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The Interpretation of Freezing Point Lowering Data in Terms of Polymerization

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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:

$$Q = \sum_{l=1}^{k} l(A_l) = \sum_{l=1}^{k} lK_l x^l,\ x = (A).\ K_1 = 1 \qquad (2)$$

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

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

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

$$x\frac{\mathrm{d}N}{\mathrm{d}x} = \sum_{l=1}^{k} lK_l x^l \tag{4}$$

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

$$x\,\mathrm{d}N/\mathrm{d}x = Q \tag{5}$$

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

$$\frac{x}{N}\frac{\mathrm{d}N}{\mathrm{d}x} = n \tag{6}$$

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

$$\frac{x}{N}\frac{\mathrm{d}N}{\mathrm{d}x} = 1 + \alpha x\frac{\mathrm{d}N}{\mathrm{d}x} \tag{7}$$

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

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

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.

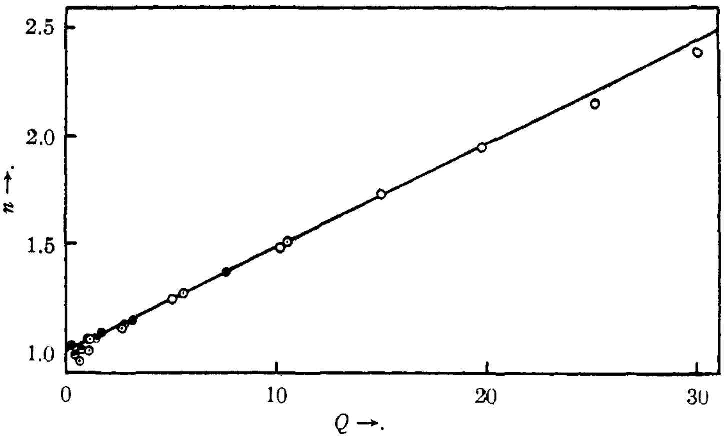

Fig. 1.—Polymerization of *p*-nitrophenol dissolved in naphthalene. Q in grams/100 grams solvent.

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 $\beta = 3.80$.

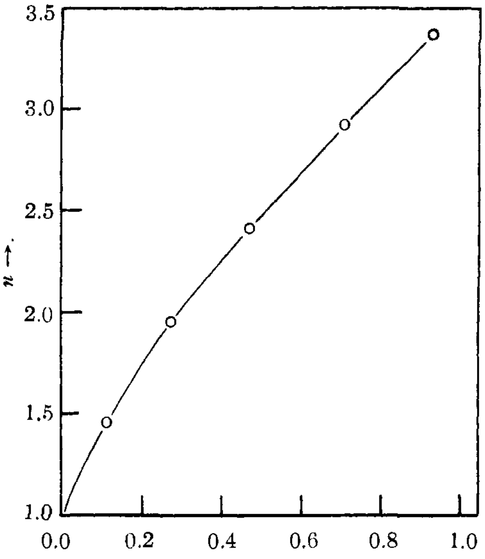

Fig. 2.—Polymerization of formanilide dissolved in *p*-xylene. *Q* is in moles/kg. of solvent.

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.

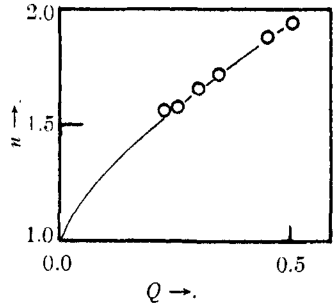

Fig. 3.—Polymerization of *n*-butyramide in benzene solution. *Q* in moles/liter solvent.

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 Standard State of Copper. A Study of the Copper–Cupric Electrode

BY LEON M. ADAMS AND DENTON J. BROWN

Electrodes composed of all but the softer metals have the tendency to show irregularities of potential which seem to depend somewhat on the previous treatment of the metal. Many methods have been tried for eliminating these irregularities. In 1914, Lewis and Lacey[1] devised an electrolytic method. They claim that a metal that has been plated upon platinum under high current densities from a solution of its salt will be strainless. In the case of copper, an acidified solution of copper sulfate was used. Copper prepared in this manner has a higher reducing potential than that of the copper amalgam. From theoretical considerations, a two-phase amalgam should be strainless and will give the potential of the standard state if there is no compound formation and if the mercury is not appreciably soluble in the metal. The solubility of mercury in copper is unknown, but if we assume that there is no compound formation, the value obtained by Lewis and Lacey would indicate an enormous solubility of mercury in copper which does not seem reasonable. So any large difference would indicate compound formation between copper and mercury. There are such compounds reported in the literature.

In this work, an application of von Weimarn's law was used in the preparation of the copper crystals at 25°. Copper sulfate in silica gels was reduced by organic reducing agents. The gel prevented the mechanical mixing of the copper sulfate with the reducing agent so that the rate of diffusion controlled the rate of reduction of the $CuSO_4$. By this method, it was hoped to secure the standard state of metallic copper.

Materials and Apparatus

The copper amalgam used was prepared by electrolysis of a half molal solution of cupric sulfate, slightly acidified, using about five amperes per sq. dm. of mercury surface and a copper anode. The amalgam was kept under this solution after preparation. Mercurous sulfate was prepared by electrolysis according to the method of Hulett.[2] The cupric sulfate used had been recrystallized from an acidified solution of the C. P. crystals. Conductivity water and distilled mercury were used in preparing the reagents. Silica gels were prepared by mixing equal volumes of N acetic acid and sodium silicate solution (sp. gr., 1.06). Before the mixture gelled, it was made 0.04 N with cupric sulfate. After the mixture gelled, a 2% solution of semicarbazide hydrochloride was poured on top of the gel and placed in an air-bath maintained at 25 ± 0.1°. In about a month, the gel was removed with concentrated sodium hydroxide solution, and the resulting crystals of copper removed and washed with water. Finely divided copper was obtained by pouring an ammoniacal solution of cuprous sulfate into an excess of dilute sulfuric acid. This was always prepared fresh. Measurements were made on a Leeds and Northrup "Type K" potentiometer, using a Weston cell with a Bureau of Standards certificate. The thermostat consisted of a bath of distilled water maintained at 25 ± 0.05°.

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(1) Lewis and Lacey, THIS JOURNAL, **36**, 804 (1914).

(2) Hulett, *Phys. Rev.*, **32**, 32 (1900).