

1938

Relationship between the electron-sharing ability of radicals and the association of organic compounds

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RELATIONSHIP BETWEEN THE ELECTRON-SHARING ABILITY OF RADICALS
AND THE ASSOCIATION OF ORGANIC COMPOUNDS

by

Franc Arthur Landee

A Thesis Submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject Plant Chemistry

Approved:

Signature was redacted for privacy.

In charge of Major work

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Dean of Graduate College

Iowa State College
1938

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TABLE OF CONTENTS

	Page
Acknowledgments	4
Statement of Problem	5
Part One - The effect of substitution of radicals of varying E.S.A. into the solute, or associating body, as evidenced by changes in the apparent molecular weight of the same . .	8
Foreword.	8
Theory.	9
Experimental part	12
The association in the vapor state	12
The association in solution.	25
Discussion of Results	43
Part Two - The effect of substitution of radicals of varying E.S.A. into the solvent, or associating medium, as evi- denced by changes in the apparent molecular weight of the solute.	46
Foreword.	46
Theory.	47
Experimental part	70
Solvation effect	70
The effect of E.S.A. on the solvation reaction	78
Discussion of Results	102
Part Three - Application of the theory to related phenomena in organic chemistry	104
Foreword.	104
The association of liquid compounds	105

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	Page
The enolization of ketonic compounds.	110
Summary.	116
Literature Cited	118

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STATEMENT OF PROBLEM

The search for an activity series of organic radicals that would allow one to predict with certainty the progress and completeness of all reactions involving compounds of these radicals as well as the physical and chemical properties of the compounds themselves is one that has occupied the time and energy of many investigators.

In the first of a series of papers attacking this problem Hixon and Johns (30) made the statement, "If the electron theory of valence holds, then the polar properties of any series of compounds such as $R(OH)$, $R(COOH)$, $R(CH_2 COOH)$, $R(CH_2 CH_2 COOH)$, $R(NH_2)$, $R(SH)$, $R(AsO(OH)_2)$, etc., must be a function of the 'electron-sharing ability' of the radicals R , if we exclude from consideration under R all groupings which themselves have polar linkages." These investigators were able to show, by making use of the dissociation constants in water of the above compounds, as listed in Landolt-Börnstein, that one order or series of the radicals concerned is sufficient to show the variation in acidity of all the types of compounds studied. This order of radicals, which is by definition an arrangement in the order of their "electron-sharing abilities" has been given an arbitrary scale of units with the hydrogen radical equal to zero as the base. In agreement with the original conception of electron-sharing ability these radicals which substituted for hydrogen in a compound caused an increase in the acidic strength of the compound, were called positive radicals and given positive values of electron-sharing ability.

It is realized that the term electron-sharing ability (abbr. E.S.A.) is a rather comprehensive term and that the E.S.A. of a radical is no doubt

influenced by many things such as dipole moment, molecular weight, steric hindrance, resonance, etc., but it is maintained that the E.S.A. of a radical is a function of the radical itself and as such should govern the influence of a radical upon a compound or reaction into which the radical is substituted. For example, since the ionization of an organic acid or base is a reversible reaction and the course of such a reaction is governed by the E.S.A. of the radicals concerned, the course of other reversible reactions should be governed by the same function of the radicals. This has been found to be true in the cases studied: i.e. the condensations of mercaptans with chloral (35) and the reversible splitting of the organomercury iodides into mercuric iodide and diorganomercury (34). Other papers concerning E.S.A. have correlated this theory with the dissociation in water of the organomercury nitrates (33), the α -substituted pyrrolidines (23), the α -substituted pyrrolines (57), the N -substituted pyrrolines (23), and the dissociation in methanol and ethanol of examples of the above types of compounds (28). Other investigators have made applications of the theory to the variations of the refractive indices of organic compounds with substitution (21), the variation of optical activity with substitution (46) and the displacement of the frequency of Raman lines as radicals of varying E.S.A. were attached to the bond emitting the radiation (41).

It is the purpose of this paper to investigate the phenomena of molecular association in all of its phases and to apply if possible the theory of electron-sharing ability to such equilibria.

The paper will be divided into three main parts:

1. The Effect of Substitution of Radicals of varying E.S.A. into the Solute, or Associating Body, as evidenced by changes in the Apparent Molecular Weight of the Same.

2. The Effect of Substitution of Radicals of varying E.S.A. into the Solvent, or Associating Medium, as evidenced by changes in the Apparent Molecular Weight of the Solute.
3. Application of the Theory to Related Phenomena in Organic Chemistry.

PART ONE

The Effect of Substitution of Radicals of Varying
Electron-Sharing Abilities into the Solute,
or Associating Body, as Evidenced by
Changes in the Apparent Molecular
Weight of the Same

Foreword

The knowledge that association of elements and compounds may occur in both the vapor and dissolved states was born almost as soon as methods were devised for measuring the molecular status of materials in these states. Thus Dumas, Mitscherlich, Meyer, Biltz, Pettersson and others collected data concerning the metals, non-metals, salts and oxides which showed the above mentioned phenomenon taking place in the vapor state while Raoult, Beckmann, Paterno, Auners, Vant Hoff and others developed the theories and collected the data that form the basis for our modern knowledge of association of organic compounds in solution.

In studying the collected data that were available Turner (60) came to the conclusion that the tendency toward association of an organic compound in solution is dependent upon the presence of certain electronegative groups such as:

-OH, -CONH₂, -COOH, -NOH, -CN, -SH, -CSNH, -CSOH, -NH₂, -NO, -CHO

The associating power of these groups drops off very rapidly in the order given, measurable association not usually occurring past the -NH₂ group.

It is not difficult to see the importance of the role played by hydrogen and especially hydrogen attached to oxygen in this series. Indeed the

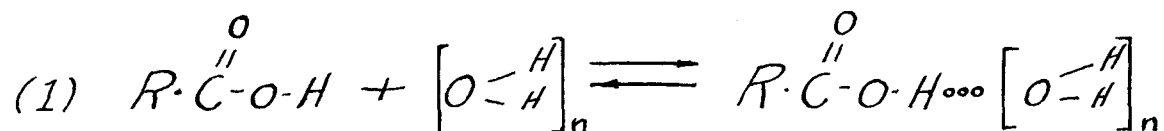
most modern manner in which to consider association is to consider it as being due to the formation of 2 - covalent hydrogen bridges or bonds between the associating molecules. This type of bond is by no means new having been first suggested by Latimer and Rodebush (38) in 1920, nor is it confined alone to association phenomena. The formation of such a bond within a single molecule is termed "chelation", while a still more common example is afforded us by hydration.

In this, the first section of the report, it is meant to investigate the variations in the ability of the hydrogens, in several of the above-mentioned electronegative groups, to form such bonds (and cause association) as radicals of different E.S.A. are attached in turn to the associating group.

Theory

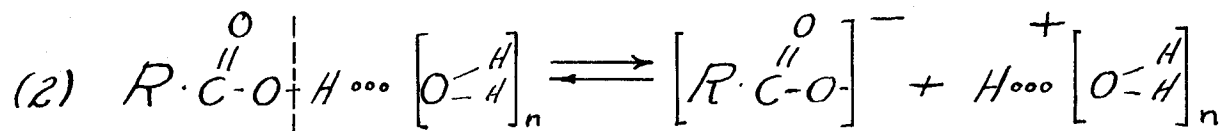
It is by applying the idea of hydrogen bridges that we are able to predict a relationship between the associating tendency of a compound and the E.S.A. of the radicals attached to the associating group of the compound. This can be done by considering the probable mechanism of the ionization of organic acids in water from the standpoint of E.S.A., bearing in mind that the same arguments apply to alcohols and amines.

It is extremely likely that the first reaction that occurs in such instances is the hydration of the dissolved acid by the formation of just such a bond as has been mentioned. This may be represented by the following equation (1) in which the dotted line represents the hydrogen bond:



This step would take place as soon as solution occurred and is not restricted to water solutions, but also happens in other solvents such as alcohols, ethers, ketones, esters, aldehydes, etc., which contain an oxygen to which the hydrogen of the acid may be attached. The properties of such a compound dissolved in such solvents are obviously those of the solvated or complex molecule.*

In the case of such a solvent as water which has a very high dielectric constant, a further reaction might be expected to occur on the basis of Coulomb's law. This is the weakening or even scission of all essentially ionic bonds in the molecule to give oppositely charged ions, and in the case of carboxylic acids in water (also alcohols and amines to a smaller extent) such ionization does occur and the negatively charged organic radical and the hydrated proton, or hydrogen ion are formed as shown by the following equation (2):

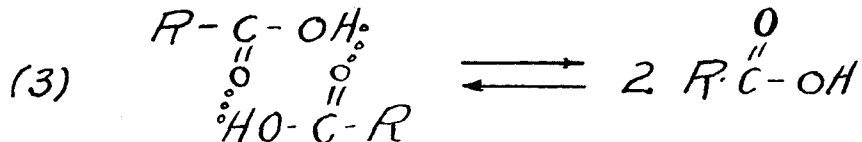


It must be obvious that for the same solvent, the difference in the ionization or completeness of equation (2) of a series of acids will depend only upon the relative ionic or covalent nature of the original O-H bond of the acid. For a series of acids of the same structure this will depend only upon the nature and properties of the radical attached to the carboxylic group. As indicated before, if the radical has a high negative value of E.S.A. (example CH₃-) the bond in question will tend toward the covalent type and but little ionization will occur, while a radical of high positive value of

* A comprehensive list of references covering this subject is given by Fricke (26).

E.S.A. (example CCl_3^-) will result in an ionic bond and strong ionization will occur.

If on the other hand the solvent in which the acid is dissolved is one (such as benzene or hexane) with which there is no opportunity for the formation of solvated complexes as shown in equation (1), two molecules of the acid will combine with each other by the formation of two hydrogen bridges as shown in equation (3):

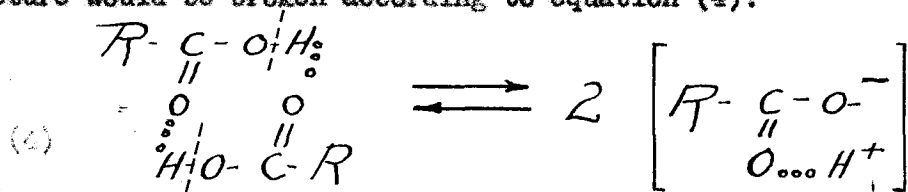


This is "association" and the structure for the complex molecule is known to be correct, in the case of the formic acid complex at least, by virtue of the investigation of the electron diffraction pattern of formic acid vapor as carried out by Pauling and Brockway (47). The fact that the upper limit of association of these acids in solution appears to be close to two is also argument for the double molecule postulated.*

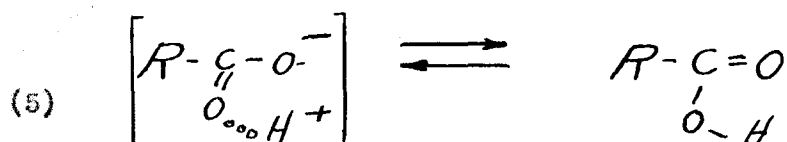
The double molecule of the acid may be seen to contain a ring structure in which the two original O-H bonds are integral parts. Therefore we may say, by the theory of electron-sharing ability, that the substitution of radicals of higher and higher positive values of E.S.A. into the acid considered should change the nature of these O-H bonds more and more into the ionic type until a point would be reached (depending upon the dielectric

* There is no doubt that this formation of double molecules also takes place in a solvent such as water or alcohol, but in these cases since the solvent molecules so far outnumber the solute molecules (in dilute solutions), the tendency is for the solvation reaction to predominate over the association reaction by virtue of mass action. This solvent action will be discussed in greater detail in Section 2 of this paper.

constant of the solvent) at which "ionization" would occur and the ring structure would be broken according to equation (4):



The resulting compound or "ion" would immediately rearrange by a simple shift of electrons to form the original acid (5):



Thus "those radicals which cause high ionization of acids and alcohols in dissociating solvents should cause low association of acids and alcohols in associating solvents and vice versa."

It is the verification of this hypothesis that shall occupy the experimental section of this part of the report. For reasons that shall be discussed with the experimental results the effect postulated should be quite small and such was found to be the case.

Experimental part

Association in vapor. The choice of compounds to investigate with regard to their molecular status in the vapor state was very easy inasmuch as only one type of organic compound is known to be associated under such conditions, i.e., the carboxylic acids. Since the effect to be studied was expected to be quite small, compounds of the type R·COOH in which the radicals show large variations in E.S.A. were desired. The compounds finally chosen are listed in Table No. 1 together with the physical constants to be

used in the calculation of the results. The purities were determined by titrating a weighed sample with barium hydroxide using phenolphthalein as an indicator. It will be noticed that the dichloro-acetic acid has a high neutralization factor indicating that a small amount of the monochloro derivative is present. The electron-sharing abilities of the various radicals concerned were taken from the original paper by Hixon and Johns (30).

The apparatus used is shown by diagram No. 1. The principle involved is in the measurement of the pressure developed by a compound when confined in a known volume at known conditions of temperature and concentration. In practice the following procedure was followed. The compound to be investigated was sealed in a small glass bulb and carefully weighed. The fragile tip was then bound tightly with a small piece of strong nichrome wire and the entire assembly placed in the mercury well at the bottom of the barometric leg of the apparatus as shown in detail A of diagram No. 1. The oil bath was then heated to 160 - 170°C. and the air pumped from the standard volume flask and barometric leg by means of a pump attached to the outlet tube of the mercury well. When this pump was removed the atmospheric pressure forced the mercury back up the barometric leg almost to the measuring index of the standard volume flask. By connecting the pressure bottle to the mercury well and applying a small amount of excess pressure the mercury level could be brought to the index, indicating that the entrapped gases (Hg vapor, residual air, etc.) were occupying a volume of 142.22 cc. at the temperature of the oil bath. The excess pressure required to do this was measured (accuracy 0.5 mm.) on the open tube manometer also connected to the pressure bottle. Inasmuch as the total pressure involved in lifting this column of mercury is the sum of the atmospheric and the so-called excess pressure, it was always necessary

TABLE NO. 1

Table showing Physical Properties of the acids investigated

Compound	Formula	Mol Weight (Theory)	Purity	Boiling Point (760 mm)	Dissociation Constant in H ₂ O (25°)	Electron Sharing Ability of Group
n-Butyric	C ₄ H ₇ COOH	88.0	99.4 %	162.5°C	1.5 X 10 ⁻⁵	- 1.45
Acetic	CH ₃ COOH	60.0	99.95%	118°C	1.8 X 10 ⁻⁵	- 1.40
Benzoic	C ₆ H ₅ COOH	122.0	99.99%	249.2°C	6.6 X 10 ⁻⁵	4.2
Monochloro-Acetic	CH ₂ ClCOOH	94.5	99.87%	186°C	155 X 10 ⁻⁵	6.7
Dichloro-Acetic	CHCl ₂ COOH	128.9	100.8%	191°C	5140 X 10 ⁻⁵	7.7
Trichloro-Acetic	CCl ₃ COOH	163.4	99.92%	195°C	121,000 X 10 ⁻⁵	8.4

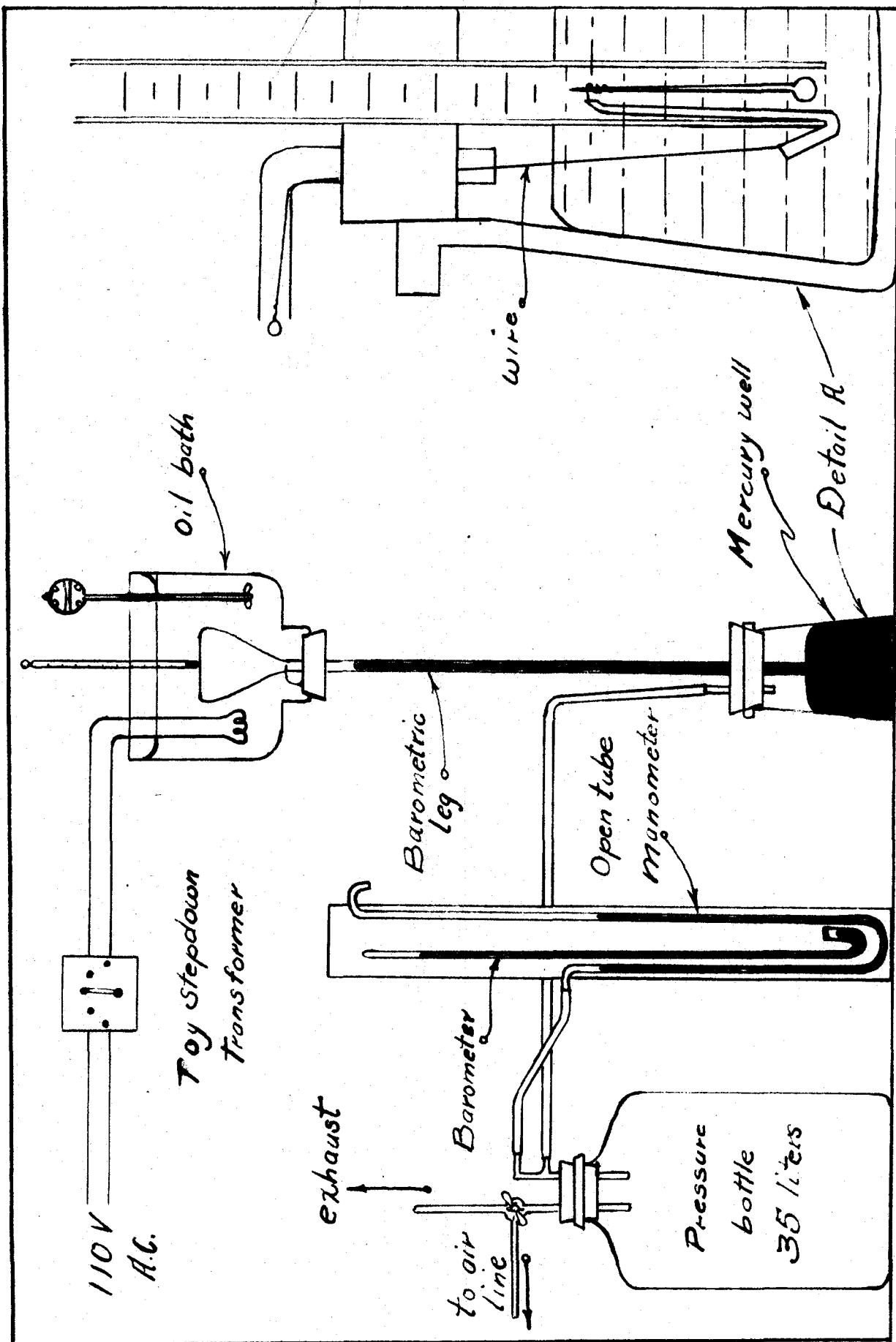


Diagram No 1 Apparatus for Measuring Vapor Densities.

to read the barometric pressure after each reading so that possible changes in this supposedly constant factor could be made. By this procedure the pressure of the residual gas in the flask was measured over the range of temperatures desired. The transformer which supplied the current to the heating unit was tapped in 2-volt stages over the range 0 to 30 volts so by the judicious choice of the available taps the temperature of the oil bath could be held at the temperature desired (accuracy 0.2°C.) for the fifteen-minute periods allowed for temperature equilibrium.

When the preliminary standardization procedure was completed, the pressure tube was removed momentarily from the mercury well and the fine wire attached to the capillary given a sudden sharp pull. The tip was broken and the now-opened capillary ascended rapidly to the top of the mercury column. Immediately sufficient pressure was applied to the apparatus to drive the mercury and sample bulb well above the measuring index until the entire sample had volatilized. This was to avoid all chance of entrapping some of the compound under the mercury along the cooler portions of the barometric leg. As soon as all the compound had volatilized, the pressures exerted by the acid at various temperatures were measured. In Table No. 2 is given a sample of the data received on acetic acid. In calculating the molecular weight of the gas the ordinary gas laws were used. The volume of the standard volume flask was 142.22 cubic centimeters at 25°C. and the correction for volume change of container with temperature was considered too small to be applied. The formula for calculating the equilibrium constant:

$$K_p = \frac{(P-R)760}{(2-R)^2 P_{acid}}$$

can easily be derived from the equilibrium expression:

$$K_p = \frac{P(\text{CH}_3\text{COOH})_2}{[P(\text{CH}_3\text{COOH})]^2}$$

by using the definition:

$$R = \frac{\text{Experimental molecular weight}}{\text{Theoretical molecular weight}}$$

The results have been put into graphical form on graph No. 1 in order that the quality of the agreement may be seen. From the slope of the line the heat absorbed at constant volume by the reaction under consideration has been calculated and found to be about -15,700 calories. This value has been determined several times before, once by Fenton and Garner (25) who obtained -13,790 calories and once by MacDougal (40) who obtained -15,800.

The other compounds in the chosen series were measured in the same way. Due to the fact that they are all less volatile than acetic acid, correspondingly smaller samples must be used and accordingly less accurate results were obtained. To show the worst of this the data obtained with two runs made with trichloro-acetic acid are given in Table No. 3. As may be seen the results are very close to the theoretical so it may be safely asserted that no measurable association occurred. However, since the temperatures were higher and the pressures were lower (both factors tending to reduce association) our results do not have the same order of accuracy that they had in the case of acetic acid. If we allow that the accuracy of the results is certain within two molecular weight units we would have:

$$R = \frac{165.4}{163.4} = 1.012$$

and

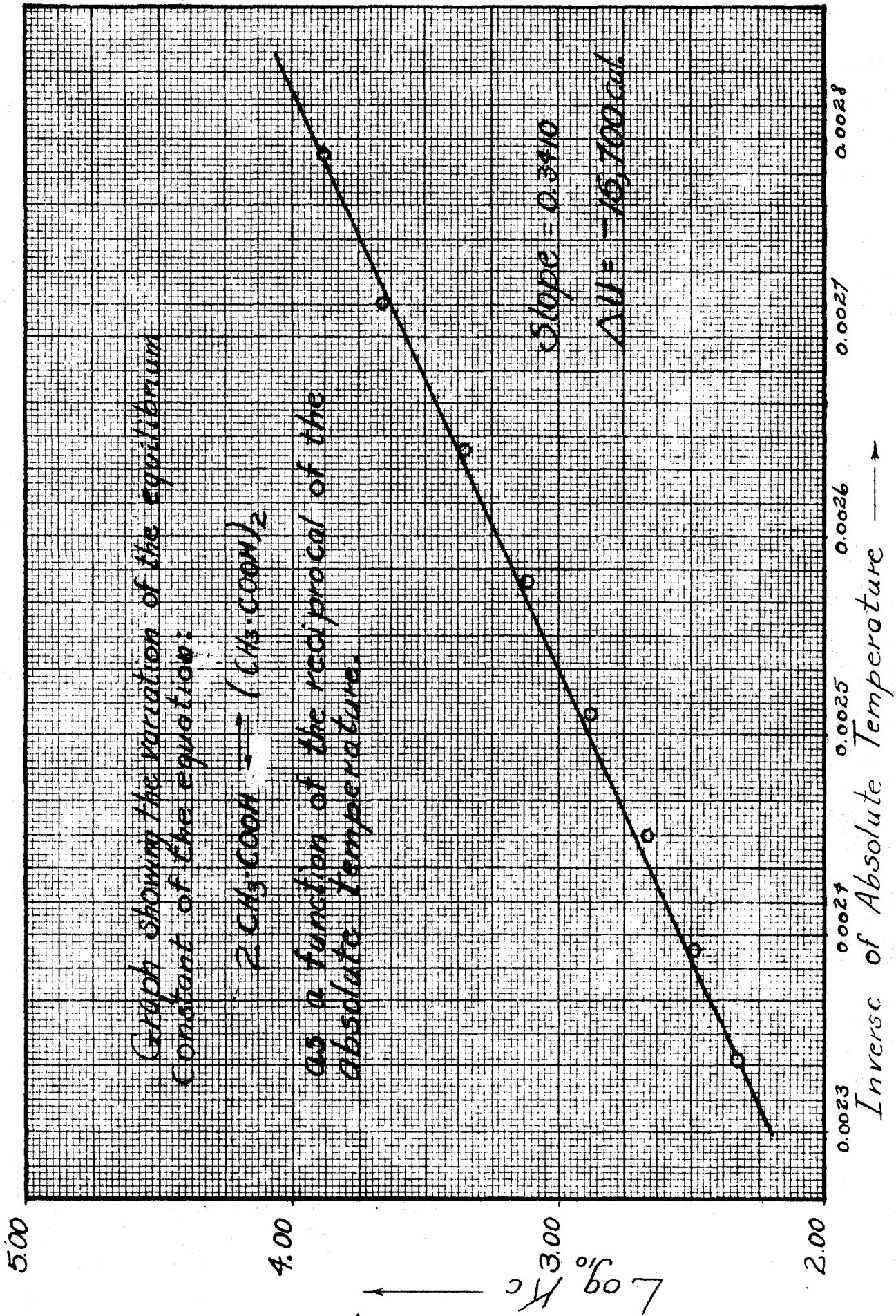
$$K_p = \frac{(.012)}{(.988)^2} \frac{760}{50} = 0.187$$

TABLE NO. 2

Molecular Weight of Acetic Acid Vapor as a Function of Temperature
(Theory 60.00)

Temp. of Run °C	Total Pressure Residual Air Compound mm	Pressure of Residual Air mm	Pressure of Compound mm	Calculated Molecular Weight	R <u>Calc.</u> ^{MW} <u>Theory</u> ^{MW}	K _p	K _c	Log ₁₀ K _c
155°C (428°A)	243.2	97.9	145.3	64.17	1.069	0.418	179	2.250
145°C (418°A)	233.6	95.3	138.3	65.90	1.098	0.662	277	2.443
135°C (408°A)	222.8	92.8	130.0	68.55	1.143	1.14	464	2.667
125°C (398°A)	210.9	90.1	120.8	71.90	1.198	1.94	772	2.888
115°C (388°A)	199.1	87.8	111.3	76.05	1.267	3.38	1,312	3.119
105°C (378°A)	187.3	85.2	102.1	80.75	1.345	6.02	2,275	3.357
95°C (368°A)	174.7	82.4	92.3	86.95	1.449	12.2	4,480	3.652
85°C (358°A)	165.9	80.5	85.4	91.50	<u>1.525</u>	20.7	7,410	3.870

(Sample Weight 0.04960 gram or 0.000827 mol.)



Graph No I

TABLE NO. 3

Molecular Weight of Trichloroacetic Acid in the Vapor
State as a Function of Temperature

Temp. of Determination °C	Run No. 1		Run No. 2	
	Pressure of Acid	Calculated Molecular Weight	Pressure of Acid	Calculated Molecular Weight
170	50.7 mm	161	--	--
165	49.9 mm	162	48.7	162
160	50.8 mm	158	47.9	163
155	48.5 mm	163	47.6	162
150	48.2 mm	162	47.5	160
145	47.9 mm	161.5	46.4	162
140	condensed		45.6	163
	Sample	0.04190 grams 0.000256 mol.	Sample	0.0408 grams 0.000250 mol.

Thus the association constant of trichloro-acetic acid may well be as large as 0.19 for any temperature between 140° and 170°C. as far as the author's results are concerned.

The other acids measured showed appreciable association as is shown by the data in Table No. 4. Benzoic acid is omitted from this table because no consistent results could be obtained owing to its low vapor pressures at the highest temperatures possible with the apparatus. Indications are, however, that it is only slightly less associated than is acetic acid at the same temperature.

The association constants contained in Table No. 4 are arranged in graphical form on graph No. 2 whereby it may be seen that the prediction made in an earlier portion of this paper has been upheld by experiment, for as the electron-sharing ability of the substituted radical does increase so does the association of the corresponding acid decrease.

Inasmuch as the ratio of the dissociation constants in water of the two acids chloro-acetic and acetic is:

$$\frac{K_{ion}^{25^{\circ}} (CH_2Cl \cdot COOH)}{K_{ion}^{25^{\circ}} (CH_3 \cdot COOH)} = \frac{155 \times 10^{-5}}{1.8 \times 10^{-5}} = 86$$

while the ratio of the dissociation constants ($\frac{1}{K_p}$) of the double molecules of the same two acids in the vapor phase is:

$$\frac{K_{diss}^{135^{\circ}} (CH_2Cl \cdot COOH)}{K_{diss}^{135^{\circ}} (CH_3 \cdot COOH)} = \frac{(\frac{1}{1.74})}{(\frac{1}{1.14})} = 1.5$$

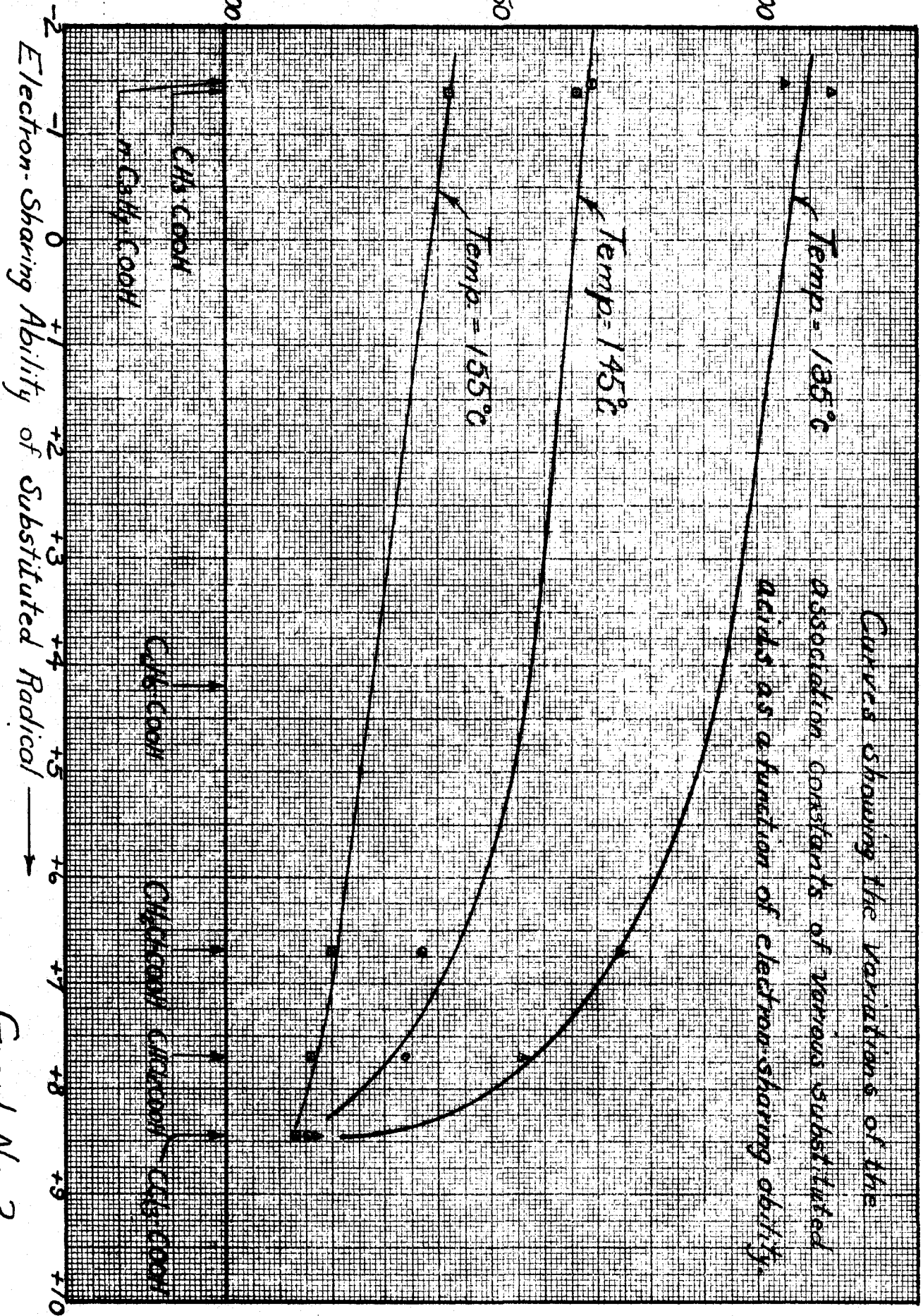
the smaller effect of variation of E.S.A. in the substituted radical in the second place can be realized. It is interesting to speculate as to the probable reason for this and also why the carboxylic acids are the only type of

TABLE NO. 4

The Association Constants (K_p) of various Substituted Acetic Acids in the Vapor State as a function of Temperature

Temp. °C	Butyric Acid C_3H_7COOH	Acetic Acid CH_3COOH	Monochloro- Acetic Acid $CH_2ClCOOH$	Dichloroacetic Acid $CHCl_2COOH$	Trichloro- Acetic Acid CCl_3COOH
160					
155		0.418	0.20	0.16	
150					
145	0.690	0.662	0.37	0.34	(0.18) ?
140					
135	1.05	1.14	0.74	0.56	
130					
125	1.90	1.94	--	--	--

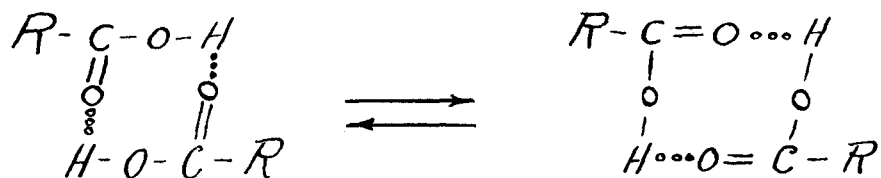
Association Constant (K_a) of Substituted Acid →



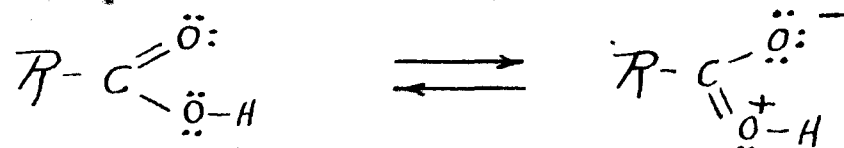
Graph No 2

organic molecules to be associated in the vapor state.* Since the vapor densities of alcohols, and of mixtures of alcohols with ketones, with ethers, and with esters are known to be normal, the presence of an OH with a group of the type C=O, or C-O-C, or C-O-R cannot be responsible for the association of the carboxylic acids.

If we examine closely the structure of the double acid complex, we may note that the following equilibrium may be written on the basis of an electronic shift:



This is "resonance" and it is well known from the work of Pauling and his collaborators the importance of this type of equilibrium in stabilizing a molecule. The contribution to the stability of the single molecule of the type R COOH by resonance between the structures:



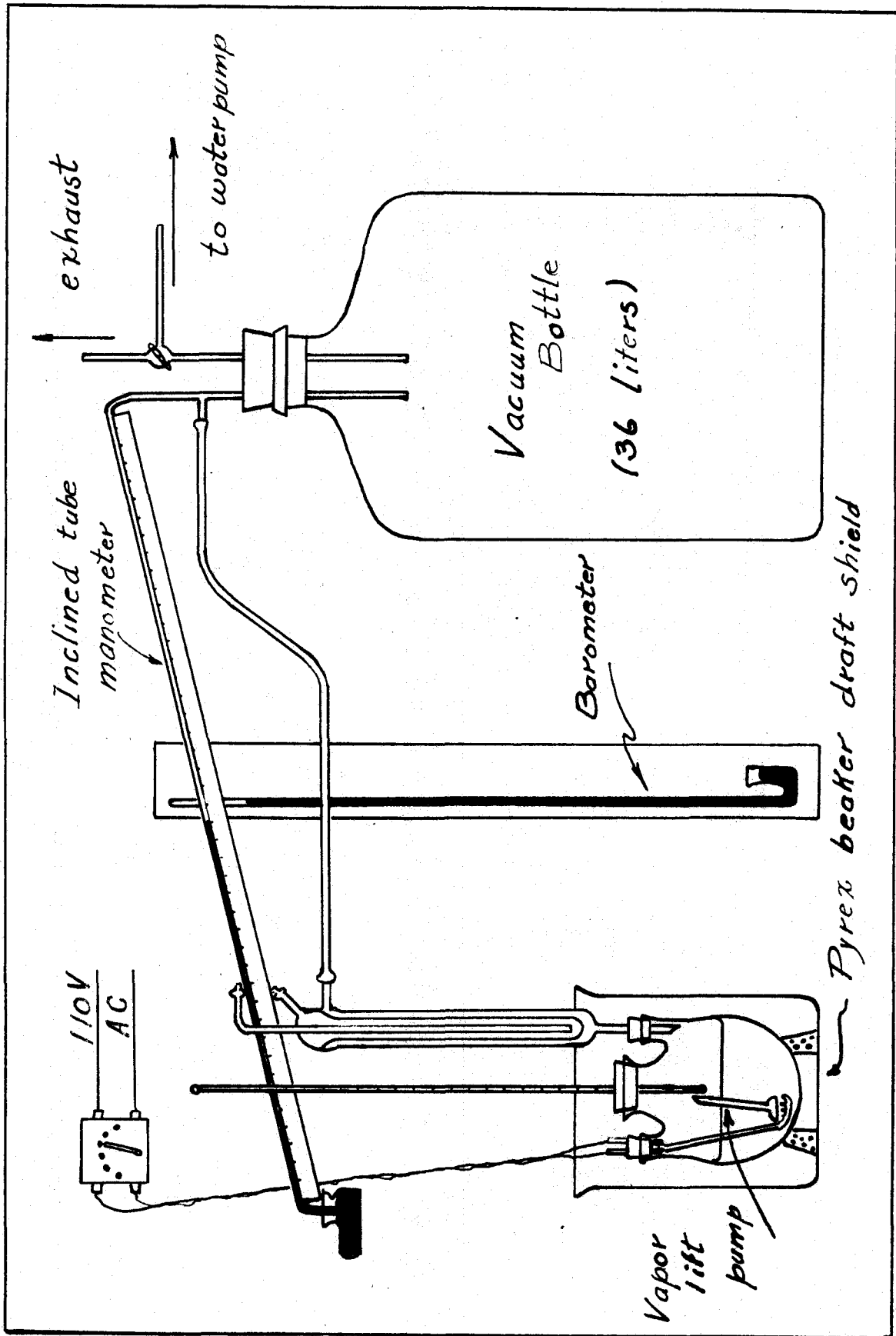
has been estimated from thermochemical data and found to be of the order of 27,000 calories (48), so the contribution to the stability is quite large. Inasmuch as complete resonance (i.e. formation of identical structures) can readily be obtained in the case of the double molecule and can only be obtained in the case of the single molecule with 100% ionization, the double molecule should have energy of stabilization over and above that of the single molecule. This is the basis for the statement made several times previously

* Schulze (54) concluded from his experiments that nitrobenzene might be slightly associated under such conditions.

that the effect of substitution should be less in the case of association than in the case of ionization.

Association in solution by ebullioscopic and cryoscopic methods. The choice of possible compounds to investigate in solution was much greater than was the case in the vapor phase problem since many classes of compounds are known to be associated under such conditions. However, the same series of acids used before was still available and so was also used for this section of the work. The choice of solvent was also to be decided and this proved to be somewhat of a problem. In solvents such as benzene, toluene, naphthalene, chloroform, carbon disulfide, ethylene dibromide, chlorobenzenes, chlorotoluenes (17), etc., in which there is no opportunity for the formation of a solvated complex, the carboxylic acids of all types are known to be practically 100% associated to the double molecule at even low concentrations. It has been shown, however, that even in these solutions normal molecular weights and weights approaching the normal may be obtained if sufficiently dilute solutions are used (50). The apparatus available to the author required a more concentrated mixture to give accurate results so a solvent, in which the carboxylic acids were only slightly associated at medium concentrations, was desired. Such a solvent was found to be ethyl ether in which Beckmann (12) determined the molecular weight of benzoic acid to be 134.5 at a temperature of 34°C. and a concentration of 1.8 normal.

The method adopted by the author for this investigation used an apparatus with which the difference in pressure, that would cause a solution and solvent to boil at the same temperature, could be measured. This apparatus is shown on diagram No. 2. The ether or ethereal solution was contained in the three-neck flask and boiled at a constant rate (as indicated by drops from



Apparatus for Measuring the Vapor Pressure of Solutions. Diagram No 2

the condenser tip), the boiling temperature being governed by the pressure above the liquid in the flask. This pressure, or rather vacuum, was measured accurately by means of the inclined tube manometer shown, with which an accuracy of $1/20$ mm. could be obtained. As before it was necessary to read the barometer at the beginning and end of each run and make corrections for any change in atmospheric pressure. The actual temperature of ebullition was given by the tenth degree thermometer over the bulb of which the boiling liquid was pumped by the vapor lift pump. With the apparatus as shown it was possible to boil ether for six hours at a time without a change of over 0.01°C . occurring in the boiling point, if corrections were made for the changes of atmospheric pressure occurring during that interval.

The actual procedure used in making a run was as follows: the round bottom flask was disconnected from the condenser and transformer, cleaned and weighed to 0.1 gram on a sensitive pan balance. About 200 - 250 grams of anhydrous ether were then added and weighed to 0.1 gram. The flask was again connected to the rest of the apparatus and the ether boiled at atmospheric pressure and at the standard rate for 30 minutes to expel all dissolved gases. The pressure was then gradually lowered until the ether was boiling at a temperature of about 19.5°C . This was done slowly and with a good circulation of water through the condenser to prevent the loss of ether. After boiling at 19.5°C . for about 10 minutes to insure that temperature equilibrium had been obtained, the pressure was gradually raised until a boiling point of 19.95°C . (approx.) was reached. From then on the "natural leak" of the apparatus was allowed to increase the pressure and hence the boiling point. Due to the large volume of the vacuum bottle, this change in pressure was very slow and a period of from ten to fifteen minutes was always required for

the boiling point of the ether to ascend from 19.97°C. to 20.00°C. As soon as the 20-degree mark was reached the inclined manometer and the barometer were read. In the same way determinations were made at various temperatures up to the boiling point of ether at atmospheric pressure. The ether was then cooled below room temperature, the condenser momentarily removed and an accurately weighed quantity of the material to be investigated added to the ether. The condenser was then replaced and the vapor pressure of the solution determined at various temperatures exactly as before. At the end of a run, the round bottom flask was weighed to determine the loss of ether. This loss usually amounted to about half a gram.

The method was checked with naphthalene which is known to exhibit normal molecular behavior in such a solution. The data obtained are given on the following page by which one may see the excellent agreement obtained. The molecular weights were calculated by use of the simple Raoult formula:

$$\frac{dP}{P_0} = \text{mol fraction (solute)}$$

Several sources of error may be pointed out in the method and calculations employed. It may readily be seen that the ability to obtain checks will not depend on how exactly the boiling temperature can be determined but rather on how accurately the solution and pure solvent can be made to boil at the same temperature. The thermometer used had a spacing of about 1 mm. between tenth degree graduations so it was possible by means of a magnifying eyepiece to observe to within 0.005°C. when the mercury thread was exactly at the half-way point of the lines indicating the even degree and half-degree marks. However, as is usual with thermometers of such a fine bore and large bulbs, the device had an appreciable pressure coefficient, that is, changes

DATA SHEET NO. 1

Weight ether — 215.5 gram — 2.912 mol
Weight naphthalene — 20.00 gram — 0.1562 mol

$$\text{Calculated mol fraction} = \frac{0.1562}{2.912} = 0.0508$$

Run No.	Temperature of Run	Vapor Pressure of Pure Ether	dP for Solution	Determined Mol Fraction
1	20.00	440.8 mm	- 22.41 mm	0.0508
2	22.50	487.1 mm	- 24.65 mm	0.0506
3	25.00	537.0 mm	- 27.10 mm	0.0505
4	27.50	591.3 mm	- 29.99 mm	0.0506
5	30.00	652.1 mm	- 33.92 mm	0.0519
6	32.50	713.3 mm	- 36.20 mm	0.0508

Calculations

Run	Molecular Wgt.
1	128.0
2	128.7
3	128.9
4	128.7
5	
6	<u>128.0</u>
	128.5

in the pressure of the atmosphere surrounding the bulb are able to produce changes in the zero point of the instrument. Inasmuch as the pure solvent and the solution when boiling at the same temperature were necessarily at different pressures, the error introduced by this pressure coefficient may be seen. The magnitude of this error was determined in the following manner. The pressure coefficient of the thermometer was measured by the Bureau of Standards method as outlined by Reilly and Ræe (53) whereby it was found that 480 mm. of mercury would raise the zero point 1/10 degree centigrade. Hence the solvent and solution employed in run No. 6 (32.50°C.) while apparently at the same temperature, due to the pressure difference of 36.2 mm., the one boiling at the lower pressure (i.e. the solution) was necessarily about 0.008 - 0.009 above 32.500°C. This is equivalent to about 0.2 mm. in pressure, also too high, and so the true dP for this run would be larger, or about 36.40. This result would give a molecular weight of about 127.2. On the other hand, if we are to use the more thermodynamically correct expression for Raoult's law:

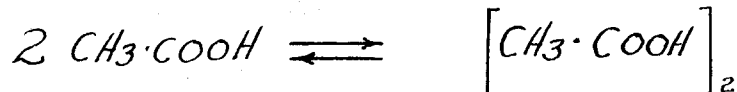
$$\text{Molecular Weight} = \frac{\chi m}{\rho V} / \text{Log}_e \frac{P_0}{P}$$

{	χ = wgt. naphthalene
	ρ = density ether
	V = vol. of solution
	m = mol. wgt. of ether
	P_0 = V.P. of ether
P = V.P. of solution	

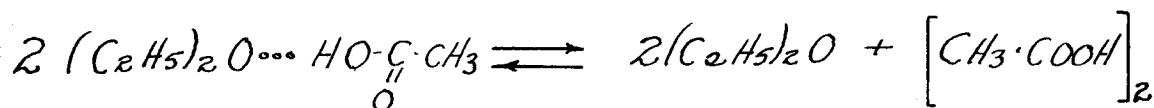
We find that the molecular weight for naphthalene in ether according to run No. 6 is about 129.5. Hence these two errors just about compensate for each other and in making the calculations neither was considered. Probably the interpretation of any molecular weight data, obtained by cryoscopic or ebulliscopic methods, to such a fine degree is unjustifiable because of our lack of knowledge of the liquid state.

The data obtained upon acetic acid solutions using this apparatus and

procedure are given in tabular form in Table No. 5 and in graphical form on graph No. 3. No attempt was made to calculate any equilibrium constants or heats of reaction from these data since the results shown are probably not governed predominantly by any reaction such as this:



but instead by a reaction such as this:



Instead the association indices "R" where R represents the ratio of the measured molecular weight to the theoretical were calculated. These indices are given in Table No. 6 and plotted on graph No. 4 of this report. The data were put into this form for only one concentration, namely 0.05 mol fraction, and the figures used were well rounded values in all cases, for example, trichloro-acetic acid gave R's of about 0.96 to 0.98 at all temperatures and concentrations investigated, so in the table and on the graph the average value of 0.97 (approx.) was used.

A search of the literature revealed that data were available on three of the acids used in this series, namely benzoic, monochloro-acetic, and trichloro-acetic. The results found by Beckmann (12) on benzoic acid have been mentioned before and the approximate agreement may be seen. Raoult (52) determined the vapor pressure of ether from trichloro-acetic acid solutions at 15°C. and obtained normal values indicating no association. The author's results check this within several percent. However, the agreement between the author's values for monochloro-acetic and the the values found by Tollen are not very good. Tollen (59), by the boiling point method, found values of about 90 - 92, while the author found values from 95 - 97, depending upon con-

TABLE NO. 5

Table Showing the Molecular Weight of Acetic Acid in Diethyl Ether as a Function of Temperature and Concentration

Temp. °C	Measured Molecular Wgt.		
	Run No. 1 Mol frac.= 0.025	Run No. 2 Mol frac.= 0.0492	Run No. 3 Mol frac.= 0.0935
20.00	73.0	73	74.2
22.50	71.0	71.8	73.3
25.00	68.5	69.5	72.8
27.50	70.0	70.1	71.9
30.00	69.4	70.1	71.3
32.50	68.4	68.6	71.2

(Theoretical Mol. Wgt. 60.0)

TABLE NO. 6

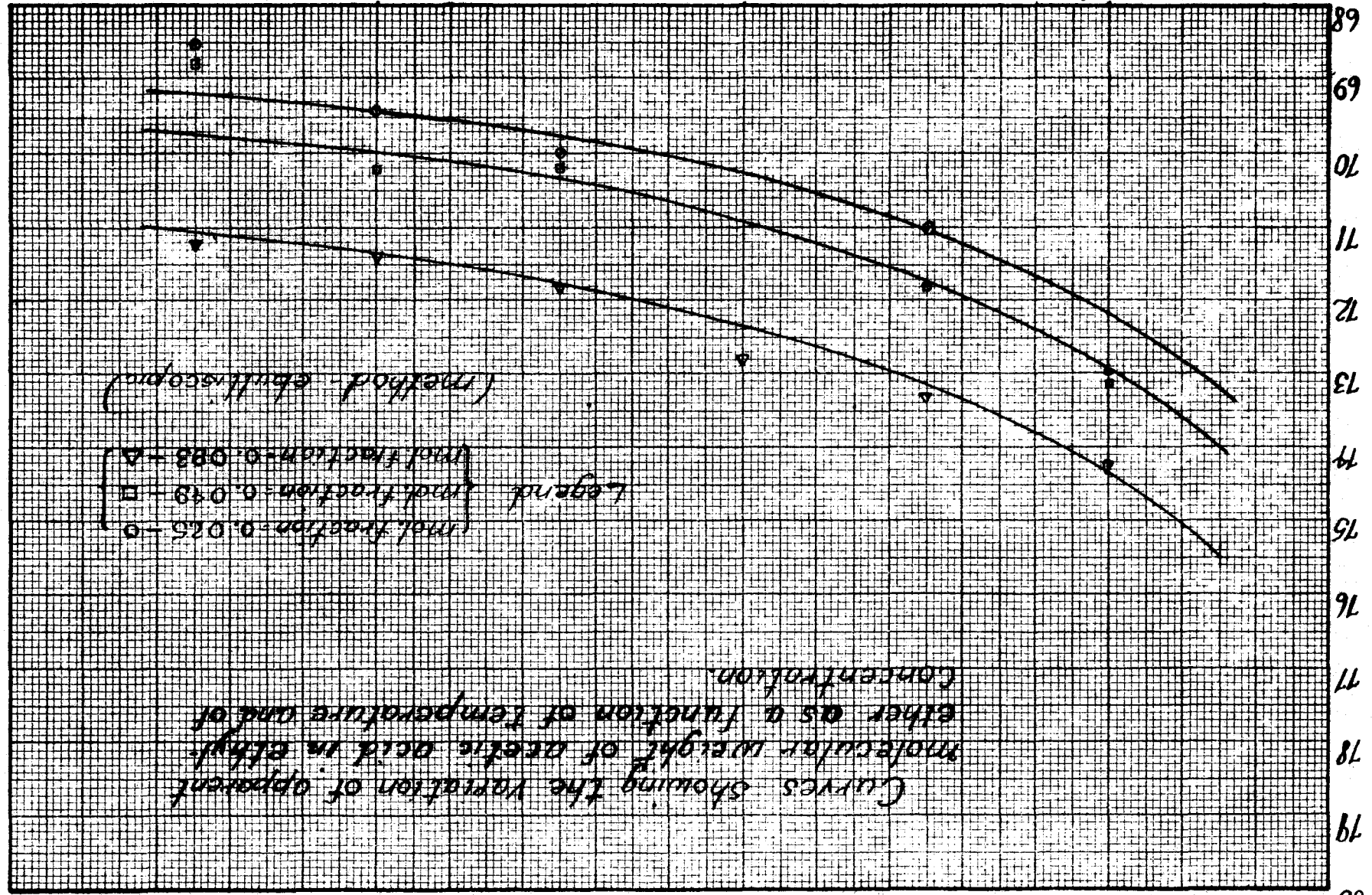
Table Showing the Association Indices of Various Carboxylic Acids as a Function of Temperature

Temp. °C	CH ₃ COOH M.F.=0.0492	C ₆ H ₅ COOH M.F.=0.0492	CH ₂ Cl COOH M.F.=0.0494	CHCl ₂ COOH M.F.=0.0627	CCl ₃ COOH M.F.=0.0512
20.00	1.22	1.10	1.04	0.99	
22.50	1.20	1.10	1.04	0.99	
25.00		1.08	1.02	0.99	0.97
27.50	1.17	1.07	1.01	0.98	
30.00	1.17	1.05	1.01	0.98	
32.50	1.14	1.05	1.005	0.98	

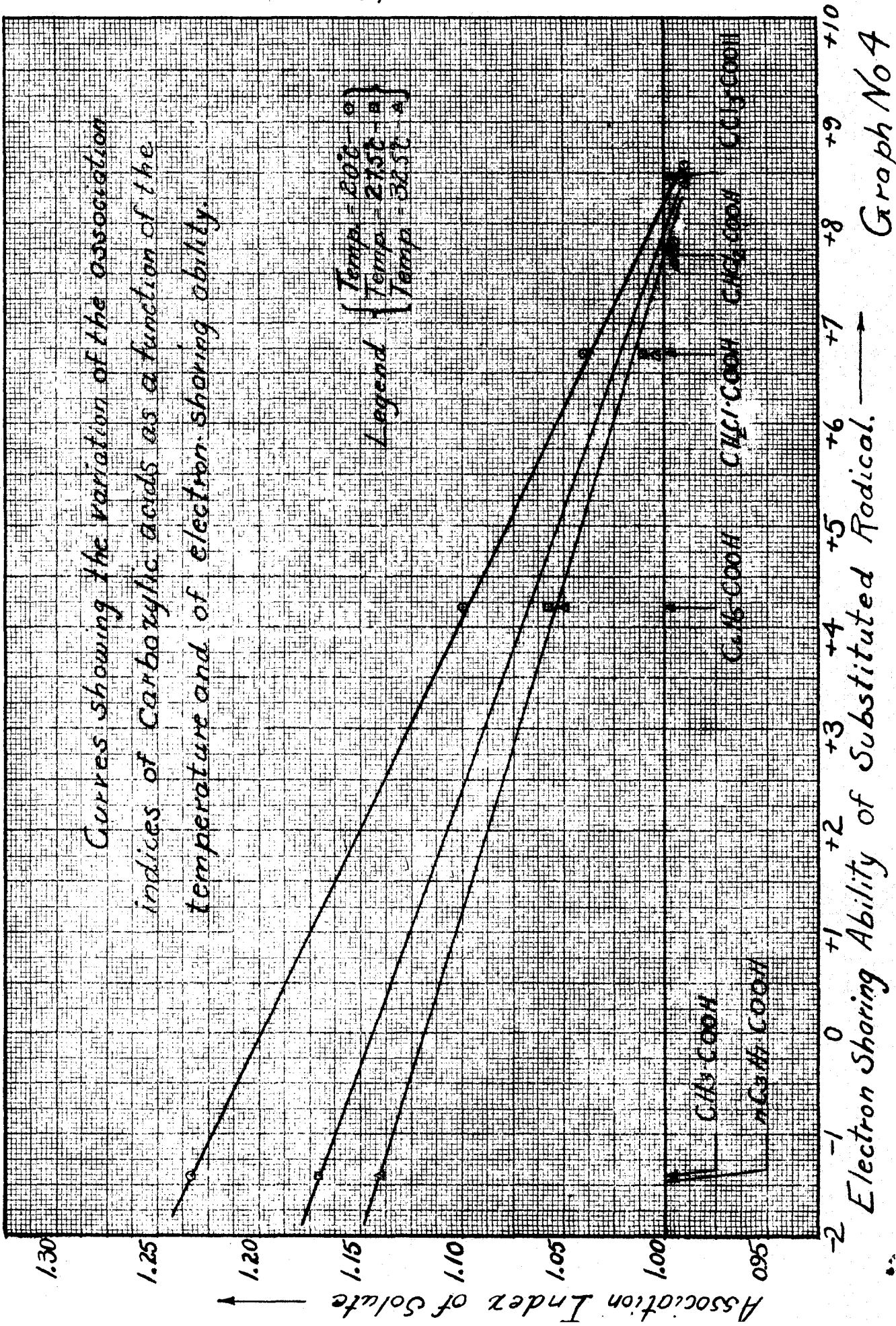
Graph No 3

Temperature of Determination →
 20°C
 25°C
 30°C

Measured Molecular Weight of Solute →



Curves showing the variation of the association indices of Carboxylic acids as a function of the temperature and of electron sharing ability.



Graph No 4

centration. No reason is known for this discrepancy.

Reverting to the graphical summary of the results as given on graph No. 4, it may be seen that again verification has been obtained for the hypothesis that the substitution of radicals of higher E.S.A. into a carboxylic acid should reduce its measured association with respect to the other members of the series.

In addition to the results on ethyl ether, which have been discussed, data were also obtained on the same series of acids using acetone (B.P. 56°C.) and methyl acetate (B.P. 57°C.) as solvents. In methyl acetate, slightly more association was found but curves of the same general type were obtained as in the case of diethyl ether. In acetone absolutely no association could be found, even acetic acid showing a molecular weight about the normal. Evidently the complex between the acetone and the acid molecules is very easily formed and very stable. Factors affecting the stability of these complexes will be discussed in the second section of this paper which deals with this solvent effect.

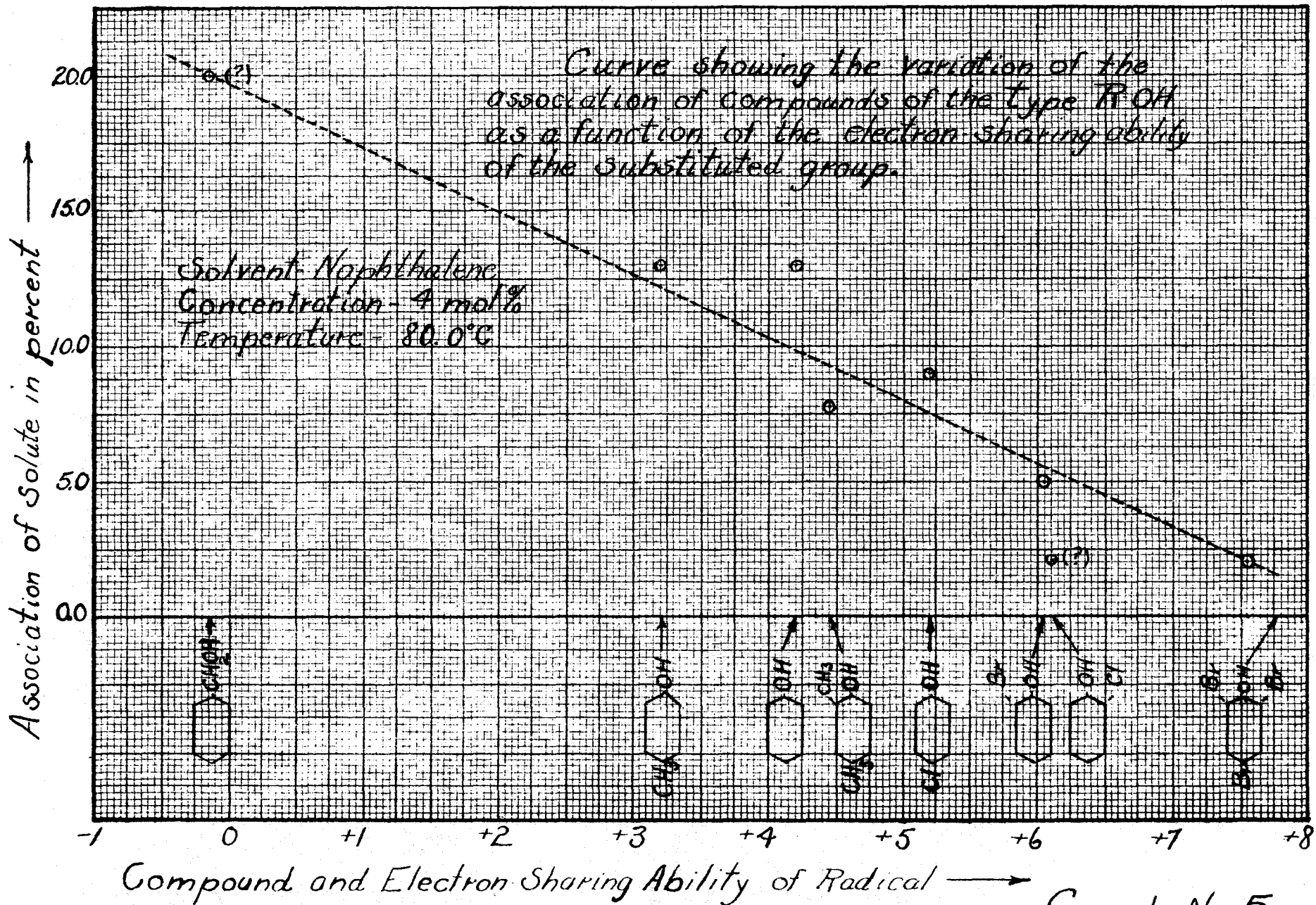
Other series of compounds (than the R·COOH) could be used as the solutes in suitable solvents and presumably the same phenomena would be observed. If this were to be done, it would be necessary to choose for substitution only radicals that contained no groups that could associate or be associated with in order that consistent results be obtained. Inasmuch as there are considerable data in the literature that can be treated in a more or less satisfactory manner by the hypothesis in question, this will be discussed and the remainder of the author's values omitted.

Auwers (2, 3, 4, 5, 6, 7, 8), Biltz (18) and their coworkers completed an enormous amount of work involving the association of organic compounds in

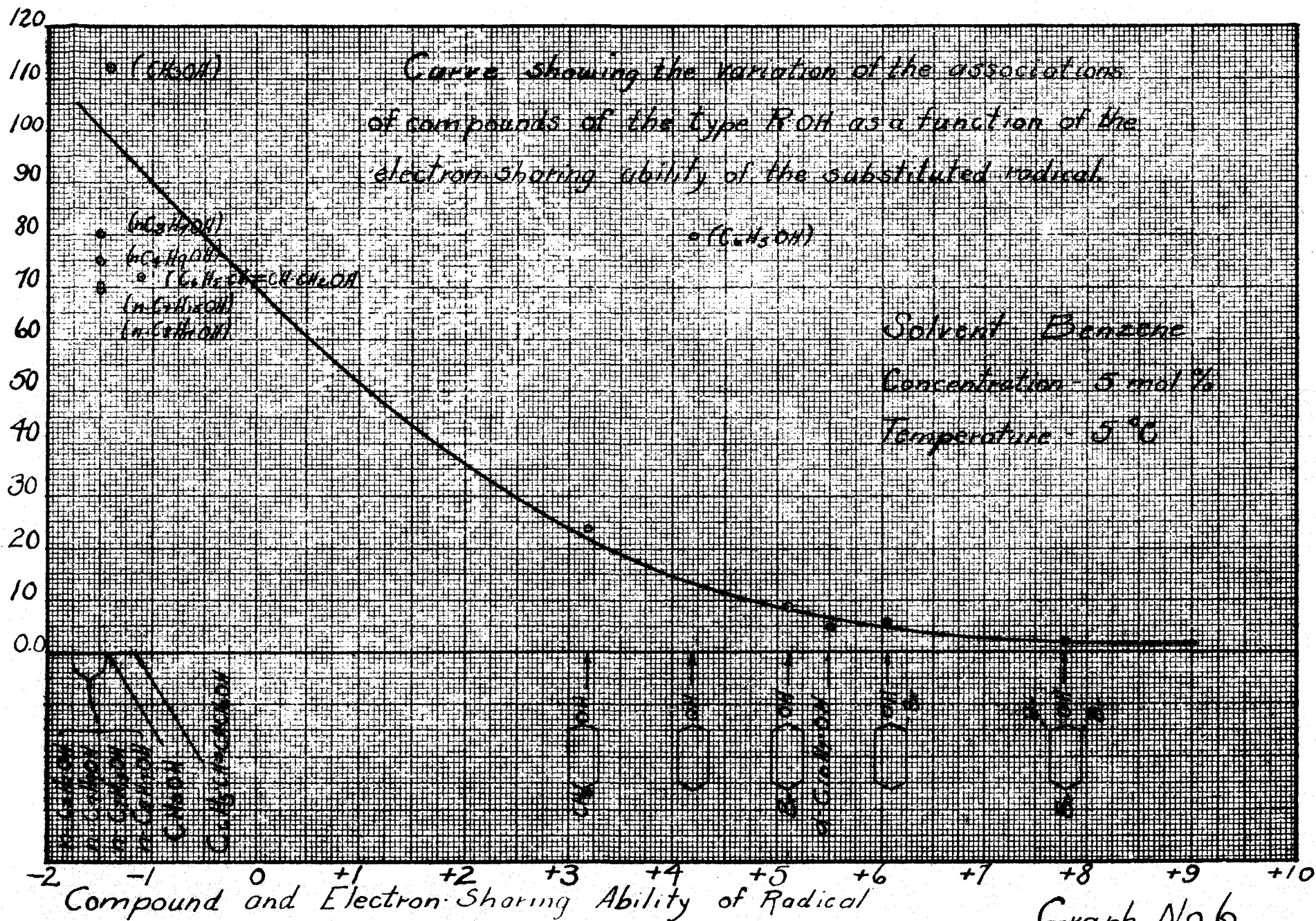
benzene and naphthalene. Some of these compounds, notably the alcohols and phenols, are associated only to a slight extent under such conditions, and hence differences in the E.S.A. of the radicals concerned should be operative in causing measurable differences in association. The results of Auwers have been put into graphical form on graph No. 5 whereby it may be seen that approximate agreement with those postulated is obtained. A search of the literature revealed no examples of molecular weight determinations of the aliphatic alcohols in naphthalene, hence no points for these radicals could be plotted. The slope of the curve is therefore very uncertain which is the reason for its dotted character.

On graph No. 6 are plotted the results found in the literature for the same series in benzene. The agreement with the results postulated is very good with one exception, i.e., phenol. No explanation can be offered for the large discrepancy in this case, although it may be pointed out that the separation of a solid solution instead of the pure solvent, in a cryoscopic determination, always gives results that may be interpreted as association of the solute. The general increase of association of the R-OH series in benzene over that found for the same series in naphthalene is very probably due to the 75°C. difference in the determination temperatures of the two solvents, that of benzene being the lower, and not to any great difference in the solvent action of the two solvents.

An interesting point regarding E.S.A. may be brought out by a discussion of the associations of the aliphatic alcohols. As may be seen from graph No. 6, as the molecular weight and length of the hydrocarbon chain increase, so does the measured association decrease, reaching an asymptotic minimum at about C_7H_{15} or C_8H_{17} . Since the E.S.A.'s of all these radicals are essentially



Graph No 5



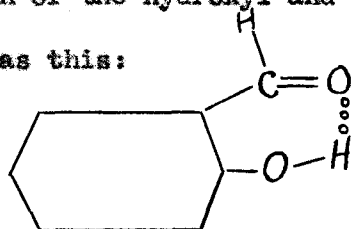
Graph No 6

the same, this behavior is contrary to our hypothesis regarding E.S.A. and association. It is believed that this is the effect of the "steric hindrance factor" of E.S.A. making itself known in an exalted manner due to the close position of the associating group to the substituted radical. A similar effect is not found in the case of the acid series $R\text{COOH}$ where the group is further away. In alcohols containing strongly branched chains such as triethyl carbinol, the effect is still larger while the simplest alcohol possible, i.e., $H-OH$ is the most highly associated of all.

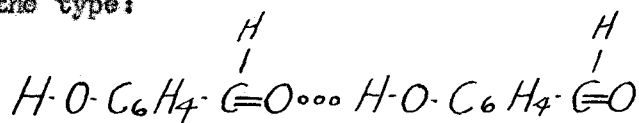
Curves such as those given on graphs Nos. 5 and 6 may be obtained indefinitely with the data available in the literature covering various classes of compounds in various solvents. In all cases investigated by the author, good to fair agreement with the hypothesis was obtained. As mentioned before, care must be taken to choose only radicals that contain no associating groups or groups that may be associated with. An example of the type of result obtained by this sort of error is as follows:

Phenol in naphthalene is associated about 14% at a concentration of 0.04 mol. solute in 100 grams of solvent. *O*-hydroxy benzaldehyde is associated not more than 1% under the same conditions, hence the conclusion might be drawn that the aldehyde group is a group of very large electron-sharing ability. If this were true, then *p*-hydroxy benzaldehyde should also be associated considerably less than 14% because the substitution of a group of large E.S.A. in either the ortho or para position of a phenol cuts down association. However, *p*-hydroxy benzaldehyde associates about 78% at the same concentration as the other compounds. This apparent contradiction can be explained very readily. In the case of the ortho derivative, there is opportunity for the formation of a "chelated" molecule by the establishment of a

bond between the hydrogen of the hydroxyl and oxygen of the aldehydic group to give such a molecule as this:



This type of molecule has been amply confirmed by many workers (55) using divers methods of attack such as absorption spectra, vapor pressure and so forth. Since the hydrogen in such a molecule is already associated, it cannot be used to form doubly covalent bonds with other molecules, hence the low association of *o*-hydroxy benzaldehyde. On the other hand in the *meta* and in the *para* derivatives the hydroxy group is so far removed from the aldehydic group that the possibility of such an intra-molecular bond is excluded on stereochemical grounds. In this case the increase of the molecular complexity of these compounds may be attributed to the formation of molecules of the type:



Thus the effect of the E.S.A. of the radicals concerned has been vastly overshadowed by other effects. This is quite a general happening when groups containing oxygen are substituted in the three positions of the benzene ring of a phenol as may be seen from the data in Table No. 7.

However, the theory of electron-sharing ability can be applied to compounds of this type if we keep the conditions constant except for the radicals substituted. On graph No. 7 are plotted the associations in percent of various organic compounds of the type:

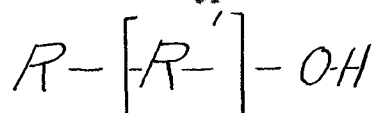
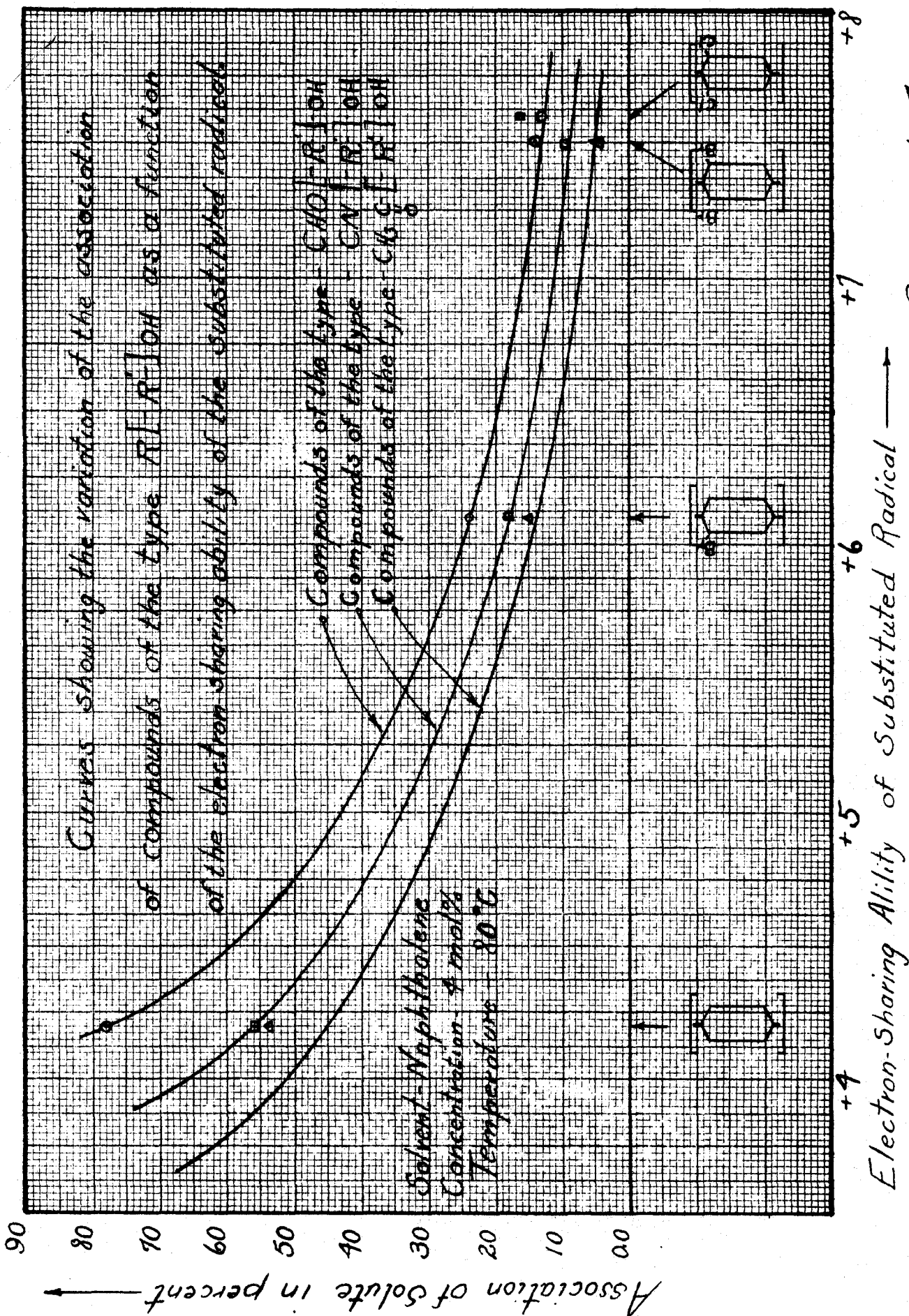


TABLE NO. 7

Associations in percent of Substituted Phenols in Naphthalene (4)

Position of Substituted Radical	Radicals Substituted			Association of Related Compounds Under Same Conditions
	- CHO	- NO ₂	- COOH - CO ₂ CH ₃	
Ortho	1	3	71	C ₆ H ₅ OH 14%
Meta	43	22	150	C ₆ H ₅ CHO 0% (in benzene)
Para	78	27	55	C ₆ H ₅ COOH 78%
				C ₆ H ₅ NO ₂ 1% (in benzene)
				C ₆ H ₅ CO ₂ CH ₃ 0%

Concentration 0.04 mol in 100 gram of Solvent



Graph No 7

as radicals of varying E.S.A.'s are substituted within the parentheses.

By this method of treatment (which gives good correlation) the assumption is made that the E.S.A. of the substituted radical is not changed by the auxiliary group occupying the para position, an assumption that is probably far from the truth. However, the relative order of the radicals would not be changed and this is the important thing in any case.

Discussion of results

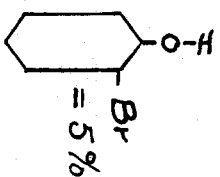
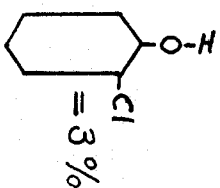
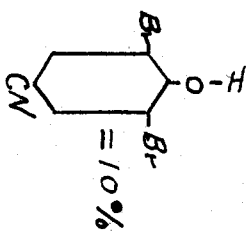
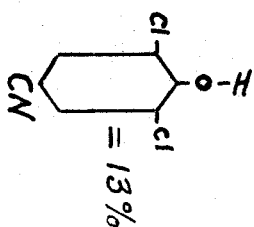
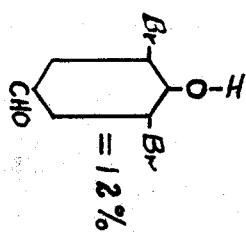
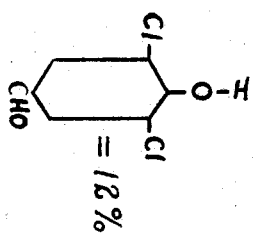
The tables of data and the curves presented in the preceding pages all do show the close relationship between the electron-sharing ability of radicals and the association of compounds containing these radicals. The order and direction of the effect is as predicted by use of the theoretical considerations in the initial pages of this report.

It has also been shown that depending upon the solvent, the solute, and various other factors, the effect sought may be masked by other occurring phenomena of greater magnitudes. In connection with this, the role of steric hindrance in producing the results observed should be considered, for it is true that in the series of radicals being investigated the positive electron-sharing ability and the steric hindrance do increase in approximately the same order. While the fact cannot be denied that a portion of the results could be attributed to steric hindrance, this factor can not be applied in some cases, e.g., the para substituted phenols or the carboxylic acids, and in many others it can be shown to be inoperative. Thus Auwers and Orton (9) found that phenol and ortho-cresol were associated to about the same extent while ortho-chlorophenol was associated scarcely at all under the same conditions. Furthermore, the ortho bromophenol was associated slightly more than the chloro derivative. These facts are easily explained by the hypoth-

esis of electron-sharing ability, while the steric hindrance of the radicals concerned seems to play but little part. Numerous examples in which the chloro and bromo derivatives have about the same association index may be found in Table No. 8. By steric hindrance the chloro should be more highly combined (i.e., chloro is smaller group), while by electron-sharing ability they should be about the same and this is what is found to be the truth of the matter. Since the iodo derivatives are found to be less associated than the chloro or bromo analogues in practically every case, it was concluded that in this instance the group had become large enough to bring the steric hindrance factor into play. For this reason no iodo derivatives were considered in the first section of the paper.

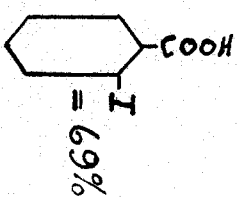
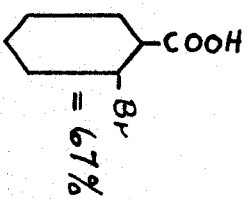
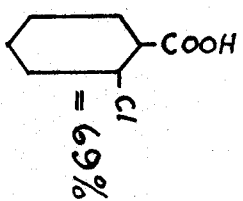
In conclusion it must be emphasized again that the conclusions reached with regard to the carboxylic acids and the alcohols apply also to all other classes of associating compounds in which the formation of doubly covalent hydrogen bonds is the modus operandi. Data are not so numerous for these cases although fair correlation can be shown for the primary amines and oximes. In connection with these the work of Hunter (31) in establishing the fact that hydrogen is necessary for association should be mentioned.

Table No 8



Association of similar Chloro- and Bromo-derivatives in Naphthalene.

(Method = Cryoscopic)
Temperature = 80°C



(Concentration = 0.04 Mol in 100g.)

PART TWO

The Effect of Substitution of Radicals of Varying Electron-Sharing Ability in the Solvent as Evidenced by Changes in the Apparent Molecular Weight of the Solute

Foreword

The effect of the choice of solvent upon the association of the solute is very great. For nearly every associating body a range of solvents (and concentrations) can be found that will take the solute from a molecular status of several times normal to one that is normal or even less than normal. This does not seem illogical considering the very great concentration of the solvent molecules with respect to the solute and the intimate action that is known to exist between the solvent and solute in many cases.

Such a variation in properties has attracted the attention of many researchers and various ideas and theories have been advanced to explain the observable phenomena. The most widely accepted of these is one that would correlate the "associating power" of a solvent upon a solute with the dielectric constant or specific inductive capacity of the solvent, the relationship being an inverse one. This theory has had fair success in explaining solvent action and is apparently on a firm theoretical basis. However, the author would like to show that in the light of the more modern theories of valency the theoretical foundation is really rather unsound and to show that the facts available can be explained more simply and with better results by viewing the problem in the light of "Electron-Sharing Ability."

Theory

The present theory of solvent effect upon association has the same theoretical background as the theory covering the solvent effect upon dissociation, in fact the first-mentioned theory was derived by analogy and comparison with the second. Let us then, consider the hypothesis covering the solvent action upon dissociation of the solute.

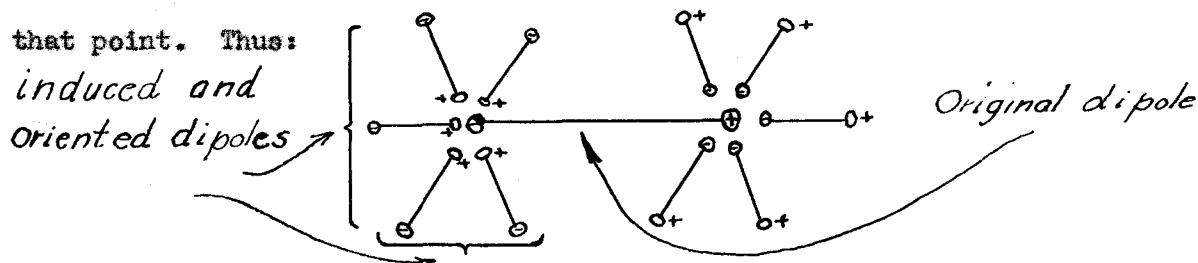
There is a law, known as Coulombs law, that gives us the attraction or repulsion of two charges "a₁" and "a₂" separated by a distance "d" in a medium of dielectric constant "D":

$$F = \frac{1}{D} \left(\frac{a_1 a_2}{d} \right)$$

$$\left\{ \begin{array}{l} F = \text{force in dynes} \\ d = \text{distance incm.} \\ a_1, a_2 = \text{charges in E.S.U.} \\ D = \text{dielectric constant} \end{array} \right.$$

Thus, because of the inverse relationship of "D" to "F" in a medium of high dielectric constant, the force between the charges is reduced and a smaller external force would be sufficient to separate the charges than would be required to separate the same charges in air.

The mechanism of this behavior is as follows: when a dipole (two charges separated by a small distance) is immersed in a medium of high dielectric constant*, the field produced by the dipole tends to orient the permanent dipoles of the fluid and to produce temporary dipoles each of which are oriented in such a manner that their field is opposite to that of the original dipole at that point. Thus:



* Physically speaking, the possession, by a medium, of a high dielectric con-

The effect of all these induced and oriented dipoles is to reduce the field of the original dipole and since the original charges of that dipole can only exert an attraction through their fields, their attraction for one another is thereby lessened. Hence in a medium in which a field can produce or orient dipoles, an ionic bond (which is an example of such a dipole and has an accompanying field) is the means of its own destruction. In a solvent of high dielectric constant, e.g., one in which a small field is able to produce a large orientation and induced effect, the ionic bond may be so weakened that it practically falls apart and the phenomenon of ionization occurs. This hypothesis which is known as the Nernst-Thompson rule, has been experimentally investigated by many workers, especially Walden (61), and very good agreement between theory and fact has been obtained. Furthermore, the application of the more modern theories of valence and ideas concerning the nature of the ionic bond only strengthen this theory.*

In his investigation of the ionizing power of solvents, Walden also derived an order of radicals, the substitution of which increased the dielectric constant of the solvent in question. This order is:

-I, -Br, -Cl, -F, -NH₂, -CN, -COOH, -CHO, -CO, -NO₂, -OH

and the arrangement is in order of the increasing effect.

Several years previously Anvers derived from experimental data a series of radicals that when substituted in a solvent exerted a "normalizing" influence on the molecular weight of the dissolved solute. This series

stant indicates the presence of permanent dipoles in the medium, or a molecular structure such that an external field is able to stretch the electrical charges of the molecules apart to produce temporary dipoles, or both.

* It should be noted, however, that exceptions can be found (notably in inorganic structure) and the search for the weakening effect on the bond by the use of other experimental methods, such as Raman frequency variations, yield very meager results (62).

is:

-Cl, -Br, -I, -NO₂, -COOR, -CN, -CHO, -NH₂, -COOH, -OH

and the arrangement is again the order of the increasing effect, that is, in solvents containing the OH radical there should be but little association. The similarity of the two series in question is at once apparent and Nernst, Meldrum and Turner (45) all suggested that the dielectric constant of the solvent was probably the controlling factor in the association of the dissolved solute. The following table (No. 9) taken from Turner's book, "Molecular Association" shows the agreement obtained by such a hypothesis. As may be seen, there is rough qualitative agreement in many cases. However, the oxygen containing solvents such as the alcohols, ketones, ethers and so forth show wide divergences from their predicted behavior in numerous instances, and there is an obvious need for a theory or postulate that will give better all around agreement.

Let us return momentarily to the mechanism by which an ionic bond is weakened in a medium of high polarizing ability. If the two charges, positive and negative, in the original dipole can be considered as exchanging places very rapidly, we can see that the oriented and the induced dipoles would also have to reverse their direction just as rapidly in order that the same weakening effect be produced. For a very rapid alternation in the relative position of the charges of the original dipole and hence the same rate of change of the polarizing field of the dipole, the induced and oriented dipoles of the solvent might be expected to lag behind and not keep pace with the change and so the relative weakening effect of the polarization of the solvent would be diminished. This inability of the solvent to keep pace with high frequencies is a well-known effect* and is the explanation of the

* See Smyth for a more detailed account of the effect and the experimental evidence confirming it.

TABLE NO. 9

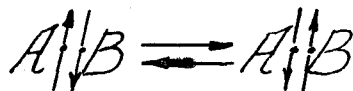
Association of Organic Compounds
in Various Solvents

Concentration 30 milligram mole/100 cc
Dielectric Mol. Wgt.
Constant Benzolic Acid (122)
of Solvents Acetic Acid (60)
Mol. Wgt. Formamide (121)

Solvent	Dielectric Constant	Mol. Wgt.	Association
Water	66	240	157
Ethylene Cyanide	61.2	180	
Nitrobenzene	40.0	280	
m-Dinitrobenzene	20.6	167	
p-Dinitrobenzene	18.4		
Ethyl Alcohol	18.0	125	157
Acetone	17.0	119	117
Sulfur Dioxide	14.0	222	120
Phenol	9.7	133	
Acetic Acid	6.3	129	
p-Formaldehyde	6.4	142	128.5
p-Bromotoluene	5.07		106
Ethylene Dibromide	4.86		118
p-Dibromobenzene	4.57	230	
Bromoforn	4.37		121.8
p-Methyltoluate	4.28	166	
Chloroforn	4.13	214	
Ether	4.12	126	
Naphthalene	3.2	212	
Nitrogen Peroxide	2.5	210	120
Benzene	2.3	236	117
p-Xylene	2.15		213
Cyclohexane	2.07	230	
Carbon Disulphide	2.5	243	135

variation of the dielectric constant of a fluid with the wavelength of the radiation acting upon it.

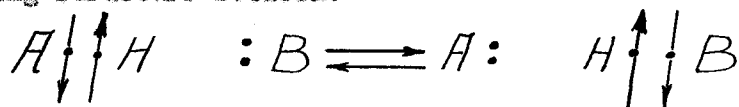
According to quantum mechanics the formation of an ionic bond between two atoms results in the actual transfer of an electron from one atom to the other, the ions thus formed being held together because of coulombic attraction. Such a valence bond does constitute a small dipole and would be expected to have a strength dependent upon the dielectric constant of the fluid in which it was immersed. Sodium chloride is an example of a compound containing an ionic bond and one that does ionize in solvents of sufficiently high polarizability. On the other hand the formation of a covalent bond between two atoms results in the sharing of an orbital electron of negative spin from one atom with an orbital electron of positive spin from the other atom, the energy of bonding between the two atoms being the result of resonance of the molecule between the structures:



where the direction of the arrows indicate the direction of spin of the bonding electrons. In such a bond there is no transfer of charge from one atom to another, or if any such transfer is thought to take place, it must be completely and very rapidly reversed. It is obvious that such a bond will be effected not at all by any solvent effect caused by polarization. The compound methane is an example of a compound containing only covalent bonds and it is well known that this compound shows no evidences of ionic dissociation in solvents of even the highest dielectric constant.

The bond formed by hydrogen upon association is of this second type, that is, if the hydrogen apparently links together two groups or atoms, "A" and "B", we will not be able to say to which atom the hydrogen is really

attached, in fact such a statement has no meaning as the true state of affairs is a resonating structure between:



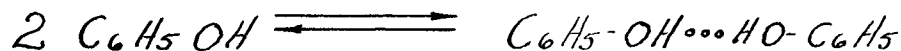
in which the hydrogen is attached momentarily to one and then to the other of the groups concerned. In such a bond or "hydrogen bridge", as in a true covalent bond, any transfer of charge must be very rapidly reversed. Estimates of the rate of this reversal have produced a figure in the order of 10^{15} times a second. The field of any "hydrogen bridge" would then so far outstrip any solvent effect that no solvent could exert any influence on the strength of the bond, speaking from the standpoint of dielectric constant and polarizability. Reference to the data in Table No. 9 will in fact show that solvents such as ether and alcohol are just as effective in preventing association as is water although the constant in question for water is 66 as against 18 for alcohol and 4 for ether.

If the dielectric constant does not have any effect, what then are the characteristics of a solvent that cause it to affect the solute in such a powerful manner? It is the opinion of the author that the chemical structure and composition are the most important factors and these are important only inasmuch as they afford or give opportunity to the solute to form solvated complexes with the solvent.* Several examples of this action will be given.

On graph No. 8 are plotted the associations in naphthalene of phenol and various substituted phenols as a function of concentration. First let us consider the case of phenol itself. If we can assume that at low concen-

* This interpretation of solvent action is not entirely original with the author. Meisenheimer and Dorner (44) as well as Philbrick (51) have previously expressed the belief that the formation of solvated complexes is a big factor in the solvent effect.

tration the association proceeds to the double molecule, we may write the equation:



for which the equilibrium expression and constant are as follows:

$$K_{\text{C}_6\text{H}_5\text{OH}}^{80^\circ} = \frac{C_{(-\text{OH}\cdots\text{HO-})}}{[\text{COH}]^2}$$

$\left\{ \begin{array}{l} K_{\text{C}_6\text{H}_5\text{OH}}^{80^\circ} = \text{association constant of} \\ \text{phenol to double molecule} \\ \text{(C}_{10}\text{H}_8\text{)} \\ C_{(-\text{OH}\cdots\text{HO-})} = \text{concentration of double} \\ \text{molecules of grouping (-OH}\cdots\text{HO-)} \\ \text{COH} = \text{concentration of single mole-} \\ \text{cules containing OH groups} \end{array} \right.$

At a mol percent concentration of 6.0 the experimentally found molecular weight for phenol is 113. This represents an association of 20%, hence 34 molecules of every hundred must have combined to give 17 double molecules.

If we take as our unit of measurement one mol per one hundred grams of solution, the following values of concentrations may be written:

$$C_{(-\text{OH}\cdots\text{HO-})} = (.06 \times .17)$$

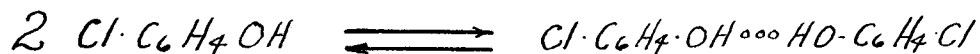
$$C(\text{OH}) = (.06 \times .66)$$

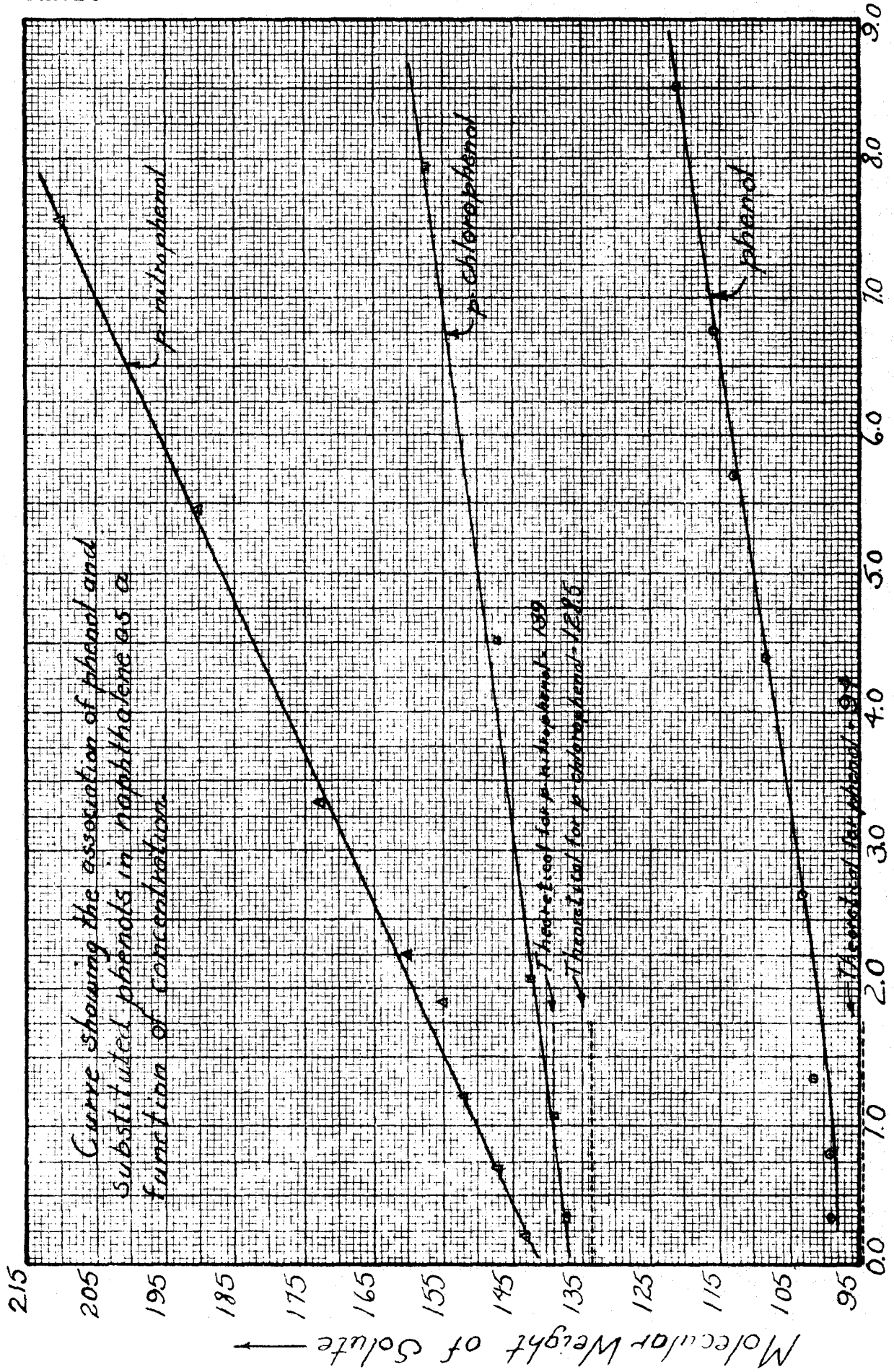
from which by substitution we may obtain:

$$K_{\text{C}_6\text{H}_5\text{OH}}^{80^\circ} = \frac{(0.17)}{(0.06)(0.66)^2} = 6.51$$

In column one of Table No. 10 are given the $K_{\text{C}_6\text{H}_5\text{OH}}^{85}$ calculated for various concentrations. As may be seen the constant varies slightly but is sufficiently constant for our purpose.

If we substitute a group of large electron-sharing ability in the para position of the phenol, the association will be cut down as was shown in part one of this paper, and so we find that para chlorophenol associates only to a molecular weight of 152 at a concentration of 6.0 mol percent. This is association of about 17% and so far the equation:





Concentration of Solute in mol% in 100g. of Solvent → Graph No 8

we would have the following equilibrium expression and constant:

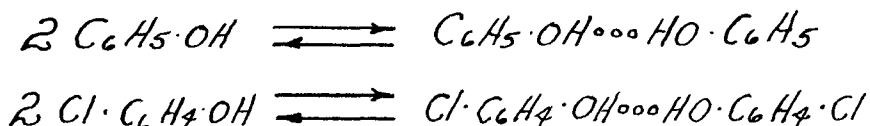
$$K_{Cl-C_6H_4OH}^{80^\circ} = \frac{C_{(Cl-OH \cdots HO-Cl)}}{[C_{Cl-OH}]^2} = \frac{(0.155)}{(0.06)(0.19)^2} = 5.42$$

These constants, calculated for various concentrations, will be found in column 2 of Table No. 10 and as will be noticed, they do indicate that the chloro derivative is less associated than phenol.

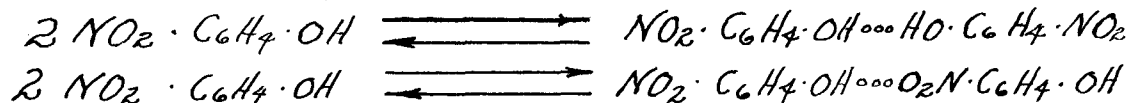
Now if in place of the -Cl group we substitute a group of about the same electron-sharing ability, say the -NO₂ group, we have every reason to believe that the nitro derivative will associate to about the same degree as the chloro and that:

$$K_{Cl-C_6H_4OH}^{80^\circ} = K_{NO_2-C_6H_4OH}^{80^\circ}$$

at the same concentrations. However, by referring to graph No. 8 we may see that at a concentration of 6.0 mol percent, p-nitrophenol has an experimental molecular weight of 196 which represents an association of 41% or about double that of the chloro derivative. As was pointed out in section one of this report, this is because the associating hydrogen is able to form a covalent bond with either an -OH group or a -nitro group and the effect of the additional chances for association has overridden the smaller effect of electron-sharing ability. Thus while phenol and p-chlorophenol can only associate as follows:



p-nitrophenol may form hydrogen bridges in the two following manners:



and the latter equation is the one that is responsible for the exalted association of the nitrophenol. For these two equations we would have two equi-

librium relations and two constants and these would be:

$$K_{NO_2 \cdot C_6H_4OH}^{80^\circ} = \frac{C(OH \cdots HO^-)}{[C_{OH}]^2}, \quad K'_{NO_2 \cdot C_6H_4OH}^{80^\circ} = \frac{C(-NO_2 \cdots HO^-)}{C_{NO_2} \cdot C_{OH}}$$

Let us hold fast to our original declaration that:

$$K_{Cl \cdot C_6H_4OH}^{80^\circ} = K_{NO_2 \cdot C_6H_4OH}^{80^\circ}$$

and solve for the values of $K_{NO_2 \cdot C_6H_4OH}^{80^\circ}$ at various concentrations.

Obviously, for low concentration of solute and low values of the K^{80°

the following relationship will hold because of the nature of our compounds:

$$C(OH) = C(NO_2) \text{ (approx.)}$$

Therefore:

$$K'_{NO_2 \cdot C_6H_4OH}^{80^\circ} = \frac{C(-NO_2 \cdots HO^-)}{[C(OH)]^2}$$

and by addition and definition:

$$K_2 = K_{NO_2 \cdot C_6H_4OH}^{80^\circ} + K'_{NO_2 \cdot C_6H_4OH}^{80^\circ} = \frac{C(OH \cdots HO^-) + C(-NO_2 \cdots HO^-)}{[C_{OH}]^2}$$

or:

$$K_2 = \frac{C \text{ (all the double molecules)}}{C \text{ (all the single molecules)}}$$

The above expression must be the one that holds in an actual solution of our compound in naphthalene and so by the use of the available data we should be able to evaluate the K_2 's for various concentrations. As was said before, at a concentration of 6.0 mol percent our compound has a measured molecular weight of 196 which represents an association of 41% and indicates that 58 of every hundred molecules must have combined to give 29 double molecules. Hence:

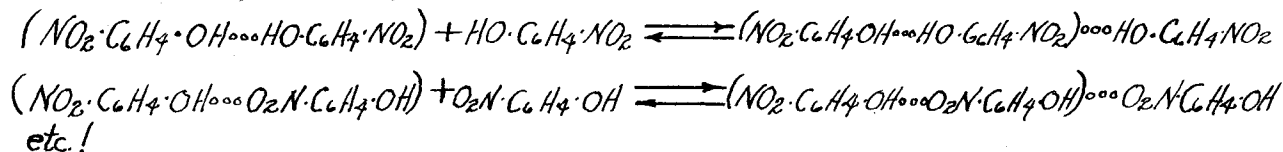
$$C \text{ (double molecules)} = (.06 \times .29)$$

$$C \text{ (single molecules)} = (.06 \times .42)$$

and

$$K_2 = \frac{(.29)}{.06(.42)^2} = \underline{\underline{27.3}}$$

However, a little thought will show that this expression is not exactly correct for the following reason. In the case of the double molecules formed from our compound with two functional groups, the double molecule is just as able to associate further as is a single molecule. This is made more evident by these equations:



hence in the calculation above, the denominator of the fraction, which should be an expression of the concentration of the groups ready to associate, should be changed to:

$$K_2 = \frac{(0.29)}{(0.06)(0.42+0.29)^2} = 9.6$$

since each of the 26 double molecules is equally as able to furnish associating groups as is each of the single molecules. This expression while more accurate than the proceeding one, makes no allowance for any triple molecules, which although present in correspondingly smaller amounts still are the equal of any single molecule as far as associating possibilities are concerned. Hence:

$$K_2 = \frac{(0.29)}{(0.06)(0.85)^2} = 6.7$$

which takes in account this factor is a still more accurate expression. Still more corrections could be applied to compensate for molecules of higher order but they are very small and amount to less than the experimental error in the determination of the percentage association of our compound and so have been omitted.

The K_2 's calculated in this manner are given in column 4 of Table No. 10. By subtracting the K^{80}_1 from the K_2 's, we may arrive at values for the K^{80}_1 which are the constants we were solving for. These are to be found

TABLE NO. 10

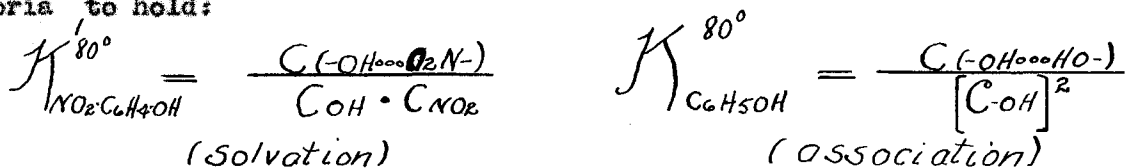
Table Showing the Equilibrium Constants of Association of Phenol and Substituted Phenols in Naphthalene at Various Concentrations

Conc. in Mol Percent	$K_{C_6H_5OH}$	$K_{ClC_6H_4OH}$	$K_{NO_2C_6H_4OH}$	K_2	$K_{NO_2C_6H_4OH} /$
1.0	7.5				
2.0	5.8	4.9	4.9	6.8	1.9
3.0	5.2	5.2	5.2	6.7	1.5
4.0	5.3	5.2	5.2	6.6	1.4
5.0	5.6	5.0	5.0	6.6	1.6
6.0	6.5	5.4	5.4	6.7	1.3
7.0	7.0	5.5	5.5	6.6	1.1

in column 5 of Table No. 10. As may be seen they are rather small in comparison with the $K_{\text{S}}^{80^\circ}$ thus showing that the exalted associating power of p-nitrophenol is not only due to the increased chances for association to the double molecule but also to the fact that its two functional groups give double, triple, quadruple and so forth molecules that still are as capable of association as the single molecule.

Now suppose we dissolve phenol in nitrobenzene and state that our unit of concentration is as before one mol in one hundred grams of solvent. Since the molecular weight of nitrobenzene (123) is so near to that of naphthalene (128), a one mol percent solution of phenol in one solvent is comparable to a one mol percent solution of phenol in the other. Furthermore, since we know the behavior of phenol in one solvent, we should be able to calculate the behavior of phenol in the other because we can calculate all reactions that may take place between the solute and the new solvent. These reactions, we have postulated, are the governing factors in association and the dielectric constant differences should play no part.

To proceed. In the nitrobenzene we would expect the two following equilibria to hold:



Suppose we start with a 2.0 mol percent solution of phenol. Then by

Table No. 10:

$$K_{\text{NO}_2 \cdot \text{C}_6\text{H}_4\text{OH}}^{80^\circ} = 1.9 \quad , \quad K_{\text{C}_6\text{H}_5\text{OH}}^{80^\circ} = 5.8$$

* Philbrick (51), by an independent calculation came to essentially the same conclusion with regard to the relative tendency of the hydroxyl group to combine with the nitro group or with other hydroxyl groups.

In one hundred grams of nitrobenzene there is 0.81 mol. As some of the phenol will be combined with the nitro group we may state as a very close approximation that:

$$C(-NO_2) = 0.80$$

$$\frac{C(-OH \cdots ON)}{C(-OH)} = 1.5 \quad , \quad \frac{C(-OH \cdots HO-)}{[C(-OH)]^2} = 5.8$$

Momentarily let us assume that the only reaction possible for the phenol is the solvation one. At equilibria we would have:

$$\frac{C(\text{double molecules})}{C(\text{single molecules})} = \frac{(.02)(1-\alpha)}{(.02)\alpha} = 1.5$$

from which $\alpha = 0.40$. This means that of every 100 original molecules of phenol, 60 would be solvated and 40 would be free. If on the other hand we assume that association is the only reaction possible for the phenol, we would find that of every 100 original molecules, 86 would still be free while the other 14 would have combined to give 7 double molecules. The true state of affairs of course is a compromise in which both reactions compete for the single phenol molecules. At equilibrium, solving as best we can without resorting to fractional molecules, we would find that every 100 original molecules would be divided as follows:

57	- solvated with nitrobenzene
39	- single
<u>4</u>	- combined to give two double molecules
100	

At a first glance one might suspect that an exact cryoscopic determination on such a solution would reveal the small amount of association indicated by the two double molecules. However, another factor enters the picture at this point. Well over half of the phenol is solvated by nitrobenzene. This means that this solvent has become part of the solute and hence due to its forsaking its solvent duties, the relative concentration of the solute

has been increased above 2.0 mol percent. Cryoscopically this would mean a larger experimental freezing point depression, which we would ultimately interpret as being due to the fact that our phenol had a molecular weight below normal in nitrobenzene. It so happens that at the concentration with which we are dealing (2.0 mol percent) these opposing effects just about cancel each other so we must predict that phenol in nitrobenzene will give normal results ($\pm 2-3\%$) at this concentration.

Let us consider a concentration of 7.0 mol percent. We would have the following constants:

$$K_{C_6H_5OH}^{80^\circ} = 1.0 \qquad C_{NO_2} = (0.78) \qquad K_{NO_2 C_6H_4OH}^{80^\circ} = 1.1$$

In exactly the same manner as before we may find that the distribution of 100 original molecules will be as follows at equilibrium:

37 - solvated with nitrobenzene
41 - single
22 - combined to give 11 double molecules
100

At this concentration the solvation has dropped off considerably while the association has increased enormously. In fact so much so that we must predict an experimental value of about 105 - 106 for the molecular weight of phenol in nitrobenzene at a concentration of 7.0 mol percent.

In view of these conclusions the experimental work of Ampola and Carlinfanti (1) covering this case is of particular interest and their data calculated to mol percent concentrations and plotted by the author are given on graph No. 9. As may be seen the agreement between the calculated and experimental is very good. Our equations have allowed us to predict quite accurately the behavior of phenol in nitrobenzene from the region of low con-

centration, where it gives results less than normal, to the region of comparatively high concentration, where it slowly approaches the behavior of phenol in naphthalene.*

It is true that the dielectric constant relationship of these two solvents is such that on the basis of the old theory we could predict that phenol would have a low or lower molecular weight in nitrobenzene than in naphthalene. For this reason our calculated example is unfortunate in that it does not rule out this old theory while confirming the new. Therefore the calculation on another type of compound will be briefly carried out.

Benzoic acid has in naphthalene at a concentration of 4.0 mol percent a molecular weight of 217. This represents an association of 78% and indicates that 88 of every hundred molecules have associated. Therefore:

$$K_{C_6H_5 \cdot COOH}^{80^\circ} = \frac{(0.04)(0.44)}{[(0.04)(0.12)]^2} = 163$$

Meta chlorobenzoic under the same conditions, and as is expected, associates slightly less or about 77%. Thus:

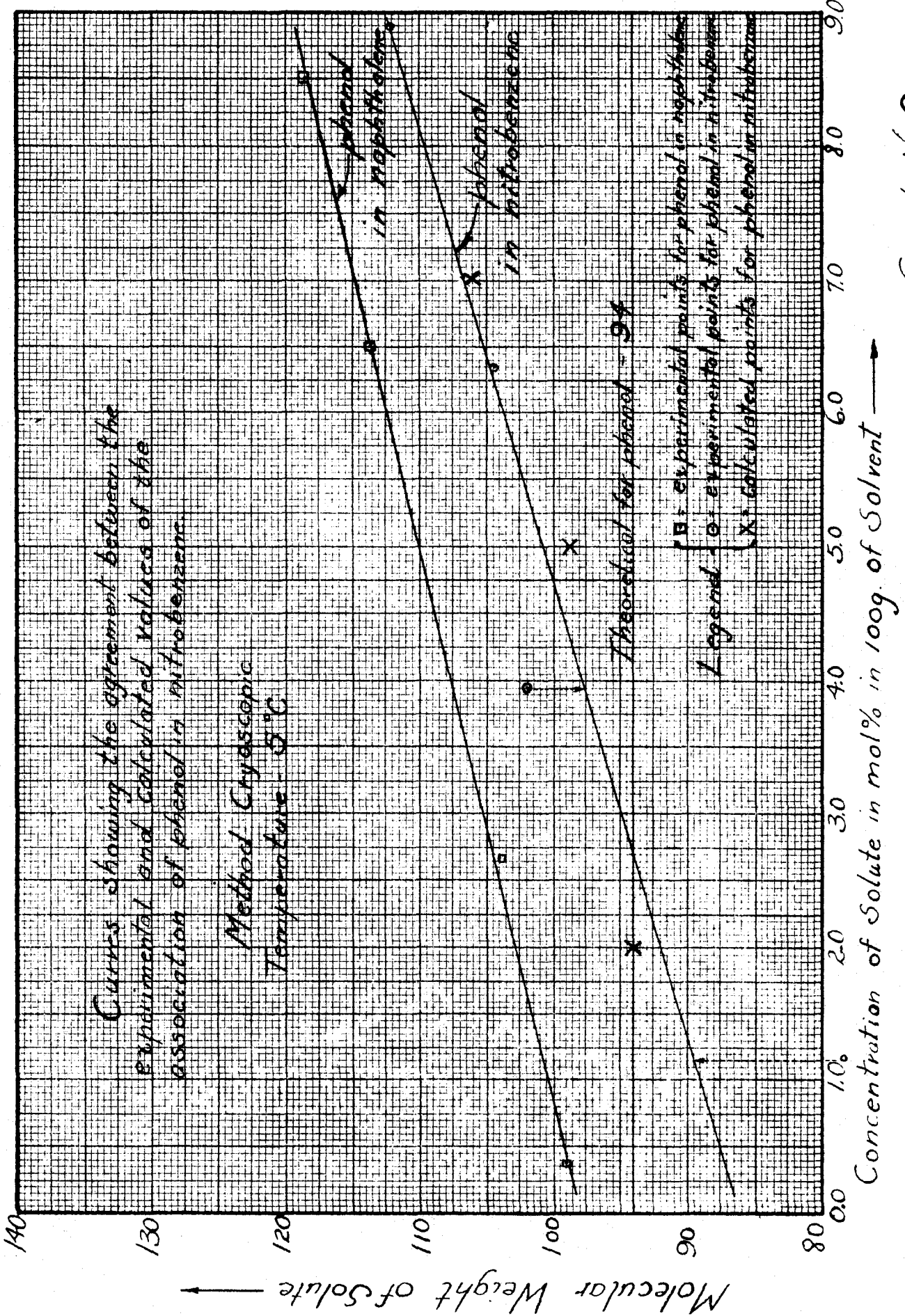
$$K_{Cl \cdot C_6H_4 \cdot COOH}^{80^\circ} = \frac{(0.04)(0.435)}{[(0.04)(0.13)]^2} = 643$$

As before we would expect that m-nitrobenzoic would show similar behavior and that:

$$K_{Cl \cdot C_6H_4 \cdot COOH}^{80^\circ} = K_{NO_2 \cdot C_6H_4 \cdot COOH}^{80^\circ}$$

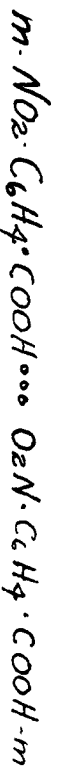
However, it is known that m-nitrobenzoic associates to such an extent that a molecular weight of 298 may be obtained in a solution of strength equal to the above examples. This is association of 78 % or a doubling up of 88 of

* Inasmuch as even the simplest equilibrium expressions and constants have never been entirely successfully applied to cases of association see Lassettre (37), the use of such expressions here is in itself quite an assumption. However, the author feels that the failure to successfully apply such equations is due to just such phenomena as are here discussed, solvation effect and simultaneous reactions. This point will be discussed in more detail later.



Graph No 9

every 100 molecules. Attributing as before this increase in association to the double molecules of the type:



we may write at once the equilibrium expression and constant for their formation, since they are obviously in such small quantities.

$$K_{80^\circ} = \frac{C_{(NO_2 \cdots HOOC)}}{C_{(NO_2)} \cdot C_{(COOH)}} = \frac{(0.04)(0.005)}{(0.09)(0.12)(0.09)} = 1.0$$

Hence the carboxyl group of acids tends to associate with another carboxyl group rather than with a nitro group. Now if benzoic, or chlorobenzoic or nitrobenzoic acid (their associations are about the same) be dissolved in nitrobenzene, we would have as before the two reactions competing for the carboxyl groups, and at equilibrium we would have the two expressions given below in force:

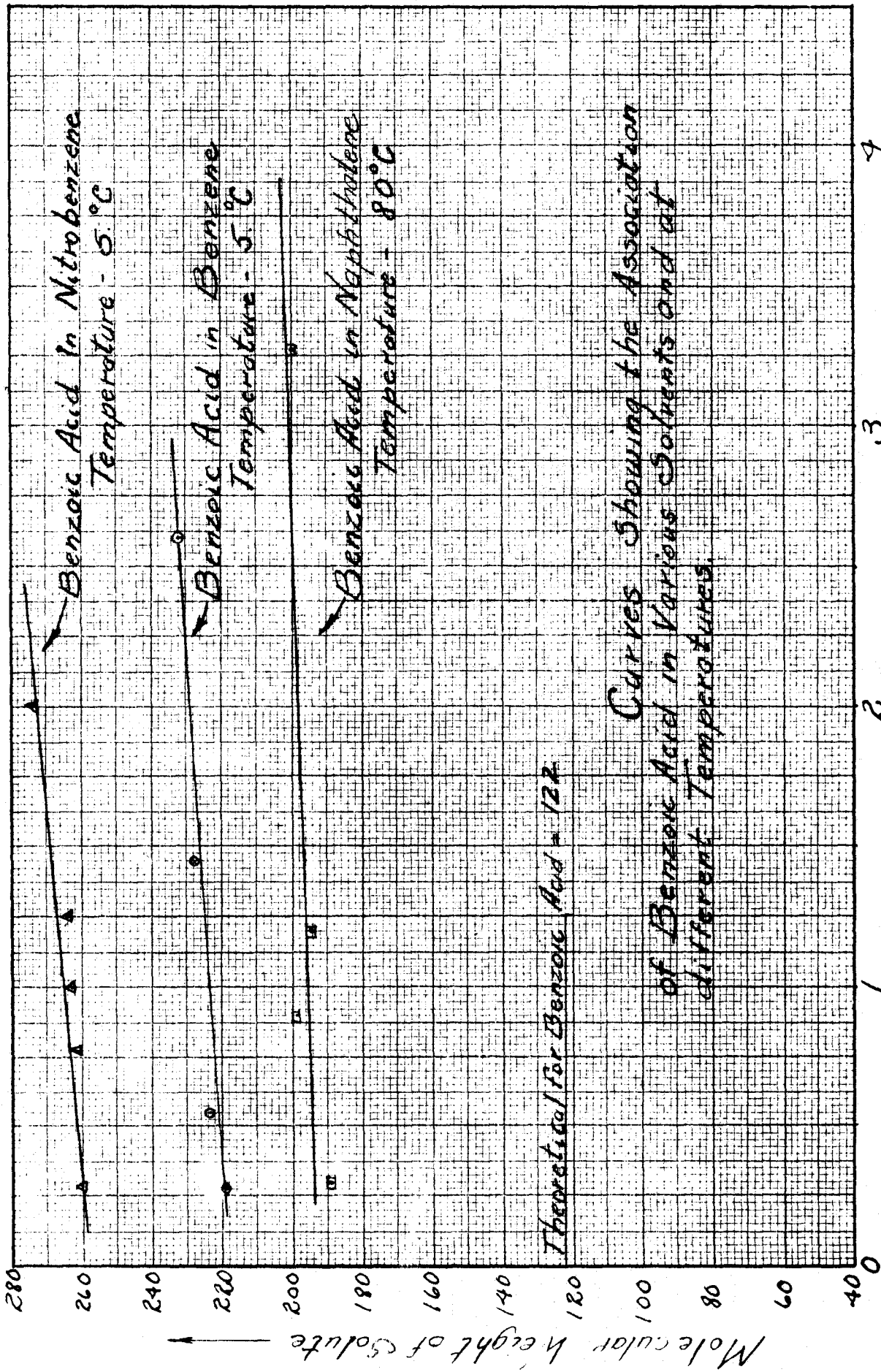
$$643 = \frac{C_{(COOH \cdots HOOC)}}{[C_{(COOH)}]^2} \quad 1.0 = \frac{C_{(COOH \cdots O_2N)}}{(0.8)(C_{(COOH)})}$$

The solvated molecules would be rather scarce as would the single molecules and our acid as in naphthalene would still be highly associated. In fact the little lowering of apparent molecular weight due to solvation could not amount to over 4 or 5%. Therefore we may state that in nitrobenzene, the association of benzoic, m-chlorobenzoic and m-nitrobenzoic acids should be very nearly as high as in naphthalene. This is at a temperature of 80°C., the temperature at which naphthalene freezes. If we drop to 5°C., the temperature at which nitrobenzene freezes and the only temperature for which data are available, we might expect that increased association could be found under these conditions as compared with that found in naphthalene at 80°C. This is essentially true as is shown by the experimental data of Beckmann and

Lockemann (16) which are plotted on graph No. 10.

There is another reason for expecting or at least explaining the high result in nitrobenzene. The possibility of benzene and naphthalene solvating dissolved solute because of the double bonds present in such solvents has not been considered in the foregoing treatment. Evidence can be presented from other sources to show that such solvation is not unlikely and even in the field of association it is known that the removal of the double bonds of a solvent (by reduction) always results in a medium in which compounds show increased association. Thus in cyclohexane, dicyclohexyl, or in the hydrocarbons, compounds exhibit their highest molecular weights. In these solvents (since all solvent effects are at a minimum) the application of equilibrium expressions and constants to an associating solute, whose association structure is known, should yield good agreement. An example of such a case would be benzoic acid in cyclohexane at vanishingly low concentrations. Unfortunately no data can be found in the literature covering this case or any similar to it.

It is a well-known fact that aromatic double bonds are less reactive than alifatic ones, and this has been explained as being due to the fact that the opportunities for resonance in the aromatic compounds have resulted in the formation of a more stable molecule. For the same reason nitrobenzene is a more stable molecule than benzene. What is more natural than to expect that as the compound becomes more and more unreactive the solvent effect would decrease and nitrobenzene (in case it can be shown that the nitro group is unable to exert any influence) would turn out to be a solvent in which benzoic acid, for example, would show higher molecular weights than it would in benzene. This is an experimental fact as may be shown by the curves on graph No. 10.

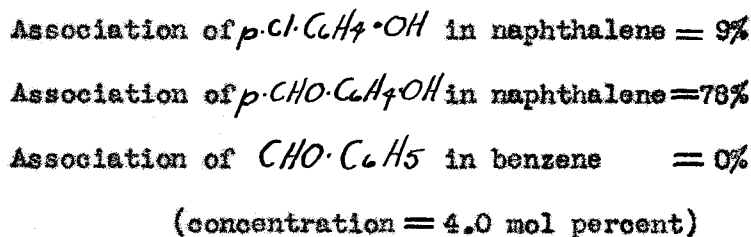


Graph No 10

Let us resume our calculations. If we calculate (at a total concentration of 4.0 mol percent) the ratio of "solvated" to "associated" molecules of phenol in benzaldehyde as a solvent, we obtain the value:

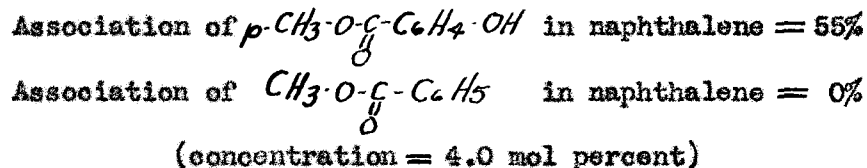
$$\text{Ratio} = \frac{C (\text{solvated molecules})}{C (\text{associated molecules})} = 99.9$$

hence in benzaldehyde very little phenol could associate. The experimental data used were as follows (4, 10):



The association in benzaldehyde has never been measured but it is a general rule that very little association can occur in aldehydes.

The same type of calculation using the data:



gives a ratio for phenol in methyl benzoate of:

$$\text{Ratio} = \frac{C (\text{solvated molecules})}{C (\text{associated molecule})} = 95 (\text{approx.})$$

hence very little association of phenol could occur in esters.

By use of the voluminous data for the association of phenols and their derivatives in naphthalene that have been made available by Auwers, we can establish, by a series of calculations of the above type, an order of "normalizing" power of the solvents $\text{C}_6\text{H}_5\cdot\text{R}$ and can attribute most of normalizing

power to the R group. The order of these R groups is as follows:

very little	Cl	
difference	Br	NO ₂ , COOR, CN, CHO, NH ₂ , COOH
	I	

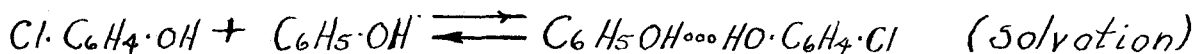
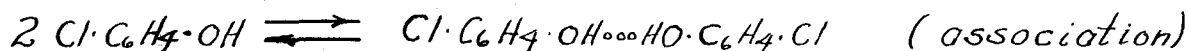
and they are arranged in such an order that those on the right give solvents that have the greatest normalizing effect on the solute. As may be seen this order is exactly as that found experimentally by Auwers with the exception of the hydroxyl group which could not be placed as it was our standard of measurement.

Hence by the proper interpretation of the experimental data concerning one compound and its derivatives in one solvent, we can calculate the behavior of our compounds in other solvents. This, by making use of the idea that the reaction or the possible reaction of the solvent in solvating the solute is the most important factor. The reason that the theory of dielectric constant gives even partial agreement is due to the coincidence (?) that most groups that are able to form associated bonds with hydrogen, contain oxygen and oxygen compounds usually have quite high dielectric constants. The inverse is not true, however, high dielectric constant does not mean good solvating effect, vis., the nitro group.

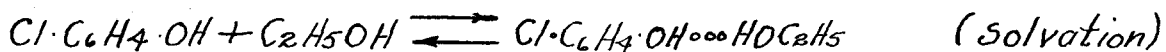
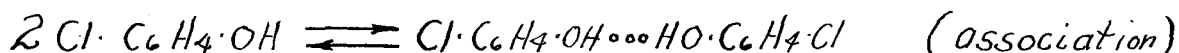
The above order was derived with respect to phenol but can be derived with respect to other compounds (benzoic acid or aniline) and associating groups and when this is done, it will be found that essentially the same order is obtained. Thus the order is independent of the solute and does represent a true order solvation. In individual cases, exceptions can and might be expected to occur. Thus ordinarily -OH should be ahead of -COOH in this series but if the solute also happens to contain -COOH, then the -COOH of the solvent is far ahead of the -OH in the series of normalizing factors.

This is undoubtedly due to the fact that the -COOH groups are able to form the ring structure of such extraordinary stability.

In deriving this normalizing series it will be noticed that the same radical (in the case considered $C_6H_5^-$) was always considered as being attached to the normalizing groups R-, and hence the order we derived is only valid for solvents that are substituted benzenes. Let us consider what would happen if this fundamental group is varied, that is, what would be the difference in the solvent action of two solvents containing the same normalizing group but different fundamental groups. The pair of solvents, phenol and ethyl alcohol, is an example of this combination. Let us consider the reaction possibilities of p-chlorophenol when dissolved in each of these solvents. In phenol we would have the following possibilities:



and due to mass action we would expect the second reaction to predominate and hence p-chlorophenol in phenol could be only slightly associated. In alcohol we would also have two reactions possible:



and the molecular status of p-chlorophenol will depend upon the completeness of the second equation. In part one of this paper we learned that ethyl alcohol is more highly associated than phenol, conditions being equal, and we showed that this was due to the lower electron-sharing ability of the ethyl group as compared with the phenyl group. For this reason we may predict that the solvation equation will be more complete in alcohol than in phenol solutions and that the normalizing action of the -OH group (or any

other normalizing group for that manner) is inversely affected by the electron-sharing ability of the attached radical as long as we limit our radicals to those that contain no normalizing groups or at least only those that have a very small effect such as the halogens. It is the verification of this hypothesis and the general theory preceding it that shall occupy the experimental section of this portion of the paper.

Experimental

Solvation effect. The data for this particular section of the paper were obtained predominantly in benzene solutions and in a molecular weight apparatus of improved design that has been described previously in the literature (35). The experimental attack chosen to show the formation of intermolecular complexes and their effect on the molecular weight of solutes was as follows: a substance of fair associating power was added to benzene and its molecular weight at various concentrations measured cryoscopically. Next, to known solutions of this compound in benzene were added measured amounts of a non associating body and the total freezing point depression of the solvent, as caused by the twin solutes, was then measured.

If there was no reaction between the two solutes, then their effects would be additive and the total freezing point lowering would be the sum of the individual lowerings, which could be calculated from previous knowledge. Any deviation from this behavior could only be interpreted as being due to some reaction between the two solutes.

Several pairs of compounds were investigated in this way, but only one pair will be discussed in any great detail since all examples tried yielded the same results. The compounds chosen for discussion are para-chlorophenol

with benaldehyde and in Table No. 11 are given the data pertaining to the molecular behavior of these compounds in benzene solution as determined by the author. These results are also given in graphical form on graph No. 11 from which it may readily be seen that the phenol shows appreciable association and the aldehyde shows none at all. The slightly high result in the case of the aldehyde was thought to be due to the oxidation of part of the compound to benzoic acid upon handling. This product would associate completely in benzene and the curve resulting would have zero slope as does ours.

So much for the case of solutions containing but one solute. In Table No. 12 are given the experimental freezing point depressions found of benzene solutions containing both p-chlorophenol and benaldehyde as solutes. Assuming that the aldehyde can in no way alter its molecular status (i.e., solvating the phenol does not change the number of aldehyde molecules instrumental in lowering the freezing point) we can make some interesting calculations regarding the molecular status of the phenol.

For example:

In run No. 2 the experimental depression is 1.870°C . Since there is present 0.0126 mol of benzaldehyde in one form or another, by our hypothesis:

$$(0.0126)(51.4) = 0.648^{\circ}\text{C}.$$

and 0.648°C . of the experimental lowering found can be attributed to the aldehyde. This leaves a lowering of 1.222°C . to be caused by the phenol or just the lowering that would be caused by 0.0238 mols of particles of phenol, either single or doubled. Obviously this 0.0238 mol is made up of the association products of a slightly larger quantity of phenol say 0.0250 mol of single molecules as a first estimate. Referring to graph No. 11 we may see that p-chlorophenol in benzene at a concentration of slightly above 0.0250

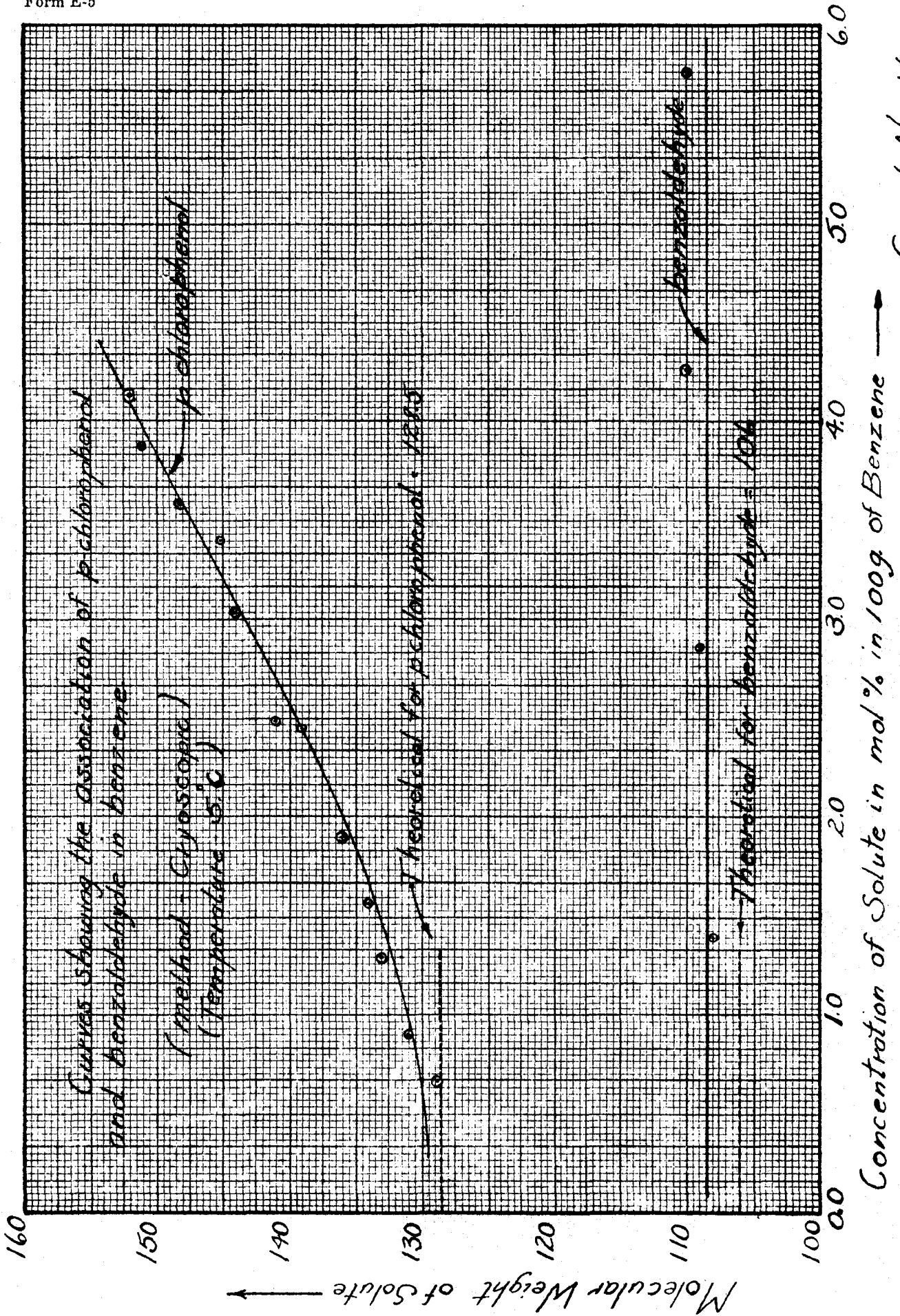
TABLE NO. 11

A. Association of p-chlorophenol in Benzene as a Function of Concentration

Run No.	Grams Solute in 100 Grams Solvent	Mols Solute 100 in 100 Grams Solvent		Calc. Mol Wgt.	% Association
1	0.847	0.659	0.338	128.9	0
2	1.658	1.29	0.640	133.	3 %
3	2.438	1.89	0.921	136.	6 %
4	3.210	2.49	1.172	141.	10 %
5	3.912	3.04	1.391	144.	12 %
6	4.609	3.58	1.599	148.	15 %
7	5.29	4.12	1.794	152.-	18-%
1	1.168	0.91	0.457	131.	2 %
2	2.010	1.56	0.772	134.	4 %
3	3.155	2.45	1.172	139.-	8 %
4	4.341	3.38	1.535	145.	13 %
5	4.964	3.86	1.562	151.	17 %
6	--	--	--	--	--

B. Association of Benzaldehyde in Benzene as a Function of Concentration

Run No.	Grams Solute in 100 Grams Solvent	Mols Solute 100 in 100 Grams Solvent		Calc. Mol Wgt.	% Association
1	1.483	1.40	0.706	108	
2	3.021	2.85	1.422	109	
3	4.504	4.25	2.108	110	nil
4	6.043	5.70	2.821	110	
5	7.550	7.12	3.552	109	



Graph No 11

TABLE NO. 12

The Freezing Points of Solutions Containing both p-chlorophenol and Benzaldehyde as Solutes in Benzene as a Solvent

Run No.	Grams Cl C ₆ H ₄ OH in C ₆ H ₆	Grams Cl C ₆ H ₄ OH in C ₆ H ₆	Mols Cl C ₆ H ₄ OH in C ₆ H ₆	Grams C ₆ H ₅ CHO in C ₆ H ₆	Mols C ₆ H ₅ CHO in C ₆ H ₆	Grams C ₆ H ₅ CHO in C ₆ H ₆	Mols C ₆ H ₅ CHO in C ₆ H ₆	Total Mols of Solute Added to 100 Grams C ₆ H ₆	Freezing Point Depression (found)	Mols of Solute Found by Freezing Point Depression
1	4.34	0.00	0.0338	0.00	0.000	0.000	0.0338	0.0338	1.535°C	0.0298
2	4.34	1.37	0.0338	0.0126	0.0126	1.37	0.0464	0.0464	1.870°C	0.0364
3	4.34	2.74	0.0338	0.0252	0.0252	2.74	0.0590	0.0590	2.275°C	0.0443
4	4.34	4.11	0.0338	0.0378	0.0378	4.11	0.0716	0.0716	2.690°C	0.0523
5	4.34	5.48	0.0338	0.0504	0.0504	5.48	0.0842	0.0842	3.170°C	0.0617

mols per 100 grams is associated to a molecular weight of 140 units. Therefore:

$$\frac{X}{0.0238} = \frac{140}{128.5} \text{ or } X = 0.0259 \text{ mol}$$

and 0.0259 mol of p-chlorophenol in benzene will associate to give 0.0238 mol of product, which will give a lowering of 1.222°C. This phenol has the following molecular distribution:

Mols of single molecules — 0.0217
Mols of double molecules — 0.0021

Total — 0.0238

To find the quantity of phenol solvated by the aldehyde we have only to subtract the "free" phenol (0.0259 mol) from the total phenol (0.0338) which gives us 0.0079 mol. Therefore the complete table of the molecular distribution of the phenol under the conditions described would be:

		Total
Single molecules	0.0217 mol	— (1)(0.0217)
Double molecules	0.0021 mol	— (2)(0.0021)
Solvated molecules	0.0079 mol	— <u>(1)(0.0079)</u>

0.0338

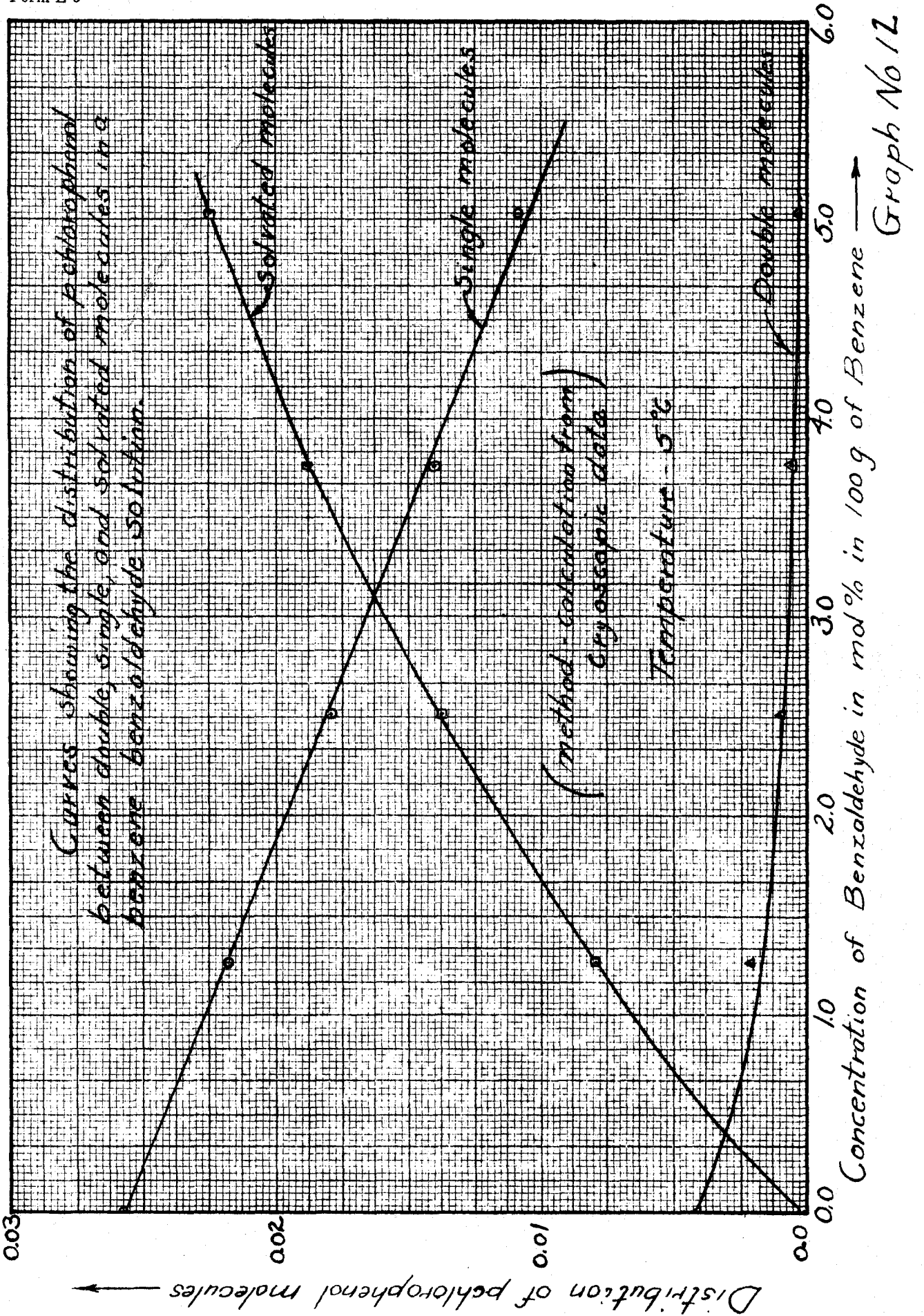
These results as well as those calculated for the other concentrations are given in Table No. 13 of this paper and are plotted on graph No. 12. The curves of this graph do show that the hydrogen of the phenol is able to form associated bonds with the aldehyde group and that as the concentration of this group increases so does the concentration of the single and double molecules of phenol decrease. It requires but little imagination to see that in pure benzaldehyde as a solvent the phenol at low concentrations would be very nearly 100% solvated as was predicted earlier in this paper. Therefore, normal or rather slightly subnormal molecular weights should be obtained in this system.

Handwritten note: $\frac{140}{128.5} = 1.089$

TABLE NO. 13

The Molecular Status of p-chlorophenol and Benzaldehyde Simultaneously Dissolved in Benzene as a Solvent

Run No.	Mols of C_6H_4OH in 100 gram C_6H_6	Mols of C_6H_5CHO in 100 gram C_6H_6	Calculated Mols of Phenol Present as Single Molecules	Calculated Mols of Phenol Present as Doubled Molecules	Calculated Mols of Phenol Present as Solvated Molecules	Calculated Mols of Aldehyde Present as Single Molecules	Calculated Mols of Aldehyde Present as Combined Molecules
1	0.0338	0.0	0.0257	0.00405	0.00	0.00	0.00
2	0.0318	0.0126	0.0217	0.0021	0.0079	0.0047	0.0079
3	0.0335	0.0252	0.0179	0.0011	0.0137	0.0115	0.0137
4	0.0335	0.0378	0.0140	0.0005	0.0188	0.0190	0.0188
5	0.0315	0.0504	0.0108	0.0003	0.0224	0.0280	0.0224



Similar calculations were made upon the data received for this pair of solutes at various lower concentration with similar results as is also the case of the pairs of solutes, p-chlorophenol with ethyl benzoate, and p-chlorophenol with nitrobenzene. The solvation or normalizing power of the three groups concerned are in the order required by the series derived in the theoretical section of this part of the paper, that of nitrobenzene being just measurable, using p-chlorophenol as a standard.

Effect of electron-sharing ability on the solvation reaction. In order to secure information concerning the effect of electron-sharing ability variations on the previously discussed solvation reaction, the molecular weights of two standard solutes, namely benzoic acid and ethyl alcohol, were determined in several series of solvents. Each solvent series consisted of a number of compounds of the same type, that is each compound contained a normalizing group such as an ester, carbonyl, or hydroxyl linkage, and to these normalizing groups were attached radicals of different electron-sharing abilities. These attached radicals were chosen to give as large a separation in electron-sharing ability as possible and to give compounds of about the same melting point. This was necessary so that the cryoscopic determinations made in all solvents would be at approximately the same temperature and hence would be comparable with one another.

The determinations themselves were carried out by the standard procedure as outlined by Reilly and Rae (53). A thermometer with 1/10 degree graduations was used to determine the freezing point depressions. It was found that some of the solvents investigated (notably benzophenone) crystallized so slowly the ⁺excessive supercoolings were obtained unless the precaution was taken of raising the temperature of the water bath to the fusion temperature ^{prevented}

of the solvent as soon as the latter was induced to crystallize by a small crystal of the solid form. In this way uniform supercoolings of 0.3°C were obtained throughout the series and the molecular weights found were not corrected for this factor since in general the correction would not amount to over several percent and the overall accuracy of cryoscopic determinations is of that same order.

Naphthalene was used in all cases to determine the Molal freezing point constants of the solvents. These constants as determined by the author are given in tabular form in Table No. 14 together with the same values as found in the literature.

In the tables 15 to 20 inclusive and on the accompanying graphs are given the data obtained on the first series of solvents which were disubstituted ketones of the type R-CO-R. In compiling these data and arranging the results so that the predicted correlation might be graphically shown, the question arose as to the choice of units of concentration for use in comparison. The usual procedure followed to show the variations of the molecular status of the solutes is to compare equal molal concentrations of the solutes in 100 grams of the solvent. This was done in the case before us, the concentrations chosen being $\frac{1}{100}$ of a mol of benzoic acid and $\frac{3}{100}$ of a mol of ethyl alcohol in 100 grams of the solvent concerned. However, since we were studying the reaction or possible reaction of the solvent molecules with the solute molecules, in order to get comparable results we should compare the two molecular species, molecule to molecule, or in other words use true mol percents. This was also done and the association indices of our solutes using this basis of concentration were also calculated. Due to differences of the densities of the solvents, neither of the above units is

TABLE NO. 14

Molal Freezing Point Constants (K_f) Of
Various Solvents Of The Type R CO R and R OH

Solvent	Melting Point of Solvent	Author's	Literature Value	
		Value K_f	K_f	Source
CH ₃ CO C ₆ H ₅	19°C	5.67	5.65	Carelli and Montanari (27)
C ₆ H ₅ CO C ₆ H ₅	46°C	9.80	9.88	Eykman (24)
pcl C ₆ H ₄ CO C ₆ H ₄ Cl p	142°C	10.5	--	none reported
CH ₂ Cl CO CH ₂ Cl	41°C	5 - 6	--	none reported
p CH ₃ C ₆ H ₄ OH	36°C	7.50	7.55	Eykman (24)
C ₆ H ₅ OH	42°C	7.21	7.20 - 7.50	I.C.T.
p Cl C ₆ H ₄ OH	42°C	not determined	8.58	Jona - (32)
O ClC ₆ H ₄ OH	6°C	7.75	7.72	Jona - (32)
2-4-6,Cl ₃ C ₆ H OH	67°C	9.61	--	none reported

TABLE NO. 15

A. Association of Benzoic Acid in Acetone
As a Function of Concentration

	Grams Solute in 100 grams Solvent	Mols Solute 100 in 100 grams Solvent	Mol % Solute	Calculated Molecular Weight	Association Index
	4.07	3.33	1.90	115	0.942
Benzoic Acid (122)	5.34	4.37	2.48	118	0.966
	6.12	5.02	2.84	117	0.960
	8.64	7.08	3.95	121	0.991
	-	-	-	-	-

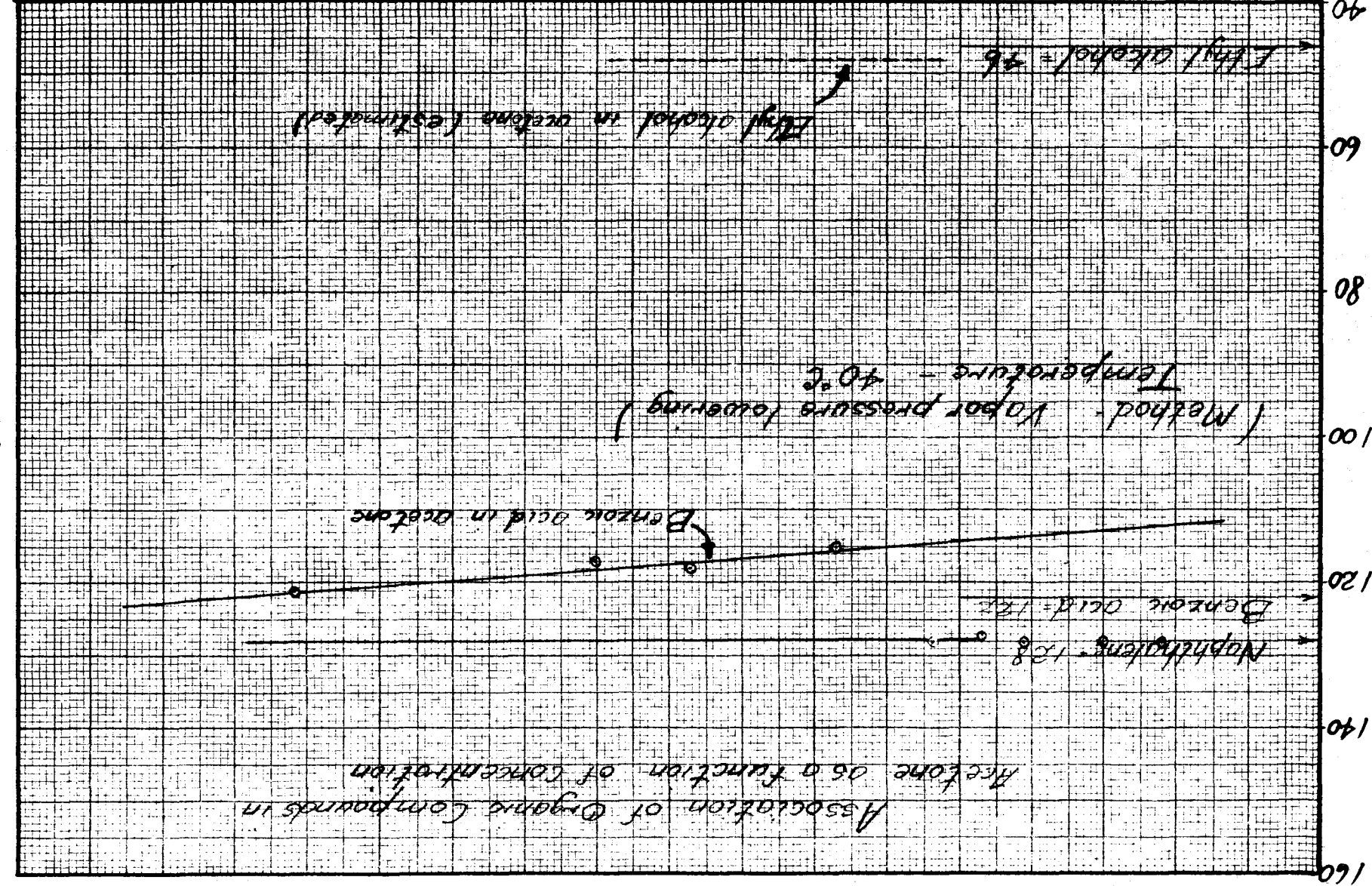
(Vapor pressure lowering method)

B. Association of Naphthalene in Acetone
As a Function of Concentration

	Grams Solute in 100 grams Solvent	Mols Solute 100 in 100 grams Solvent	Mol % Solute	Calculated Molecular Weight	Association Index
	2.65	2.06	1.08	128	1.000
Naphthalene (128)	2.97	2.32	1.34	127	0.992
	3.45	2.70	1.54	128	1.000
	-	-	-	-	-

(Vapor pressure lowering method)

Association of Organic Compounds in Acetone as a function of concentration



Graph No. 13

Concentration of solute in mol/l in 100g. of solvent. →

Molecular Weight of Solute →

TABLE NO. 16

A. Association of Benzoic Acid in Methyl Propyl
Ketone as a Function of Concentration

	Grams Solute in 100 grams Solvent	Mols Solute 100 in 100 grams Solvent	Mol % Solute	Calculated Molecular Weight	Association Index
	1.22	1	0.85	113	0.93
	2.44	2	1.70	115	0.94
Benzoic Acid (122)	3.66	3	2.52	117	0.96
	4.88	4	3.33	120	0.98
	6.10	5	4.13	122	1.00
	7.32	6	4.81	124	1.02

(by boiling point method)

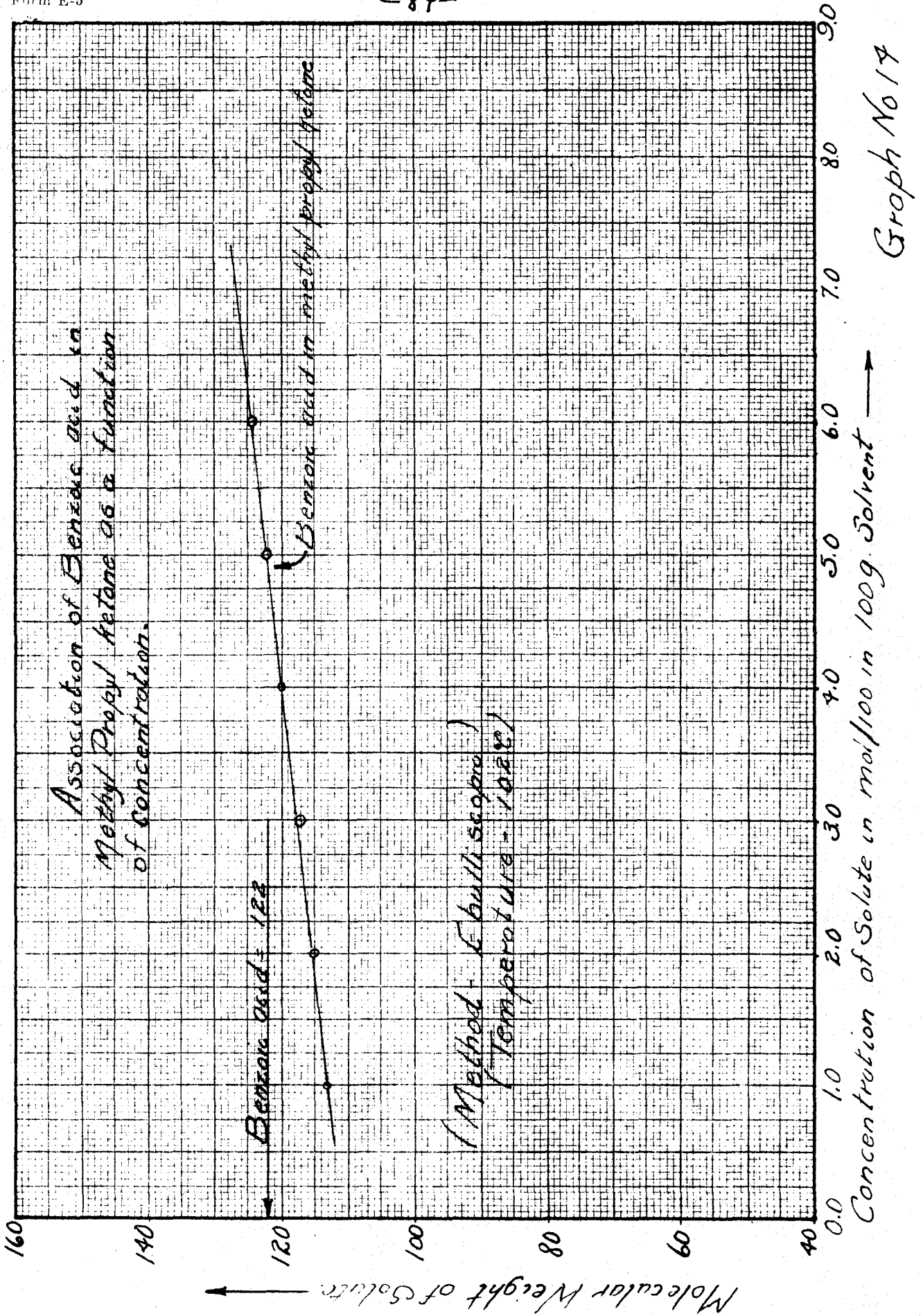


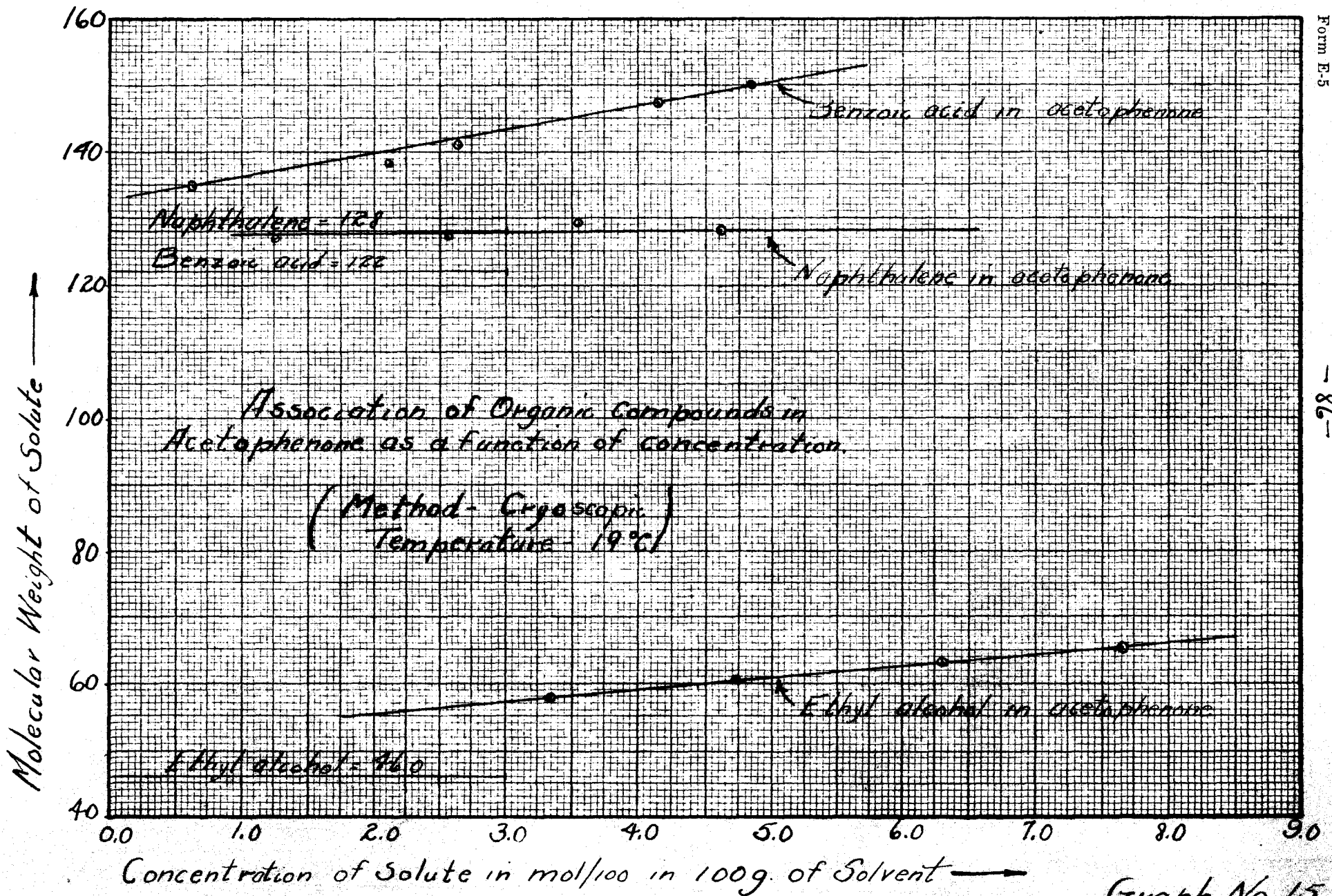
TABLE NO. 17

A. Association of Benzoic Acid and Ethyl Alcohol in Acetophenone as a Function of Concentration

	Grams Solute in 100 grams Solvent	<u>Mols</u> Solute 100 in 100 grams Solvent	Mol % Solute	Freezing Point Depression	Calculated Molecular Weight	Association Index
Benzoic Acid (122)	0.816	0.67	0.80	0.34°C	135	1.11
	2.581	2.12	2.48	1.05°C	139	1.13
	3.250	2.66	3.10	1.30°C	141	1.16
	5.063	4.15	4.75	1.95°C	147	1.20
	5.895	4.83	5.48	2.22°C	150	1.23
Ethyl Alcohol (46)	1.54	3.34	3.86	1.52	57.2	1.24
	2.17	4.71	5.35	2.03	60.5	1.31
	2.89	6.28	7.02	2.60	63.0	1.37
	3.52	7.65	8.42	3.06	65.0	1.41
	--	--	--	--	--	--

B. Molecular Weight of Naphthalene in Acetophenone

	Grams Solute in 100 grams Solvent	<u>Mols</u> Solute 100 in 100 grams Solvent	Mol % Solute	Freezing Point Depression	Calculated Freezing Point Constant
Naphthalene (128)	1.605	1.25	1.48	0.72	5.74
	3.290	2.57	3.03	1.47	5.71
	4.521	3.54	4.08	2.02	5.61
	5.90	4.61	5.25	2.60	5.65
				Average	(5.67)



Graph No 15

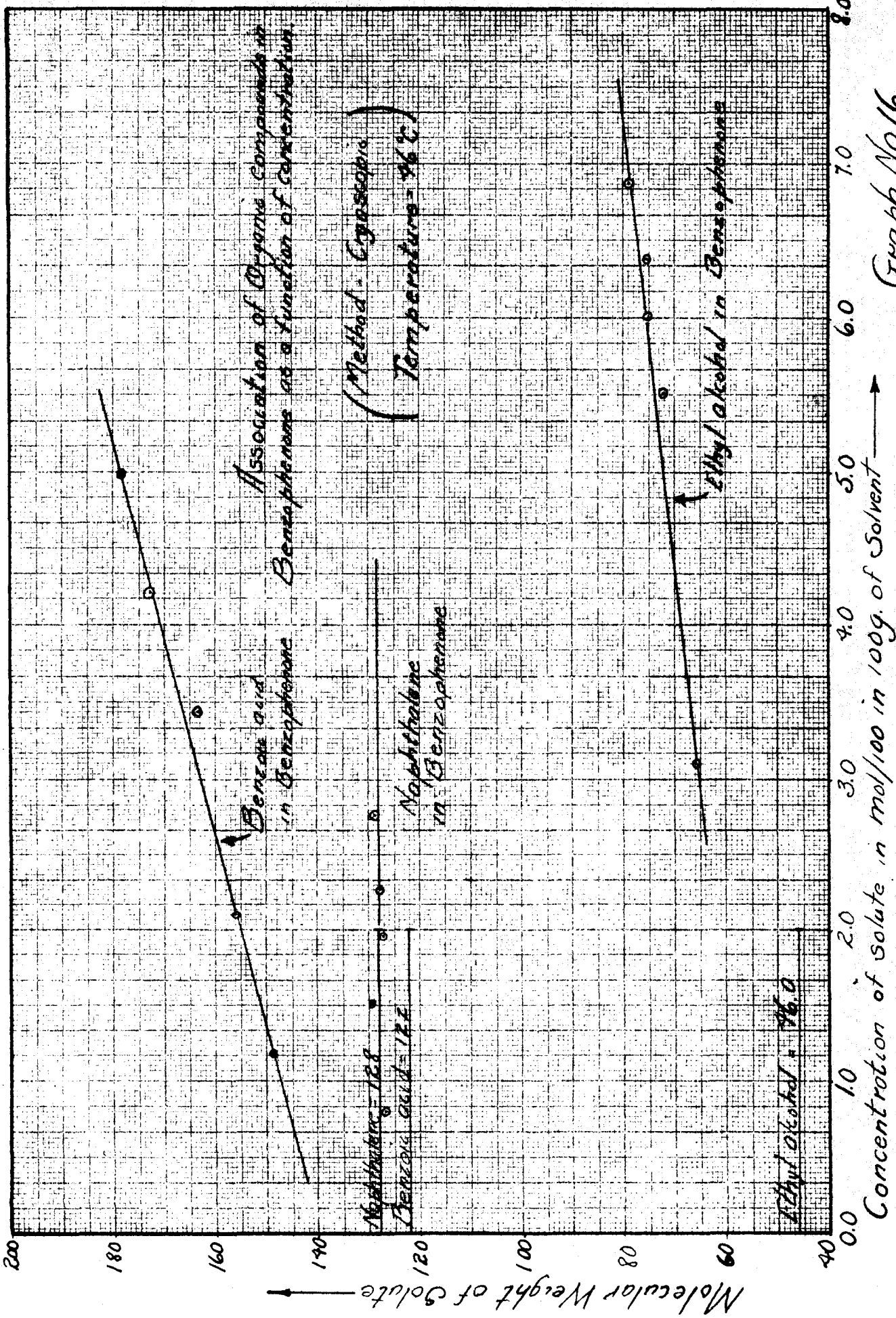
TABLE NO. 18

A. Association of Ethyl Alcohol and Benzoic Acid in Benzophenone as a Function of Concentration

	Gram Solute in 100 grams Solvent	<u>Mols</u> 100 Solute in 100 grams Solvent	Mol % Solute	Freezing Point Depression	Calculated Molecular Weight	Association Index
Benzoic Acid (122)	1.410	1.16	2.07	0.93°C	149	1.22
	2.548	2.09	3.66	1.60°C	156	1.28
	4.201	3.44	5.89	2.53°C	163	1.34
	5.115	4.19	7.09	2.91°C	173	1.42
	6.082	4.99	8.33	3.35°C	178	1.46
Ethyl Alcohol (46)	1.421	3.09	5.33	2.13°C	65.5	1.42
	2.539	5.51	9.12	3.46°C	71.8	1.56
	2.762	6.01	9.85	3.61°C	75.0	1.63
	2.938	6.38	10.4	3.80°C	75.6	1.64
	3.162	6.88	11.1	3.91°C	79.2	1.72

B. Molecular Weight of Naphthalene in Benzophenone

	Gram Solute in 100 grams Solvent	<u>Mols</u> 100 Solute in 100 grams Solvent	Mol % Solute	Freezing Point Depression	Calculated Freezing Point Constant
Naphthalene (128)	1.010	0.79	1.40	0.78°C	9.89
	1.926	1.502	2.66	1.42°C	9.69
	2.464	1.926	3.38	1.90°C	9.84
	2.918	2.278	3.98	2.24°C	9.81
	3.521	2.752	4.77	2.69°C	9.77
				Average	(9.80)



Graph No 16

TABLE NO. 19

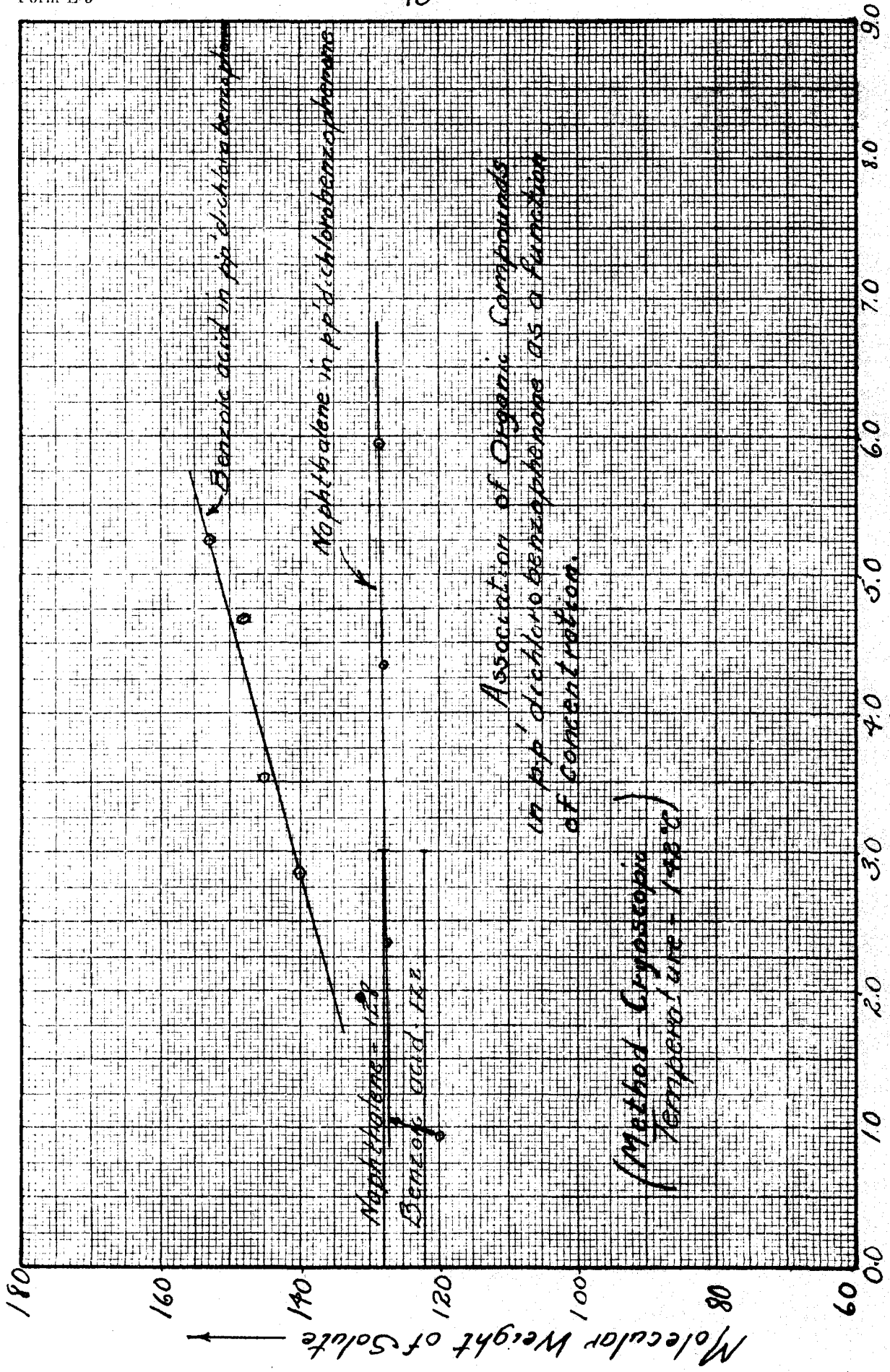
A. Association of Benzoic Acid in p.p' Dichlorobenzophenone as a Function of Concentration

	Grams Solute in 100 grams Solvent	$\frac{\text{Mols}}{100}$ Solute in 100 grams Solvent	Mol % Solute	Freezing Point Depression	Calculated Molecular Weight	Association Index
Benzoic Acid (122)	2.390	1.96	4.76	1.85	131	1.07
	3.495	2.86	6.66	2.53	140	1.15
	4.283	3.51	8.08	3.00	145	1.19
	5.721	4.69	10.5	3.92	148	1.21
	6.40	5.25	11.6	4.25	153	1.25

(Molecular weight of solvent is 250)

B. Molecular Weight of Naphthalene in p.p' Dichlorobenzophenone

	Grams Solute in 100 grams Solvent	$\frac{\text{Mols}}{100}$ Solute in 100 grams Solvent	Mol % Solute	Freezing Point Depression	Calculated Freezing Point Constant
Naphthalene (128)	1.10	0.91	2.22	0.94	10.90
	2.86	2.34	5.53	2.26	10.20
	5.30	4.34	9.78	4.20	10.15
	7.27	5.96	12.9	5.71	10.07
			Weighted average		(10.15)



Benzoic acid in *pp'*-dichlorobenzophenone

Naphthalene in *pp'*-dichlorobenzophenone

Naphthalene = 128

Benzof. acid = 122

Association of Organic Compounds
in *pp'*-dichlorobenzophenone as a function
of concentration.

(Method Grayscopic
Temperature: 148°C)

Graph No 17

TABLE NO. 20

A. Association of Benzoic Acid in Phosgene (15)
as a Function of Concentration

	Grams Solute in 100 grams Solvent	$\frac{\text{Mols}}{100}$ Solute in 100 grams Solvent	Mol % Solute	Calculated Molecular Weight	Association Index
	0.59	0.48	0.47	247	2.02
Benzoic Acid (122)	0.79	0.65	0.64	244	2.00
	1.18	0.97-	0.94	255	2.09
	1.61	1.32	1.29	267	2.19

B. Determination of Molal Boiling Point Constant
of Phosgene

Grams Solute in 100 grams Solvent	$\frac{\text{Mols}}{100}$ Solute in 100 grams Solvent	Boiling Point Rise	Calculated Boiling Point Constant
0.66	0.52	0.160	3.10
1.35	1.05	0.307	2.91
2.13	1.67	0.493	2.97
2.74	2.14	0.635	2.96
		(average -	2.99)

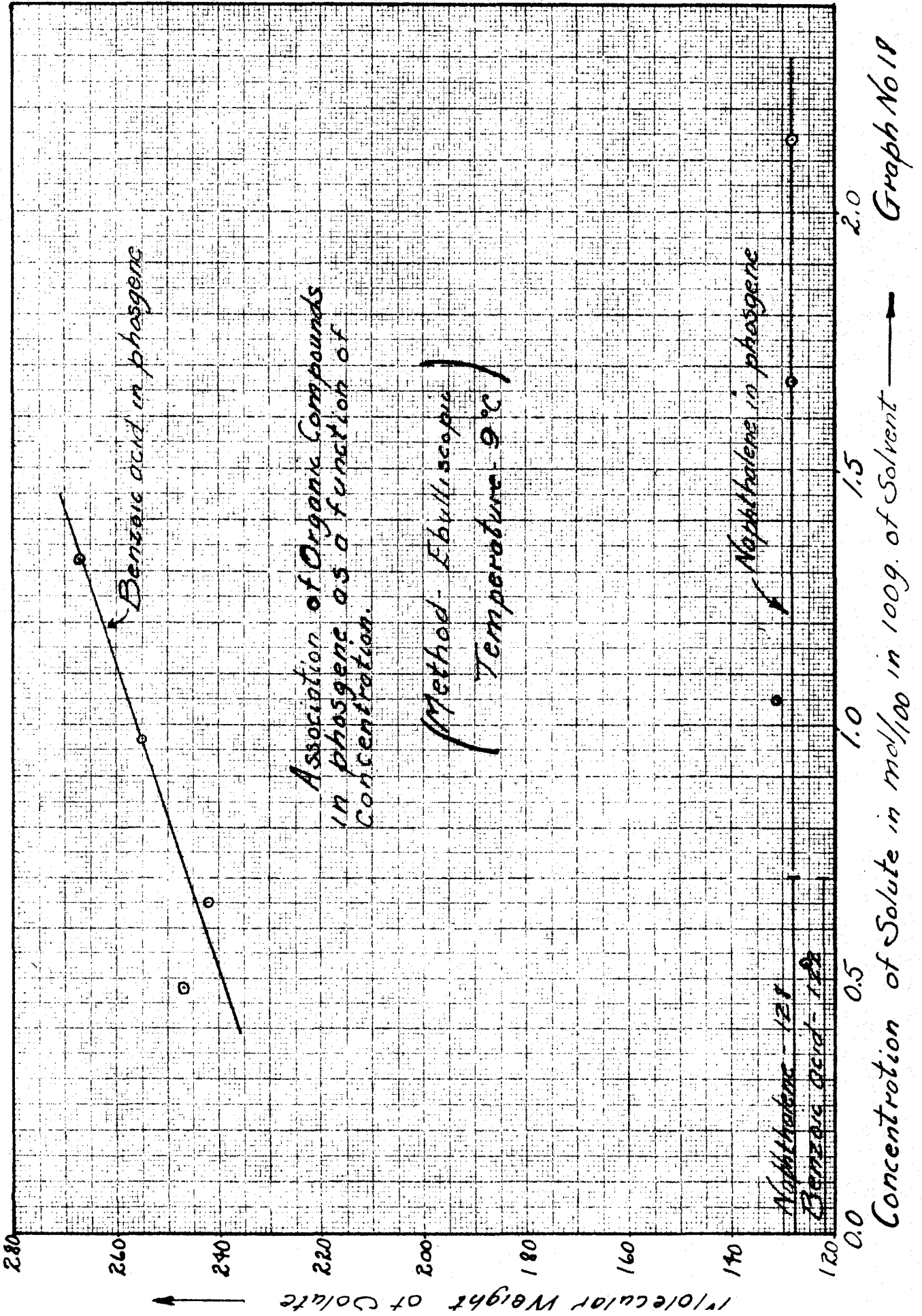
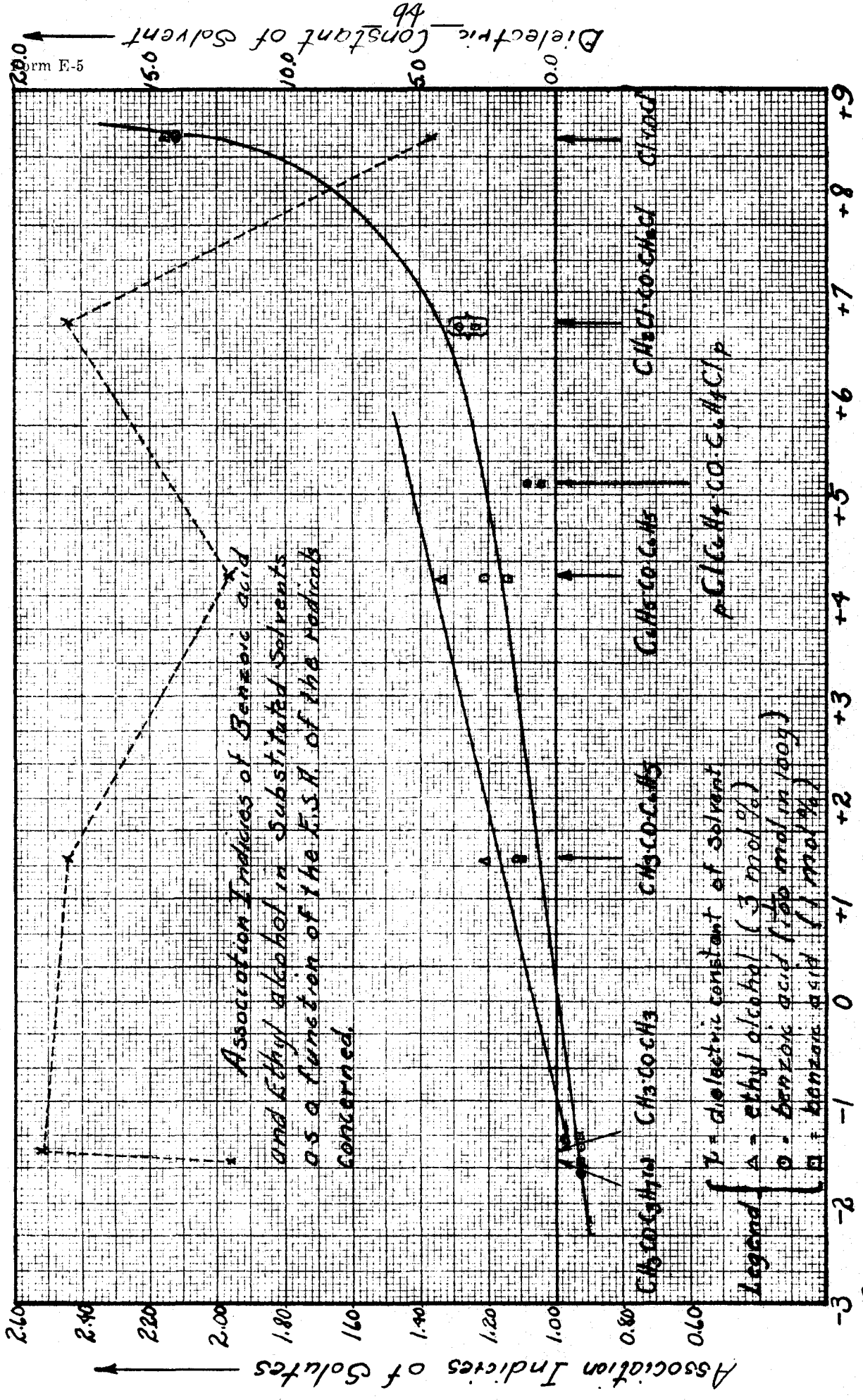


TABLE NO. 21

Association Indices of Benzoic Acid and Ethyl Alcohol at
Standard Concentrations in Various Solvents of the Type R·CO·R Together
With Various Physical Constants of the Solvents

Solvent	Temp. of Deter. °C	Dielectric Constant of Solvent	E.S.A. of R. Groups Concerned	Association Indices of Solutes				Source of Data
				Benzoic Acid 1 mol in 100 gr. 1 mol% 100	3 mol in 100 gr. 3 mol% 100	Ethyl Alcohol 1 mol in 100 gr. 3 mol%	3 mol in 100 gr. 3 mol%	
$\text{CH}_3\text{-}\overset{\text{O}}{\parallel}{\text{C}}\text{-CH}_3$	40	(19.0)	-1.45	0.94	0.93	0.99	.98	Author
$\text{CH}_3\text{-}\overset{\text{O}}{\parallel}{\text{C}}\text{-C}_3\text{H}_7$	102	(12.0)	-1.50	0.93	0.93+	-	-	Beckmann (14)
$\text{CH}_3\text{-}\overset{\text{O}}{\parallel}{\text{C}}\text{-C}_6\text{H}_5$	19	18.0	+1.40	1.11	1.10	1.22	1.20	Author
$\text{C}_6\text{H}_5\text{-}\overset{\text{O}}{\parallel}{\text{C}}\text{-C}_6\text{H}_5$	46	12.0	+4.2-	1.21	1.14	1.41	1.33	"
$\text{Cl-C}_6\text{H}_4\text{-}\overset{\text{O}}{\parallel}{\text{C}}\text{-C}_6\text{H}_4\text{-Cl}$	142	-	+5.1	1.07	1.03	-	-	"
$\text{CH}_2\text{Cl-C}\overset{\text{O}}{\parallel}\text{-CH}_2\text{Cl}$	41	(18.0)	+6.7	1.2 - 1.3	1.2-1.3	-	-	"
$\text{Cl-C}\overset{\text{O}}{\parallel}\text{-Cl}$	9	4.5	+8.5	2.12	2.13	-	-	Beckmann (15)



Solvent and E.S.A. of Radical concerned

Graph No 19

exactly that desired for perfect comparison but are close enough for our purposes.

In Table No. 21 are given the association indices of our standard solutes in every solvent investigated for each of the two units of concentration. It will be noticed that a parenthesized value is given for the indices of benzoic acid in 1 - 3 dichloroacetone. This indicates that the value is uncertain. The uncertainty arises from the fact that the author was unable to determine a satisfactory constant for the freezing point depression of this solvent. In Table No. 21 are also given the dielectric constants of each solvent as taken from the International Critical Tables. The values are given for infinite wavelength and at the fusion point of the solvent. The parenthesized values were obtained by extrapolation.

The data on Table No. 21 have been put into graphical form on graph No. 19 whereby it may be seen that as the electron-sharing ability of the radical attached to the solvent group increases so does the association of the solute increase. The curve giving the dielectric constants of the solvents shows no marked correlation while the other curve (E.S.A.) has only one exception. This is the case of benzoic acid in p-p'-dichlorobenzophenone as a solvent. The low results here may be understood when it is realized that this determination was made at a temperature of 142°C or about 110°C higher than the mean determination temperature of the other solvents in which association was found. It is well known that an increase in temperature decreases association, Beckmann (11) finding for benzoic acid in benzene the following behavior:

Temperature	Concentration	Molecular Weight
5.5°C	0.25 mol/1000	233
30°C	0.25 mol/1000	193

hence it is not surprising that benzoic acid is less associated in p-p' dichlorobenzophenone at 142°C than it is in benzophenone at 46°C. If a temperature correction could be made, the point (or points) in question could doubtless be brought closer to the curve. Unfortunately no way in which this may be done is known. True the heat of the reaction of the single benzoic acid molecule associating to the double molecule is known with considerable accuracy thanks to the work of Hendrixson (29) and of Szyskowski (58), but in our case this energy is not applicable since our reaction is not from the single to the double molecule but from the solvated to the doubled molecule.

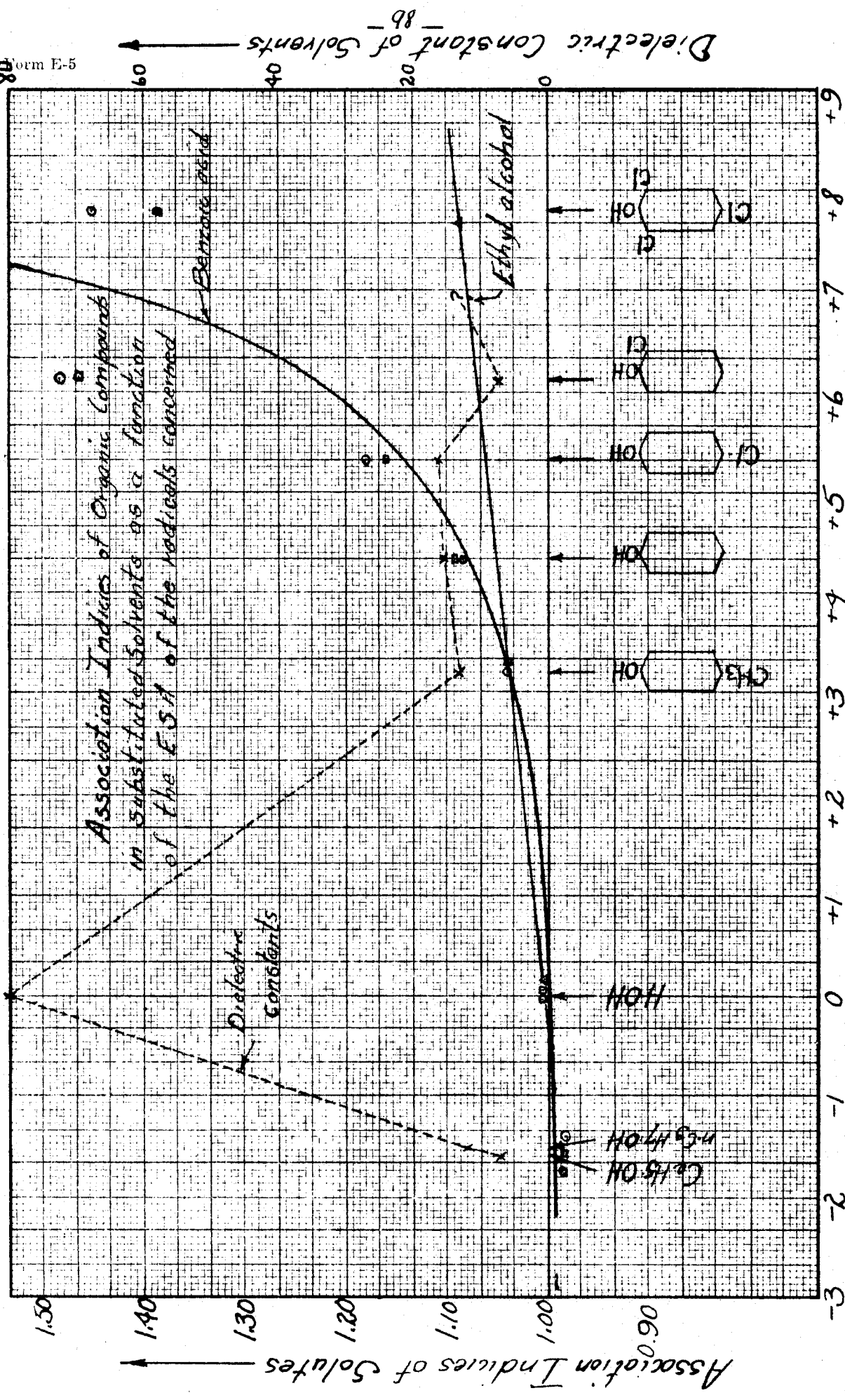
In Table No. 22 and on Graph No. 20 are given the results of the molecular weight determinations involving the same solutes in a series of solvents of the type R-OH. Again correlation is obtained between the measured solvent action and electron-sharing ability while the dielectric constant differences seem to play no part.

There is one point of particular interest on the benzoic acid curve on Graph No. 20 and that is the point which states that benzoic acid has a normal molecular weight in water. This combination of solute and solvent has been of particular interest to molecular weight investigators for some time because of the contradictions obtained by entirely different methods of attack. In the first place experiments involving the distribution coefficient of this acid between water and benzene clearly state that the molecular complexity of the acid in water should be approximately one-half that of the same acid in benzene. There is no doubt concerning the molecular status of benzoic acid in benzene inasmuch as both the cryoscopic and ebulliscope methods indicate a molecular weight about twice the normal, so we must conclude (from our distribution coefficient) that benzoic acid has a molecular weight about the normal in water. Unfortunately the low solubility of the

TABLE NO. 22

Association Indices of Benzoic Acid and Ethyl Alcohol at Standard Concentrations in Various Solvents of the Type R-OH together with Various Physical Constants of the Solvents

Solvent	Temp. of Deter. °C	Dielectric Constant of Solvent	E.S.A. of R-groups Concerned	Association Indices of Solutes		Source of Data
				Benzoic Acid	Ethyl Alcohol	
C_2H_5OH	80	7.0	-1.60	0.98	0.98	Landsberger (56)
C_3H_7OH	97	11.6	-1.50	0.98	0.98	Author
H OH	0.0	80.0	0	1.0	1.0	1.0
$CH_3C_6H_4OH$	36	13.0	3.2	1.04	1.04	---
C_6H_5OH	41	15.0	4.2	1.08	1.09	1.0
P Cl C_6H_4OH	42	(16.)	5.2	1.18	1.16	---
O Cl C_6H_4OH	8	7.0	6.1	1.49	1.47	---
2-4-6-Cl ₃ C ₆ H ₂ OH	66	---	7.8	1.45	1.38	1.09
						1.06



Graph No 20

Solvent and E.S.A. of Radical concerned

acid in cold water prohibits any direct determination in this solvent by a cryoscopic method. However, the acid is soluble enough at the boiling temperature so a determination may be run in this manner, and Peddle and Turner (49) carried out this evaluation. They noticed that the benzoic acid appeared to have appreciable vapor pressure from the water solutions at the boiling temperature and were at pains to correct for this error, nevertheless their data when calculated gave the acid association in water above that found in benzene. Molecular weights of 235 - 255 were found at concentrations of 6 - 7 grams of acid in 100 grams of water.

Since many distribution experiments involving water with other solvents (in each of which there is no doubt as to the molecular status of benzoic acid) give benzoic acid a normal or slightly subnormal value of molecular weight in the water, the author came to the conclusion that the ebulliscope method of Peddle and Turner must have been in error in this particular case and that the high molecular results received by them were due to causes other than association. Evidence was sought from other sources to substantiate this conclusion and will be discussed briefly.

It was found that an interesting and quite accurate calculation can be made of the molecular weight of any compound in a solvent in which it is slightly soluble, by the use of the Vant Hoff reaction isochore provided the variation of solubility with temperature and the heat of solution per gram can be found. These data are known for benzoic acid in water, Massol (43) having found a heat of solution of 53.2 calories per gram, while Bourgoïn (20) determined the following temperature-solubility values:

Temperature (degrees cent.)	Solubility (grams/100 gram)
4.5	0.182
10.0	0.207
17.5	0.268
31.0	0.425
40.0	0.555
60.5	1.213
70.0	1.781
75.0	2.193

In writing Vant Hoff's reaction isochore we have:

$$\frac{\partial \log S}{\partial T} = \frac{Q}{RT^2} \quad \text{or} \quad \frac{1}{S} \frac{\partial S}{\partial T} = \frac{Q}{RT^2}$$

In solving this equation for Q, the molal heat of solution, we obtain:

$$Q = \frac{RT^2}{S} \left(\frac{\Delta S}{\Delta t} \right)$$

$$Q = q M$$

$\left\{ \begin{array}{l} R = \text{gas constant} \\ T = \text{absolute temperature} \\ S = \text{solubility} \\ \Delta S = \text{change in solubility} \\ \Delta T = \text{change in temperature} \\ Q = \text{molal heat of solution} \\ q = \text{heat of solution per gram} \\ M = \text{molecular weight of solute} \end{array} \right.$

By using the data given above, the following substitutions can be effected:

$$Q = M(53.2) = \frac{2(298)^2}{0.346} \frac{0.156}{13.5}$$

from which:

$$\text{Molecular weight} = 112$$

and this is just about the result to be expected if benzoic acid does not associate in water inasmuch as it is known to ionize to a small extent.

In an effort to discover what would give the irregular results found by Peddle and Turner, the author repeated their determination using the boiling point apparatus described in part one of this report. Good agreement with the values found by the earlier investigators was obtained. However, the vapor pressure of benzoic acid from boiling water solutions appears to be much greater than has been suspected heretofore. In making a

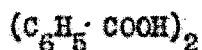
run, crystals of solid benzoic acid could be seen returning with the condensed water down the inner tube of the reflux condenser. Inasmuch as the vapor pressure of solid benzoic acid at 100 C (as determined by steam distillation) is about 1 - 2 mm and in the solution used the mol fraction was about 0.009, this should not have been. In an effort to find just what was the vapor pressure of the acid from such a solution, the author fractionally distilled solutions of known concentration of acid and titrated each condensed fraction with standard $\text{Ba}(\text{OH})_2$ to determine the acid content. Knowing the mol fraction of acid in the boiling solution and in the condensed vapor, one can calculate, using the vapor pressure of water at the observed boiling point, just what the vapor pressure of the acid under such conditions must have been. The result obtained was about 185 - 200 mm. If this correction, which is much greater than that used by Peddle and Turner, is applied to their results, molecular weights of about 140 - 150 for benzoic acid are obtained. These are much closer to those determined by other methods and it may be said with quite a degree of certainty that this exalted vapor pressure of the acid from the solution is the cause of the difficulties found in the literature.

It is interesting to speculate as to the cause of the exalted vapor pressure of the organic compound in this instance. In associating solvents and in the liquid state, benzoic acid is highly associated, the average molecular weight being about 240. In water the average molecular weight is about 120 and this is because our molecule has been solvated by the water to give a complex:



This would have a molecular weight of 140 and as such should be much more

volatile than a molecule of the type:



Whether the solvated molecule would be stable in the vapor phase or whether it would merely enter this phase and decompose cannot be definitely said. However a determination of the apparent vapor pressure of benzoic acid from water solutions boiling under different pressures should throw much light on this question.

Reverting to the original subject it may be said that in addition to the two series $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}$ and $\text{R}\cdot\text{OH}$ which have been discussed in detail, the molecular weight of benzoic acid was also determined in two more series, one consisting of substituted ethers of the type $\text{R}\cdot\text{O}\cdot\text{R}$ and the other of compounds of the type $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}\cdot\text{C}_6\text{H}_5$ where R varied from CH_3- to $-\text{Cl}$. In both cases substantially the same type of agreement as before was obtained so the details of the procedure and results have been omitted.

Summary and conclusions

It must be admitted that the value of the data determined in part two for substantiating the hypothesis regarding electron-sharing ability and the solvent action is seriously diminished by the temperature differences apparent in the determinations. These temperature differences are obvious in Tables No. 20 and 21, and on Graphs No. 19 and 20 is shown their effect in reversing the solvation order of the solvents. As pointed out previously, however, in every case a correction to a mean temperature would improve the correlation between the data and the theory. Another factor that can not be so easily surmounted is the effect of steric hindrance upon the solvation reaction and hence upon the association of the solute. As pointed out in

part one of this paper the E.S.A. of a radical and its steric hindrance increase together in many cases and care must be taken in interpreting experimental results because of this fact. Unfortunately insufficient data are at hand to enable us to state definitely that the steric hindrance factor plays no part in the production of the phenomena displayed. Rather all that can be said is that the dielectric constant of the solvent appears to play no part in governing solvent behavior and that the solvation reaction appears to be the controlling factor. This factor is dependent upon many things, concentration, temperature, steric hindrance, electron-sharing ability and so forth. Until more data are obtained and what is more important until a better method of experimental attack is developed, the relative importance of each of these contributing causes must remain uncertain.

A search of the literature revealed insufficient data to enable us to form anything resembling a complete series for compounds of other types than those previously mentioned. However, many isolated examples may be found that are in accord with that expected by our solvation theory and the effect of electron-sharing ability.

PART THREE

The Application of the Theories
Developed in Part One and Two to Related Phenomena

Foreword

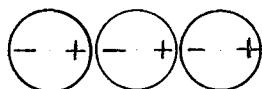
The original paper of Hixon and Johns on electron-sharing ability points out the manner in which the properties of a single molecule are affected by changes of the E.S.A. of the radicals concerned. The ideas presented in their paper have been applied to numerous problems involving the properties of the single molecule and many papers have been written on these subjects.

So must also the theories presented in this paper find application in other fields related to the title subject. In contrast to the paper of Hixon and Johns, the properties studied and correlated by the author are not those of the single molecule, but those of the associated complexes formed between various molecules as affected by the E.S.A. of the radicals concerned. If, as thought by many chemists, no organic reaction or change takes place without the reaction first passing through an addition compound stage, the importance of electron-sharing ability to organic reactions, rearrangements, orientations, and so forth, may be realized.

Several applications of the theories developed in the preceding parts of this paper will be made to the data in the literature.

The function of electron-sharing ability in governing association in the pure liquid phase

It is well known that many liquid substances such as water, alcohols, acids, amines, etc., are highly associated in the liquid state. Parallelism, to a certain extent has been shown for the dielectric constant of a liquid and its degree of association, Smyth (56) devoting a considerable portion of his book to this interpretation of the problem. The method of association by this explanation would be the simple coupling of molecules because of their dipole moments in some such fashion as this:



However it is easy to show that the most highly associated liquids, in fact nearly all compounds that do associate even slightly, do contain or can obtain by some tautomeric shift, hydrogen in such a form that it can form doubly covalent bonds. Therefore the author would suggest that the same factor that governs the association in solution (i.e., the E.S.A. of radicals attached to the associating group) also governs the association of compounds in the liquid state.

Unfortunately no method above criticism is known for determining the molecular weight of a liquid, if such a term can even be said to have a meaning. All methods available involve the study of some physical constant of the compound in question and the comparison of this value with the calculated value as derived from a study of the same constant for liquids that are known or appear to be normal. The deviation of the found and calculated value of the constant is interpreted as being due to association and the

degree of association is proportional to the degree of deviation.

The boiling point of a liquid compound is one of the constants adapted to such a study and an empirical relationship known as Longinescu's (39) relation has been derived that shows a relationship between the absolute boiling point of a liquid, its density at 0°C and the number of atoms of any type in the molecule. The relation is:

$$\frac{T}{d\sqrt{n}} = \frac{T'}{d'\sqrt{n'}} = \frac{T''}{d''\sqrt{n''}} = \dots = K$$

$\left\{ \begin{array}{l} T, T', T'', \text{etc.} = \text{absolute boiling} \\ \text{points} \\ d, d', d'' = \text{density at } 0^{\circ}\text{C} \\ n, n', n'' = \text{number of atoms per} \\ \text{molecule} \\ K = \text{Longinescu's constant} \end{array} \right.$

This constant has been evaluated by a study of the required constants of normal liquids such as chlorobenzene, carbon disulfide, ethylene bromide, ethyl cinnamate, octyl ether, *etc.* and so forth and found to have a value of 100.

Therefore:

$$n = \left[\frac{T}{d(100)} \right]^2$$

and since acetic acid has a boiling point of 118°C (391°A) and has a density of 1.065 at 0°C we may substitute these values in the above equation and find that "n" or the number of atoms in each molecule in the liquid state is equal to 13.5. Since the formula CH_3COOH requires but 8, we may say that our association index in this case is 13.5/8 or about 1.7-. Propionic acid by the same calculation gives an index of about 1.6 while benzoic acid with a boiling point of 249°C (522°A) and a density of 1.15 has an association index of 1.3.

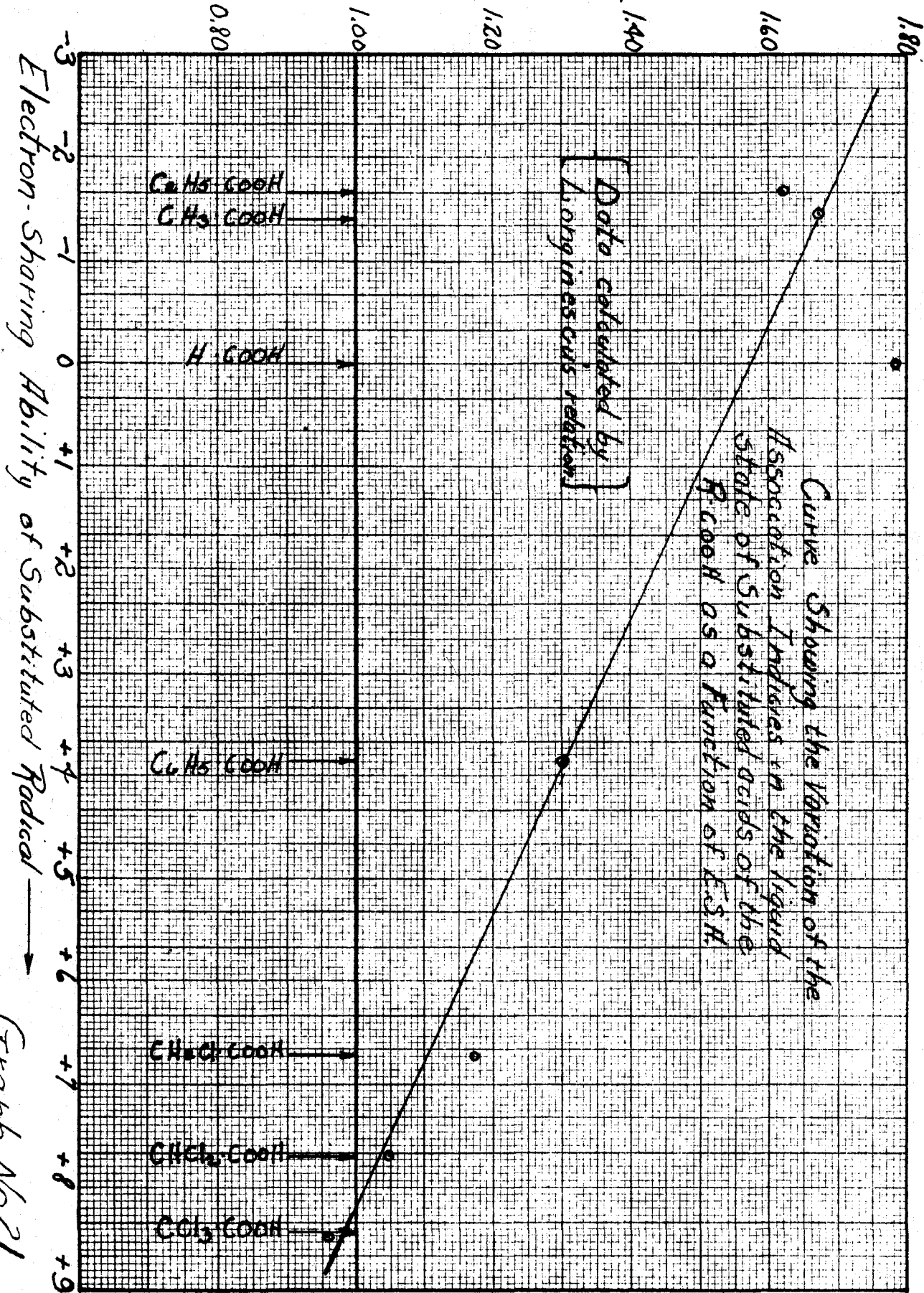
It is realized that this method is only approximate and that the results must be considered more from a qualitative than a quantitative standpoint, nevertheless these results do compare favorably with those secured by other methods so they must contain some elements of truth. Therefore this relation

was used to calculate the association indices of a series of substituted carboxylic acids, (of the type $R-COOH$). These results are plotted on Graph No. 21 against the electron-sharing ability of the substituted radical. The result is precisely that predicted. The associations do decrease in a regular fashion as the electron-sharing ability of the substituted radical increases.

Another method of estimating association in the liquid is that due to Ramsey and Shields which involves the measurement of the surface tension and the density of the liquid being studied. While it is true that the Ramsey-Shields equation has been modified by many investigators and the results determined using this method criticized on many grounds, it is nevertheless true that methods involving the surface tension are still considered valuable in determining association in the liquid phase. On Graph No. 22 is given a curve that shows the variation of the association indices of compounds of the type ROH as a function of the electron-sharing ability of the substituted radical. As may be seen the agreement with our hypothesis is good. This curve was plotted from data obtained by investigators using the old Ramsey-Shields equations. Newer investigations involve a function of the surface tension and the density at the boiling point of the liquid being examined. This function called the "specific cohesion" is thought to be a better physical constant of a liquid to be used as an indicator of association. At least the use of the specific cohesion function does remove many discrepancies in the data that were placed there by the old equation. This is especially true of the higher molecular weight compounds. On Graph No. 22 is also given a curve of the same type as the one mentioned previously except that the specific cohesion function was used to obtain the data.

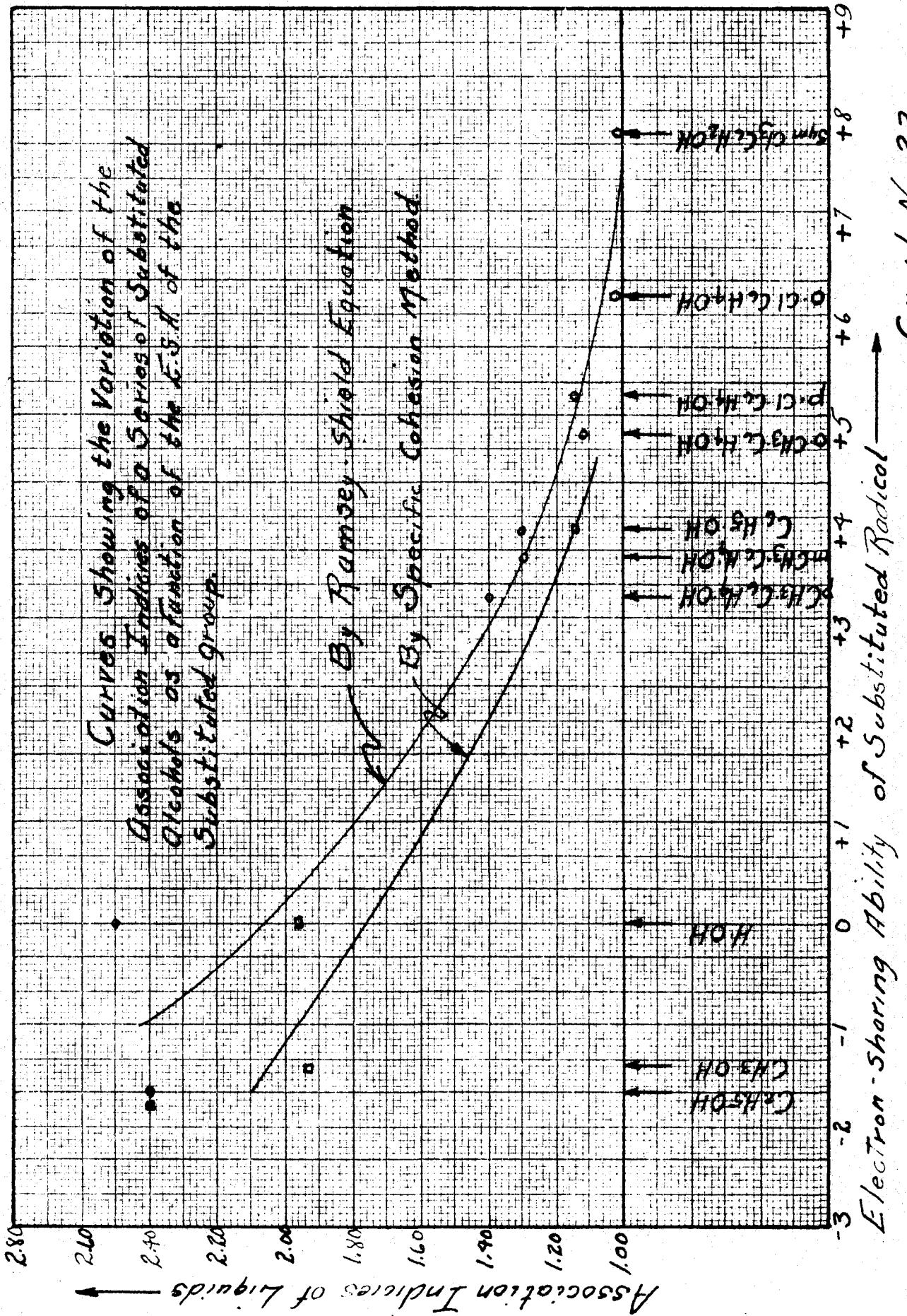
Still another method of measuring association in the liquid is that due

Association Indices of Liquids



Electron-Sharing Ability of Substituted Radical →

Graph No. 21



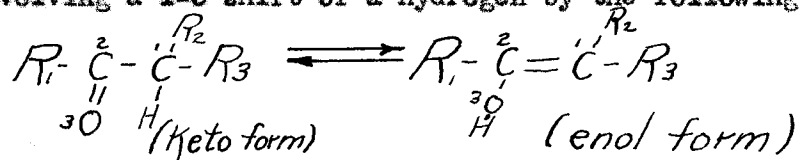
Graph No 22

to Bingham and his coworkers which involves measurements of the fluidity of the compound in question. Data obtained by this method have been plotted on Graph No. 23) whereby it may be seen that our hypothesis is again upheld by the experimental data. It seems to be a characteristic of this method that high results are obtained. By their fluidities, even compounds such as chlorobenzene, biphenyl, ethylene chloride, and so forth, are judged to be appreciably associated. This is contrary to the finding of other methods in most cases.

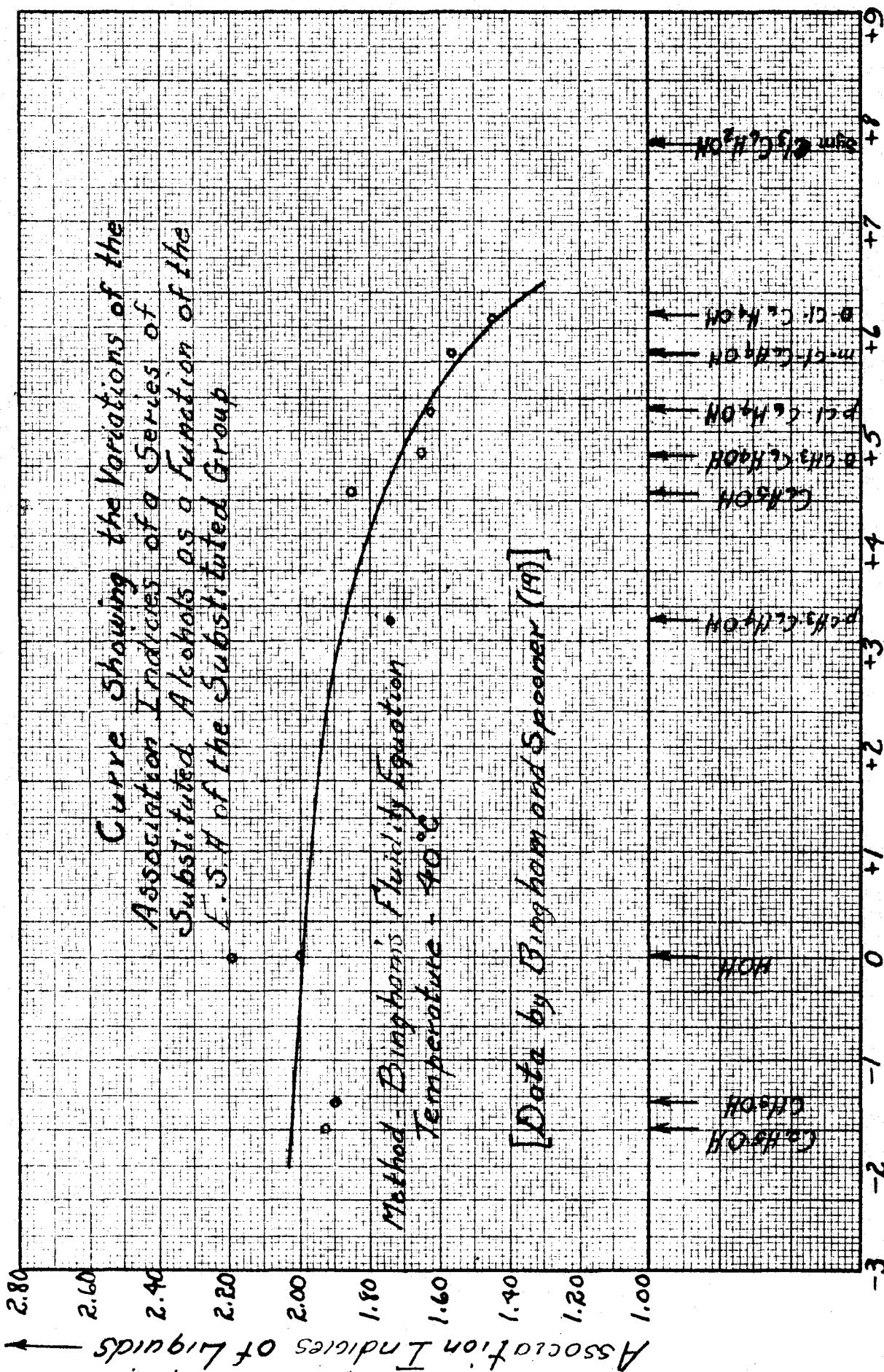
In conclusion it may be stated that apparently no matter what method we (choose to) measure association in the liquid phase, we (will always) find that the observed values will depend upon the electron-sharing abilities of the radicals concerned. This dependence will always be in the same direction as that predicted, and found, for association of organic compounds in solution. Hence the contributing factors in each case must be the same, i.e., the presence of doubly covalent hydrogen.

The function of electron-sharing ability in governing the enolization of ketonic compounds

Compounds of the type $R_1-\overset{\overset{R_2}{|}}{\underset{\underset{O}{||}}{C}}-\overset{\overset{R_3}{|}}{C}-H$ are known to undergo a tautomeric rearrangement involving a 1-3 shift of a hydrogen by the following reaction:



This equilibrium has been studied by various investigators, notably Conant and Thompson (22) and the variation of the various groups concerned shown to have a very great effect upon the percent enol form in the equilibrium mixture.

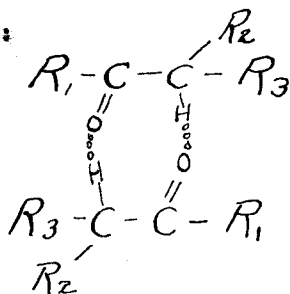
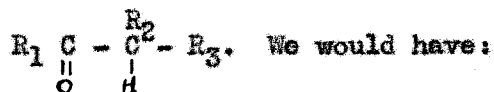


Electron Sharing Ability of Substituted Radical → Graph 23

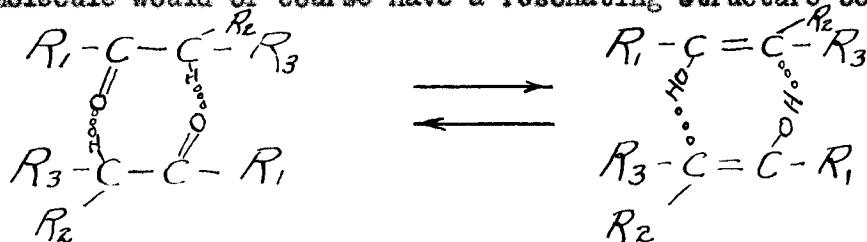
The author would like to show that perhaps the electron-sharing ability of the substituted radical is the governing factor in this equilibrium. The data available do substantiate this belief but they cannot be said to be voluminous enough to give conclusive proof.

In the first place the exact manner in which enolization is effected is still more or less of a mystery. It is known that equilibrium cannot be reached in the gaseous state and that the solvent used has a great effect on the rapidity with which equilibrium is reached and the percent enol obtained in the equilibrium mixture. As a general rule those solvents that promote association also promote enolization. Thus in hexane the highest enolizations are found while in water and alcohol very low values of enol percentage are possible. It therefore appears that the formation of intramolecular compounds between molecules of the solute, or association, promotes enolization* while solvation of the solute by solvent molecules promotes the reverse reaction.

Let us consider a possible association of a compound of the type



This molecule would of course have a resonating structure between the forms:

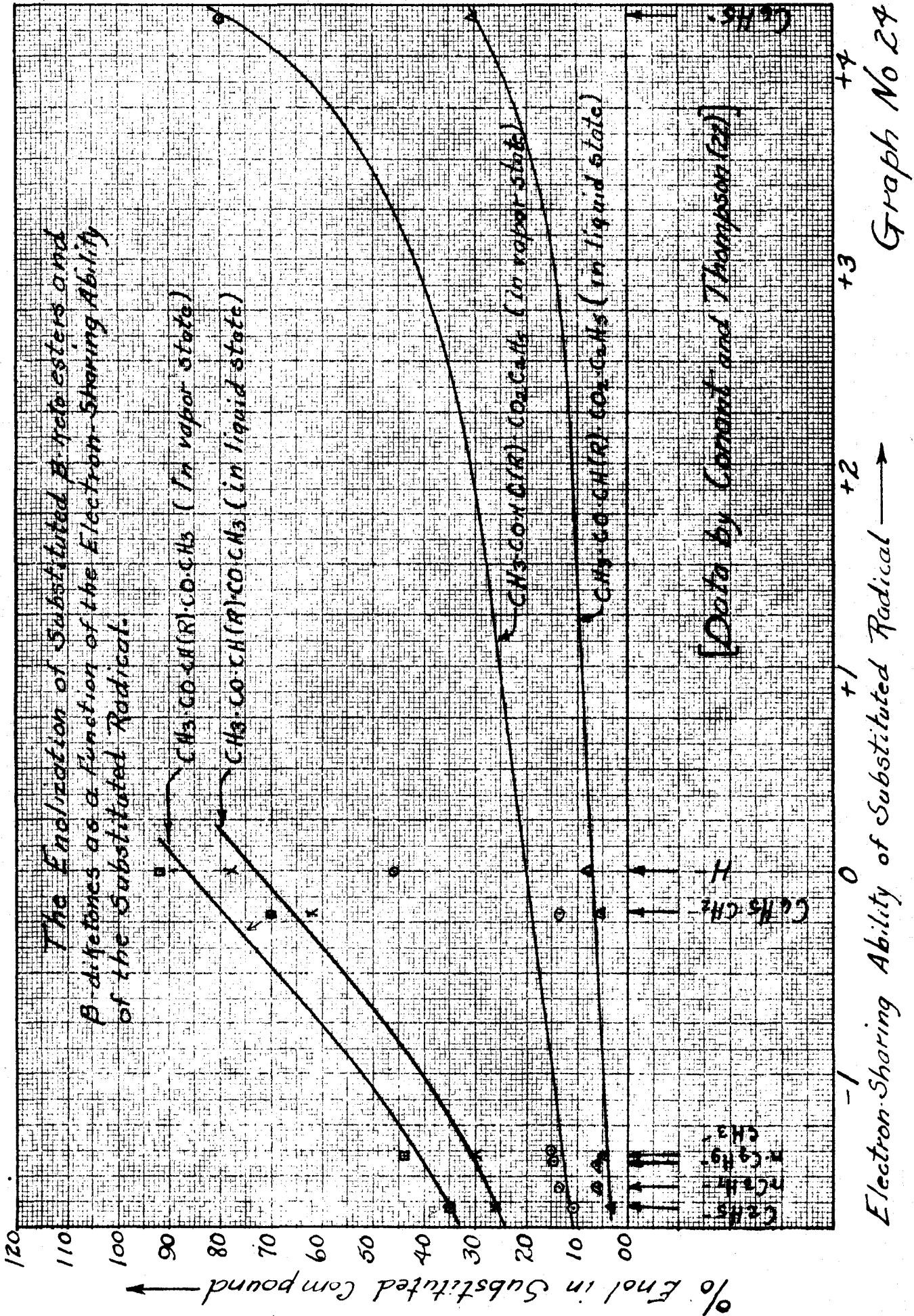


* In connection with this it might be mentioned that Mascarelli and Musatti (42) found that acetoacetic ester is associated 55% at a concentration of $4.2 \frac{\text{mol}}{100}$ in hexane.

The dissociation of one form of our molecule would yield only keto form while the rupture of the other form would yield only the enol. This dissociation of course would depend only on the relative strength of the various association bonds present, which would depend (among other things) upon the properties of the radicals substituted into the compound in question. Let us make a few deductions by making use of the theories regarding the effect of electron-sharing ability upon such bonds as developed in parts one and two of this paper.

In the first place the substitution of a radical of high value of electron-sharing ability directly upon the carbon atom concerned in the tautomeric shift (i.e. position R_2) should lessen the strength of the associated bond formed by this atom. This would be evidenced by an increase in the percent of enol to be found in the equilibrium mixture. The available data covering this case have been put into graphical form on Graph No. 24 whereby it may be seen that agreement is obtainable between the predicted and experimental values as far as they are available.

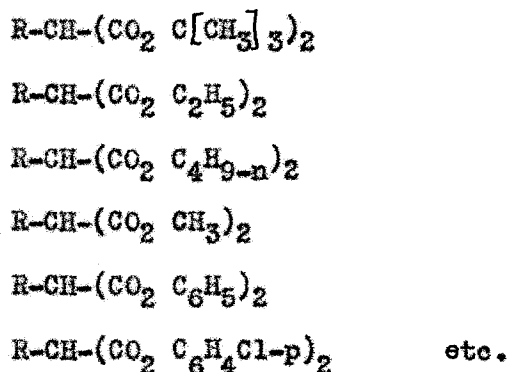
In the second and third cases (i.e. those regarding substitution in the R_1 - and R_3 - positions) no such definite prediction can be made because in these cases the effect of the substituted radical must be transmitted through a carbon atom before being evidenced by changes in the properties of the oxygen and of the carbon atoms occupying the end positions of the triad system. The chances are that the effect would be somewhat smaller than in case one and that the carbon atom would be influenced more than the oxygen atom. Thus the substitution of radicals of high values should increase the enolization obtained for such a system. Still less data are available for checking this postulate and nothing like a complete series may be obtained to



show the result. Several compounds that show the effect are given below:

Compound	Percent Enol in Liquid
$\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_3$	78
$\text{H} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_3$	98 (approx.)
$\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_3$	99
$\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_5$	100

The data needed to settle the question with regard to these three types of substitution could no doubt be obtained by a study of the enol content of a series of substituted malonic esters in either the gaseous phase or in hexane solutions. Malonic ester is enolized only slightly so it should be possible to secure data for a series in which R- varied from methyl to o-chlorophenol without having the enolization approach too close to 100% to show differences in the radicals concerned. If, as is possible judging from the enolization of the compound $\text{CH}(\text{CO}_2\text{CH}_3)_3$, the enolizations are too small to show the differences desired the relative enolization of the entire series could be increased by using a different ester group on the malonic acid. Thus the following series of substituted malonic esters should have increasing relative enolizations:



and each series should show the variations of the electron-sharing ability of the substituted group.

SUMMARY

1. Theoretical considerations have been made to show that the association of organic compounds should be an inverse function of the electron-sharing ability of the radical or radicals attached to the associating group.
2. Methods have been devised for measuring the association of the substituted carboxylic acids in the vapor state and as solutes in various solvents and the above prediction shown to be substantiated by the data received.
3. A brief review of the literature concerning molecular weights has been given to show that the hypothesis in question applies to classes of compounds other than the carboxylic acids. A discussion of other factors that effect measured association is given.
4. Theoretical considerations have been made to show that the reaction or possible reaction of the solvent in solvating the solute, and not the dielectric constant, should be the controlling factor in any discussion of the effect of a solvent in increasing or decreasing the association of a solute.
5. Approximate calculations have been made to show the feasibility of the solvation reaction in controlling the molecular status of the solute and a derivation of the normalizing power of a series of solvents made on this basis.
6. The theory of electron-sharing ability has been applied to the solvation reaction and reasons shown for believing that the associating power of solvent is a direct function of the electric-sharing ability of the radical or

or radicals attached to the solvating group.

7. Experimental data have been received for standard solutes in several series of solvents in an effort to prove the soundness of the above application of the theory of electron-sharing ability. Unfortunately, due to uncontrollable factors such as temperature differences and steric hindrance, the interpretation of the laboratory results proved to be very difficult. It was concluded that the electron-sharing ability of the radical concerned did have an effect and that it was in the direction predicted, but the degree to which the solvation reaction depended only upon this characteristic of the radical could not be determined.

8. Various other phenomena that may be controlled by electron-sharing ability have been mentioned and a brief discussion of each case given.

9. Various additions and corrections to the literature concerning molecular weights and association have been made.

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