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Edwin N. Lassettre

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PART I

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The Interpretation of Freezing Point Lowering Data in Terms of Polymerization

BY EDWIN N. LASSETTRE

Introduction

In the course of reviewing data on molecular weights in solution, a new method of calculating equilibrium constants was discovered which throws considerable light upon the behavior of polymerized compounds in various solvents. This method and a few applications are described in the following paper. More extensive applications will be published soon in an article in *Chemical Reviews*.

The investigation of the molecular weights of organic compounds in various non-polar substances brought to light the fact that many solutes must be considered highly polymerized to account for the high molecular weights obtained and for the increase of molecular weight with concentration. The final result of such investigations has been to divide polymerized materials roughly into two classes. For substances of the first class the molecular weight approaches an upper limit with increasing concentration; this class includes for example, the aromatic acids whose molecular weights approach a value twice the formula weight. The molecular weights of substances of the second class increase almost linearly with concentration and apparently approach no limit; this class includes phenol and substituted phenols, anilides, acid amides, and alcohols. Polymers of all of these substances are supposedly held together by hydrogen bonds. The reactions of polymerization and depolymerization are apparently fast.

The original problem for which a solution was sought was to determine a set of equilibrium constants for successive polymerization reactions which would account for a linear increase in apparent molecular weight with concentration. It was found that a unique set of equilibrium constants could be produced which would account for this state of affairs. The method used is quite general and can be applied to any data of this type, although it is convenient only when the molecular weight data can be expressed by a simple function of the concentration.

Calculation of Equilibrium Constants When the Molecular Weight is a Linear Function of the Concentration.—The following set of variables is useful for the discussion

Q = concentration in formula weights/kg. of solvent
N = concentration in molecular weights/kg. of solvent
m = apparent molecular weight of solute
M = formula weight of solute
$n = m/M$ = mean polymerization number
(A) = concentration of species A

It is clear from these definitions that $n = Q/N$.

In the following discussion a molecule of the species from which the polymer is constructed will be called an element of the polymer, and a polymer containing j elements will be called a polymer of order j.

These three hypotheses are made concerning the experimental situation: (i) The freezing point abnormalities are due to the presence of polymers. (ii) The reactions involved are so rapid that equilibrium is established completely by the time the measurements were made. (iii) The polymers obey the law of mass action with all activity coefficients unity.

Let an element of a polymer be designated by A and a polymer of order l by A_l. The equilibria present in the solution can be represented as

$$2A \rightleftharpoons A_2,\ 3A \rightleftharpoons A_3,\ \ldots,\ lA \rightleftharpoons A_l$$

Application of the law of mass action to this set of equilibria gives

$$(A_2)/(A)^2 = K_2,\ \ldots,\ (A_l)/(A)^l = K_l \qquad (1)$$

the K's being equilibrium constants.

Equations (1) are still true if there are several polymers, all of order l but differing in structure. In case there are isomers, (A_l) means the sum of the concentrations of all the isomers and K_l is the sum of the equilibrium constants for all the isomers.

The concentration Q is obtained by summing $l(A_l)$ over all l:

$$Q = \sum_{l=1}^{k} l(A_l) = \sum_{l=1}^{k} lK_lx^l,\ x = (A),\ K_1 = 1 \quad (2)$$

where the relations (1) have been used to eliminate (A_l). Similarly,

$$N = \sum_{l=1}^{k} (A_l) = \sum_{l=1}^{k} K_lx^l \qquad (3)$$

In these formulas, k is the order of the largest polymer.

Hypothesis (iii) requires that the constants K_l be independent of x. We take the derivative of (3) with respect to x and multiply by x, obtaining

$$x\frac{dN}{dx} = \sum_{l=1}^{k} lK_l x^l \tag{4}$$

The right-hand member of equation (4) can be immediately identified as Q by comparing with (2), thus leading to the formula

$$x\,dN/dx = Q \tag{5}$$

and (5), together with the definition of n, leads to

$$\frac{x}{N}\frac{dN}{dx} = n \tag{6}$$

We are now discussing the case of a relation between n and Q of the form $n = 1 + \alpha Q$ where α is a constant. If n and Q are replaced by the expressions (5) and (6) we obtain

$$\frac{x}{N}\frac{dN}{dx} = 1 + \alpha x\frac{dN}{dx} \tag{7}$$

The problem is now reduced to solving this differential equation. The solution provides a relation between N and x, and if this be expanded into a power series in x, the coefficients will be the desired constants as is obvious from (3).

Equation (7) is easily solved and the constant of integration can be evaluated by the conditions that $\lim_{x \to 0} \frac{N}{x} = 1$ and $N = 0$ when $x = 0$. The final solution obtained in this way is

$$N = xe^{\alpha N} \tag{8}$$

The expansion of N in powers of x can be accomplished most conveniently by use of Lagrange's theorem.[1] The final result is

$$N = \sum_{l=1}^{\infty} \frac{x^l\,(\alpha l)^{l-1}}{l!} \tag{9}$$

Comparison of this series with (3) shows that

$$K_l = (\alpha l)^{l-1}/l! \tag{10}$$

This set of constants will account for a linear relation between n and Q and it is the only set of constants compatible with hypotheses (i), (ii), and (iii) which will suffice, because the solution of the differential equation is unique. Furthermore the number of constants is infinite and hence an infinite number of polymers is required; it is to be expected that this fact will not be particularly significant.[2]

That large polymers should be necessary to account for the molecular weights is not particularly surprising nor unlikely. Crystal structure investigations have indicated that some crystals, such as water, can be regarded as big polymers held together by hydrogen bonds, and deviations of molecular weights from formula weights are large. On the other hand, it is not proposed that all deviations from the laws of perfect solution should be accounted for by such equilibria, and, in fact, it is known that this cannot be the case. Systematic deviations occur for virtually all solutes at sufficiently high concentrations and for many solutes the deviation is proportional to the concentration. In the discussion of these problems it is therefore necessary to confine one's attention to solutes for which the deviation is so large that it can be attributed only to a polymerization.

Calculation of Equilibrium Constants when the Relation is not Linear.—The case in which n is not a linear function of Q can be treated also. If n be expressed in the form

$$n = 1 + f(Q,N) \tag{11}$$

where $f(0,0) = 0$, and if $f(Q,N)$ be expanded and only the first two terms retained, the following equation is obtained

$$n = 1 + \alpha Q + \beta N \tag{12}$$

If the substitutions (5) and (6) are made and the equation treated as before, the equilibrium constants are found to be

$$K_l = \frac{\prod_{q=0}^{l-2} [\alpha l + (l - q)\beta]}{l!} \tag{13}$$

$$q = \text{an integer}$$

and the solution of the differential equation is

$$N = x(1 + \beta N)^{(\alpha+\beta)/\beta} \tag{14}$$

The equation (12) can easily be tested by substituting $N = Q/n$, leading to

$$n(n - 1)/Q = \beta + \alpha n \tag{15}$$

A plot of $n(n - 1)/Q$ *vs.* n will quickly decide whether or not the equation is applicable. Negative values are permitted for β provided $\alpha + \beta > 0$. When $l = 2$, $K_2 = \alpha + \beta$ and the significance of the sum of the constants is established.

Interpretations of the Relations between the Equilibrium Constants.—It is not surprising that

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(1) Whittaker and Watson, "Modern Analysis," 4th ed., Cambridge University Press, 1927, p. 132.

(2) A rough indication of the region of validity of the relations can be obtained by considering a deviation of the type RN^P where R is a constant and P is an integer. If experimental measurements are available from $N = 0$ to $N = N_0$ with an accuracy $\pm\epsilon$, then that value of P which makes the deviation largest when $N > N_0$ is $P = -1/\log N_0$ provided $N_0 < 1$. Under these conditions it can be shown that the first P equilibrium constants are unaffected by the deviation from linearity while the $(P + 1)$st constant is changed by R/P.

relations should exist between the equilibrium constants of such closely related substances as a series of polymers. The substances most closely resembling polymers whose thermodynamic properties have been investigated are the normal paraffin hydrocarbons, and the entropies and heats of formation of these compounds are known to be approximately linear functions of the number of carbon atoms. It is of interest to examine the conclusions following from the assumption that the partial molal entropies and heats of formation of polymers of the type discussed in this paper are also linear functions of the number of elements of the polymers. This assumption leads to the conclusion that the standard free energy change of the reaction

$$A_l + A = A_{l+1} \qquad (16)$$

is a constant independent of l, say $\Delta F^\circ = -RT \ln \beta$, and hence the equilibrium constant of the reaction

$$lA = A_l$$

is

$$K_l = \beta^{l-1} \qquad (17)$$

The previous deductions of this paper will be interpreted by comparison with this result.

If in equation (13) α be put equal to zero we obtain $K_l = \beta^{l-1}$, which is identical with (17). By examining (12) we see that in this case the mean polymerization number is a linear function of N.

The other extreme case is obtained by putting β equal to zero. In this case the equilibrium constants are given by (10). The equilibrium constant of the reaction (16) is

$$K = \alpha\left(\frac{l+1}{l}\right)^{l-1} \qquad (18)$$

and

$$\Delta F^\circ = -RT \log \alpha - RT(l-1) \log (l+1)/l \quad (19)$$

Equation (19) is the sum of a constant term and a term which is zero when $l = 1$ and increases steadily to RT as l becomes large. The term which depends on l does not contain an empirical constant and hence it seems that it does not depend upon the structure of the polymer. This suggests that the variable term arises from the entropy change rather than from the change in heat content.

It appears then that a small deviation from the hypotheses which lead to equation (17) is sufficient to change materially the form of the function which represents the variation of the mean polymerization number with concentration.

Application to Freezing Point Data for *p*-Nitrophenol in Naphthalene and Discussion of Error.—Figure 1 shows a plot of mean polymerization number against concentration for *p*-nitrophenol in naphthalene solution. The data are due to Auwers and collaborators,[3] and were determined by freezing point lowering measurements. The different symbols used to designate experimental points indicate independent determinations. The curve is closely linear up to concentrations of 20 g./100 g. solvent and above this point does not markedly deviate from linearity.

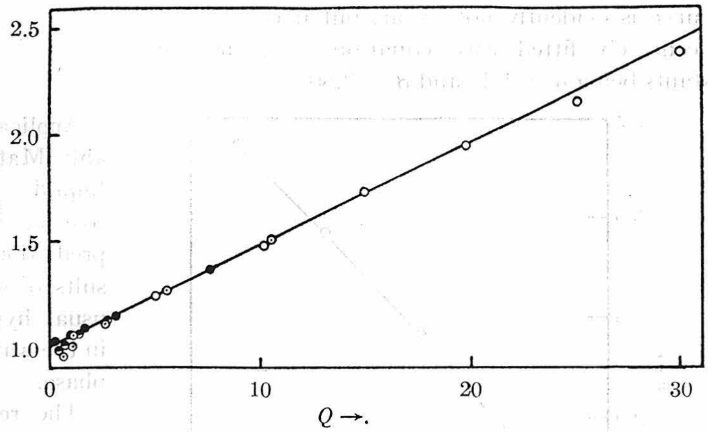

Fig. 1.—Polymerization of *p*-nitrophenol dissolved in naphthalene. Q in grams/100 grams solvent.

The terms of the series (9) will be significant only when their value exceeds the experimental error in the determination of N. Since it is of interest to obtain an estimate of the number of significant terms, we can proceed by estimating experimental error for a given value of N and finding how far it is possible to go in the series and still have the individual terms exceed the estimated experimental error in N. The highest measured value of N is 0.91 and the point deviates from the straight line by 0.06 unit, corresponding to an error in N of approximately 0.02 unit. The value of x corresponding to $N = 0.91$ is 0.495. The most optimistic estimate is obtained by taking x to be 0.495 and experimental error to be 0.02. The sixth term of series (13) exceeds 0.02 while the seventh term is less than 0.02. In order to have the whole remainder of (9) less than 0.02 it is necessary to take terms up to and including $l = 9$.

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(3) K. Auwers, *Z. physik. Chem.*, **18**, 595 (1895); K. Auwers and K. Orton, *ibid.*, **21**, 337 (1896); K. Auwers, *ibid.*, **30**, 300 (1899).

From these calculations it seems that not more than nine terms of series (9) are necessary to account for the observed data and not more than the first six terms exceed experimental error. The calculations further show that the deduction of a dependable relationship depends upon the data being accurate and extensive. For example, if experimental error had been 0.4 (about 0.3%) the fourteenth term of the series would still have exceeded experimental error.[4]

Application to Molecular Weight Data for Formanilide and *n*-Butyramide.—Figure 2 shows n against Q for formanilide in *p*-xylene as solvent. The data are due to Auwers[5] and were determined by freezing point lowering experiments. The curve is evidently not linear, but it can be very accurately fitted with equation (12), the constants being $\alpha = 1.43$ and $\beta = 3.80$.

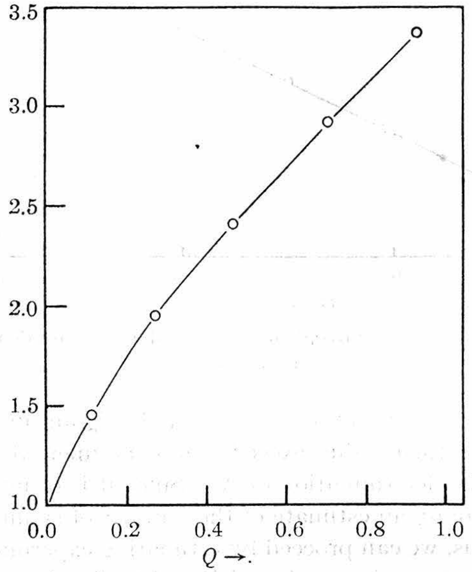

Fig. 2.—Polymerization of formanilide dissolved in *p*-xylene. Q is in moles/kg. of solvent.

Figure 3 shows n against Q for *n*-butyramide in benzene. The data are due to Meldrum and Turner[6] and were determined from boiling point raising experiments. The data are somewhat erratic, but are fitted by (12) with $\alpha = 0$ and $\beta = 3.5$.

Due to the existence of extensive data on freezing point lowering, the relations could be extensively tested, and they have been found to account for the data in many but not in all cases. Moreover, the simple approximating function (16) accounts for a much more extensive group of observations than might have been expected.

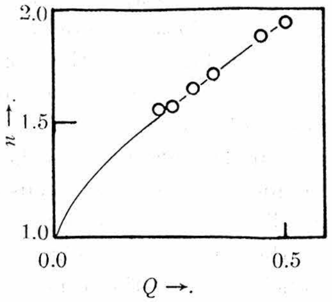

Fig. 3.—Polymerization of *n*-butyramide in benzene solution, Q in moles/liter solvent.

Application to the Distribution of Polymerizable Materials between Water and an Organic Liquid.—The application of this treatment of freezing point lowering data should permit the prediction of equilibrium constants from the results of distribution experiments, subject to the usual hypothesis that the molecules are single in the water phase and polymerized in the organic phase.

The recent investigations of Philbrick[7] have indicated that the distribution ratio may have sudden discontinuities at very low concentrations. The equations developed in the preceding sections of this paper would not, of course, account for such behavior as this but the equations are capable of accounting for some of the high concentration data. Table I shows the distribution ratio of phenol between water and pentachloroethane[8] and the calculated values of the ratio with particular values of the parameters α and β of equation (12). In this table

$$k = \frac{\text{concentration of single molecules in organic phase}}{\text{concentration of single molecules in water}}$$

and

$$D = \frac{\text{formal concentration in organic phase}}{\text{formal concentration in water}}$$

The calculated and observed values agree within about 1%.

Other distribution data also can be accounted for, but the uncertainty in extrapolation to low concentrations makes a decisive selection of constants impossible at present.

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(4) Due to the fact that freezing point experiments are not isothermal, errors are introduced into the equilibrium constants. From the van't Hoff equation, using 5000 calories for ΔH, it is calculated that a change of about 3% per degree occurs in the equilibrium constant of the reaction $A_l + A = A_{l+1}$.

(5) K. Auwers, *Z. physik. Chem.*, **42**, 513 (1903).

(6) A. N. Meldrum and W. E. S. Turner, *J. Chem. Soc.*, **97**, 1605 (1910).

(7) F. A. Philbrick, THIS JOURNAL, **56**, 2581 (1934).

(8) W. Herz and W. Rathmann, *Z. Elektrochem.*, **19**, 552 (1913).

TABLE I

DISTRIBUTION OF PHENOL BETWEEN PENTACHLOROETHANE AND WATER

$k = 1.085$, $\alpha = 0.83$, $\beta = 0$

Q	$D_{\text{obsd.}}$	$D_{\text{calcd.}}$
0.0495	1.18	1.17
.110	1.27	1.28
.226	1.51	1.51
.432	1.94	1.92
.708	2.53	2.56
1.170	3.51	3.50

I wish to thank Professor Linus Pauling for suggesting this problem, and for his help and encouragement throughout the work. I wish also to thank Professor Roscoe G. Dickinson for the many helpful discussions we have had.

Summary

1. A method of calculating equilibrium constants of polymerization reactions from freezing point, boiling point, and distribution data is described.

2. The method is applied to various compounds and it is shown that the data are often fitted by the empirical relation $n = 1 + \alpha Q + \beta N$.

3. The distribution of phenol between pentachloroethane and water is accurately accounted for by the same type of equation as accounts for freezing point lowering data.

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THE HYDROGEN BOND AND ASSOCIATION[1]

EDWIN N. LASSETTRE

Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California

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CONTENTS

I. INTRODUCTION

The phenomenon of association was known to chemists at a very early date, but its wide-spread character became most evident in the latter part of the nineteenth century through the extensive investigations of molecular weights in solution. In 1891 Nernst (28) made an important contribution to the field by successfully accounting for the distribution of

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[1] Contribution No. 585.

benzoic acid between water and benzene, assuming doubled molecules in the benzene phase.

At first it was supposed that organic compounds are polymerized only when they contain hydroxyl groups, but this was disproved by Auwers (2), who showed that the anilides are polymerized in most cases. Auwers also showed that the ortho-substituted phenols are less likely to be polymerized than the meta and para compounds, and the much later work of Sidgwick (39) showed that other properties also of ortho-substituted compounds may be strikingly different from those of the meta and para compounds.

Latimer and Rodebush in 1920 (25) proposed a theory which correlated and explained many of these facts and which is now generally accepted. The proposal of Latimer and Rodebush was that, under suitable conditions, a proton can form a bond between two atoms. Such a bond is customarily called a hydrogen bond.

Newer methods of investigation have provided extensive experimental material which in general confirms the theory in a remarkable manner. The investigation of crystal structures of both inorganic and organic compounds has revealed several structures which can be explained from the hydrogen bond point of view. One of the most important contributions was made by Pauling and Brockway (29), whose electron diffraction investigation of formic acid led to the determination of the structure of the dimer and thus opened the way to a better understanding of the polymerization of the organic acids; similar results have been provided by the crystal structure studies of oxalic acid and other carboxylic acids. Another recent and very important contribution to our knowledge of both the existence and properties of hydrogen bonds has been made by Wulf and collaborators (20, 42), who investigated the infra-red absorption spectra of many organic compounds in solution and were able to interpret the spectra in terms of hydrogen-bond formation.

In the present paper the older data, relating particularly to molecular weights and distribution ratios, are reviewed and correlated with the newer theories whenever possible. No attempt is made to include the results of crystal structure, electron diffraction, or absorption spectra investigations, but the deductions from classical data are compared with these results whenever possible and the concepts which have arisen from these investigations are freely used. For purposes of continuity in presentation the results are not necessarily presented in chronological order.

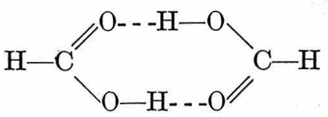
II. MOLECULAR WEIGHTS. GENERAL CONSIDERATIONS

The three most important classical methods of determining molecular weights involve the measurement of vapor density, freezing-point lowering, and boiling-point raising. For the sake of clarity a brief discussion of the freezing-point equation will be given. This equation depends upon the validity of Raoult's law and upon the assumptions of perfect gases. The assumption that the solid phase is *pure solvent* is very important; the formation of solid solutions completely invalidates this equation. The presence of a solid solution would make the freezing-point lowering less than expected and might be interpreted as polymerization. The studies of freezing-point lowering with which we shall be concerned were not accompanied by an investigation of the solid phase, but it is thought that solid solutions do not often occur in these cases. The possibility of deviations from the laws of perfect solutions due to causes other than polymerization is dealt with empirically by giving as a standard the molecular weight determination of a normal compound for each solvent concerned if possible.

III. THE ENERGY OF THE HYDROGEN BOND FROM VAPOR DENSITY AND DISTRIBUTION DATA

The heats of dissociation of polymers held together by hydrogen bonds can be obtained in a few cases from data on the change in equilibrium constant with temperature, determined by measurement of vapor density or of distribution ratio. The vapor densities of three organic acids have been carefully studied. The vapor densities of formic or acetic acid could be consistently interpreted in terms of a dimer in equilibrium with a monomer, and from the measurements values of the dissociation energy were obtained. Two other reactions, the polymerizations of benzoic and salicylic acids, have been studied in solution by investigating the change with both temperature and concentration of the distribution ratio between two immiscible solvents. These latter results are highly uncertain, but are apparently the only ones available for reactions in solution.[2]

One of the most investigated polymers is the dimer of formic acid. The electron diffraction investigation of Pauling and Brockway (29) has shown that the dimer has the structure



where the broken lines indicate hydrogen bonds. The geometry of this configuration is such that the hydrogen lies on the straight line joining the two oxygens, and the two carboxyl groups lie in the same plane. This

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[2] A more complete discussion of bond energies is to be found in a paper by Huggins (J. Org. Chem. **1,** 407 (1936)).

structure involves two hydrogen bonds, as shown. The heat of dissociation of formic acid divided by 2 should be approximately the hydrogen bond energy. The reaction

$$2HCOOH \rightleftharpoons (HCOOH)_2$$

has been the subject of a very careful study by Coolidge (15), who found the heat of dissociation of formic acid to be 14,125 cal. per mole, corresponding to the value 7063 cal. per mole for the energy of the hydrogen bond.

The vapor density of acetic acid has been studied by Fenton and Garner (16), who obtained 14,900 cal. per mole as the heat of dissociation. The vapor density of acetic acid has also been studied by MacDougall (26), who found 16,400 cal. per mole for the heat of dissociation. The latter result is probably more reliable than the former, since the study was made at such low pressures that the perfect gas laws are valid. If MacDougall's value is adopted, the bond energy is 8200 cal. per mole, assuming the same structure as for formic acid. This value is not in particularly good agreement with that obtained from formic acid and indicates that the introduction of substituents considerably changes the bond energy. Hexoic acid was also studied by Fenton and Garner, but no consistent results were obtained.

All the above values are for the gaseous materials, and it is desirable to have a value for reactions in solution. A study of the distribution of benzoic acid between two phases was made by Hendrixson (21) long ago. The distribution experiments were interpreted by assuming that the benzoic acid in the organic phase is partially polymerized into a double molecule and in water exists entirely as single molecules. It was possible to interpret the data with an equilibrium constant of the reaction

$$2C_6H_5COOH \rightleftharpoons (C_6H_5COOH)_2$$

and a distribution constant. By performing experiments at various temperatures the heat of dissociation was obtained. With benzene as the organic phase the heat of dissociation was found to be 8710 cal. per mole, and with chloroform 8350 cal. per mole. From these data the apparent hydrogen bond energies are found to be 4400 and 4200 cal. per mole, respectively. These measurements are subject to a serious uncertainty due to the transfer of water into the organic liquid layer by hydration of the acid.

Salicylic acid was also studied by Hendrixson (21), the solvents being again benzene and chloroform. The heats of dissociation obtained were 5630 cal. per mole and 7680 cal. per mole, respectively. The values will not be interpreted in terms of bond energies, because the presence of the hydroxyl group in the ortho-position makes such an interpretation uncertain. The fact that these energies are lower than those for benzoic acid may be due to the presence of the hydroxyl group or to the fact that an increase in hydration occurs which invalidates the results. That hydration is not a negligible factor is shown by the work of E. Cohen and collaborators (14, 13) and also by Szyszkowski (41), who investigated the solubility of benzoic acid in dry benzene and in benzene containing varying amounts of water. It was found that the solubility in benzene is increased by the presence of water. The solubility of benzoic acid in benzene at 25°C. was found to be about 3 per cent lower than that in benzene saturated with water, while the solubility of salicylic acid was about 30 per cent lower. This suggests that the distribution experiments on benzoic acid are approximately right, while those for salicylic acid are likely to be considerably in error. Other data bearing on this subject are presented in a following section.

IV. THE QUALITATIVE INTERPRETATION OF EXPERIMENTS ON THE LOWERING OF THE FREEZING POINT IN TERMS OF POLYMERIZATION

The ease of reversal of reactions involving hydrogen bonds precludes the study of polymers by actual isolation and subsequent study of their properties. The properties of the polymers are obtained by inference from the study of complicated mixtures of polymers of all orders. The properties of greatest interest in the study of a given compound, or compounds, are the arrangements of the atoms in space, or structure, and the rate and equilibrium of the reactions which the compound undergoes with other compounds. A consideration of molecular weights obtained by the classical methods might well provide information concerning the equilibrium constants of certain reactions involving the polymers, but can provide information concerning the structure of polymers only by inference, if at all. Nevertheless certain reasonable conclusions concerning structure can be drawn by considering molecular weights, provided we keep in mind the large accumulation of experimental evidence on internuclear distances resulting from studies of x-ray and electron diffraction by various compounds. This will be illustrated by the qualitative considerations of the remainder of this section, and data will be given which indicate the general properties to be expected of compounds which can form hydrogen bonds.

It is found, in general, that the molecular weights of organic compounds containing the groups $—NH_2$, —OH, —COOH, =NOH, and =NH are abnormally high in non-polar solvents such as benzene, carbon tetrachloride, and naphthalene, and the apparent molecular weights increase as the concentration increases, while molecular weights of the same compounds in such solvents as acetic acid are often found to be normal. These facts are illustrated by figures 1 and 2 (8, 31). In these figures *n* represents (apparent molecular weight)/(formula weight) and Q the concentration in formula weights per kilogram of solvent, unless otherwise indicated. Naphthalene and benzene are included for purposes of comparison. The freezing-point lowering constant for benzene has been taken to be 5.10 in all cases (32). The large abnormalities in non-polar solvents are interpreted as due to polymerization of the solute, while the normal molecular weights in water and acetic acid are interpreted in the usual way, as due to the reaction of the solute with solvent. The reaction of solute and solvent will not change the molal concentration of the solute, and hence will not affect a molecular weight determination by the freezing-point lowering method except in very concentrated solutions. This interpretation is a reasonable one from the hydrogen bond point of view because all the groups listed above could form hydrogen bonds with water or acetic acid. It is expected that such hydrogen bonds will be formed, owing to the large concentration of solvent, although polymerization need not disappear

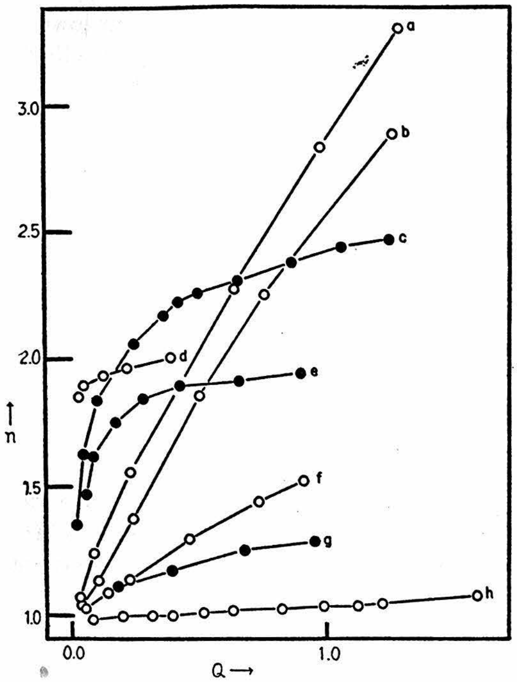
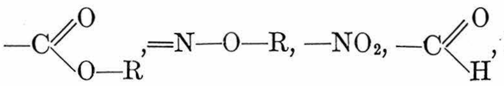


FIG. 1. Polymerization number plotted against concentration for typical polymerized solutes in benzene solution. Q in moles per kilogram of solution. a, formanilide; b, ethyl alcohol; c, acetoxime; d, benzoic acid; e, *d*-camphor oxime; f, benzhydrol; g, aniline; h, naphthalene.

completely in these solvents, and, in fact, does not always disappear, as we shall see later.

The polymerization discussed in the preceding paragraph depends upon the presence of a hydrogen atom attached to the proper sort of group. This is shown by the normal behavior of compounds containing the groups



$-\mathrm{C}\begin{array}{l}/\!\!/\mathrm{O}\\ \backslash\mathrm{O{-}R}\end{array}, =\mathrm{N{-}O{-}R}, -\mathrm{NO_2}, -\mathrm{C}\begin{array}{l}/\!\!/\mathrm{O}\\ \backslash\mathrm{H}\end{array}, \mathrm{R'{-}O{-}R}$, in which hydrogen

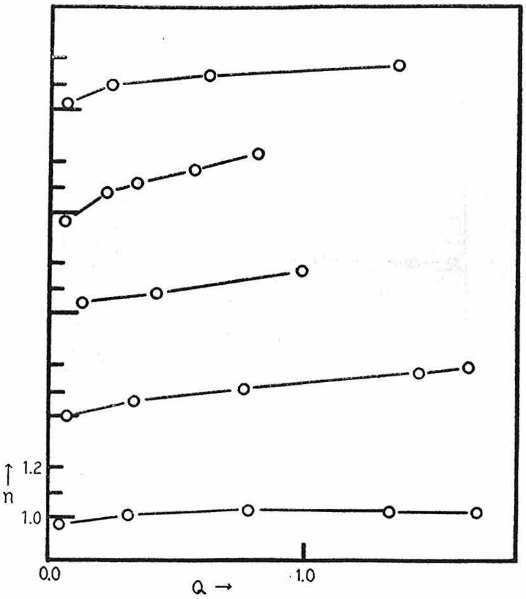


FIG. 2. The polymerization numbers of organic compounds in acetic acid solution. Q in moles per kilogram of solution. Reading from top to bottom: ethyl alcohol, benzhydrol, benzene, benzoic acid, acetoxime. The ordinate for the lowest curve is repeated for each of the upper curves.

has been replaced by another group, as illustrated by the data presented in figure 3 (8, 31). Although the apparent molecular weights of the compounds increase as the concentration increases, this increase is of the same order of magnitude as that found for naphthalene, and is therefore attributed to other causes than polymerization. The fact that the alcohols and phenol have normal molecular weights in water indicates that polymers of solute which are held together by molecules of water do not occur in these cases. Further, it seems that a large dipole moment is not sufficient to cause marked polymerization, since even such a strongly polar compound as nitrobenzene does not show an abnormal molecular weight in benzene solution.

The data given in figures 1, 2, and 3 are not always from the most recent investigations, but instead are representative of the most extensive data in the literature.

One other fact concerning figure 1 should be noted, namely, that for acids and oximes the value of n appears to be approaching an upper limit, while for alcohols, anilides, acid amides, and phenols the value of n increases indefinitely and almost linearly as the concentration increases. This indicates that polymers of low order are predominant in solutions of acids and oximes, while higher polymers occur in solutions of alcohols, anilides, etc. Of the two oximes shown, one appears to be approaching an upper limit of $n = 2$, while the second appears to be approaching an upper limit of $n = 3$ or more. Both the dimer and trimer of these oximes would

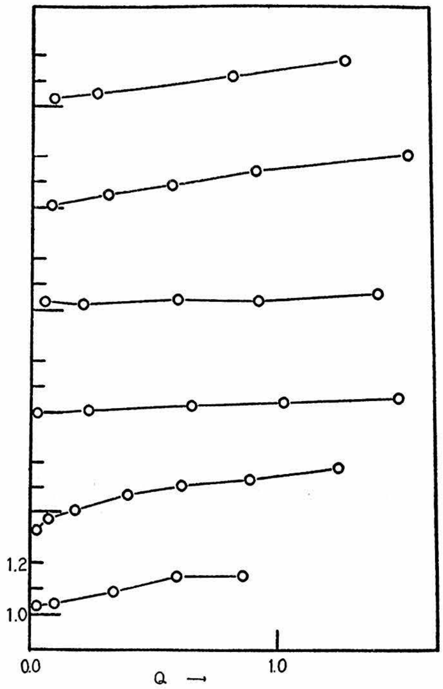


FIG. 3. Polymerization numbers of organic compounds which do not contain hydrogen attached to oxygen. The solvent is benzene. Q in moles per kilogram of solution. Reading from top to bottom: acetone, nitrobenzene, phenetole, ethyl benzoate, benzaldoxime ethyl ether, benzaldehyde. The ordinate for the lower curve is repeated for each of the upper curves.

probably be rings held together by hydrogen bonds of the N- - -H—O type. That the trimers would occur in one case and not in the other might be due to a change in the =N—O—H bond angles in the two cases. These conclusions are borne out, for alcohols and acids, by distribution experiments which will be discussed shortly. The structures of the acid dimers are probably the same as that of formic acid. Neither molecular weight nor distribution data, except in very dilute solution, can be entirely accounted for by a dimer, so there may well be higher polymers in the solution.

The molecular weights of ethyl mercaptan, amyl mercaptan, and thiophenol have been investigated in benzene solution and found to be normal, indicating that the group —S—H does not form hydrogen bonds to any appreciable extent. A related conclusion, that —OH does not form hydrogen bonds to sulfur, is drawn from the fact that benzoic acid is found to be as largely polymerized in carbon disulfide solution as in benzene. A few hydrazones have been studied in naphthalene solution and found not to be appreciably polymerized (6).

V. EVIDENCE FROM MOLECULAR WEIGHT DETERMINATIONS FOR CHELATION IN AROMATIC COMPOUNDS

The investigations of the physical properties of the nitrophenols give evidence of another type of hydrogen-bond formation for which we shall use the name *chelation.*[3] Of their physical properties which have been investigated we shall consider in this section only the molecular weights.

A consideration of figure 4 (6) shows that the molecular weights of the *m*- and *p*-nitrophenols are abnormally high in naphthalene solution, while that of *o*-nitrophenol is normal. This difference in behavior of the ortho compounds is attributed to the formation of an internal hydrogen bond of the type shown in figure 5. The formation of an internal hydrogen bond would be expected to reduce the polymerization of *o*-nitrophenol, since the energy of this substance in the monomolecular form would be lowered by hydrogen-bond formation relative to non-chelated molecules, such as for *m*- and *p*-nitrophenol, whereas the ortho polymers would be about the same as the meta and para polymers, and hence the equilibrium between single molecules and polymers would lie farther towards single molecules for *o*-nitrophenol than for *m*- and *p*-nitrophenol. These experimental data indicate that a hydrogen atom already used to form a chelate ring cannot, at the same time, form a hydrogen bond to a neighboring molecule. The foregoing explanation was apparently first given by Sidgwick

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[3] The term "chelation" is used by the English chemists to designate hydrogen bonds of all types. In this paper the term is used, for purposes of convenience, to designate only internal hydrogen-bond formation.

(36) and has been amply confirmed by the work of Wulf and collaborators from their study of absorption spectra.

The discussion of the nitrophenols shows that a study of molecular weights provides a means of detecting chelation in aromatic compounds. If the molecular weights of the meta and para compounds are abnormally high and increase with increasing concentration, while the molecular weight of the ortho compound is normal, it can be concluded immediately that the meta and para compounds form polymers through hydrogen-bond formation, and that the ortho compound is chelated. Figures 6a, 6b, and 6c (6) show the experimental data for the hydroxybenzaldehydes, the methyl esters of the hydroxybenzoic acids, and the azo compounds of phenol, re-

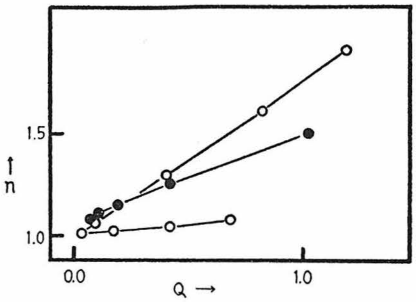


FIG. 4. Polymerization numbers of the nitrophenols in naphthalene solution. From top to bottom: *p*-, *m*-, and *o*-nitrophenol.

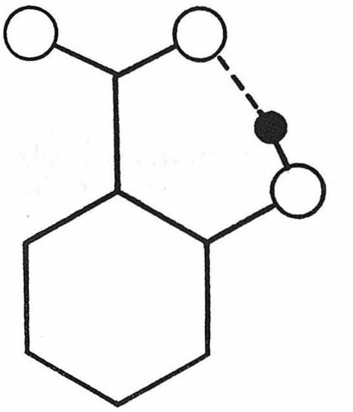


FIG. 5. Diagram of *o*-nitrophenol. The circles are oxygen atoms and the black dot is a hydrogen atom. The dimensions of the nitro group are those given by Brockway, Beach, and Pauling (11), while the other dimensions were obtained from a table of radii (30). The broken line represents a hydrogen bond.

spectively, in naphthalene solution. From these figures it appears that the ortho compounds are all chelated and hence that the azo, aldehyde, and carboxylic ester groups are capable of forming hydrogen bonds with the hydroxyl hydrogen. These results are in agreement with those of Wulf and collaborators. It should be noted that the structures of the azo, aldehyde, and ester groups are such that a six-membered ring can be formed, similar to that for *o*-nitrophenol shown in figure 5.

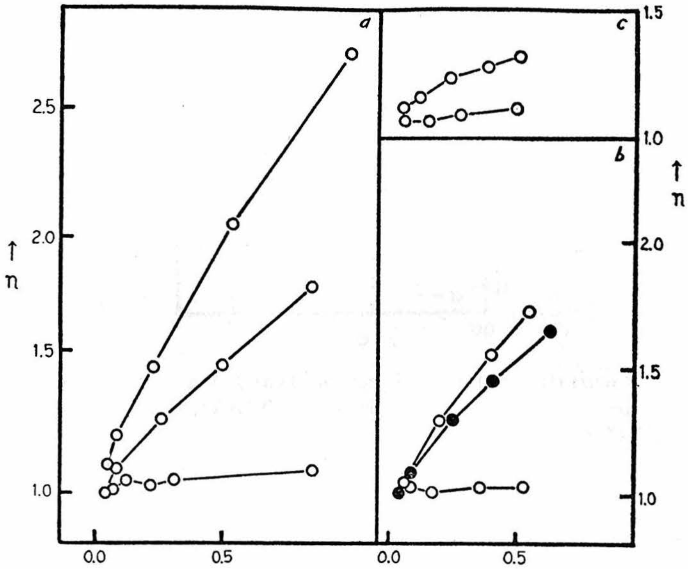
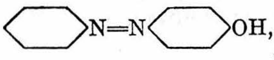
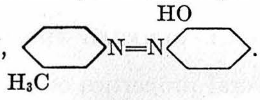


FIG. 6. (a) Polymerization numbers for the hydroxybenzaldehydes in naphthalene solution. Top to bottom: para, meta, ortho. (b) Polymerization numbers of methyl esters of the hydroxybenzoic acids in naphthalene solution. Top to bottom: para, meta, ortho. (c) Polymerization numbers of the azophenols in naphthalene solution. Top to bottom: ,  $\underset{\mathrm{H_3C}}{\bigcirc}\mathrm{N{=}N}\overset{\mathrm{HO}}{\bigcirc}$. The abscissae for a and b are the same.

All the preceding examples have been substituted phenols, but the phenomenon of chelation is not confined to these compounds. Compounds of the type


$\underset{\mathrm{X}}{\bigcirc}\mathrm{NHCOCH_3}$

are apparently chelated when the group X is a nitro or aldehyde group, but the chelation is weak when X is a methoxyl group. These facts are illustrated by the data presented in figure 7 (2) for compounds in naphthalene solution. The chelation is assumed to occur between the hydrogen of the amine group and the group X. The chelate rings contain six members in all cases shown, except the methoxy compound, which will be discussed later.

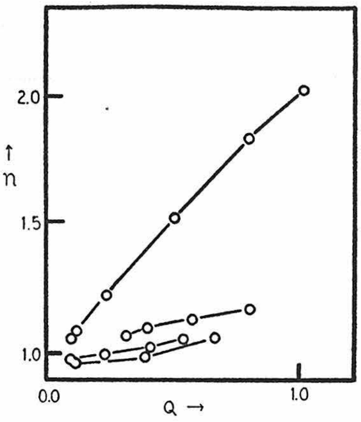


FIG. 7. Polymerization numbers of acetanilide and ortho-substituted acetanilides. Top to bottom: $C_6H_5NHCOCH_3$, o-$C_6H_4(OCH_3)NHCOCH_3$, o-$C_6H_4(CHO)COCH_3$, o-$C_6H_4(NO_2)NHCOCH_3$.

TABLE 1

Relative solubilities of o-, m-, and p-nitrophenols

Solvent	H_2O	H_2O	C_2H_5OH	C_4H_9OH	CH_3COCH_3	Ether	C_6H_6	C_6H_6
Temperature	60°	20°	60°	60°	23°	17°	60°	20°C.
ortho/para	0.200	0.388	1.63	0.855	1.46	2.67	127.5	193.4
meta/para	0.739	1.84	1.03	0.560	1.17	1.03	1.04	2.76

VI. THE GENERAL PHYSICAL PROPERTIES OF CHELATED COMPOUNDS

Several properties of chelated compounds are strikingly different from the properties of the non-chelated isomers in a way which can be interpreted from the hydrogen bond point of view.

It has been emphasized by Sidgwick that vapor pressures and solubilities of chelated compounds differ largely from those of the non-chelated isomers. For example, the vapor pressures at 100°C. of *o*-, *m*-, and *p*-nitrophenol are, respectively, 2.92 mm., 0.196 mm., and 0.083 mm. (37). To interpret these facts we consider the energy change attending a transfer of material from the liquid to the vapor phase. In liquid *m*- and *p*-nitrophenol hydrogen bonds exist between neighboring molecules, while in liquid *o*-nitrophenol chelate bonds exist and hence the energies of all three isomers are approximately the same. In the vapor phase chelation will persist in *o*-nitrophenol, but the polymers of the *m*- and *p*-nitrophenols will tend to be dissociated, and therefore the energy absorbed upon vaporization of the meta and para compounds will be larger than for the ortho compound, thus leading to lower vapor pressures. In table 1 are shown the ratios of the solubilities of *o*- and *p*-nitrophenol, and of *m*- and *p*-nitrophenol in various solvents (38). Whereas the solubilities of the *m*- and *p*-nitrophenols are about the same in all solvents and the solubilities of the ortho, meta, and para compounds are roughly the same in the oxygenated solvents, the ortho compound is enormously more soluble in benzene than are the meta and para compounds. To find the reason for this behavior we consider the energy change occurring upon solution. The energies of the *o*-, *m*-, and *p*-nitrophenols as solids should be about the same, for the reason given above for liquids, and in an oxygenated solvent they should be about the same, since the meta and para compounds form bonds with the solvent while the ortho compound either remains chelated or forms bonds with the solvent. The energy changes are therefore about the same for all compounds in this case, and hence the solubilities should be about equal in oxygenated solvents. In benzene solution, however, the ortho compound remains chelated, while the meta and para compounds are dissociated; hence the energy absorbed by the meta and para compounds is larger and their solubility should be smaller.

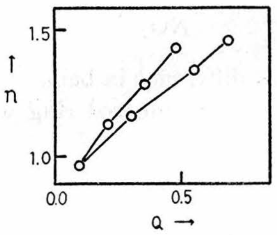


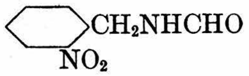
FIG. 8. Polymerization numbers of the nitrobenzylacetamides in naphthalene solution. Top to bottom: *p*-$C_6H_4(NO_2)CH_2NHCOCH_3$, *o*-$C_6H_4(NO_2)CH_2NHCOCH_3$.

Sidgwick and his coworkers (39) have investigated the phase rule diagrams of systems containing an organic component and water. It was found that when the organic component was chelated the critical solution temperature was much higher than for non-chelated isomers. The interpretation of this fact is apparently more complex than the interpretation of vapor pressure or solubility data.

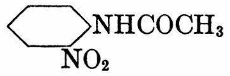
VII. EXAMPLES OF MOLECULAR WEIGHT STUDIES WHICH ILLUSTRATE THE STEREOCHEMICAL PROPERTIES OF HYDROGEN BONDS

The examples of section V have indicated some of the types of compounds in which six-membered chelate rings are found to occur. In this section examples showing the effect of varying the number of members in the chelate ring will be examined, together with others intended to illustrate the effect of varying bond angles and distances.

A consideration of figure 8 (2) shows that the compound

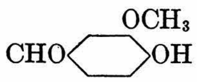


is not chelated to any large extent, while we have already seen that the compound

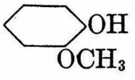


is strongly chelated. This difference in behavior is attributed to the fact that in the first case a seven-membered ring would have to be formed. We have already seen that the compound

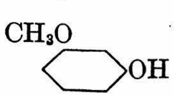
is weakly chelated in naphthalene solution. In this compound only a five-membered ring can be formed. The compound



has been studied in naphthalene solution, and it was shown that although it is less polymerized than *p*-hydroxybenzaldehyde there is nevertheless some polymerization and hence the chelation is not complete. The results of molecular weight studies (4) on the two compounds



and



show that the ortho compound is chelated. These results indicate that the six-membered ring is somewhat more stable than the five-membered ring, and a seven-membered ring is much less stable than a five-membered one. The conclusions are expected to be dependent upon the bond angles and internuclear distances in the ring. The general conclusions concerning the stability of the various rings are the same as those reached by Wulf and collaborators (20, 42) from their studies of absorption spectra. These investigators studied many more examples than are given here, and their conclusions are correspondingly more certain.

Figure 9 shows molecular weight data for *o*- and *m*-cyanophenol (6) and phenol in naphthalene solution. It is evident that the ortho compound is not chelated to any appreciable extent. It would be wrong, however, to conclude that the cyanide group is incapable of forming hydrogen bonds with the hydroxyl group, because from figure 12 we see that the introduction of the cyanide group into phenol enormously increases the polymerization. The reason for this apparently anomalous behavior is that the cyanide group is directed straight out from the benzene ring, and hence the distance between oxygen and nitrogen becomes too great for a strong hydrogen bond to be formed.

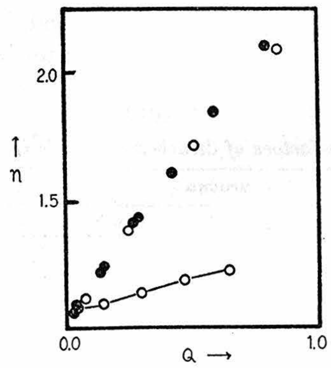


FIG. 9. Polymerization numbers of the cyanophenols in naphthalene solution. Upper curves: ●, *o*-cyanophenol; ○, *p*-cyanophenol. The lower curve is phenol.

In view of the preceding results it would seem reasonable to suppose that a dicarboxylic acid would tend to chelate, provided the hydrocarbon chain became long enough to permit the carboxyl groups to get close to one another. Measurements on the molecular weights of dicarboxylic acids in phenol by Robertson (34) have indicated that this is actually the case. The results of these experiments were not recorded directly by the investigator, who instead gave a number A, which is essentially the percentage change in polymerization number n for a lowering of 3.5°C. In table 2 are shown values of A for ethylmalonic, methylsuccinic, and sebacic acids; benzene is included for comparison purposes. Both ethylmalonic and methylsuccinic acids are polymerized, but sebacic acid is polymerized only slightly if at all. It can be shown by constructing a model that the hydrocarbon chain is long enough to permit chelation in sebacic acid, with eight carbon atoms in the chain between the carboxyl groups, but not in methylsuccinic or ethylmalonic acid.

From molecular weight measurements it is known that the polymerization numbers of benzoic, *o*-nitrobenzoic, and *m*-nitrobenzoic acids are approximately the same at a concentration of 0.5 molal in naphthalene solution (6), which indicates that there is no marked amount of chelation in *o*-nitrobenzoic acid. Since a seven-membered ring would have to be formed, it is not surprising that no marked chelation occurs. No molecular weight data exist for *o*-methoxybenzoic acid, but distribution experiments have been performed on this compound in both toluene and chloroform solutions (40). The attempt to determine the equilibrium constant for chloroform solution was unsuccessful, but in toluene solution the compound was found to be much less polymerized than benzoic acid. This indicates that the ortho compound is chelated, but the possibility of hydration renders the interpretation uncertain until more experimental data are available. It is to be noted that a six-membered ring could be formed in this case.

TABLE 2

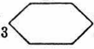
Association factors of dicarboxylic acids in phenol solution

COMPOUND	*A*
Ethylmalonic acid	31
Methylsuccinic acid	47
Sebacic acid	16
Benzene	12

The relative vapor pressures of *o*-, *m*-, and *p*-hydroxybenzoic acids are 1320.0, 5.0, and 1, respectively, at 100°C. (35), indicating that the ortho compound is chelated (see section VI). On the other hand the relative vapor pressures of the *o*-, *m*-, and *p*-nitrobenzoic acids are 20.9, 7.3, and 1, respectively, at 100°C., indicating that the ortho compound is only weakly chelated if at all. These results confirm the relative stabilities of six- and seven-membered rings. Unfortunately it is not possible to say from these data whether the hydrogen involved in the chelate ring of *o*-hydroxybenzoic acid comes from the hydroxyl group or from the carboxyl group.

VIII. THE EFFECT OF CHANGE OF SOLVENT UPON THE MOLECULAR WEIGHTS OF DISSOLVED COMPOUNDS

The effect of change of solvent upon the molecular weights of dissolved materials was actively investigated in the early part of the twentieth century in connection with the hypothesis of Nernst that polymerization is least in solvents of high dielectric constant. The general result of these investigations was to confirm this rule, and the results appear to be so well known that they will be omitted here unless they are intimately connected with the properties of the hydrogen bond.[4]

The earliest and perhaps the most complete systematic investigation of the effect of solvent change was that of Auwers (5). The solvents used were of the type CH_3X, where the X group was varied. The solutes used were substituted phenols and benzoic acids. The general result of this investigation was summarized by Auwers with the statement that the order of the groups in producing polymerization was —CH_3, —Cl, —Br, —I, —NO_2, —CO_2R, —CN, —CHO, —NH_2, —CO_2H, —OH. The groups furthest to the left were most effective in producing polymerization when in the solvent and least effective when in the solute. The experiments were rough, and in a few cases solid solutions seemed to be formed, but the order given has in general been confirmed by subsequent investigations. The position of the amino group in this series is a little surprising in view of the small polymerization of aniline in benzene solution (see figure 1). The result indicates that the amino group forms much stronger hydrogen bonds with other groups than with itself. This property of the amino group also makes itself felt in connection with other properties than polymerization (36).

The investigations of Meldrum and Turner (27) on the acid amides and anilides in the solvents benzene, chloroform, alcohol, acetone, ether, and water have shown that although polymerization proceeds about as expected in the first five solvents, the amides and anilides are much more widely polymerized in water than might be expected, and in fact those compounds which are least polymerized in benzene tend to be most polymerized in water. Of the solvents listed only alcohol and water have hydrogen atoms which can form hydrogen bonds, alcohol having one and water two. From the order of Auwers and the interpretation given to it, it seems reasonable to suppose that in case a solvent can donate two hydrogen atoms, one to each of two molecules of a solute, a polymer may be formed which is held together by a molecule of solvent. Water is the only such solvent among those listed and is at the same time that solvent in which most anomalies occur. For one compound, methylacetanilide, which contains no hydrogen which can form hydrogen bonds and hence for which no polymerization is expected, it is actually found that in benzene, chloroform, alcohol, acetone, and ether the molecular weight is normal, while in water the molecular weight is about three times the formula weight. This com-

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[4] For an account of these results see Turner, *Molecular Association*, Longmans, Green and Co. (1915).

pound is appreciably volatile at the boiling point of water, but this fact was known to Meldrum and Turner and precautions were taken to reduce the error to a minimum, although the molecular weight was not actually corrected for the volatility of the solute. The opinion of the investigators was that the high molecular weight cannot be entirely accounted for by the volatility of the compound. If this result is correct it is difficult to see how this high molecular weight can be explained other than by assuming that two molecules of solute are held together by one of water. The experiments of Peddle and Turner (31) on the molecular weights of salicylic and benzoic acids in water solution deserve mention, because they provide an inconsistency which has not yet been explained. At the boiling point of water these acids have molecular weights approximately twice the formula weight, even after corrections have been applied for the volatility of the two acids. These experiments cannot as yet be said to contradict flatly the experiments on the distribution of benzoic and salicylic acids between benzene and water, because they were performed at a different temperature, but they come dangerously close to contradicting the distribution experiments. From molecular weight measurements in benzene such as those shown in figure 1 it is known that benzoic acid is probably not more than doubled in benzene at the freezing point, and hence the distribution experiments cannot be explained by assuming a doubled molecule in water and a quadrupled one in benzene. This contradictory evidence led Peddle and Turner to conclude that the polymerization of compounds in water solution was not a real effect but was due to some simplification in the structure of water caused by the addition of solute. This hypothesis seems unlikely, especially in view of the fact that Raoult's law has been verified for such a compound as mannite in water solution (17). The whole problem is now at a point at which more experimental investigation is called for.

The behavior of benzoic acid in a few of the more common solvents is shown by the data given in table 3 (9, 12). The number recorded is the mean polymerization number at a concentration of 0.5 mole per kilogram of solvent. The measurements were on the raising of the boiling point, except for that in nitrobenzene which was an experiment on the lowering of the freezing point. Benzoic acid is polymerized in all the non-polar solvents given and is not appreciably polymerized in any of the oxygenated solvents except nitrobenzene. Nitrobenzene behaves in the same fashion with other polymerizable compounds.

Experiments in pure solvents provide us with two extreme pieces of information at temperatures which are often widely different, one on the behavior in a pure non-polar solvent and the other on the behavior in a pure hydrogen-bond-forming solvent. It is desirable to have a complete view of the isothermal changes in polymerization which occur when one goes continuously from one of these extreme cases to the other. Such a picture is obtained from a consideration of the experiments of Barger (7) on the molecular weights of compounds in mixed solvents. By means of an ingenious method Barger was able to measure the molecular weights of solutes in solvents which were mixtures of two components, of which one component was a non-polar material, such as benzene, and the other component a hydrogen-bond-forming material, such as an alcohol. A series of measurements upon a polymerizable solute was then made in a series of solvent mixtures of varying composition. A set of data typical of the results obtained, with a few exceptions, is shown graphically in figure 10. The concentration of solute is indicated in the legend and was kept constant in all measurements of a given series. As ordinate is plotted the mean polymerization number of solute and as abscissa the percentage composition of the solvent. The striking feature of the figure is that the introduction of a small amount of hydrogen-bond-forming solvent materially decreases the polymerization number. This can be interpreted most easily by assuming that the solvent combines with the solute and breaks up the polymer; this interpretation was given by Barger in 1905.

TABLE 3

Polymerization numbers of benzoic acid (0.5 molal) in various solvents, with naphthalene for comparison

SOLVENT	n FOR BENZOIC ACID	n FOR NAPHTHALENE
Acetone	0.99	1.00
Acetic acid	1.00	1.17
Ethyl ether	1.04	0.98
Ethyl alcohol	1.06	
Ethyl acetate	1.09	1.04
Chloroform	1.82	1.00
Benzene	1.96	1.10
Carbon disulfide	2.14	1.03
Phenol	1.16	1.09
Nitrobenzene	1.69	

Figure 10 thus indicates that pyridine forms strong hydrogen bonds with formanilide. This is in complete agreement with the investigations of Innes (23), who showed that organic acids and related compounds have normal molecular weights in pyridine. Presumably these data can be analyzed by applying the law of mass action, but the solutions are so concentrated and the equilibria are so complex that this does not seem worth while.

The curve found by Barger for guaiacol in mixtures of methyl alcohol and chloroform shows a pronounced maximum at about 15 per cent alcohol. Guaiacol has already been shown to be a definitely chelated compound and its chelated character is borne out in this experiment, since in pure chloroform the polymerization number is small. Guaiacol was the only chelated compound investigated and the only one for which a maximum was observed, so it seems probable that the two are connected. An interpretation in terms of hydrogen bonds leads to the conclusion that the addition of methyl alcohol tends to break the chelate bond, but the experimental data are so incomplete that this conclusion is not justified at present. More investigation of this point would be desirable.

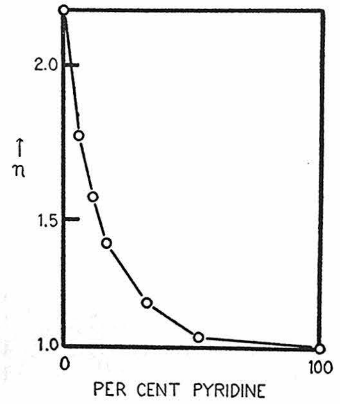

FIG. 10. Polymerization number of formanilide dissolved in mixtures of pyridine and toluene. The concentration of formanilide was 0.5 mole per liter of solution throughout. The percentage composition of solvent is plotted as abscissa.

IX. EXPERIMENTS UPON THE DISTRIBUTION OF HYDROGEN-BOND-FORMING COMPOUNDS BETWEEN TWO IMMISCIBLE SOLVENTS

In the distribution experiments which are considered here one phase is always water and the other an organic liquid. Interpretation of these experiments is always made by assuming that the molecules are single in the water phase, and polymerized, if at all, only in the organic phase. One of the most serious difficulties which attend the interpretation of distribution experiments is the possibility of hydration. Quantitative investigation of this factor has been made in recent years and a description of some of these results will be given first.

By studying the solubilities of certain organic acids in solutions of both dry benzene and benzene saturated with water Szyszkowski (41) has been able to correct the dissociation constants, obtained from distribution experiments, for hydration. The increase in solubility of the acid gave directly the concentration of hydrated molecules. Since water is comparatively insoluble in benzene the solution will be dilute with respect to water, so it was assumed that the hydrate of most importance at these low concentrations is that containing one molecule of water. With these assumptions it is possible to compute the equilibrium constant for the dissociation of non-hydrated double molecules by a straightforward application of the law of mass action. In the course of these experiments Szyszkowski found that in order to account for the distribution ratio of *o*- and *m*-nitrobenzoic acids between water and benzene it is necessary to assume, in addition to a dimer, quadruple molecules in the benzene phase. The results are shown in table 4. The concentrations are in moles per kilogram. The letters shown in the table have the following meanings: K' is the equilibrium constant, uncorrected, of the reaction $A_2 \rightleftharpoons 2A$, Δ is the percentage change in solubility of the acid upon saturating benzene with water, K_2 is the equilibrium constant of the reaction $A_4 \rightleftharpoons 2A_2$, and K is the corrected value of K'. The values of K differ considerably from those of K'. If we look at K' we conclude that *m*-nitrobenzoic acid is much less polymerized than salicylic acid, while if we look at K we arrive at the opposite, and correct, conclusion. This experiment indicates the need for caution in comparing the results of distribution experiments. An examination of the table shows that both salicylic and *o*-nitrobenzoic acids are less polymerized than benzoic acid, while *m*-nitrobenzoic acid is more polymerized, indicating that *o*-nitrobenzoic acid is weakly chelated.

TABLE 4

Dissociation constants of aromatic acids from distribution ratios at 25°C.

ACID	K_2	K'	Δ	K
	moles per kilogram	*moles per kilogram*	*per cent*	*moles per kilogram*
Benzoic		2.63×10^{-3}	3.1	4.74×10^{-4}
Salicylic		3.30×10^{-3}	31.2	8.45×10^{-3}
o-Nitrobenzoic	1.75×10^{-2}	4.60×10^{-2}	60	8.38×10^{-3}
m-Nitrobenzoic	0.70	1.15×10^{-2}	26.7	2.49×10^{-4}

Szyszkowski also investigated the question of whether these acids could form compounds with one another. This was done by measuring the solubility of mixtures of the two compounds. It was observed that the solubility of the mixture is greater than the sum of the solubilities of the separate acids. The excess is attributed to compound formation between the two acids and upon assuming that the combination is one to one the equilibrium constant, K_{12}, of the reaction $AB \rightleftharpoons A + B$ is obtained. The constants K_{12} for various pairs are shown in table 5. The constants are of the same order of magnitude as the dissociation constants of the dimers of the pure constituents, but otherwise seem to bear no particular relation to them.

This work illustrates the importance of investigating the question of hydration and indicates that distribution experiments which do not take this effect into account may give misleading results. In the present stage of experimental development distribution experiments are chiefly useful for detecting polymerization and for finding the relations between the equilibrium constants of successive polymers.

The general results of distribution experiments show that the organic acids can be considered as polymerized largely into doubled molecules, while phenol polymerizes into high-order polymers. This fact is illustrated by figure 11, which shows the distribution ratio as a function of the concentration for phenol between water and pentachloroethane. If only a dimer were present the curve would be a straight line. In connection with the polymerization of phenol a recent investigation by Philbrick (33) of the distribution between water and several organic solvents shows a dimer of phenol to be present, except possibly in carbon tetrachloride solution. The investigations were made in very dilute solution, and it is shown that the distribution ratio is a linear function of the concentration in the water phase at low concentrations. This is just the behavior expected when a dimer is predominant. The equilibrium constants of the reaction 2A $\rightleftharpoons A_2$ for various solvents are shown in table 6. The order of solvents in

TABLE 5

Dissociation constants of mixed compounds of aromatic acids

MIXTURE	K_{12}
Salicylic + *o*-nitrobenzoic acids	6.30×10^{-3}
m-Nitrobenzoic + salicylic acids	2.19×10^{-3}
m-Nitrobenzoic + *o*-nitrobenzoic acids	8.94×10^{-4}

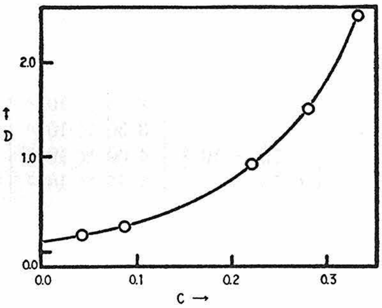

FIG. 11. Distribution of phenol between pentachloroethane and water

producing abnormalities is in agreement with that of Auwers. Philbrick also reported a sharp point of inflection in the distribution ratio curve at low concentrations, which has not previously been observed and which has not yet been completely accounted for. More extended investigation of this phenomenon is called for. The distribution ratio between carbon tetrachloride and water does not vary sufficiently to permit the calculation of an equilibrium constant.

The most extensive investigation of the distribution of organic acids between two solvents is that of Smith and White (40), who used the solvents toluene, chloroform, and benzene. The experiments were not corrected for hydration, and the equilibrium constants vary quite specifically with both solvents and substituents. This is illustrated by the fact that in toluene solution the dissociation constants of the dimers of *o*- and *p*-toluidic acids are 22.3 × 10^{-3} and 1.74 × 10^{-3}, respectively, while in chloroform solution the constants are 1.38 × 10^{-3} and 198.0 × 10^{-3}, respectively, the order being completely changed. This fact and others like it discourage any attempt to interpret the results.

TABLE 6

The equilibrium constants for the dimer of phenol in various solvents

SOLVENT	K
	moles per liter
$C_6H_5CH_3$	0.843
C_6H_5Cl	0.648
C_6H_6	0.575
$C_6H_5NO_2$	0.196

X. THEORY OF THE CALCULATION OF EQUILIBRIUM CONSTANTS FROM DATA ON THE LOWERING OF THE FREEZING POINT AND FROM DISTRIBUTION DATA

In the preceding sections data have been presented which indicate that the properties of solutions of organic acids can be satisfactorily accounted for by assuming equilibria between single and double molecules. There remains the problem of applying the law of mass action to solutions which contain higher polymers.

It is assumed that the solutions under discussion contain polymers constructed from some fundamental molecular unit designated by A, the polymer of order l being designated by A_l. The essential variables are as follows:

Q = concentration in formula weights of A per kilogram of solvent,
N = concentration in total moles of solute per kilogram of solvent,

n = moles of solute per formula weight of A (evidently $n = Q/N$),
(A_l) = concentration of polymer A_l in moles per kilogram of solvent, and
$K = (A_l)/(A)^l$ = equilibrium constant of the reaction $lA \rightleftharpoons A_l$.

The following three hypotheses are made: (i) Abnormalities (e.g., in freezing points) are due to the presence of polymers. (ii) The reactions involved are so rapid that equilibrium is completely established at the time of measurement. (iii) The polymers obey the law of mass action with all activity coefficients unity. These three hypotheses suffice for the proof of the following two mathematical theorems.

Theorem A. There exists one and only one set of constants K_l which leads to a relation between n, Q, and N of the form

$$n = 1 + f(Q, N) \tag{1}$$

where $f(Q, N)$ is a given continuous function with continuous derivatives of all orders, $f(0, 0) = 0$, and $f(Q, N) \geqslant 0$.

Theorem B. If $f(Q, N)$ of equation 1 has the form

$$f(Q, N) = \alpha Q + \beta N \tag{2}$$

where α and β are any constants independent of n, Q, and N, the equilibrium constants are given by

$$K_l = \frac{1}{l!}\prod_{q=0}^{l-2} [\alpha l + \beta(l - q)], \qquad q = 0, 1, 2, \cdots, l - 2;\ l = 1, 2, 3, \cdots, \tag{3}$$

and in addition

$$N = (A)(1 + \beta N)^{\frac{\alpha+\beta}{\beta}} \tag{4}$$

In order that K_l be positive we must have $\alpha + \beta > 0$, and $\alpha > 0$.

The inverse of theorem A, namely, that to each set of constants there corresponds only one function $f(Q, N)$, is not true without further restrictions. This arises because N and Q are not independent. If we substitute the relation $Q = nN$ in equation 1, we obtain $n = 1 + f(nN, N)$, and this equation can be solved for n, having, in general, several roots from which we must select that root which satisfies the condition that $n = 1$ when $N = 0$. This will determine the root uniquely, and the resulting equation will have the form $n = 1 + \phi(N)$, $\phi(0) = 0$. With the problem in this form only one function $\phi(N)$ will correspond to a given set of constants K_l and vice versa. The same is true when we eliminate N from the equation instead of Q. These facts may be illustrated by using the special function equation 2. Making the substitution $N = Q/n$ and solving for n we obtain

$$n = \{1 + \alpha Q \pm \sqrt{(1 + \alpha Q)^2 + 4\,\beta Q}\}/2$$

n reduces to unity when $Q = 0$ only provided we take the positive sign for the radical, hence

$$n = \{1 + \alpha Q + \sqrt{(1 + \alpha Q)^2 + 4\,\beta Q}\}/2$$

This matter is of some importance in actual applications of the theorems. It is to be noted that, subject to the restrictions outlined above, equation 1 determines one and only one curve in the n,Q plane, and hence, for example, any curve in figure 1 determines a unique set of K_l's and vice versa.

The proofs of these theorems will be omitted, since they are given in detail in an article to be published elsewhere (24).

In applying these results to actual data the constants α and β of equation 2 are to be determined by making use of measured values of n, Q, and N; specific methods of evaluating the constants are given in a subsequent section. Since equation 3 provides for an infinite number of constants, a discussion of the number of significant constants must be given, and this matter will be taken up in section XI in connection with a specific set of experimental data. Theorem A serves mainly to indicate the danger of an unrestrained discussion of experimental data from this point of view. Positive deviations from the laws of perfect solutions may well, and indeed do, arise from causes other than polymerization, and in these cases a treatment in terms of the above ideas would serve only to disguise the nature of the phenomena involved. It is necessary then to confine the treatment to cases for which the deviations are so large that they can be attributed only to polymerization.

TABLE 7

Dependence of K_l on ratio of α to β when $\alpha + \beta = 2$

$\alpha =$		0	1	2	3	4	5
$\beta =$		2	1	0	−1	−2	−3
$l =$	2	2	2	2	2	2	2
	3	4	5	6	7	8	9
	4	8	14	21.3	30	40	51.3
	5	16	42	83.3	143	224	329.3

If we let $l = 2$ in equation 3 we obtain $\alpha + \beta = K_2$, which is the equilibrium constant of the reaction $2A \rightleftharpoons A_2$. This establishes the physical significance of the sum of α and β. To study the physical significance of the ratio of α and β we make the following calculation. We keep $\alpha + \beta$ (that is, K_2) constant but vary the ratio of α to β; the equilibrium constants K_l, with $l > 2$, are then found to increase steadily as α increases and β decreases, the increase being larger for larger l. This is illustrated for the case $\alpha + \beta = 2$ by table 7. It is seen that as β becomes more negative the higher equilibrium constants begin to predominate more and more strongly.

This is also reflected by the fact that if, using the relation $n = Q/N$, we plot n as a function of Q from equations 1 and 2 the curve is convex more and more sharply upward as the value of β becomes more negative.

It is interesting to examine the free energy change attending the addition of a single molecule to a polymer of order l, that is, the free energy change of the reaction $A_l + A \rightleftharpoons A_{l+1}$. The equilibrium constant of this reaction is

$$K_l' = \frac{K_{l+1}}{K_l}$$

In the limiting case $\alpha = 0$ we obtain from equation 3

$$K_l' = \beta \tag{5}$$

This is just the relation expected when both the partial molal entropy and the partial molal heat content of a polymer are linear functions of the number of molecules in the polymer. This result is therefore a very reasonable one, particularly in view of the fact that the entropies and heat contents of the liquid normal paraffin hydrocarbons have been found by experiment to be nearly linear functions of the number of carbon atoms and, in fact, the thermodynamic constants of many organic compounds are known to be additive.

In the limiting case $\beta = 0$ we obtain

$$K_l' = \alpha\left(\frac{l+1}{l}\right)^{l-1} \tag{6}$$

This is seen to vary with l, in contrast to equation 5, but the factor $\left(\frac{l+1}{l}\right)^{l-1}$ varies only slowly, going from unity at $l = 1$ to 2.718 . . . at $l = \infty$. The behavior of K_l' is therefore not greatly different in the two cases $\alpha = 0$ and $\beta = 0$. In both cases equation 3 gives results which are intuitively attractive. It should be noted, however, that the appearance of the curve for n plotted against Q is so greatly different in the two cases that we can easily distinguish between them.

The application of theorem B to data on freezing-point lowering is relatively simple, since both n and Q are directly determined. The application of this theorem to the calculation of equilibrium constants from distribution ratios is, however, much more laborious. A simple theorem can be proved which facilitates somewhat the numerical calculation of α and β. It is assumed as usual that the material distributed is polymerized in the organic layer but not in the water layer. The following variables are useful:

Q = concentration in organic layer in formula weights of A per unit volume or mass as the case may be,
C = concentration in the water layer,
x = concentration of single molecules in the organic layer,
$k = C/x$ = distribution constant,
$D = Q/C$ = distribution ratio, and
N = concentration in organic layer in moles per unit of solution.

Theorem C. The molal concentration of solute in the organic layer is given by

$$N = \int_0^C D\,\mathrm{d}C \tag{7}$$

The proof of this theorem can be made by methods entirely analogous to those used for theorems A and B. To obtain N it is necessary to plot D as a function of C and integrate graphically. Having determined N, theorem B can be applied as soon as α and β are determined.

In the limiting case when $\alpha = 0$, the calculation of β from distribution experiments is especially simple. In this case by making use of equations 1, 2, and 4, and of the fact that $C = kx$, we easily obtain

$$\sqrt{\frac{1}{D}} = k^{\frac{1}{2}} - k^{-\frac{1}{2}}\beta C \tag{8}$$

In this equation k and β are constants and hence a plot of $\sqrt{1/D}$ against C will give a straight line when the equation is applicable. From the slope and intercept of the line both β and k are obtainable.

XI. THE RELATIONS BETWEEN THE EQUILIBRIUM CONSTANTS OF SUCCESSIVE POLYMERS

The possibility of obtaining a general relation between the equilibrium constants of successive polymers directly from the experimental data, as discussed in the foregoing section, is a particularly interesting one. To obtain a reliable relation, very accurate data must be available. A definite conclusion is warranted in only a very few cases, which will be discussed in the following pages of this section, and the general applicability of equation 2 to distribution and freezing-point data will be examined.

In figure 12 data are shown for p-nitrophenol in naphthalene solution (2, 5, 1). At low concentrations the data are inconsistent, but it seems that to a good approximation n is a linear function of Q and hence the relation 3 with $\beta = 0$ is valid, giving for the equilibrium constants

$$K_l = \frac{(\alpha l)^{l-1}}{l!}$$

The question of the error involved in this relation is one to which no definite answer can be given; it can only be asserted that relation 3 with $\beta = 0$ must exist in order to account in terms of polymerization for a linear relation between n and Q. We can, however, obtain a rough upper limit to the number of polymers to which equation 3 can be applied (24). This number is obtained by considering how many equilibrium constants can be omitted without introducing an error larger than the experimental error in n. The highest measured value of Q is 2.89, and n deviates from the straight line by 0.06 unit. If we adopt 0.06 as experimental error it turns out that nine equilibrium constants are needed to account for the results to within the experimental error. It is to be emphasized that this does not mean that the first nine equilibrium constants are given by equation 3, but it does imply that we are not justified in applying equation 3 beyond $l = 9$.

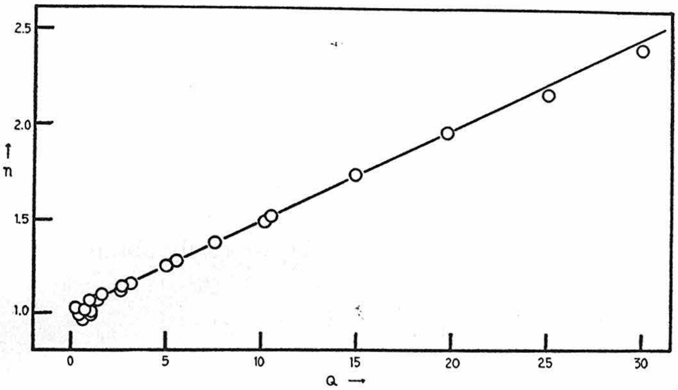

FIG. 12. Polymerization number of p-nitrophenol in naphthalene solution. Q in grams per hundred grams of solvent.

Figure 13 shows data for p-nitrophenol in p-dibromobenzene (3), and here again the relation appears to be accurately linear. The line does not approach $n = 1.00$, but approaches $n = 1.03$. This fact is attributed here to a small error in the molal freezing-point lowering constant and is therefore ignored.

Brown and Bury (12) have determined the molecular weights of benzyl and isoamyl alcohols in nitrobenzene, using a technique which had previously been subjected to a very careful investigation. By performing the experiments both in the presence of a salt hydrate and in the presence of water the water content of the nitrobenzene could be controlled accurately. Their results for benzyl alcohol in dry nitrobenzene and in fully saturated nitrobenzene are shown in figure 14. The lines are straight, although they miss the origin by about 1 per cent, which is attributed to an error in the freezing-point constant. The curves for isoamyl alcohol

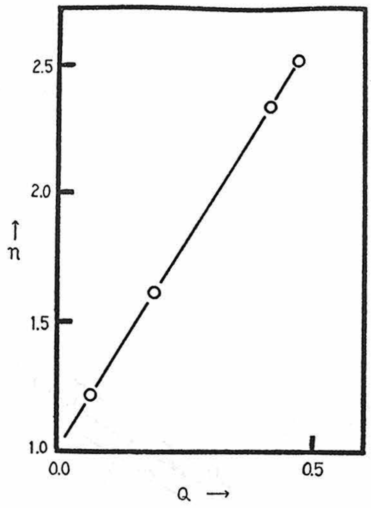

FIG. 13. Polymerization number of p-nitrophenol in p-dibromobenzene solution

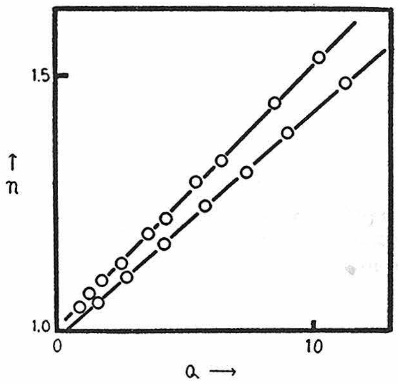

FIG. 14. Polymerization number of benzyl alcohol in nitrobenzene solution. Upper curve, dry nitrobenzene; lower curve, fully saturated nitrobenzene. Q is in grams per hundred grams of solvent.

in nitrobenzene show a distinct curvature, so the general form of equation 2 must be used. If the substitution $N = Q/n$ be made in equation 2 it can be readily verified that

$$\frac{n(n-1)}{Q} = \beta + \alpha n$$

hence by plotting $n(n-1)/Q$ against n a straight line will be obtained when the equation is applicable. When n is close to unity the term $(n-1)$ may be largely in error, so the low concentration points are expected to exhibit considerable irregularities, and, in fact, this method of plotting will in general considerably magnify any irregularities in the data. In figure 15 the data for isoamyl alcohol in dry, partially wet, and completely saturated nitrobenzene are shown. The points are somewhat irregular, but on the whole the relation seems to be a linear one, and we conclude accordingly that equation 2 represents the data satisfactorily.

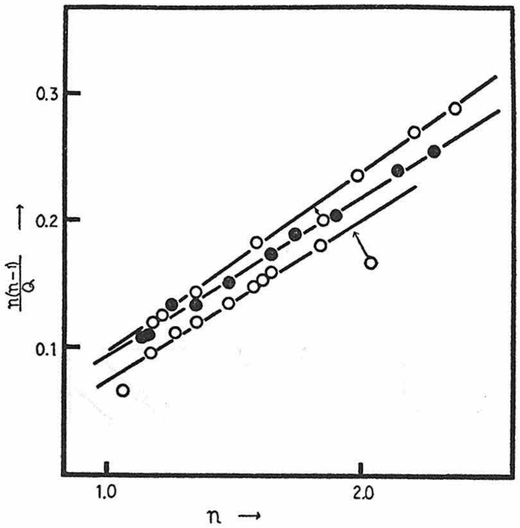

FIG. 15. $n(n-1)/Q$ plotted against n for isoamyl alcohol in nitrobenzene. Q is in grams per hundred grams of solvent. Top to bottom: fully saturated nitrobenzene, partially saturated nitrobenzene, dry nitrobenzene.

Experiments upon the distribution of phenol between water and organic solvents also indicate that equation 2 is applicable. In table 8 are shown the calculated and observed values of the distribution ratios of phenol between water and pentachloroethane. It will be observed that the agreement is within 1 per cent (see also figure 11). Figure 16 shows $\sqrt{1/D}$

against C for phenol in toluene, and the line is approximately straight. Data for phenol between water and m-xylene have been examined and equation 2 is found to be roughly applicable, although the number of experimental points is too small to permit an accurate graphical integration. Data are available for phenol between benzene and water; however, the highest concentration of phenol in benzene is 6 moles per liter of solution, and at such a concentration considerable deviations from the law of mass action are expected, so β was arbitrarily placed equal to zero in order to facilitate the calculation. The relation obtained in this way fits the data only to within about 5 per cent, but despite this fact the equilibrium

TABLE 8

Distribution ratio of phenol between water and pentachloroethane

$k = 1.085$; $\alpha = 0.83$; $\beta = 0$

Q	$D_{obsd.}$	$D_{calcd.}$
moles per liter		
0.0495	1.18	1.17
0.110	1.27	1.28
0.226	1.51	1.51
0.432	1.94	1.92
0.708	2.53	2.56
1.170	3.51	3.50

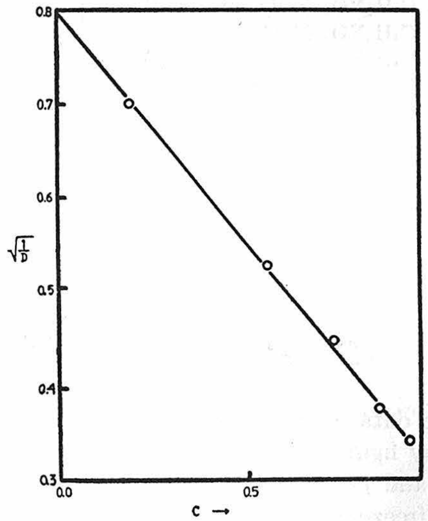

FIG. 16. Distribution of phenol between water and toluene. C is in moles per liter of solution.

constants are in surprisingly good agreement with those of Philbrick (see table 6).

The constants α and β from both the molecular weight and distribution data are collected in table 9.[5] In these cases, with the possible exception of phenol in benzene, it has been definitely shown that the equilibrium constants are given by equation 3, although the accuracy becomes less as l becomes larger. In toluene solution the constants do not agree with those of Philbrick, as is expected, since he reports a discontinuity in the distribution ratio curve at low concentrations in this solvent.

Equation 2 has been found to be capable of accounting for a large part of the existing data on anilides, amides, and substituted phenols in the cases for which the data are regular and approach the origin properly. This is illustrated by figures 17 and 18, which show data for formanilide in several solvents and p-hydroxybenzaldehyde in naphthalene solution. The data are from freezing-point measurements in all cases (6, 3). The lines are straight to within the limits of experimental error, and it is concluded that equation 2 fits the data satisfactorily.

TABLE 9

Equilibrium constants from distribution and molecular weight data

COMPOUND	SOLVENT	α	β	$K_2 = \alpha + \beta$
A. From molecular weight experiments (freezing point)				
Benzyl alcohol.......	$C_6H_5NO_2$ (fully saturated)	0.45		0.45
Benzyl alcohol.......	$C_6H_5NO_2$ (dry)	0.55		0.55
Isoamyl alcohol.....	$C_6H_5NO_2$ (fully saturated)	1.29	−0.51	0.78
Isoamyl alcohol......	$C_6H_5NO_2$ (partially saturated)	1.11	−0.30	0.81
Isoamyl alcohol......	$C_6H_5NO_2$ (dry)	1.28	−0.71	0.57
p-Nitrophenol.......	Naphthalene	0.67		0.67
p-Nitrophenol.......	p-Dibromobenzene	3.18		3.18
B. From distribution experiments at 25°C.				
Phenol.............	Pentachloroethane	0.83		0.83
Phenol.............	Benzene		+0.58	0.58
Phenol.............	Toluene		+0.67	0.67
Phenol.............	m-Xylene	0.13	+0.16	0.29

Since equation 2 seems to be sufficiently adjustable, it has been used to calculate the equilibrium constants from the experimental data in all cases except for the aliphatic alcohols, which will be discussed later.

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[5] All distribution data are from *International Critical Tables,* except that for pentachloroethane.

XII. CALCULATION OF EQUILIBRIUM CONSTANTS FROM MOLECULAR WEIGHT DATA FOR THE SUBSTITUTED PHENOLS, AND THE RELATIVE STRENGTHS OF HYDROGEN BONDS

In the discussion which follows, an attempt has been made to avoid the inclusion of data which are more than usually irregular or for which the number of experimental points is unusually small. Since the results of these calculations are of interest chiefly for comparative purposes, the applications are confined to a few well-known solvents in which a variety of compounds have been investigated.

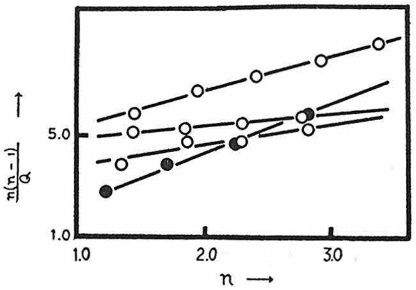


FIG. 17. $n(n - 1)/Q$ against n for formanilide in various solvents. Top to bottom: *p*-xylene, *p*-dichlorobenzene, *p*-dibromobenzene, benzene.

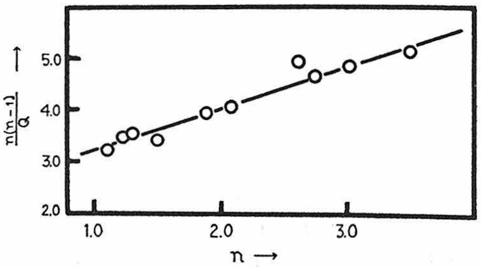
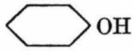
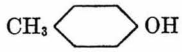
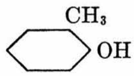
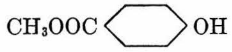
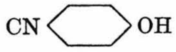
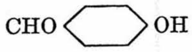
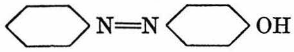
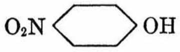
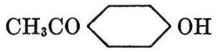
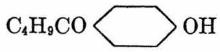


FIG. 18. $n(n - 1)/Q$ against n for *p*-hydroxybenzaldehyde in naphthalene solution

The material presented in section VI made evident the fact that introduction of a nitro group into the meta- or para-position of phenol considerably increases the polymerization number of the compound. This fact has a simple interpretation in terms of isomerism, which will be tested in this section. A para-substituted phenol of the type XC_6H_4OH can polymerize in two ways to form a dimer, either as XC_6H_4OH- - -HOC_6H_4X or as XC_6H_4OH- - -XC_6H_4OH, if the group X is capable of forming hydrogen bonds with the hydroxyl group. Let the equilibrium constants be $K_2^{(1)}$ and $K_2^{(2)}$, respectively. By means of a simple application of the law of mass action it is found that the equilibrium constant obtained from the data is $K_2 = K_2^{(1)} + K_2^{(2)}$. If a reasonable estimate of the constant $K_2^{(1)}$ can be made, $K_2^{(2)}$ can be calculated. We notice that the first isomer is held together by a bond between the two hydroxyl groups, and hence it seems reasonable to evaluate the constant $K_2^{(1)}$ by considering a compound containing a group X which does not form hydrogen bonds.

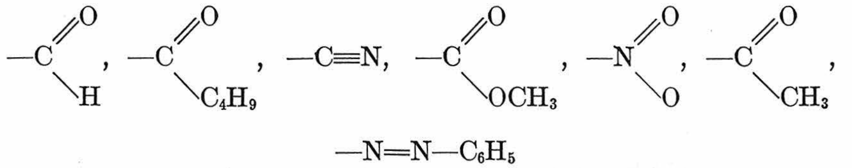
TABLE 10

Equilibrium constants for phenol, o-cresol, and para-substituted phenols in naphthalene solution

COMPOUND	α	β	$K_2 = \alpha + \beta$	$K_2^{(2)}$
	(moles per kg. of solvent)$^{-1}$	*(moles per kg. of solvent)*$^{-1}$		
	0.30*			
	0.20	0.18	0.38	
	0.20*			
	1.33	0.00	1.33	0.95
	1.00	0.63	1.63	1.25
	0.82	2.45	3.27	2.89
	0.94	−0.59	0.35	−0.03
	0.67	0.00	0.67	0.29
	1.06	−0.46	0.60	0.22
	0.86	1.65	2.51(?)	2.13

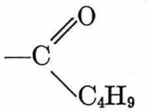
* β was arbitrarily put equal to zero in these cases.

As such a compound *p*-cresol may be selected. The same considerations hold, of course, for meta-substituted phenols as well. $K_2^{(2)}$ is clearly the equilibrium constant of a reaction which involves the formation of a bond of the type —X---H—O— and hence is a convenient measure of the bond strength. The equilibrium constants for a number of para-substituted phenols calculated from freezing-point lowering measurements (6, 3) are shown in table 10. Equation 2 was used to fit the data in all cases, and the values of K_2 are probably not reliable to more than ±0.05 unit. If the hypothesis that the constant K_2 for *p*-cresol is equal to $K_2^{(1)}$ is satisfied, then $K_2^{(2)}$ should never be negative. Actually, it does become negative in one case, for *p*-hydroxyazophenol, but the negative value is smaller than the experimental error and so is not significant. From a consideration of the constants K_2 for phenol and *o*-cresol it seems likely that the estimate of $K_2^{(1)}$ from the data for *p*-cresol gives too high a value. The strengths of the bonds between hydroxyl groups and other groups are in the order



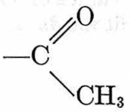
$$-\mathrm{C}(=\mathrm{O})\mathrm{H},\quad -\mathrm{C}(=\mathrm{O})\mathrm{C_4H_9},\quad -\mathrm{C{\equiv}N},\quad -\mathrm{C}(=\mathrm{O})\mathrm{OCH_3},\quad -\mathrm{N}(=\mathrm{O})\mathrm{O},\quad -\mathrm{C}(=\mathrm{O})\mathrm{CH_3},\quad -\mathrm{N{=}N{-}C_6H_5}$$

The relative positions of the groups



$$-\mathrm{C}(=\mathrm{O})\mathrm{C_4H_9}$$

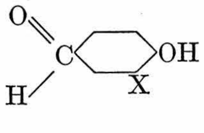
and



$$-\mathrm{C}(=\mathrm{O})\mathrm{CH_3}$$

are surprising, and indicate that other effects than isomerism contribute to the increase in polymerization number. Otherwise the order is in agreement with that of Auwers.

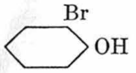
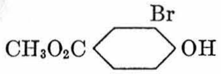
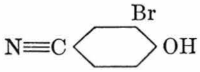
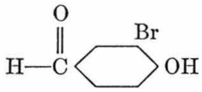
Table 11 shows a set of constants calculated from freezing-point lowering measurements (6) for para-substituted phenols which have a bromine in the position ortho to the hydroxyl group, while table 12 shows constants for a series of compounds (6) of the type



From table 12 we see that the constants decrease steadily in the order H, CH_3, Br, OCH_3, to such a low value as to indicate that the last compound is definitely chelated. This decrease in K_2 upon introducing a substituent may be due to changes in bond energy and entropy, or it may be due to conversion of a constant fraction *a* of molecules into such a form that they can not form hydrogen bonds to their neighbors. The equilibrium constants cannot decide the relative importance of these factors, of course, but it is of interest to make a calculation based on the last hypothesis and on the assumption that the introduction of bromine has no other

TABLE 11

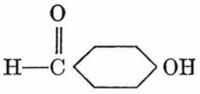
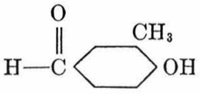
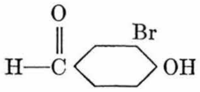
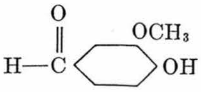
*Ortho-brominated substituted phenols in naphthalene solution**

COMPOUND	$K_2 = \alpha + \beta$	$K_2^{(2)}$
	0.07	
	0.13(?)	0.06
	0.33	0.25
	0.70	0.63

* The molecular weight data for these compounds consist of only a few points covering a small range of concentrations, and hence higher constants than K_2 cannot be significant. The values of α and β are accordingly omitted. The method of least squares was used to fit the data.

TABLE 12

Equilibrium constants for the ortho-substituted p-hydroxybenzaldehydes in naphthalene solution

COMPOUND	α	β	$K_2 = \alpha + \beta$
	(moles per kilogram of solvent)$^{-1}$	*(moles per kilogram of solvent)*$^{-1}$	
	0.82	2.45	3.27
	1.55	0	1.55
	0.14	0.57	0.71
	0.32	0	0.32

effect. Using the equilibrium constants of tables 10 and 11 we obtain the values of a shown in table 13. If the hypothesis is valid these numbers should be equal, and we see that they are closely similar. Owing to sys-

TABLE 13

Values of a for ortho-brominated compounds in naphthalene

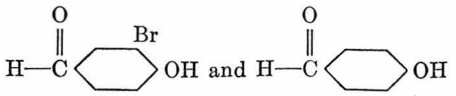
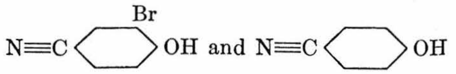
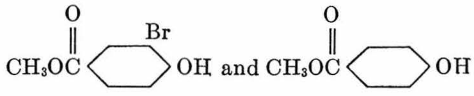
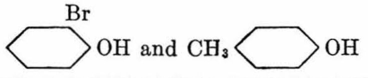
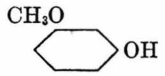
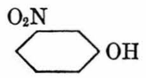
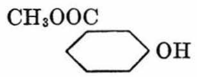
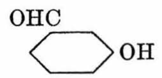
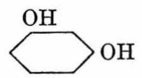
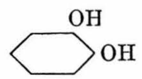
OBTAINED FROM	a
	0.52
	0.56
	0.69
	0.56

TABLE 14

Equilibrium constants for meta-substituted phenols and catechol in naphthalene solution

COMPOUND	α	β	$K_2 = \alpha + \beta$
	(moles per kilogram of solvent)$^{-1}$	*(moles per kilogram of solvent)*	
	0.44		0.44
	1.12	0.71	1.83
	0.67	0.59	1.26
	0.41	0.92	1.33
	1.04		1.04
	0.63	0.09	0.72

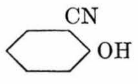
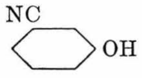
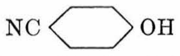
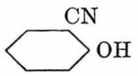
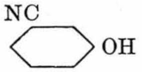
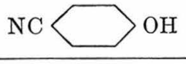
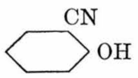
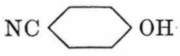
tematic deviations from the law of perfect solutions the constants in table 11 are no doubt too large, and hence the values of a in table 13 are too small. It should be pointed out that the numbers in table 13 seem much too small to account for even a weak chelate bond.

In table 14 constants are shown for some meta-substituted phenols (6). In this case the order of the groups is changed, indicating again that effects other than isomerism are important in these polymerizations.

Table 15 shows equilibrium constants for the *o*-, *m*-, and *p*-cyanophenols in three solvents. The constants are calculated from freezing-point lowering experiments (6, 3, 5). The compounds are all more polymerized in *p*-dichlorobenzene than in *p*-dibromobenzene. This difference can be attributed to the difference in the melting points of the two solvents, and, in fact, the magnitude of the difference is just that predicted by the van't Hoff equation by assuming a reasonable value of ΔH. The small values of the constants in naphthalene solution can not be attributed to a tempera-

TABLE 15

Equilibrium constants for the cyanophenols in various solvents

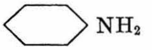
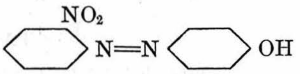
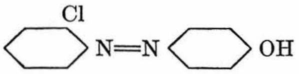
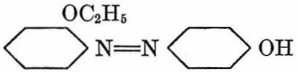
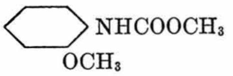
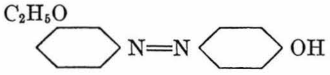
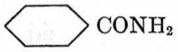
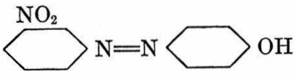
COMPOUNDS	α	β	$K_2 = \alpha + \beta$
(a) Cyanophenols in *p*-dibromobenzene			
	(moles per kilogram of solvent)$^{-1}$	*(moles per kilogram of solvent)*$^{-1}$	
	2.1	−0.6	1.5
	1.7	0.9	2.6
	1.9	3.2	5.1
(b) Cyanophenols in *p*-dichlorobenzene			
	5.0	−1.0	4.0
	3.3	2.5	5.8
	4.4	9.4	13.8(?)
(c) Cyanophenols in naphthalene			
	1.3	0.2	1.5
	1.0	0.6	1.6

ture effect, and hence must be due to some specific interaction of the solute and solvent. Since addition compounds of naphthalene with various aromatic compounds are known, the effect may be due to an actual combination of solute and solvent. The steady decrease in the dimer constant from the ortho to the para compound indicates a steric effect which becomes less important as the cyanide radical is moved away from the hydroxyl group.

Considering the quality of the available data, the interpretations in this section seem moderately satisfactory. The indications are, however, that the interpretation of such data as these awaits further advances in experimental investigations of the structure of polymers.

TABLE 16

Equilibrium constants of anilides, acid amides, and azophenols in naphthalene solution

COMPOUND	α	COMPOUND	α
	0.14		0.66
	0.77		0.28
	0.96		0.90
	0.23		0.32
	1.13		1.44
	0.50		

XIII. EQUILIBRIUM CONSTANTS FOR COMPOUNDS OTHER THAN SUBSTITUTED PHENOLS

A. Azophenols, anilides, and acid amides

The existing data on the azophenols, anilides, and acid amides are both less extensive and less accurate than on the substituted phenols, so a treatment analogous to that of section XIII can not be carried out for these compounds. Furthermore, the data offer nothing essentially new, so only a few examples will be considered in order to show the order of magnitude of the equilibrium constants. In table 16 are shown the equilibrium constants calculated from freezing-point experiments (2, 6) for a few of these compounds in naphthalene solution. The data were fitted reasonably well by a straight line, so β was arbitrarily placed equal to zero. The only surprising feature is the great difference between the methoxy compounds of *p*-hydroxyazobenzene, and no reason is known for this behavior. Table 17 shows data for three normal acid amides in benzene solution. The constants were calculated from boiling-point raising experiments (27). The data for these three compounds are fitted best by assuming that $\alpha = 0$, and the amides are the only compounds which are fitted at all well with $\alpha = 0$.

Data for formanilide exist at both the freezing point and boiling point in benzene solution (5, 27), so it should be possible to calculate ΔH for the dimer formation. The equilibrium constant at the freezing point is $K_2 = 2.4$, and at the boiling point $K_2 = 0.8$, hence $\Delta H = -2900$ cal. per mole. A structure of the dimer of formanilide can be written which involves two —N—H- - -O— bonds, but this structure seems somewhat unlikely in view of the small value for ΔH. At the boiling point only three experimental points were available, so the value is highly uncertain.

TABLE 17

Acid amides in benzene solution (boiling-point measurements)

COMPOUND	β
	(moles per liter of solvent)$^{-1}$
$C_2H_5CONH_2$	3.9
n-$C_3H_7CONH_2$	3.6
n-$C_4H_9CONH_2$	2.7

B. The aliphatic alcohols

The data for the aliphatic alcohols, which seemed at first to be the most easily interpreted, have proved to be rather confusing. As has been pointed out before, the curve for ethyl alcohol in benzene shown in figure 1 exhibits a tendency toward a point of inflection. This tendency is apparently a real one, since the molecular weight of ethyl alcohol in dilute solutions of benzene has been shown by the work of Peterson and Rodebush (32) to be constant and normal at low concentrations. The relation between the equilibrium constants is therefore more complicated than any that has yet been investigated. These data are even more remarkable, in view of the fact that the molecular weight of methyl alcohol is found by Peterson and Rodebush to increase rapidly even at very low concentration. These two examples illustrate the vital need for low concentration data in all cases. Because of the difference in behavior of methyl and ethyl alcohols even in very dilute solution, the data for these compounds have not been treated quantitatively. Data for a few higher alcohols have been analyzed under the specific hypothesis that the curve approaches the origin with a slope which is different from zero. Under this hypothesis it is found that the data for several higher alcohols can be represented by a function of the form $n = 1 + \alpha + RN^P$, where α and R are constants and P is an integer; these constants must be determined from experimental data. Application of the methods of section X shows that the equilibrium constants are

$$K_l = \frac{(l\alpha)^{l-1}}{l!} \quad \text{if } l - 1 < P$$

but

$$K_l = \frac{(l\alpha)^{l-1}}{l!} + \frac{R}{P} \quad \text{when } l = P + 1$$

TABLE 18

Equilibrium constants of normal aliphatic alcohols in benzene solution

COMPOUND	α	R	P
	(moles per kilogram of solvent)$^{-1}$		
n-Propyl alcohol	1.56	−12	5.1
n-Butyl alcohol	1.63	−6	4.0
n-Heptyl alcohol	1.80	−10	4.0
n-Octyl alcohol	1.61	−12	4.1

The first P equilibrium constants are unaffected by the term RN^P. In table 18 (10) are shown values of α, R, and P for four alcohols. These values must be considered tentative until the molecular weights at low concentration have been investigated. In the cases shown the values of R are negative and hence the larger constants tend to fall off past the point $l = 4$. The significance of this result is not clear at present.

The experimental data on aliphatic alcohols indicate that primary alcohols are most polymerized, secondary alcohols next, and tertiary alcohols least polymerized (10) (see also figure 1).

XIV. THE HYDROGEN BOND AND SURFACE ENERGY

It is a well-known fact that the total surface energies of the aliphatic hydrocarbons are closely similar to the surface energies of the alkyl amines and other alkyl compounds. This has been interpreted by Langmuir, Harkins, and other workers in this field to mean that the hydrocarbon group is directed outward at the liquid surface, while the polar group is directed inward (18). In the case of an associated liquid, such as an alcohol, it is of interest to inquire into the matter of whether the surface molecules form hydrogen bonds with the molecules on the interior. A simple calculation shows that the energies involved in a transfer of material from the surface to the vapor are of just the order of magnitude of the hydrogen bond energy.

When a liquid composed of spherically symmetrical molecules or atoms evaporates, the ratio of the total surface energy per mole to the latent heat of vaporization is approximately one-half. When a substance having a polar and a non-polar end evaporates, this ratio is less than one-half, because the surface energy is that required to move only the non-polar end to the surface, while in evaporation the whole molecule is moved out of the surface. In case the liquid is an associated one, this ratio may be much less than one-half (19). This may be interpreted as being due to the fact that in moving the molecule to the surface no hydrogen bonds need be broken, but in evaporation hydrogen bonds are broken. If it were possible to estimate the ratio of total surface energy to heat of vaporization for a material which was polar, could not form hydrogen bonds, but otherwise resembled an alcohol (in dipole moment, etc.), then any difference between this ratio and that for an alcohol could be attributed to breaking hydrogen bonds upon evaporation. As a standard material ethyl ether may be selected. The excess of energy required to move alcohol molecules from the surface to the vapor phase over that required to move ether molecules was computed from the data of Harkins and Roberts (19). The values are given in table 19. These values are of the same order of magnitude as the energy of the hydrogen bond. Some of the decrease in energy as the

TABLE 19

Energy used in breaking hydrogen bonds upon vaporization from liquid surface

TEMPERATURE	*E*
Methyl alcohol	
°A.	*cal. per mole*
363	4820
413	3870
463	2690
483	2000
503	935
Ethyl alcohol	
333	5330
383	4940
433	3670
473	2590

temperature rises can be attributed to the fact that hydrogen bonds are broken by the thermal agitation. This is evidence for the viewpoint that hydrogen bonds are broken as the material leaves the surface, and suggests that some of the facts of surface orientation might be interpreted in terms of hydrogen bonds.

XV. SUMMARY

1. From both distribution ratio and molecular weight data evidence is obtained that the organic acids polymerize in non-polar solvents, largely into double molecules, and the oximes polymerize largely into low-order polymers.

2. From molecular weight data it is concluded that alcohols, acid amides, anilides, and substituted phenols polymerize into high-order polymers, and from distribution data it is known that dimers are present in non-polar solvents.

3. Molecular weight data show that —SH groups do not form hydrogen bonds to any appreciable extent and that hydroxyl groups do not form strong hydrogen bonds to sulfur atoms.

4. Molecular weight measurements indicate that a hydrogen which is used in forming a chelate ring cannot at the same time form a hydrogen bond to a neighboring molecule.

5. The abnormal vapor pressures and solubilities of ortho-substituted aromatic compounds can be explained by the concept of chelation.

6. From a consideration of molecular weights, distribution ratios, and vapor pressures it is concluded that a six-membered chelate ring is more stable than a five-membered ring, while chelation is almost inappreciable in a seven-membered ring. Chelation is sensitive to changes in bond angles and internuclear distances, as shown by the examples of the cyanophenols and sebacic acid.

7. From a consideration of molecular weights it is concluded that combination of solute and solvent occurs when hydrogen bonds can be formed between solute and solvent, and that the polymerization of solute is thereby rapidly reduced.

8. An amino type group can form strong hydrogen bonds with groups of a different type, but only weak ones with other amino groups.

9. Molecular weight data show that polymers which are held together by molecules of solvent are comparatively rare, but evidence is put forward that such combination can occur when a nitrogen atom is involved. The conclusion is not yet definite, because the data are in serious conflict in some cases.

10. Application of a theory of computing equilibrium constants to molecular weight data shows that in general the polymerization curves of the

acid amides, anilides, substituted phenols, and some alcohols lead directly to the conclusion that a succession of polymers is present, the order of the highest polymer being uncertain. Only in two or three cases is there evidence that any polymer, of the set of successive polymers, is missing.

11. The experimental data for *p*-nitrophenol in naphthalene and in *p*-dibromobenzene solution show that the successive equilibrium constants are given by

$$K_l = \frac{(l\alpha)^{l-1}}{l!}$$

Molecular weight data on benzyl alcohol and isoamyl alcohol show that the successive equilibrium constants are given by equation 3. The successive equilibrium constants for phenol in pentachloroethane are shown to be given by equation 3, $\beta = 0$.

12. The hypothesis that the increase in polymerization attending the entrance of a substituent into the benzene ring can be explained by an increase in the number of isomers is examined and found to be only moderately satisfactory.

13. It is shown by a consideration of surface energies and heats of vaporization that the excess of energy required to remove an alcohol molecule from the surface of liquid alcohol over that required to remove an ether molecule corresponds to breaking somewhat less than one hydrogen bond per molecule removed.

In conclusion I wish to thank Professor Linus Pauling for suggesting this review and to express my appreciation for his advice and encouragement during the course of the work. I am also indebted to Professor Roscoe G. Dickinson for the many helpful discussions that we have had, and to Marjorie Lassettre for aid in the calculations and preparation of the manuscript.

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A COMPARATIVE METHOD OF MEASURING VAPOR PRESSURE LOWERING WITH APPLICATION TO SOLUTIONS OF PHENOL IN BENZENE*

The examples discussed in the two previous publications show that dilute solutions of many organic compounds in inert solvents have properties which may be explained on the basis of an equilibrium between the unpolymerized solute and polymers of all orders. The object of the present investigation is to obtain the heat of dissociation of the polymer of order two and of as many higher polymers as possible. The experimental methods which have been used in the investigation of these substances either do not permit a study to be made over an arbitrary temperature range, as in the case of freezing point lowering experiments, or include a reaction with water, as in the case of measurements on the distribution of solute between water and an inert solvent.

In the following paper a procedure is described by means of which the objections outlined above may be overcome. The experiment consists essentially in studying the distribution of a volatile solvent between two non-volatile solutes. This is accomplished by preparing two solutions of different solutes and connecting them through the vapor phase. Solvent then distills from the solutions of high vapor pressure to the solution of low vapor pressure until equilibrium is attained. The distillation is followed by measuring the volumes of the two solutions from time to time. At equilibrium the vapor pressures of the two solutions are equal, hence if the vapor pressure of one is known the ~~other~~

vapor pressure of the other can be determined. Investigations which are described in this paper show that the distillation is sufficiently rapid to permit a close approach to equilibrium.

This principle has been used by other investigators for special purposes[1,2] but the methods employed are not well adapted to use with volatile solvents.

Apparatus. A side view of the apparatus used is shown in figure I. Two erlenmeyer flasks are connected by sealing the necks to each end of a large glass tube. The two tubes A have pieces of burette scale B slipped over them and sealed in place with de Khotinsky cement. The scales were calibrated by pouring weighed quantities of mercury into the apparatus. The bulbs C serve to increase the volume to a convenient size. The apparatus is supported by means of a brass rod D which is perpendicular to the plane of the paper. The rod is soldered to a piece of curved brass E which is attached to the apparatus with de Khotinsky cement. The apparatus is suspended from a stand by means of bearings at the ends of the rod D. The whole apparatus is immersed in a small thermostat, having a glass window, in such a way that the stopcock G remains out of the water both when the burettes are vertical and when they are horizontal.

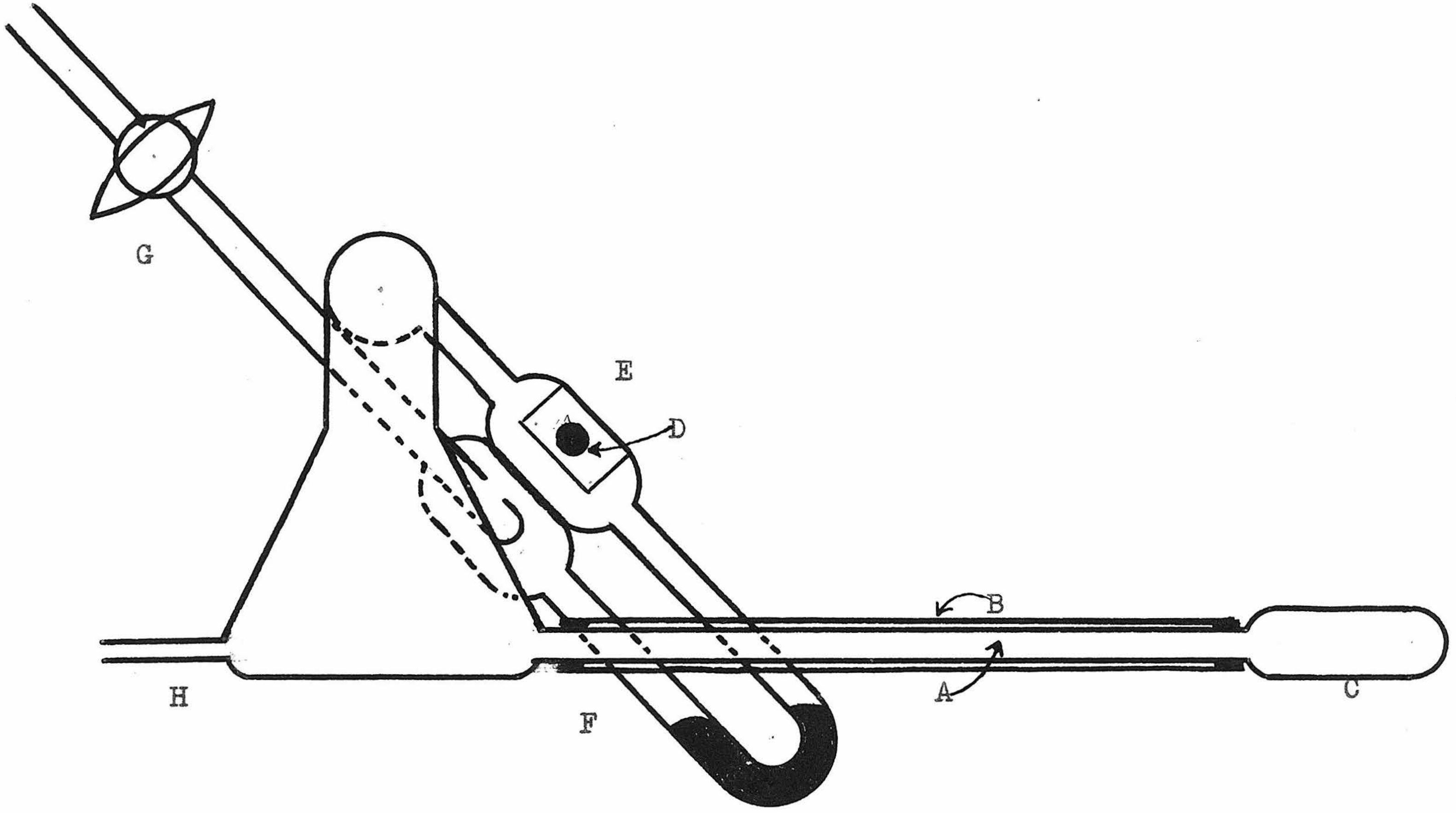

FIGURE I

Procedure and sources of error. The apparatus is filled through the tubes H, the standard solution being placed in one flask and the solution of unknown vapor pressure in the other. The tubes H are then sealed off and the air removed by pumping through the mercury trap F, which prevents the distillation of solvent into the grease of stopcock G. During transfer the apparatus is placed horizontally in the thermostat and rocked slowly back and forth around the axis D by means of an arm attached to D and extending out of the thermostat. The volumes of the solutions are determined from time to time by tilting the apparatus into a vertical position and reading the volume on the scales B. Equilibrium can be approached from the opposite direction by distilling solvent from the dilute to the concentrated solution. This distillation is accomplished by placing a piece of ice on the flask into which distillation is desired.

The precision of the experiment is limited largely by the presence of small differences in the temperatures of the two Erlenmeyer flasks. The test for temperature differences was carried out by placing dilute solutions of naphthalene in benzene in both Erlenmeyer flasks and allowing the system to approach equilibrium. Equilibrium must be attained when the two concentrations are equal. Any deviation from the equilibrium volume calculated in this way strongly indicates that the two flasks are at different temperatures. In the early stages of this experiment difficulty was encountered because the observed position of equilibrium differed from that calculated by an amount which exceeded experimental error. The source of the error was finally demonstrated by allowing the system to approach equilibrium as closely as possible and then turning the whole apparatus through 180° with respect to the thermostat. In this new position a different equilibrium was obtained. At 25°C this error was eliminated by vigorously stirring the thermostat but at 50°C it became necessary to modify the apparatus. The modification used at 50°C was essentially similar to that shown in figure I but more compact. The Erlenmeyer flasks were replaced by large glass tubes horizontally placed. The device was so constructed that it fitted snugly into a glass jar having a capacity of about a liter and a half. The jar was filled with thermostat water and some mercury to provide stirring, placed in the thermostat and rocked back and forth as before. With this device temperature gradients are greatly reduced.

The general features concerning the operation of the apparatus are best discussed with respect to Tables I and II. Table I shows the results of a series of experiments in which a solution of azobenzene in benzene was placed in one flask and a solution of naphthalene in the other. The distillation is slow but is sufficiently rapid for the solutions to approach equilibrium closely. This feature eliminates the necessity for preparing a series of standard solutions which is characteristic of

Table II

0.3159 gm. Azobenzene. 0.2199 gm. Naphthalene. Tempt. 25°C

The predicted equilibrium volume of the naphthslene solution is 15.81 cc.

Volume azobenzene solution	Volume naphthalene solution	Time hours	Total volume cc.
a) Rate immediately after filling.			
15.46	16.39	0	31.85
15.74	16.07	9.5	31.81
15.76	16.05	11.5	31.81
15.83	15.98	24	31.81
b) Rate aber transferring solvent to azobenzene side.			
16.56	15.25	0	31.81
16.38	15.42	1.25	31.80
16.23	15.56	4	31.79
16.11	15.71	22.7	31.82
c) Rate after transferring to naphthalene side.			
15.66	16.15	0	31.81
15.68	16.12	0.2	31.80
15.74	16.06	0.75	31.80
15.81	15.99	2.2	31.80
15.89	15.93	4.5	31.82
15.90	15.91	6.5	31.81
15.93	15.88	12.5	31.81
15.95	15.86	22	31.81
d) Rate after transferring to azobenzene side.			
16.14	15.68	0	31.82
16.10	15.71	0.5	31.81
16.08	15.73	1	31.81
16.06	15.75	2	31.81

Table I (continued)

Volume azobenzene solution	Volume naphthalene solution	Time hours	Total volume cc.
d) Rate after transferring to azobenzene side. (continued)			
16.04	15.77	4	31.81
16.02	15.78	7.5	31.80
16.01	15.79	14.5	31.80
16.01	15.79	24	31.80

Fom these data it is evident that the observed value for the volume of the naphthalene solution at equilibrium is 15.825 ± 0.035.

Table II

0.1603 grams of Cinnamic acid, 0.0831 grams of naphthalene

Volume cinnamic acid cc.	Volume naphthalene cc.	Time hours
a) Begun immediately after evacuation.		
15.05	15.70	0
15.01	15.71	3.5
14.97	15.74	7.5
14.95	15.76	17
b) Solvent transferred to naphthalene side.		
14.61	16.12	0
14.65	16.06	1
14.67	16.03	2
14.71	16.00	4.5
14.73	15.98	7.5
c) Solvent transferred to cinnamic acid side.		
14.98	15.73	0
14.91	15.80	2.5
14.88	15.84	5.5
14.84	15.86	15.5
d) Solvent transferred to naphthalene side		
14.74	15.98	0
14.75	15.95	0.5
14.78	15.93	4.5
14.78	15.93	12
e) Solvent transferred to cinnamic acid side.		
14.92	15.79	0
14.88	15.84	1.5
14.85	15.86	5

Table II (continued)

Volume cinnamic acid cc.	Volume naphthalene	Time hours
e) Solvent transferred to cinnamic acid side. (continued)		
14.81	15.90	11.25
f) Turned apparatus through 180°		
14.81	15.90	0
14.81	15.90	1
14.81	15.90	3.5
14.81	15.90	8

certain other modifications of this method.[2] The solutions drain quite readily into the burettes, five minutes being ample time for complete drainage. The accuracy of the volume measurement is indicated to some extent by the constancy of the total volume given in column four. The burettes were read to tenths of a scale division directly and hundredths were estimated by reading with a magnifying glass. One scale divistion corresponds to 0.43 cc.

Freezing point lowering experiments[2,3,4] show that both azobenzene and naphthalene solutions in benzene obey the perfect solution laws so the two solutions must reach equilibrium when the mol fractions are equal, at these low concentrations this requires that the concentrations be equal, to a sufficient degree of approximation. On this basis the value for the ratio of the volumes of the azobenzene and naphthalene solutions at equilibrium is calculated to be 1.0105 ± 0.0035. The uncertainty given is half the difference between the upper and lower limits to the ratio. The limits set in this experiment are somewhat closer than was ordinarily the case since more time was spent in approaching equilibrium. These runs required four days of continuous operation. The solutions were 0.1095 molar at equilibrium.

In figure II the volume of naphthalene solution (from table I) minus the equilibrium volume is plotted against the time. From these curves we see that the rate of distillation falls off very rapidly, and it does not

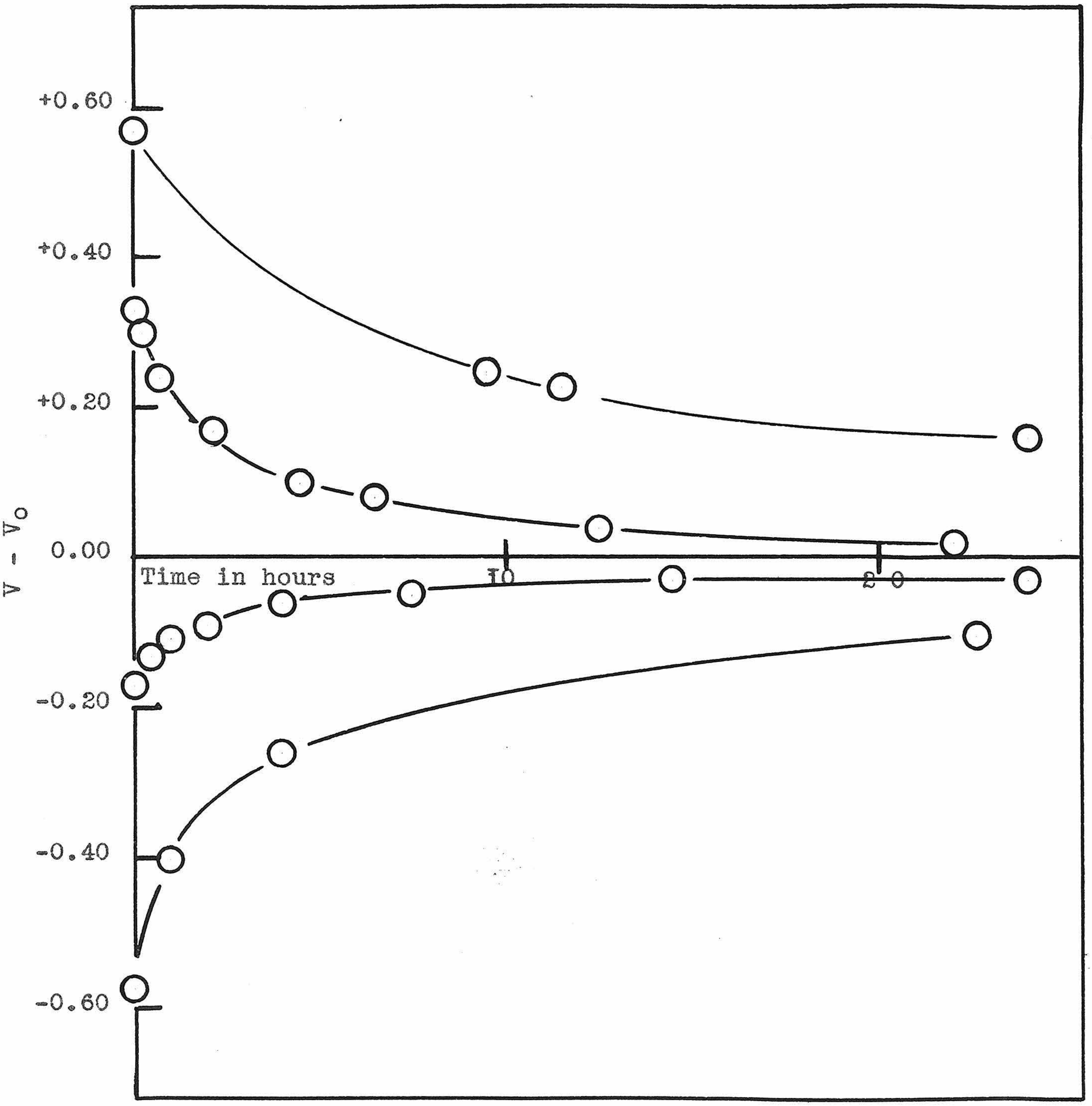

FIGURE II

V is the observed volume, V_o the equilibrium volume.

depend solely upon the distance from equilibrium but is also influenced by other factors which were not controlled in the present experiment. It is also evident that an approach to equilibrium from one side only may produce misleading results, since the rate falls off to a very small value when the volume is still considerably removed from its equilibrium value. Although the rates are not reproducible, an extensive series of tests have shown that the equilibrium can be quite accurately reproduced.

The data in table II illustrate the operation of the apparatus at even lower concentrations. In this series of measurements solutions of naphthalene were placed in one flask and solutions of cinnamic acid in the other; the solvent is benzene. At equilibrium the concentration of naphthalene is 0.0413 molar and is determined to within 0.1%. The concentration of cinnamic acid is 0.0727 formula weights per liter. That this differs from the concentration of naphthalene is due to the fact that cinnamic acid is polymerized in benzene solution. Although cinnamic acid has not been studied in benzene solution its behavior in other inert solvents strongly suggests that the polymers formed are chiefly dimeric[10]. Further study of this compound was not profitable because the equilibrium did not change sufficiently rapidly with concentration and further its solubility in benzene is rather small.

Vapor Pressure Lowering of Solutions of Phenol in Benzene

Experiments were performed upon phenol in benzene solutions both because phenol polymerizes into polymers of high order and hence the shift in equilibrium with temperature is more marked, and because accurate distribution data at 25°C. are available with which these experiments can be compared.

Materials.

Benzene.--Thiophene-free benzene was distilled with a 25 centimeter fractionating column. The middle and constant boiling fraction was used. The benzene was preserved in contact with sodium and was used immediately upon being removed from contact with the sodium.

Phenol.--A good grade of phenol was distilled and the middle fraction used. The product obtained was entirely colorless. Analysis by bromination with $KBrO_3$-KBr solution showed at least 99.7 percent phenol. The analysis was intended to show that only little water was present.

Naphthalene.--Eastman's naphthalene was used without further purification. The product melted sharply at 80.6°C. Further purification did not change the melting point.

Azobenzene.--Kahlbaum's azobenzene was used without further purification. The product melted sharply at 68.1°C.

Cinnamic Acid.--A good grade of cinnamic acid was used without further purification.

A further test of purity was afforded in testing the apparatus and all evidence tended only to indicate that the purity was sufficient.

Results on Phenol.--Solutions of phenol in benzene were prepared by weighing phenol into a volumetric flask and diluting to the mark. Samples of this solution were transferred to the apparatus as needed. Solid naphthalene was weighed directly into the apparatus.

The results obtained are shown in Table III and graphically in Figures IIIa and IIIb. In the first column under Q are given the values for the number of formula weights of phenol per liter of solution at equilibrium. The second column under N gives the number of formula weights of naphthalene per liter of solution at equilibrium. A correction has been introduced for the thermal expansion of the solutions, all concentrations being corrected to 25°C. The coefficients of expansion of the solutions are not known, but were computed from the known coefficients of expansion of pure benzene and pure phenol[5], on the assumption that the density of the mixture is a linear function of the composition. The densities of mixtures of phenol and benzene have been investigated at 20°C,[5a] and at this temperature the density is a linear function of the composition in weight percent. The uncertainties given are the differences between the values obtained when the equilibrium was approached from both sides. The time consumed in a determination varied between eight and forty-eight hours, depending on the concentration and temperature.

The loss of phenol upon evacuation was examined by condensing the vapor in an experiment and analyzing for phenol. It was found, at 25°C, that if one percent of the solution is pumped off, 0.02 percent of phenol is lost. The data in Table III are corrected for this loss.

The distillation of phenol from one flask to the other

TABLE III

25.00 ± 0.01°C

Q	N	Q/N
0.2221	0.1989	1.117 ± 0.004
0.3162	0.2738	1.155 ± 0.004
0.3471	0.2948	1.180 ± 0.002
0.4002	0.3336	1.199 ± 0.001
0.4000	0.3313	1.205 ± 0.009
0.4884	0.3946	1.237 ± 0.006
0.5023	0.4034	1.245 ± 0.004
0.6634	0.5070	1.307 ± 0.003
0.7369	0.5608	1.313 ± 0.003
1.036	0.7314	1.416 ± 0.004
1.368	0.9057	1.509 ± 0.004
	50.00 ± 0.03°C	
0.2018	0.1826	1.098 ± 0.008
0.3909	0.3391	1.152 ± 0.009
0.6386	0.5275	1.210 ± 0.008
1.521	1.045	1.433 ± 0.007

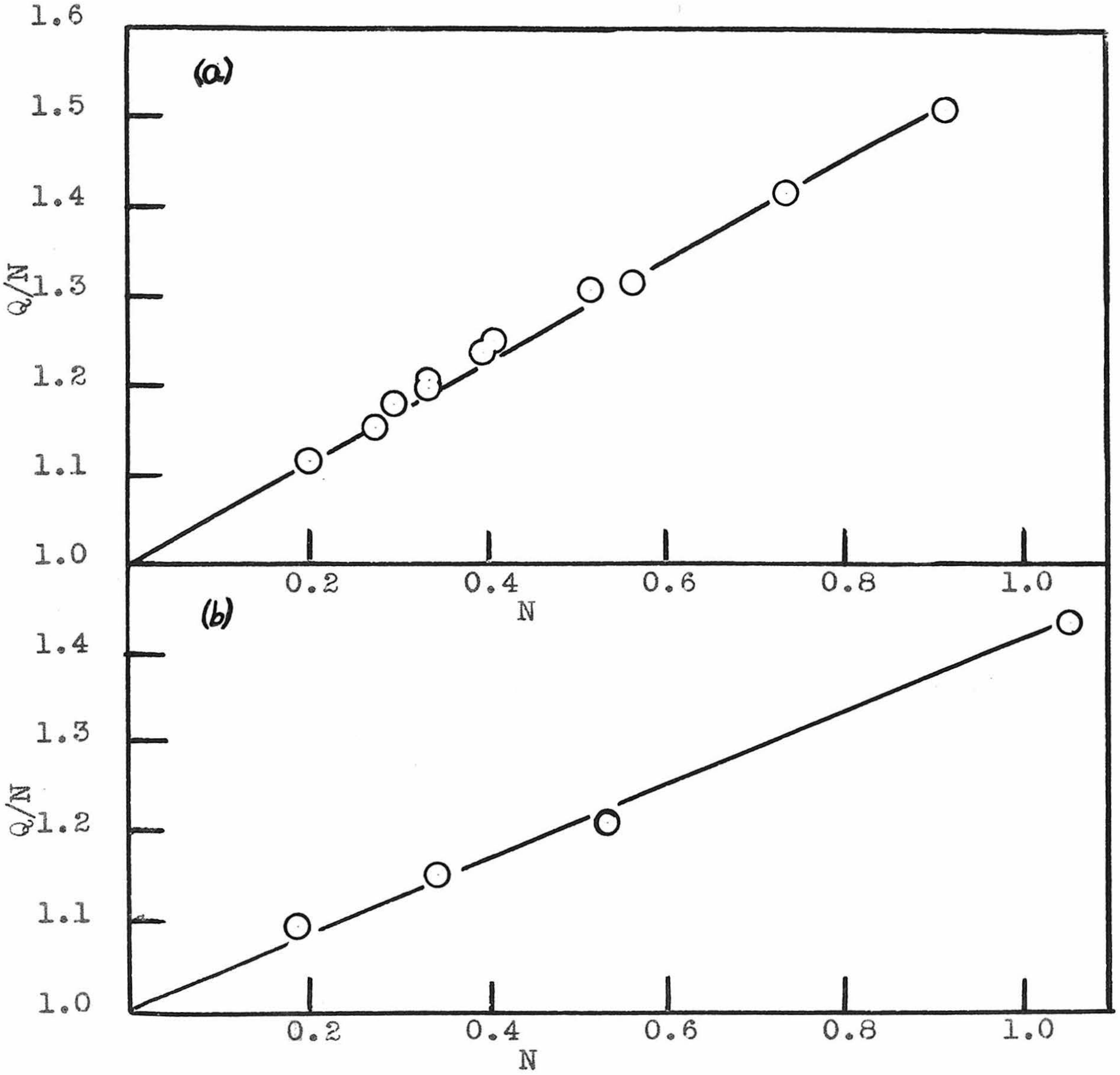

FIGURE III

Q is the concentration of phenol in formula weights per liter of solution; N is the concentration of naphthalene in formula weights per liter of solution.

was also examined under the most unfavorable conditions used, i.e., at 50°C with a phenol concentration of 1.5 molar. After a run of 15 hours the naphthalene solution was analyzed for phenol; it was found that 0.25% of the original phenol had distilled to the naphthalene side. This corresponds to an error of 0.5% in the experiment, since the distillation of phenol reduces the phenol concentration and effectively increases the naphthalene concentration. To reduce this error the time of each determination was reduced as much as possible. As a result equilibrium was not approached as closely as at 25°C. No correction for the distillation is introduced.

Interpretation of Results. If both naphthalene and phenol behaved as perfect solutes in benzene the values of Q and N would be equal. It is known that naphthalene behaves as a perfect solute in benzene[4, 6]; if we assume that phenol is polymerized and that each polymer behaves as a perfect solute then the number of moles of phenol per liter of solution at equilibrium must be equal to N, each polymer being counted as one molecule. There remains the problem of calculating the equilibrium constants of the polymerization reactions. It is easy to show that the equilibrium constant of the reaction

$$2\ C_6H_5OH \rightleftharpoons (C_6H_5OH)_2 \qquad 1$$

is equal to the slope of the curve Q/N vs. N at the point N = 0. This result is independent of the behavior of the higher polymers, depending only upon the assumption that the law of mass action is valid and that deviations ~~are~~

are due to polymerization reactions alone, i.e., no other reactions than polymerization reactions are taking place. From figure III we see that at both 25°C and 50°C the plot of Q/N against N gives a straight line to within the limits of accuracy of the experiments. We conclude therefore that the slopes of those lines give the equilibrium constants for the reaction 1 at 25°C and 50°C, respectively. The equilibrium constant at 25°C is 0.570 and at 50°C is 0.416. From these equilibrium constants and the Van't Hoff equation, neglecting the change in heat capacity, the change in partial molal heat content in reaction 1 is found to be -2400 cal./mole.

These experiments were carried out in the absence of water, the reagents were carefully dried and the apparatus thoroughly washed with dry benzene before using. A comparison of these equilibrium constants with those obtained from a distribution experiment provides some measure as to the importance of hydration in the latter experiment. An accurate study of the distribution of phenol between benzene and water has recently been carried out by Philbrick[7]. He obtains for the equilibrium constant of the reaction 1 at 25°C 0.575. This is in very good agreement with the value obtained in this experiment (0.570) and demonstrates that hydration plays only an unimportant part in this case. This is contrary to the result obtained in the case of several carboxylic acids in benzene solution[8,9].

It is now well recognized that phenol polymerizes because of the formation of hydrogen bonds. For steric reasons it seems unlikely that more than one hydrogen bond is formed in reaction 1. If this is true the heat absorbed in breaking a hydrogen bond between two phenols in benzene solution is 2400 cal/mole. This is consideralby less than would be expected on the basis of hydrogen bond energies calculated from other data and for other compounds than phenol[11]. The study of these reactions is hardly advanced enough to justify a speculation as to the cause of this small value.

We obtain but little information about higher order polymers from these data especially at 50°C. A dimer alone is definitely not sufficient to account for the variation of Q/N with N at 25°C. Whatever the behavior of the higher polymers the equilibrium constant of reaction 1 cannot be greatly different from 0.570 as was indicated by the argument previously used. If we assume that we have only a dimer with equilibrium constant 0.570 we find for the calculated value of Q/N at N = 0.5, Q/N = 1.19 while the observed value is 1.29. For higher values of N the calculated and the observed values diverge even more sharply. It seems certain that polymers of higher order than the second must play an important part in the equilibrium. As demonstrated in the first of the two preceeding papers a linear relation between Q/N and N can be exactly accounted for if we assume that polymers of all orders are present and under these conditions the equilibrium constant of the reaction

$$\ell\, C_6H_5OH \rightleftharpoons (C_6H_5OH)_\ell \qquad 2$$

is

$$K_\ell = \beta^{\ell-1} \qquad 3$$

where β is the slope of the line. It seems likely, and the data strongly suggests, that the heat content change in the general reaction 2 is just (ℓ - 1) times -2400 cal./mole, at least for small values of ℓ. The data are not, however, either accurate enough or extensive enough to render this conclusion decisive, and it seems unlikely that the present experimental technique will be adequate to deal with this matter due to the appreciable volatility of phenol. It does indicate, however, that since the effect of hydration is small, an extended study of the distribution of phenol between water and benzene both as a function of temperature and concentration would settle this point conclusively.

Summary

1. A comparative method of determining the vapor pressures of solutions of non-volatile solutes is described.
2. The method is applied to solutions of phenol in benzene and the results of previous distribution experiments are confirmed, thus demonstrating that the effect of hydration in these experiments at 25°C is unimportant.
3. An approximate value of 2400 cal./mole is obtained for the heat of dissociation of the dimer of phenol.

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*This work was carried on under the supervision of Professor Roscoe G. Dickinson.

PART II

Reprinted from The Journal of Chemical Physics, Vol. 4, No. 5, 325, May, 1936
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The Raman Spectra of Carbon and Silicon Tetrafluorides

We have photographed the Raman spectra for the tetrafluorides of carbon and silicon in both the liquid and gaseous states. The results are presented in Table I together with the Raman frequencies of CCl_4 for purposes of comparison. The relative intensities are given in parentheses.

Table I.

	ω_1 (cm^{-1})	ω_2 (cm^{-1})	ω_3 (cm^{-1})	ω_4 (cm^{-1})
CF_4	904 (10)	437 (1)	(1200)	635 (1)
SiF_4	800	(285)	(1000)	(431)
CCl_4	450	214	775	311

So far only ω_1 for SiF_4 has been found, the other three lines being apparently of small intensity. For gaseous CF_4 only ω_1 was definitely seen on the plates, and it was sharp and strong. ω_2 and ω_4 together with ω_1 were obtained from CF_4 (1) at $-120°$.

The CF_4 was prepared by treating carbon (Norit) with fluorine gas and submitting the raw product to a number of fractional distillations. It is difficult to prepare pure CF_4. The SiF_4 was prepared by a conventional method.

The assignment of frequencies is based on a number of considerations. Since ω_1 is the completely symmetrical vibration, it should appear intense and sharp in the Raman spectrum. Accordingly the strongest and sharpest observed line was assigned to ω_1. It was found, from a consideration of the Raman spectra for eight tetrahalides that certain regularities existed (approximate constancy of ratios of corresponding frequencies), and on the assumption that no discontinuities in these regularities would occur with CF_4 the frequencies ω_2 and ω_4 were assigned.

The frequencies given in parentheses were computed from empirically found ratios, or from the formulae derived from normal coordinate treatments of tetrahedral molecules by Urey and Bradley,[1] and Rosenthal.[2]

Two absorption bands in the infrared spectrum of CF_4 have been observed recently by Eucken and Bertram,[3] namely, $\omega_3 = 1350$ cm^{-1} and $\omega_4 = 653$ cm^{-1}. The latter is in fair agreement with 635 cm^{-1} found in the Raman spectrum, and the estimate (1200) for ω_3 is, considering the theory involved, in accord with $\omega_3 = 1350$ cm^{-1}. Eucken and Bertram estimate ω_2 to be 503 cm^{-1} from specific heat measurements, and this agrees only moderately well with the observed value, $\omega_2 = 437$ cm^{-1}. The disagreement is probably to be assigned to errors in the theory or measurement of the specific heats.

Don M. Yost
Edwin N. Lassettre
Siegfried T. Gross

California Institute of Technology,
Pasadena, California,
April 6, 1936.

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[1] Urey and Bradley, Phys. Rev. **38**, 1970 (1932).

[2] Rosenthal, Phys. Rev. **45**, 538 (1931).

[3] Eucken and Bertram, Zeits. f. physik. Chemie **B31**, 361 (1936).

NOVEMBER, 1936 JOURNAL OF CHEMICAL PHYSICS VOLUME 4

The Raman Spectra of Boron Trifluoride, Trichloride, and Tribromide. The Effect of the Boron Isotopes*

THOMAS F. ANDERSON, EDWIN N. LASSETTRE AND DON M. YOST, *California Institute of Technology, Pasadena, California*

(Received August 12, 1936)

The Raman frequencies $\nu_1\{1\}$, $2\nu_2\{2\}$, $\nu_3\{2\}$, and $\nu_4\{2\}$ for $BF_3(g)$, $BCl_3(l)$, and $BBr_3(l)$ were found to be 886 and 783, 1394, 1038 and 1105, 440; 471, 924, 958 and 996, 243; 279, 743, 806 and 846, and 151 cm^{-1}, respectively. The assignment of frequencies was determined by polarization experiments on BCl_3 and is confirmed for the three compounds by the results of a normal coordinate treatment. The doubling of ν_1 in BF_3 is ascribed to vibrational resonance between ν_1 and $2\nu_4$. The doubling of ν_3 in all three compounds is shown to be due to the presence of the two isotopes of boron B^{10} and B^{11}. A satisfactory assignment of the infrared frequencies of BCl_3 is made.

INTRODUCTION

THE Raman spectrum of boron trichloride has been reported by Bhagavantam and by Venkateswaran.[1] Cassie[2] has proposed an assignment for the infrared frequencies he observed for boron trichloride, but he assumed frequencies differing rather widely from the Raman frequencies as well as the presence of forbidden lines in the infrared spectrum.

We have reinvestigated the Raman spectrum of boron trichloride and report as well the Raman spectra of boron tribromide and boron trifluoride. In all three compounds a doubling of certain frequencies by the presence of the boron isotopes B^{10} and B^{11} is observed. The infrared spectrum of boron trichloride is satisfactorily explained by an assignment of frequencies which is confirmed by the results of a normal coordinate treatment.

The work on boron trifluoride was started at this laboratory in 1934 by Mr. S. T. Gross.

This and other similar investigations were assisted by a grant-in-aid of research to one of us (D. M. Y.) from the National Research Council. The boron tribromide used was prepared as an N.Y.A. project by Mr. David Pressman.

GENERAL THEORETICAL CONSIDERATIONS

The shape of the boron trichloride molecule is rather definitely shown to be that of a plane equilateral triangle with the symmetry D_{3h}. This follows from its zero dipole moment[3] and the results of electron diffraction experiments.[4] The results of the present investigation are in agreement with the assumption that the other boron trihalides also have the symmetry D_{3h}.

The BX_3 molecule then has the four symmetry modes of vibration indicated in Fig. 1. $\nu_1\{1\}$, $\nu_3\{2\}$, and $\nu_4\{2\}$ are allowed in the Raman effect with the depolarizations 0, 6/7, and 6/7, respectively.[5] Numbers in braces adjoining ν's are degeneracies. $\nu_2\{1\}$, $\nu_3\{2\}$ and $\nu_4\{2\}$ are active in the infrared. The selection rules for simple combinations and overtones obtained by the methods of group theory[6] are indicated in Table I.

The fact must be borne in mind that the presence of the isotopes of boron B^{11} and B^{10} in the approximate ratio of 4 to 1 will produce a doubling of those frequencies in which the boron atom moves appreciably. Thus in the Raman effect we should expect ν_3 and $2\nu_2$ each to appear as a doublet separated in frequencies by about 5 percent, and with the lower frequency about four times as intense as the higher. Analogous splits in frequencies should appear in the infrared spectrum with a ratio of extinction coefficients for the two components of 4 to 1. A normal coordi-

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* Contribution No. 562 from the Gates and Crellin Chemical Laboratory of the California Institute of Technology.

[1] Bhagavantam, Ind. J. Phys. **5**, 73 (1930); Venkateswaran, ibid. **6**, 284 (1931).

[2] A. B. D. Cassie, Proc. Roy. Soc. **A148**, 87 (1935).

[3] E. Bergmann and L. Engel, Physik. Zeits. **32**, 425 (1931); H. Ulich and W. Nespital, Zeits. f. Elektrochem. **37**, 559 (1931); W. Nespital, Zeits. f. physik. Chemie **B16**, 153 (1932).

[4] L. O. Brockway, Rev. Mod. Phys. **8**, 231 (1936); private communication.

[5] E. B. Wilson, Jr., J. Chem. Phys. **2**, 432 (1934).

[6] E. Wigner, Gött. Nachr., 133 (1930); G. Placzek, *The Structure of Molecules* (Blackie and Son, London, 1932); L. Tisza, Zeits. f. Physik **82**, 48 (1933); E. B. Wilson, Jr., Phys. Rev. **45**, 706 (1934).

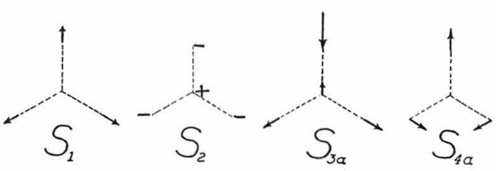

FIG. 1. Symmetry modes of the plane symmetrical BX_3 molecule.

TABLE I. *An addition table showing the selection rules for simple combinations and overtones of modes of vibration of BX_3 molecules.*

	$\nu_1\{1\}R$	$\nu_2\{1\}I$	$\nu_3\{2\}RI$	$\nu_4\{2\}RI$
$\nu_1\{1\}R$	R	I	RI	RI
$\nu_2\{1\}I$		R^*	R	R
$\nu_3\{2\}RI$			RI	RI
$\nu_4\{2\}RI$				RI

R indicates a Raman active combination; *I* indicates an infrared active combination.
* $3\nu_2$ is infrared active.

nate treatment should enable one to predict the isotopic doubling of frequencies with greater accuracy.

EXPERIMENTAL

Boron trifluoride was prepared by treating ammonium fluoborate with concentrated sulfuric acid and heating. The reaction chamber was of glass, so silicon tetrafluoride was expected as an impurity. To prepare ammonium fluoborate, boric acid was treated with hydrofluoric acid in a copper beaker; the solution was neutralized with NH_4OH and concentrated by heating. Upon cooling the solution, NH_4BF_4 crystallized out. The BF_3 so prepared was fractionated repeatedly; the final product had a melting point of −127±1°, in good agreement with the value given in the literature. The Raman spectrum of the somewhat cloudy liquid under its own vapor pressure of 6 atmospheres at the temperature of a solid carbon dioxide alcohol bath was taken using a technique similar to that previously employed for phosphorus trifluoride.[7] The Raman spectrum of the gas at a pressure of six atmospheres was taken using the 2537A line of mercury as a source of radiation. The spectrum from the gas was much more satisfactory than that from the liquid.

Kahlbaum's C.P. boron trichloride (b_{760} 12.5°) was distilled into a Raman tube and sealed in without further purification. The Raman spectrum was obtained at room temperature from the liquid under its own vapor pressure. The polarizations of the two most intense lines were roughly determined. For this purpose[8] the mercury lamp was placed below the horizontal Raman tube with a series of parallel vanes of black cardboard between lamp and tube to insure that the light entering the tube was parallel. The scattered light from the Raman tube then passed successively through a half-wave plate for 4400A, a large Nicol prism with vertical axis, and a lens which focused the light on the 0.4 mm slit of the spectrograph. With the axis of the half-wave plate at an angle of 45° to that of the Nicol, only horizontally polarized light from the Raman tube passed through to the slit. When the axis of half-wave plate and Nicol were parallel, only the perpendicular component reached the slit. The advantage of this arrangement is that all light entering the spectrograph is vertically polarized so that there is no effect of selective transmission or reflection of the light from the slit or prism faces, in contrast to previously used arrangements. Two one-hour exposures were made on the same photographic plate with the two settings of the half-wave plate. Relative intensities of the lines in the two spectra were estimated visually and compared with the relative intensities of the Rayleigh lines which are known to be polarized.

Boron tribromide (b_{740} 90.1°) was prepared by passing bromine vapor over a mixture of boric oxide and carbon at 250°. It was carefully fractionated, the fraction used having a boiling point of 91.0±0.2°. Difficulty was had in sealing the material in the Raman tube without the liberation of small amounts of bromine. The bromine was therefore removed by sealing a small amount of mercury in the Raman tube with the boron tribromide. The mercurous bromide, which was formed on shaking, settled out nicely and Raman spectra of the clear colorless liquid remaining were obtained.

RESULTS AND ASSIGNMENT OF FREQUENCIES

The observed Raman frequencies and assignments are presented in Table II. We shall discuss

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[7] D. M. Yost and T. F. Anderson, J. Chem. Phys. 2, 624 (1934).

[8] The arrangement here described, which has been in use in this laboratory for some time, was developed by Dr. Fred B. Stitt of this laboratory. He will publish a more detailed account shortly.

first the more complete results for BCl_3 and proceed then to a discussion of BBr_3 and BF_3.

Boron trichloride

The results for boron trichloride agree with those obtained by Venkateswaran[1] with the exception that the broad band he observed at 947 cm^{-1} is resolved into a triplet. This group, consisting of a sharp line and two broad lines, is reproduced in Fig. 2. The depolarization of the 471 cm^{-1} line was found to be less than 0.25; it was therefore assigned to the mode ν_1. The depolarization of the line at 253 cm^{-1} was close to unity and it was therefore taken to be ν_4. The frequency ν_3 was taken to be the expected isotopic doublet 946, 989 cm^{-1}, the broadness of this pair distinguishing it from the sharp line at 902 cm^{-1}. The latter frequency was then assumed to be $2\nu_2$ whose weaker isotopic component is obscured by the 946 cm^{-1} frequency.

When we make the assignment of infrared absorption frequencies[2] indicated in Table III, we arrive at the values for the vibrational frequencies for $BCl_3(g)$ indicated in Table II. These frequencies differ only slightly from the Raman frequencies for $BCl_3(l)$. The agreement between observed and calculated frequencies is quite satisfactory with the exception of the assignment of the frequency 845 cm^{-1}. Its nearness to the frequency 834 cm^{-1} observed in the Raman spectrum of phosgene[9] and the fact that phosgene is often a by-product in the preparation of BCl_3 and difficult to separate from it, suggest that the presence of this band may be due to a trace of phosgene in the BCl_3 used. The infrared spectrum of phosgene has not been reported. The weaker isotopic components of $\nu_3+\nu_4$ and of $\nu_1+\nu_3$ are evidently too weak to be observed, while that of $3\nu_2$ is obscured by $\nu_1+\nu_3$ from $B^{11}Cl_3$. In other cases the estimated relative intensities of the bands are in accord with the relative abundancies of the boron isotopes. Unfortunately Cassie has not published data from which extinction coefficients could be calculated. The assignment of frequencies is confirmed by the results of the normal coordinate treatment which follows this section.

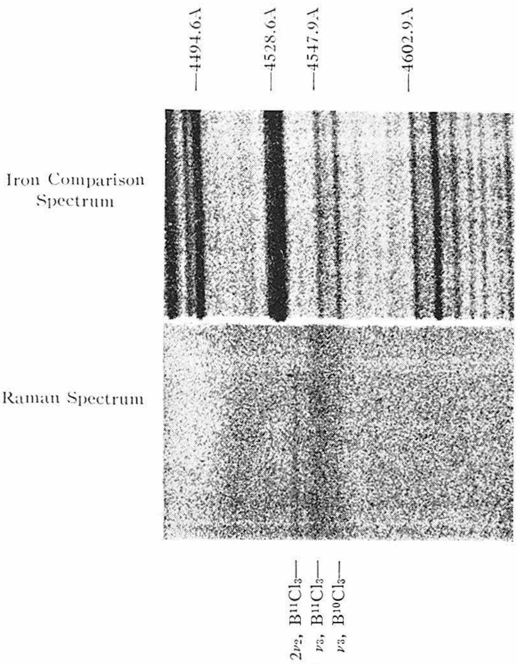

FIG. 2. The effect of the boron isotopes in the Raman spectrum of BCl_3.

TABLE II. *The Raman spectra of boron trifluoride, boron trichloride, and boron tribromide.*

SUBSTANCE	$\nu_1\{1\}$ (cm^{-1})	$2\nu_2\{1\}$ (cm^{-1})	$\nu_3\{2\}$ (cm^{-1})	$\nu_4\{2\}$ (cm^{-1})
$B^{11}F_3(g)$	886(7), 783(3)	1394($\frac{1}{2}$?)*	1038(1)	440(4*b*) ±25*
$B^{10}F_3(g)$	886(7), 783(3)	(1452)	1105($\frac{1}{2}$?)*	440(4*b*) ±25*
$B^{11}F_3(l)$	883(1), —	—	—	—
$B^{11}Cl_3(g)$†	471	924	958	243
$B^{10}Cl_3(g)$†	471	(966)	996	243
$B^{11}Cl_3(l)$	471(10)	902(3)	946(3*b*)	253(8)
$B^{10}Cl_3(l)$	471(10)	(943)	989(1*b*)	253(8)
$B^{11}Br_3(l)$	279(10)	743($\frac{1}{2}$)	806(3/4*b*)	151(8)
$B^{10}Br_3(l)$	279(10)	(780)	846($\frac{1}{2}$*b*)	151(8)

Numbers in parentheses adjoining frequency values indicate relative intensities. *b* = broad; all other lines are sharp. Numbers in braces adjoining ν's are multiplicities. Frequencies in parentheses are estimated.

* The assignment of these frequencies is provisional for $BF_3(g)$.

† Frequencies obtained from infrared data for $BCl_3(g)$.

Boron tribromide

The Raman spectrum of boron tribromide is very similar in appearance to that of boron

TABLE III. *The infrared spectrum of boron trichloride.*

$\nu_{obs.}$ (cm^{-1})	$\nu_{calc.}$ (cm^{-1})	Combination
714(4)	714	$\nu_1+\nu_4$
845(3)	834(*R*)	$COCl_2$ (?)
958(100)	958	ν_3, $B^{11}Cl_3$
996(50)	996	ν_3, $B^{10}Cl_3$
1206(2)	1201	ν_3, $B^{11}Cl_3+\nu_4$
1387(6)	1386	$3\nu_2$, $B^{11}Cl_3$
1429(6)	1429; 1452	$\nu_1+\nu_3$, $B^{11}Cl_3$; $3\nu_2$, $B^{10}Cl_3$
1912(2.5)	1916	$2\nu_3$, $B^{11}Cl_3$
1995(2)	1992	$2\nu_3$, $B^{10}Cl_3$

R = observed in Raman spectrum of $COCl_2(l)$.

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[9] Kohlrausch, *Der Smekal-Raman-Effekt* (Julius Springer, Berlin, 1931).

TABLE IV. *Calculated force constants K, H, G, and K′, calculated frequencies for trihalides containing* B^{10}, *and calculated internuclear distances B–X, for boron trihalides.*

SUBSTANCE	$K\times10^{-5}$ (dynes/cm)	$H\times10^{-5}$ (dynes/cm)	$G\times10^{-5}$ (dynes/cm)	$K'\times10^{-5}$ (dynes/cm)	$\nu_3B^{10}X_3$ calc. (cm^{-1})	$\nu_3B^{10}X_3$ obs. (cm^{-1})	$\nu_4B^{10}X_3$ calc. (cm^{-1})	$\nu_4B^{10}X_3$ obs. (cm^{-1})	B–X calc. (A)	B–X obs. (A)
$BF_3(g)$	4.24	0.60	0.88	1.73	1080	1105(?)	416	416*	1.49	1.42†
$BCl_3(g)$	3.30	0.276	0.434	0.653	1000	996	243	243	1.72	1.73
$BBr_3(l)$	2.50	0.252	0.270	0.61	843	846	151	151	1.85	1.87

* This value was assumed for ν_4, $B^{11}F_3$ in order to obtain real values for the constants.

† The sum of Pauling's double bond radii plus 0.04A was taken as an estimate for the B–F distance. See L. Pauling, L. O. Brockway and J. Y. Beach, J. Am. Chem. Soc. **57**, 2705 (1935).

trichloride with $2\nu_2$ and the isotopic shift of ν_3 both appearing. By analogy with the assignment of the BCl_3 frequencies the assignment of frequencies indicated in Table II was made; confirmation is again obtained from the normal coordinate treatment.

Boron trifluoride

The Raman spectrum obtained from boron trifluoride is much more difficult to interpret. In addition to the frequencies listed in Table II, a line, doubtless due to the presence of SiF_4 ($\nu_1=800(10)$ cm^{-1}),[10] was observed at 801(4) cm^{-1}. The line assigned to ν_4 whose center is at 440 cm^{-1}, is 50 cm^{-1} in width. Its integrated intensity is therefore quite great. We then attribute the strong doublet, which appears as ν_1 in our assignment, to vibrational resonance between ν_1 and $2\nu_4$. Aside from the presence of impurities this appears to be the only reasonable possibility of accounting for the existence of both lines. If we introduce the perturbation term

$$H'=\gamma Q_1(Q_{4a}^2+Q_{4b}^2)$$

(where the Q's represent the normal coordinates and γ is a constant) in the potential energy expression one obtains the following energy levels from the solution of the secular equation:[11]

$$\begin{aligned}\lambda_1\{2\}&=2\nu_4,\\ \lambda_2\{1\}&=\tfrac{1}{2}[2\nu_4+\nu_1+\{(2\nu_4-\nu_1)^2+8P^2\}^{\frac{1}{2}}],\\ \lambda_3\{1\}&=\tfrac{1}{2}[2\nu_4+\nu_1-\{(2\nu_4-\nu_1)^2+8P^2\}^{\frac{1}{2}}].\end{aligned}$$

We should expect λ_2 and λ_3 to appear, while the simple overtone λ_1 should be very weak in the Raman effect. P, the perturbation energy defined in the usual manner, has the value 35 cm^{-1} when it is assumed that $\nu_1=2\nu_4=835$ cm^{-1}. This value is of the usual order of magnitude for P. The assignment of other observed frequencies is confirmed by the rather satisfying results of the following normal coordinate treatment. An investigation of the infrared absorption spectrum of BF_3 would doubtless yield a unique assignment.

NORMAL COORDINATES; COMPUTATION OF ISOTOPIC SHIFTS IN FREQUENCIES

Normal coordinate treatments of the plane symmetrical AB_3 type molecule have been made by a number of authors.[12] We shall use the valence force potential function V with force constants chosen so that

$$\begin{aligned}2V=K(\Delta R_1^2+\Delta R_2^2+\Delta R_3^2)&\\ +HR_0^2(\Delta\alpha_{12}^2+\Delta\alpha_{23}^2+\Delta\alpha_{13}^2)&\\ +GR_0^2(\Delta\beta_1^2+\Delta\beta_2^2+\Delta\beta_3^2)&\\ +2K'(\Delta R_1\Delta R_2+\Delta R_2\Delta R_3+\Delta R_1\Delta R_3).&\end{aligned}$$

R_1 is here the distance $A-B_i$ and R_0 is this distance when the atoms are at equilibrium positions. α_{ij} is the angle B_i-A-B_j while β_i is the angle made by the line $A-B_i$ with the B_3 plane. The frequencies are then given by the equations:

$$\begin{aligned}&m\lambda_1-K-2K'=0,\\ &mM\lambda_2-(3m+M)G=0,\\ &m^2\lambda_{3,4}^2-\{\tfrac{1}{2}(K-K')(3m/M+2)\\ &\qquad+H(9m/2M+3)\}m\lambda_{3,4}\\ &\qquad\qquad+H(K-K')(9m/M+3)=0.\end{aligned}$$

Using the vibrational data for the boron trihalides containing the isotope B^{11} we have determined the various force constants with the

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[10] D. M. Yost, E. N. Lassettre, and S. T. Gross, J. Chem. Phys. **4**, 325 (1936).

[11] T. F. Anderson, J. Chem. Phys. **4**, 161 (1936).

[12] D. M. Dennison, Phil. Mag. **1**, 195 (1926); F. Lechner, Wien. Bericht **141**, 633 (1932); J. B. Howard and E. B. Wilson, Jr., J. Chem. Phys. **2**, 630 (1934); J. Rosenthal, Phys. Rev. **47**, 235 (1935). We have applied in part the results of Howard and Wilson in our treatment.

results indicated in Table IV. It is interesting to note that the constant G, usually assumed equal to H in the treatment of pyramidal type molecules, is nearly equal to H for heavy halogen atoms, but is considerably greater than H for light halogen atoms bound to the central boron.

Using these force constants we have calculated the frequencies ν_3 and ν_4 to be expected for the compounds containing the B^{10} isotope. The results agree well with the observed values as indicated in the table. The fact that the frequency ν_4 has little isotopic shift indicates that the symmetry modes are very nearly the normal modes in these cases.

Finally in Table IV, columns 10 and 11 are presented values of the internuclear distances calculated directly from the values of K by Badger's rule.[13] The agreement with the internuclear distances determined by electron diffraction experiments[4] is much better than would have been expected, judging from the experience of previous investigators.

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[13] R. M. Badger, J. Chem. Phys. **2**, 128 (1934); **3**, 710 (1935).

PROPOSITIONS

I. If a differential equation of the type

$$(\rho_1 P_n')' = \lambda_n \rho P_n$$

(ρ_1, ρ are known functions of x. λ_n is a parameter. The primes denote differentiation with respect to x.)

subject to the boundary conditions

$$\rho_1^{(a)} P_n(a) = \rho_1^{(b)} P_n(b) = 0$$

has a complete set of orthogonal polynomials as solutions, then a recursion formula of the type

$$xP'_n = a_n P'_{n+1} + b_n P'_n + c_n P'_{n-1}$$

always exists. (a_n, b_n, c_n denote constants.) If we adopt the convention that the coefficient of the highest power of x be unity, then $a_n = \frac{n}{n+1}$.

II. A differential equation of the type

$$\frac{d^2\psi_n}{dx^2} + \lambda_n \psi_n - V\psi_n = 0 \qquad V(+x) = V(-x)$$

subject to the boundary conditions

$$\psi_n(+\infty) = {}_n(-\infty) = 0$$

can be solved by functions of the type $\psi_n = \sqrt{\rho}\,P_n(x)$ ($P_n(x)$ = polynomial of degree n) only in case that $V(x) = \alpha x^2 + \beta$. ($\alpha$, β are constants.) The condition is both necessary and sufficient since the solutions with $V(x) = \alpha x^2 + \beta$ are Hermite Functions. The mathematical properties of the Hermite Functions can be deduced in a very simple and elegant way without either using the generating function or solving the differential equation explicitly.

III. A differential equation of the type shown in (I) can have as solutions a complete orthogonal set of polynomials only when the equation is of the hypergeometric type; that is, it has only three singular points, all of which are regular. The equation might, of course, be a confluent form in which two singularities are condensed. The interval (a,b) is assumed to be finite.

This proposition is of interest for two reasons; first, because it shows that polynomial solutions are rare, and secondly, because it reconciles two different view points concerning the origin of three term recursion formulae which occur in many of the known solutions to boundary value problems.

IV. Experimental measurements on the specific heat at constant volume for air have shown that c_v is a linear function of the pressure at constant temperature. (For an account of these measurements see Partington and Schilling, "The Specific Heat of Gases", Benn Co., 1924, page 156. Direct measurements of c_v have been made as well as calculations from c_p and the equation of state.) The question to be considered is: what is the equation of state of a gas for which the specific heat is given by

$$c_v = f(t) + \frac{a}{t} P$$

$f(t)$ = an arbitrary function of t.

a = a constant.

P = pressure

t = absolute temperature.

The equation (1) is a rough approximation to c_v for air when t is greater than -100°C. (P. and S.)

The solution is as follows:

If at any *one* volume $v = v_o$

$$P = \sum_{n=m}^{\ell} \alpha_n t^n$$

then at all *other* volumes

$$P = \sum_{n=m}^{\ell} \alpha_n t^n e^{n(n-1)\frac{(v - v_o)}{a}} \qquad \text{Provided } a \neq 0$$

This solution has interesting properties, some of which are preserved when c_v has the more general form

$$c_v = f(t) + \phi(t)\,P. \qquad (\phi(t) \text{ is an arbitrary function.})$$

V. We use the following notation:

Q = Formal concentration of solute.

N = Molal concentration of solute.

$n = \frac{Q}{N}$.

It is assumed that in a given solvent the solute can only polymerize, and that it obeys the law of mass action. If we plot n vs. Q for such a solution the beginning slope is the equilibrium constant of the reaction $2A \rightleftharpoons A_2$, i.e., $K_2 = \text{slope} = \frac{(A_2)}{(A)^2}$.

VI. If it is known by experiment that $n = 1 + f(Q)$, the problem of finding the concentration of monomer as a function of N can always be reduced to the solution of the following differential equation of the first order:

$$\frac{x}{N}\frac{dN}{dx} = 1 + f\left(x\frac{dN}{dx}\right).$$

The auxiliary conditions are: $N = 0$ when $x = 0$ and $\lim_{x \to 0} \frac{N}{x} = 1$.

VII. Using the notation of the preceding proposition, if $n = 1 + \quad Q$, the equilibrium constant of the reaction $\ell A \rightleftharpoons A_\ell$ is $K_\ell = \frac{(\alpha \ell)^{\ell - 1}}{\ell!}$, and the concentration of monomer is

$$x = N e^{-\alpha N}.$$

This case arises in practice.

VIII. We consider the distribution of a solute between two liquid phases, to be called Phase 1 and Phase 2, respectively. In Phase 1 it is assumed that the material undergoes no reaction, while in Phase 2 it may be polymerized to any extent. Let C be the concentration in Phase 1 while for Phase 2 we use the notation of V and VI. If the law of mass action is obeyed,

$$N = \int_0^{C} D \, dC \qquad (1)$$

where $D = \frac{Q}{C}$ is the distribution ratio. The law of mass action has disappeared completely from this expression. It is of interest to find that conditions under which the reasoning canbe reversed; namely, if (1) holds is the law of mass action valid? If it be assumed that the concentration of a polymer is a function of C only, and if the functional form of this relation is independent of the presence of other polymers then the converse can be proven.

IX. Nernst's Rule that polymerization is greatest in solvents of low dielectric constant can well be replaced by the rule that polymerization due to hydrogen-bond formation is least in solvents with which the solute can form hydrogen bonds.

X. Molecular weight data indicate that sulfur atoms are not involved in hydrogen-bond formation to any marked extent.

XI. Simple structural interpretations can be given to the following phenomena, in terms of hydrogen-bond formation.

a) o-nitrophenol is not polymerized in naphthalene solution but m- and p-nitrophenols are.

b) Both o- and p-cyanophenols are polymerized,in naphthalene solution, to about the same extent.

c) Sebacic acid is less polymerized in phenol solution than either ethyl malonic or methyl succinic acid.

d) The vapor pressure of o-nitrophenol is higher than that of m- or of p-nitrophenol at 100°C.

e) The solubilities of o-, m-, and p-nitrophenols are about the same in oxygenated solvents while in nonpolar solvents such as C_6H_6 the solubility of the o-compound is much greater than that of either the m- or p-compound.

XII. Molecular weight data for several organic compounds can be interpreted in terms of a succession of polymers. Application of the methods of propositions IV, V, and VI leads to the conclusion that all members of the set are present. The approach to the problem was made by plotting the data, drawing a smooth curve through it, and then asking for the set of equilibrium constants which would reproduce the curve.

XIII. Many cases of polymerization are known for which the hydrogen bond does not furnish an attractive explanation.

Summary of Thesis

Part I of this thesis is concerned with the effect of hydrogen bond formation on solutions, and Part II deals with the Raman effect. The first paper considers the application of the law of mass action to a class of polymerization reactions in solution. The substances considered are of that large group for which the molecular weights in certain solvents are linear functions of the formal concentration. It is demonstrated, first, that in order to account for such behavior over the whole range of composition polymers of all orders must be present, second, that the problem of determining the constants can be reduced to that of solving a first order differential equation and it follows that the equilibrium constants are uniquely determined, and finally, a simple explicit expression is produced which relates the equilibrium constants to the slope of the line. The second paper is a review dealing with the hydrogen bond and its influence on the properties of solutions. The data is treated systematically in accordance with the principles outlined above. The third paper deals with the development of a method of measuring vapor pressure lowering. The vapor pressures of solutions of phenol in benzene are examined, and it is shown first that the heat of dissociation of the dimer of phenol of 2500 cal./mole and second that the results of this experiment are in agreement with the results of distribution experiments. The first paper of Part II gives the results of an investigation of the Raman spectrum of CF_4. Only three lines could be obtained from liquid phase scattering and only one from vapor phase scattering. The fourth line was observed in infrared absorption by another investigator, thus providing sufficient information to calculate the entropy of the substance. The second

paper deals with the Raman spectra of the boron halides, from which is calculated the force constants, and the effect of isotopes on the spectra is discussed, several Raman lines being split due to the presence of the two isotopes B_{10} and B_{11}.