI1X(IP),
       1 PI2X(IP), PX(IP), P
    235 IF(IP-IPTS)216,236,236
    236 EPAR=FLOATF(IPAR)
    237 EPTS=FLOATF(IPTS)
    238 STDD = SQRTF(PERR/(EPTS-EPAR))
    276 PRINT 7, STDD
    278 DO 279 I=1,II
    279 PRINT 6, C(I,1), C(I,2), C(I,3),
       1C(I,4), C(I,5), CODE
    280 IF(CODE-100.0)23,23,19
    410 PI1=P1(IP)+2.0*C(3,1)*
       1P1(IP)**2 +C(2,2)*P1(IP)*P2(IP)+
       22.*C(3,2)*P1(IP)**2 *P2(IP)+2.*C(3,3)*P1(IP)**2
       3*P2(IP)**2 +C(2,3)*P1(IP)*P2(IP)**2
        PI2=P2(IP)+2.0*C(1,3)*P2(IP)**2
       1+C(2,2)*P1(IP)*P2(IP)+
       2C(3,2)*P1(IP)**2 *P2(IP)+2.*C(3,3)*P1(IP)**2 *P2(IP)**2 +
       32.*C(2,3)*P1(IP)*P2(IP)**2
        PI11=1.+4.*C(3,1)*P1(IP)+C(2,2)*P2(IP)+
       14.*C(3,2)*P1(IP)*P2(IP)+4.*C(3,3)*P1(IP)*P2(IP)**2
       2+C(2,3)*P2(IP)**2
        PI12=C(2,2)*P1(IP)+
       12.*C(3,2)*P1(IP)**2 +4.*C(3,3)*P1(IP)**2 *P2(IP)+
```

```
   22.*C(2,3)*P1(IP)*P2(IP)
    PI21=C(2,2)*P2(IP)+
   12.*C(3,2)*P1(IP)*P2(IP)+4.*C(3,3)*P1(IP)*P2(IP)**2
   2+2.*C(2,3)*P2(IP)**2
    PI22=1.+4.*C(1,3)*P2(IP)+C(2,2)*P1(IP)+
   1C(3,2)*P1(IP)**2 +4.*C(3,3)*P1(IP)**2
   2*P2(IP)+4.*C(2,3)*P1(IP)*P2(IP)
425 P=P2(IP)+P1(IP)+C(3,1)*P1(IP)**2 +C(3,2)*P1(IP)
   1**2 *P2(IP)+C(2,2)*P1(IP)*P2(IP)+C(3,3)*P1(IP)
   2**2 *P2(IP)**2 +C(2,3)*P1(IP)*P2(IP)**2 +C(1,3)*P2(IP)**2
426 ERR=(PI1-PI1X(IP))**2  +
   1(PI2-PI2X(IP))**2
427 GO TO (220,232),KK
  1 FORMAT (4I3)
  2 FORMAT (5F10.0)
  6 FORMAT(6E13.6)
  7 FORMAT (E13.6)
    END
```

APPENDIX C

DETERMINATION OF VAPOR PHASE DIMERIZATION CONSTANTS FROM PRESSURE-TEMPERATURE DATA

By Sherril D. Christian, Harold E. Affsprung and Chii Lin

Measurements of vapor density, pressure and temperature frequently are used in determining association constant; however, in most vapor density experiments, the relative error in the measured density is considerably greater than the relative errors in temperature and pressure. We have devised a scheme for calculating dimerization constants and enthalpies of dimerization from measurement of the variation of the pressure, p, with absolute temperature, T, for a given volume of gas. Density measurements are not required. The technique is illustrated with data for acetic acid, obtained using a vapor density apparatus described previously.[1]

For species which dimerize, but undergo no higher polymerization, the equilibrium constant for the dimerization reaction may be written

$$K = A \exp. (- \Delta H/RT) = \frac{(M - M_m)M_m}{(2M_m - M)^2 p}$$

where A is related to the entropy of dimerization, ΔH is the enthalpy of dimerization, M is the average molecular weight of the vapor and M_m is the molecular weight of the monomer of the associating species. It is assumed that ΔH and A are constant over a range of temperatures and that the monomeric and dimeric species individually obey the ideal gas law. If vapor density is constant, M may be replaced by aT/p, where a is a constant of proportionality. Upon making this substitution and multiplying by T, equation (1) becomes

$$AT\ \exp.(-\Delta H/RT) = \frac{(aT/p - M_m)(T/p)M_m}{(2M_m - aT/p)^2} = \frac{(ax - M_m)xM_m}{(2M_m - ax)^2} \qquad (2)$$

where x is defined as T/p, and both T and x are measureable quantities.

Taking logarithms of both sides of equation (2) and differentiating with respect to 1/T, one obtains

$$-(\Delta H/R + T) = \frac{(3ax/M_m - 2)}{(ax/M_m - 1)(2-ax/M_m)} \cdot \frac{d\ln x}{d(1/T)} \qquad (3)$$

Note that $\Delta H/R + T$ is virtually constant over a considerable range of temperatures, provided that $\Delta H/R \gg T$. (In the case of acetic acid vapors, $\Delta H/RT \backsim 25$)

In equation (3), values of $d\ln x/d(1/T)$ are directly determinable from p vs. T measurements, and the function

$$\frac{(3ax/M_m - 2)}{(ax/M_m - 1)(2 - ax/M_m)} = f(ax/M_m)$$

depends only on the parameter ax/M_m. Plots of $f(ax/M_m)$ vs. ax/M_m and $d(1/T)/d\ln x$ vs. x may be constructed on the same log-log graph; and, if $\Delta H/R + T$ is constant, equation (3) requires that the two curves be identical in shape but translated with respect to each other. The displacement of the abscissas should equal log (a/M_m) and the displacement of the rodinates should be log $(-\Delta H/R - T)$. Thus, both a and ΔH may be determined by translating one of the curves so that it coincides as nearly as possible with the other.

The method of curve-fitting is illustrated with the aid of the Figure. A standard curve of $f(ax/M_m)$ vs. ax/M_m (on a log-log scale) is plotted as the solid line. Values of $d(1/T)/d\ln x$ (determined from a least squares quartic fit of $\ln x$ vs. $1/T$ data) are plotted vs. x on the same graph, for acetic acid vapors at pressures and temperatures ranging from about 5 mm., 15° to 9 mm., 85°. The values of the parameters determined by translating the $d(1/T)/d\ln x$ curve to force it to fit as nearly as possible the standard $f(ax/M_m)$ curve are:

$$a = 2.06 \text{ mm. gm. } {}^\circ K^{-1} \text{mole}^{-1} \text{ and } \Delta H = 15.6 \text{ kcal/mole.}$$

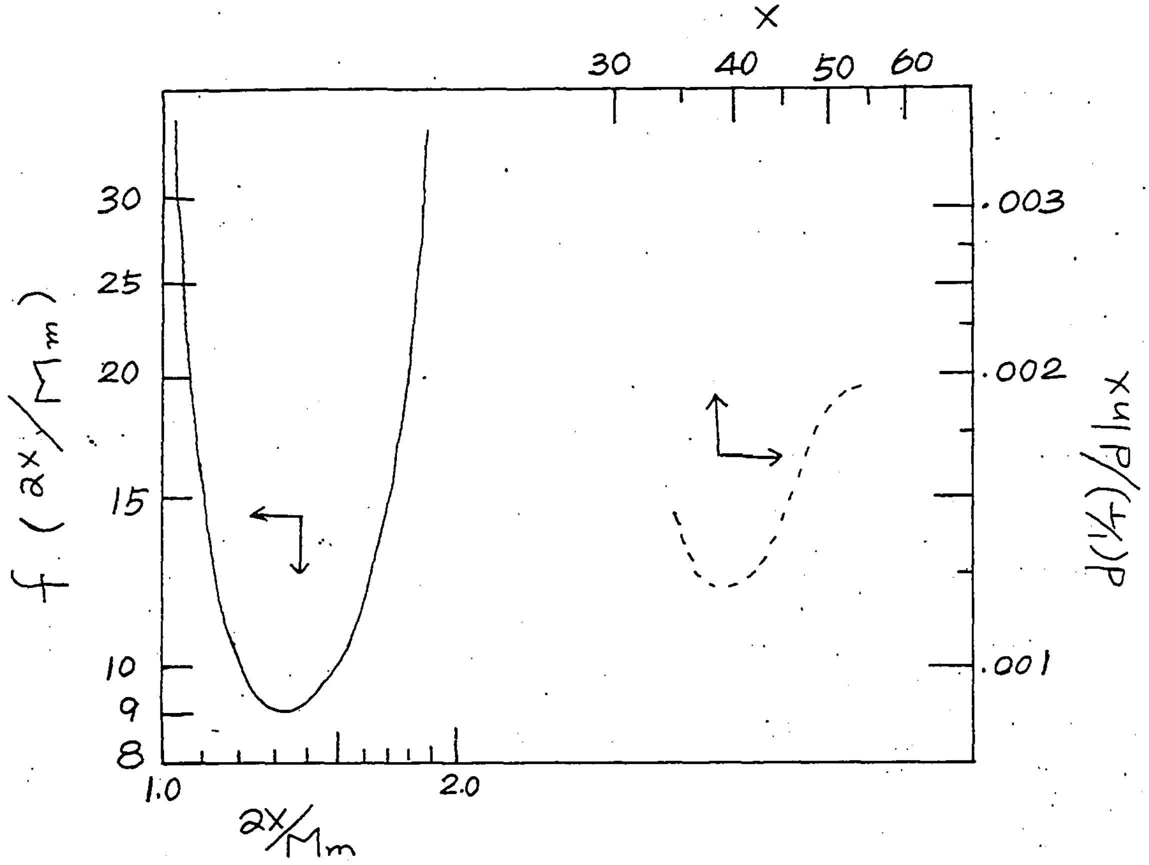
From these values, the constants in equation (1) may be evaluated. The following expression may thereby be obtained for the equilibrium constant:

$$\log_{10}K(\text{mm.}^{-1}) = -11.14 + 3410/T$$

Thus result may be compared to the expressions

$\log_{10}K(\text{mm.}^{-1}) = -11.789 + 3590/T$ obtained by MacDougall[2] (for temperatures and pressures ranging from 25° to 40° and 3 to 23 mm.) and

$\log_{10}K(\text{mm.}^{-1}) = -10.931 + 3347/T$ reported by Taylor[3] (for temperatures and pressures ranging from 50° to 150° and 13 to 34 mm). At 300°K our result leads to $K = 1.70 \text{ mm}^{-1}$ as compared to values



Standard $f(ax/M_m)$ vs. ax/M_m curve and $d(1/T)/d\ln x$ vs. x curve for acetic acid vapors of 1.51 mm^{-1} and 1.71 mm^{-1} calculated from the data of MacDougall and Taylor, respectively.

It is somewhat difficult to relate errors in the measured P,T values to errors in the calculated values of ΔH and K. For the run indicated in the figure, the average deviation of p values from values calculated using the least squares quartic equation is 0.07 mm. From a comparision of slopes obtained graphically with those obtained by differentiating cubic and quartic power series expressions representing the data, we estimate that, except for points near the extremities of the range of x, the approximate error in d(1/T)/dlnx is everywhere less than 5×10^{-5} $°K^{-1}$. This corresponds to a maximum uncertainty in ΔH of about 0.7 kcal. Judging from the reproducibility of values of H and a obtained from repeated attempts to bring the theoretical and experimental curves into coincidence, the curve-matching process appears to introduce an uncertainty in K at 300°K of less than 0.1 mm^{-1}. The tailing off of the computed curve at large values of x (see figure) is an artifact of the method of curve-fitting, and causes little difficulty in locating the position of the minimum of the derivative curve.

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DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF OKLAHOMA,
NORMAN, OKLAHOMA, USA

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