

On the Thermodynamics of NonElectrolyte Solutions and Its Technical Applications III. Systems with Associated Components

O. Redlich and A. T. Kister

Citation: *J. Chem. Phys.* **15**, 849 (1947); doi: 10.1063/1.1746359

View online: <http://dx.doi.org/10.1063/1.1746359>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v15/i12>

Published by the [American Institute of Physics](#).

Additional information on J. Chem. Phys.

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT



**ACCELERATE COMPUTATIONAL CHEMISTRY BY 5X.
TRY IT ON A FREE, REMOTELY-HOSTED CLUSTER.**

[LEARN MORE](#)

THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 15, NUMBER 12

DECEMBER, 1947

On the Thermodynamics of Non-Electrolyte Solutions and Its Technical Applications

III. Systems with Associated Components

O. REDLICH AND A. T. KISTER
Shell Development Company, Emeryville, California

(Received November 25, 1946)

The influence of continuous association of one component on the free energy of a non-electrolyte solution is derived from a few assumptions. The result is in accord with available data for hydrocarbon-alcohol solutions. Systems of two associating components and the general interpretation of the free energy of non-electrolyte solutions are briefly discussed.

1. INTRODUCTION

THE examination of the thermodynamic properties of non-electrolyte solutions reveals a variety of characteristic types. The interpretation of these types is desirable both for the extension of our basic knowledge and for technical applications such as the design of efficient distillation columns.

Systems of an associating and a non-associating component represent one of these types, easily recognized in a diagram of the function $\log(\gamma/\gamma_0)$ (γ and γ_0 activity coefficients) against the mole fraction x . The advantages of the examination of this particular function and its representation by

$$\log(\gamma/\gamma_0) = B(1-2x) + C[-1+6x(1-x)] + D(1-2x)[1-8x(1-x)] + \dots, \quad (1)$$

have been discussed in the second paper of this series.¹ It has been found that associating systems can be approximated by (1) with appreciable values of the coefficients B and D , while C is small.

¹ To be published in Ind. and Eng. Chem.

It is the object of this paper to derive this peculiar behavior from a suitably chosen model. In other words, an attempt is made to find the relationship between the free energy and the stoichiometric mole fraction x for a solution which consists of molecules H of a non-associating substance like a hydrocarbon and monomeric and associated molecules A , A_2 , $A_3 \dots A_n \dots$ of an associated substance like an alcohol.

Obviously this problem can be solved only by means of an approximation which is based on far-reaching simplifying assumptions. The decisive point is the proper selection of the assumptions. If they are not far-reaching enough, the calculation becomes too complicated and the number of empirical constants so large that the result has no value at all. On the other hand, the assumptions should not slur over any characteristic feature, and above all, they must be consistent.

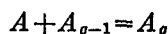
The relations derived in this paper are based on three assumptions, each of which is more or less well supported by previous knowledge. They are:

(a) The free energy of interaction can be approximated by Scatchard's method.^{1a}

(b) The non-ideal or interaction parts of partial molal quantities (free energy, heat content, volume) of members of a homologous series are proportional to the molecular size. This is a somewhat generalized form of a hypothesis which has been introduced first by Kratky and Musil² in a study of the osmotic pressure of high polymers. It has been used since by many authors in this field.

The justification of this assumption lies in the fact that the non-ideal functions directly represent the interaction between molecules, and that any part of a molecule (like an OH-group or a CH₂-group) interacts with its environment approximately the same way irrespective of being part of a larger or a smaller molecule.

(c) It is assumed that the association constant for the reaction



does not depend on the order g of the association. This hypothesis has been considered by Lassettre,³ later used by Kempter and Mecke⁴ and thoroughly discussed by other authors.⁵ The basic idea is similar to that of the second assumption.

The three assumptions differ in significance. Assumptions (a) and (b) are fair approximations required for a reasonably simple derivation. Assumption (c), however, restricts the discussion to a certain type of association. Other types undoubtedly exist. For instance, for a solution of acetic acid in a hydrocarbon association to double molecules rather than "continuous" association should be expected.

Starting from different assumptions, Flory^{5a} and Tobolsky and Blatz^{5b} obtained a different result for a related problem.

^{1a} G. Scatchard, Chem. Rev. 8, 321 (1931); J. Am. Chem. Soc. 56, 995 (1934); Trans. Faraday Soc. 33, 160 (1937).

² O. Kratky and A. Musil, Oesterr. Chem. Ztg. 40, 144 (1937); Z. Elektrochemie 43, 326 (1937).

³ E. N. Lassettre, J. Am. Chem. Soc. 59, 1383 (1937); Chem. Rev. 20, 281 (1937).

⁴ H. Kempter and R. Mecke, Zeits. f. physik. Chemie (B) 46, 229 (1940).

⁵ J. N. Wilson, Chem. Rev. 25, 400 (1939); R. S. Rasmussen, Thesis, California Institute of Technology, Pasadena (1941); J. Kreuzer and R. Mecke, Zeits. f. physik. Chemie (B) 49, 309 (1941); E. G. Hoffman, *ibid.* 53, 179 (1943); J. Kreuzer, *ibid.* 53, 213 (1943).

^{5a} P. J. Flory, J. Chem. Phys. 14, 49 (1946).

^{5b} A. V. Tobolsky and P. J. Blatz, J. Chem. Phys. 13, 379 (1945).

2. NOTATION

The present problem requires a clear distinction between stoichiometric and "true" mole numbers and fractions. The symbol x is used for the stoichiometric mole fraction of the associating substance (alcohol) so that $1-x$ represents the stoichiometric mole fraction of the non-associating component (hydrocarbon). The "true" mole numbers, etc., are denoted according to the following scheme:

molecule	H	A	A_2	A_3	\cdots	A_g	\cdots
mole number	n_0	n_1	n_2	n_3	\cdots	n_g	\cdots
mole fraction	N_0	N_1	N_2	N_3	\cdots	N_g	\cdots
activity coefficient	β_0	β_1	β_2	β_3	\cdots	β_g	\cdots

We adopt the rule that the symbol \sum indicates summation over the values 1, 2, 3... of the subscript, not including zero.

With

$$n = \sum n_g; \quad N = \sum N_g; \quad N^* = \sum gN_g \quad (2)$$

the relations between the quantities so far introduced are

$$N_0 = \frac{n_0}{n_0 + n}; \quad N_h = \frac{n_h}{n_0 + n}; \quad N = \frac{n}{n_0 + n} = 1 - N_0;$$

$$N^* = \frac{\sum gn_g}{n_0 + n}; \quad (3)$$

$$x = \frac{n_1 + 2n_2 + 3n_3 + \cdots}{n_0 + n_1 + 2n_2 + 3n_3 + \cdots} = \frac{\sum gn_g}{n_0 + \sum gn_g}, \quad (4)$$

since a polymerisate of g single alcohol molecules contributes g molecules to the analytical or stoichiometric mole number. The last equation can be transformed, by means of (3), in the following way

$$x = \frac{N^*}{N_0 + N^*}; \quad 1 - x = \frac{N_0}{N_0 + N^*}; \quad \frac{x}{1 - x} = \frac{N^*}{1 - N}. \quad (5)$$

The significance of the quantity N and numerous related functions has been discussed at very great length by several authors. Various elaborate systems of nomenclature were suggested. It is obvious that a ratio like N^*/N is some measure of the degree of association, and that other functions can be constructed, any of which characterizes the state of association.

3. THE "TRUE" MOLE FRACTION

Since the free energy will be expressed as a function of the "true" mole fraction N , the relationship between this function and the stoichiometric mole fraction x is required. It can be derived from the assumptions (b) and (c).

According to (c), the association equilibrium is characterized by

$$N_g \beta_g = K N_1 \beta_1 \cdot N_{g-1} \beta_{g-1}, \quad (6)$$

where K has the same value for all values of g . Repeated application of this equation to the values $g-1, g-2 \dots 2$ and multiplication of the obtained relations leads to

$$N_g \beta_g = K^{g-1} (N_1 \beta_1)^g. \quad (7)$$

According to assumption (b), the true activity coefficients are connected by

$$\log \beta_g = g \log \beta_1, \quad (8)$$

so that

$$N_g = K^{g-1} N_1^g. \quad (9)$$

Similar formulas have been previously used without justification by assumption (b).

Equations (2) and (9) furnish

$$\begin{aligned} N &= N_1 + K N_1^2 + K^2 N_1^3 + \dots \\ &= \sum (K N_1)^g / K = N_1 / (1 - K N_1); \end{aligned} \quad (10)$$

$$N_1 = N / (1 + K N);$$

$$\begin{aligned} dN/dN_1 &= 1 + 2K N_1 + 3(K N_1)^2 + \dots \\ &= \sum g (K N_1)^g / K N_1 = 1 / (1 - K N_1)^2, \end{aligned} \quad (11)$$

so that, with the aid of (2) and (9)

$$\begin{aligned} N^* &= \sum g N_g = \sum g (K N_1)^g / K \\ &= N_1 / (1 - K N_1)^2. \end{aligned} \quad (12)$$

Equation (10) furnishes

$$\begin{aligned} (1 + K N) &= 1 / (1 - K N_1); \\ N(1 + K N) &= N_1 / (1 - K N_1)^2. \end{aligned} \quad (13)$$

From (5), (12), and (13) we obtain

$$N^* = (1 - N)x / (1 - x) = N(1 + K N) \quad (14)$$

or, arranged in powers of N ,

$$N^2 + N/[K(1-x)] - x/[K(1-x)] = 0, \quad (15)$$

so that

$$N = \{-1 + [1 + 4Kx(1-x)]^{1/2}\} / [2K(1-x)]. \quad (16)$$

The negative sign of the root is excluded by the

fact that N must be positive. This formula satisfies, of course, the obvious conditions

$$N = x \text{ for } K = 0; \quad (17)$$

$$N = 0 \text{ for } x = 0; \quad (18)$$

$$N = 1 \text{ for } x = 1. \quad (19)$$

The application of this relation will be discussed later.

4. THE FREE ENERGY

The free energy will be represented in two ways. First, in the conventional way by means of the stoichiometric and experimental quantities:

$$\begin{aligned} (F - F^0) / 2.3RT &= (1-x) \log(1-x) \\ &+ x \log x + Q, \end{aligned} \quad (20)$$

where the function

$$Q = (1-x) \log \gamma_0 + x \log \gamma \quad (21)$$

corresponds to Scatchard's "excess free energy." The activity coefficients of the hydrocarbon and the alcohol are denoted by γ_0 and γ , respectively. The quantities F and Q refer to that amount of solution which contains $(1-x)$ moles of hydrocarbon and x moles of alcohol.

The free energy can also be represented in terms of the "true" mole fractions:

$$\begin{aligned} (F - F^0) / 2.3RT &= (N_0 \log N_0 \\ &+ \sum N_g \log N_g + Q^*) / (N_0 + N^*), \end{aligned} \quad (22)$$

$$Q^* = N_0 \log \beta_0 + \sum N_g \log \beta_g, \quad (23)$$

where the "true" activity coefficients are denoted by β_0 and β_g . The denominator $N_0 + N^*$ reduces the right hand side of (22) to the amount of solution containing $1-x$ and x moles of the components since the numerator refers to N_0 moles of hydrocarbon and $\sum g N_g = N^*$ moles of monomeric alcohol.

According to assumption (a) the quantity Q^* can be represented by Scatchard's equation

$$Q^* = (\sum b_{0g} V_0 V_g N_0 N_g + \sum b_{gh} V_g V_h N_g N_h) / (V_0 N_0 + \sum V_g N_g), \quad (24)$$

where b_{0g} denotes Scatchard's coefficient of interaction between a solvent molecule and a polymer of order g , divided by $2.3RT$. The coefficient b_{gh} indicates the interaction of two polymers of order g and h . Since Q^* is a homogeneous function of first degree in N_0 and N_g , the activity coef-

ficients are given by

$$\log \beta_0 = \partial Q^* / \partial N_0; \quad \log \beta_g = \partial Q^* / \partial N_g. \quad (25)$$

It can be concluded from Tyrer's measurements⁶ of the densities of methanol-benzene solutions that the apparent molal volume of the alcohol varies not more than a few tenths of one percent over the whole range. The approximation

$$V_g = g V_1 \quad (26)$$

is therefore amply sufficient. By introducing (26) into (24) and carrying out the differentiation indicated in (25), one recognizes that condition (8) requires that the interaction coefficients b_{0g} and b_{gh} be independent of the subscripts g and h , i.e., that

$$b_{0g} = b_{01}; \quad b_{gh} = b_{11}, \quad (27)$$

whatever the values of g and h are.

Equations (24) to (27) furnish

$$\begin{aligned} \log \beta_0 &= V_0(b_{01} - b_{11})z^2; \\ \log \beta_g &= g V_1[(b_{01} - b_{11})(1 - z^2) + b_{11}], \end{aligned} \quad (28)$$

where

$$\begin{aligned} z &= V_1 N^* / (V_0 N_0 + V_1 N^*) \\ &= V_1 x / [V_0(1 - x) + V_1 x] \end{aligned} \quad (29)$$

represents the volume fraction of the alcohol.

The change from the "true" to the experimental or stoichiometric activity coefficients can be carried out by means of (20) to (23). More convenient is a direct calculation based on the fact that the activities, as experimental quan-

ties, do not depend on any assumption regarding the molecular state. Denoting the activities in the reference states by a_0^0 and a_1^0 , we have, therefore,

$$(1 - x)\gamma_0 = N_0 \beta_0 / a_0^0; \quad x\gamma = N_1 \beta_1 / a_1^0. \quad (30)$$

From (3), (5), (10), and (14), we derive

$$\begin{aligned} N_0 / (1 - x) &= N_0 + N^* = 1 - N + N^* \\ &= 1 + KN^2; \end{aligned} \quad (31)$$

$$\frac{N_1}{x} = \frac{N}{1 + KN} \cdot \frac{N_0 + N^*}{N^*} = \frac{1 + KN^2}{(1 + KN)^2}. \quad (32)$$

Equations (28) to (32) furnish

$$\begin{aligned} \log \gamma_0 &= \log(1 + KN^2) \\ &\quad + V_0(b_{01} - b_{11})z^2 + \log a_0^0; \end{aligned} \quad (33)$$

$$\begin{aligned} \log \gamma &= \log[(1 + KN^2)/(1 + KN)^2] \\ &\quad + V_1[(b_{01} - b_{11})(1 - z)^2 + b_{11}] + \log a_1^0. \end{aligned} \quad (34)$$

The reference states are defined by the usual convention that

$$\log \gamma_0 = 0 \text{ for } x = 0; \quad \log \gamma = 0 \text{ for } x = 1, \quad (35)$$

the corresponding limits $N = 0$ and $N = 1$ being given by (18) and (19). Therefore,

$$\begin{aligned} \log \gamma &= \log[(1 + K)(1 + KN^2)/(1 + KN)^2] \\ &\quad + V_1(b_{01} - b_{11})(1 - z)^2. \end{aligned} \quad (36)$$

The function $\log(\gamma/\gamma_0)$ is useful for a comparison with experimental data. With the abbreviation

$$A = 2x \log(1 + K) - 2 \log(1 + KN) \quad (37)$$

it is represented by

$$\begin{aligned} \log(\gamma/\gamma_0) &= A + (1 - 2x) \log(1 + K) \\ &\quad + (b_{01} - b_{11})[V_1(1 - z)^2 - V_0 z^2]. \end{aligned} \quad (38)$$

Developing the expression in brackets in terms of

$$v = (V_1 - V_0)/(V_1 + V_0), \quad (39)$$

one obtains

$$\begin{aligned} V_1(1 - z)^2 - V_0 z^2 &= 2 V_1 V_0 / (V_1 + V_0) \\ &\quad \times \{1 - 2x - v[-1 + 6x(1 - x)] + \dots\}. \end{aligned} \quad (40)$$

The term containing v is a second order term which is outside the scope of the present discussion. Indeed, the error introduced by (27) can be estimated in a somewhat complicated calculation and is found to be of the same order of

TABLE I. Values of the association function A .
(- sign for $0 < x < \frac{1}{2}$; + sign for $\frac{1}{2} < x < 1$.)

K	x	0.05 0.95	0.1 0.9	0.2 0.8	0.3 0.7	0.4 0.6
1		0.0107	0.0163	0.0199	0.0165	0.0090
2		.0290	.0433	.0494	.0396	.0224
3		.0486	.0702	.0777	.0610	.0330
4		.0680	.0962	.1036	.0801	.0429
5		.0870	.1206	.1269	.0976	.0519
6		.1049	.1426	.1475	.1126	.0600
8		.1386	.1835	.1854	.1397	.0738
10		.1693	.2193	.2176	.1625	.0856
12		.1974	.2512	.2457	.1825	.0959
14		.2233	.2800	.2707	.2001	.1049
16		.2472	.3063	.2933	.2160	.1130
20		.2904	.3528	.3328	.2434	.1268
25		.3376	.4024	.3742	.2722	.1416
30		.3786	.4450	.4094	.2966	.1512

⁶ D. Tyrer, J. Chem. Soc. 99, 871 (1911).

magnitude as the v -term in (40). This term, therefore, will be neglected or taken care of by means of an empirical coefficient so that with

$$B = \log(1+K) + (b_{01} - b_{11}) \cdot 2V_1V_0/(V_1 + V_0) \quad (41)$$

the result

$$\log(\gamma/\gamma_0) = A + B(1-2x) \quad (42)$$

is obtained.

The linear B -term represents the usual first approximation of the interaction between the two components. The coefficient B , however, contains $\log(1+K)$ and is to be expected, therefore, to be unusually large for associating systems. The "association function" A depends on the association constant K and the mole fraction x in a complicated way and determines the peculiar behavior of systems with an associating component.

5. THE ASSOCIATION FUNCTION

The association function (37) is odd with respect to the variable $(1-2x)$. In other words, if A' represents the value of A for x' , and A'' the value for $x'' = 1-x'$, then $A' + A'' = 0$. To prove this, we calculate first

$$1 + KN = (1 - 2x + r)/2(1 - x); \\ r = +[1 + 4Kx(1 - x)]^{1/2} \quad (43)$$

from (16). Then we see that, since $r' = r''$,

$$(1 + KN')(1 + KN'') = (1 - 2x + r) \\ \times (-1 + 2x + r)/4x(1 - x) = 1 + K, \quad (44)$$

after an appropriate rearrangement. Equation (37) then furnishes

$$A' + A'' = 2(x + 1 - x) \log(1 + K) \\ - 2 \log(1 + K) = 0. \quad (45)$$

For small values of K , the square root r can be developed into a power series. The development up to the second order furnishes

$$A = K^2x(1-x)(2x-1)/2.303, \quad (46)$$

valid for small values of K and any value of x .

Likewise one obtains for small values of x and any value of K

$$A = 2x[\log(1 + K) - K/2.303]. \quad (47)$$

If $K \ll 1$ and therefore (46) holds, Eq. (42) is

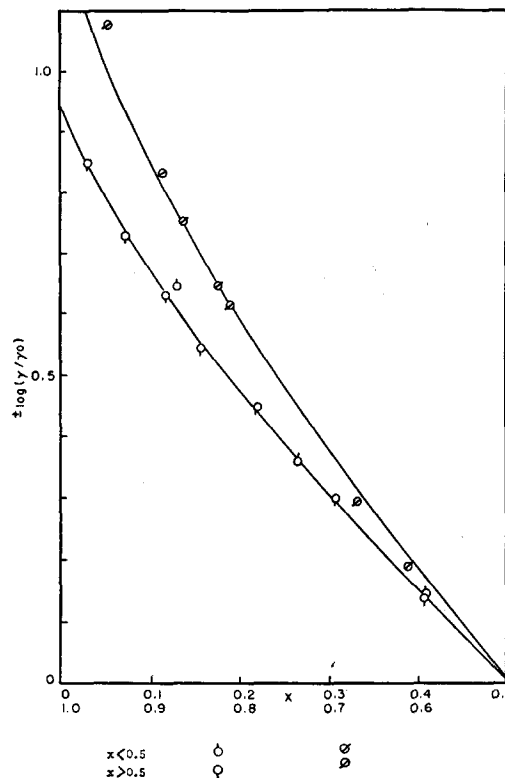


FIG. 1. Toluene-methanol and n -heptane-methanol (760 mm).

represented by (1) with

$$C = 0; \quad -8D = K^2/2.303, \quad (48)$$

i.e., the association function furnishes the D -term. For greater values of K appreciable deviations arise though the general course is still similar. It has been realized already by Scatchard that association leads to a term of this type.

Table I contains values of the function A .

6. EXPERIMENTAL DATA

The results of Benedict *et al.* on toluene-methanol and n -heptane-methanol at atmospheric pressure are shown in Fig. 1. In this figure, the absolute magnitudes of the function (42) are plotted against the mole fraction x of the associating component in such a way, that the values x and $(1-x)$ of the abscissa coincide. In a diagram of this kind, the two branches of $[\log(\gamma/\gamma_0)]$ are represented by a single curve if, and only if, \log

⁷ M. Benedict, C. A. Johnson, E. Solomon, and L. C. Rubin, Trans. Am. Inst. Chem. Eng. **41**, 371 (1945).

(γ/γ_0) is an odd function of $(1-2x)$, i.e., if the values of $\log(\gamma/\gamma_0)$ for x and $(1-x)$ have opposite sign and equal magnitude.

The data of Benedict *et al.* were checked by means of the method described in the first paper of this series and found very well consistent. The scattering, as shown in Fig. 1, is small. The diagram shows immediately that the two branches of $[\log(\gamma/\gamma_0)]$ for $x < 0.5$ and $x > 0.5$ can be represented by a single curve which deviates considerably from a straight line. The curve for toluene-methanol in Fig. 1 corresponds to Eq. (42) with $B=0.95$ and $K=3.8$ in the association function (37). This curve represents the data well within the small experimental errors. The data for *n*-heptane-methanol are fairly well represented by the curve in Fig. 1 corresponding to $B=1.25$ and $K=6.6$.

The results of Ferguson⁸ on *n*-hexane-methanol at 45°C can be represented by $B=1.71$ and $K=30$. Data for *n*-heptane-ethanol⁹ at 30°C scatter considerably more. Even so, the expected influence of the association of ethanol is unmistakable.

In these examples the coefficient C (Eq. (1)) is practically zero. Frequently, however, an additional, usually small, C -term is required for the representation of experimental data. Recently published data¹⁰ of benzene-methanol for 35°C are satisfactorily represented by means of $B=1.050$; $C=-0.116$; $K=6.1$, the data on carbon tetrachloride-methanol by means of $B=1.105$; $C=-0.148$; $K=6.1$. The deviations of the mole fraction of the vapor and of the pressure are of the same order as those obtained by Scatchard, Wood and Mochel with three independent coefficients for each system.

The characteristic influence of association is more or less clearly noticeable in the data available for benzene-phenol,¹¹ benzene-aniline and benzene-benzonitrile,¹² benzene-propanol,¹³ and in various systems with ethanol and butanol.¹⁴

⁸ J. B. Ferguson, J. Phys. Chem. **36**, 1123 (1932).

⁹ J. B. Ferguson, M. Freed, and A. C. Morris, J. Phys. Chem. **37**, 87 (1933).

¹⁰ G. Scatchard, S. E. Wood, and J. M. Mochel, J. Am. Chem. Soc. **68**, 1957, 1960 (1946).

¹¹ A. R. Martin and C. M. George, J. Chem. Soc. **1933**, 1414.

¹² A. R. Martin and B. Collie, J. Chem. Soc. **1932**, 2662.

¹³ Siang Chieh Lee, J. Phys. Chem. **35**, 3558 (1931).

¹⁴ C. P. Smyth and E. W. Engel, J. Am. Chem. Soc. **51**, 2660 (1929).

The association indicated by the vapor pressures of the system triethylamine-water¹⁵ is undoubtedly due to water since triethylamine is not appreciably associated.¹⁶

A qualitative check may be seen in the fact that the values of B are very large and that the values of K , with the exception of $K=30$ for hexane-methanol, are reasonable. No term similar to the association function A has been found in any system of non-associating components. It may be concluded, therefore, that this function actually is characteristic of associating systems.

According to (10) and (19), the mole fraction of the monomer in the pure alcohol is

$$N_1 = 1/(1+K). \quad (49)$$

Since this quantity as a property of the pure component cannot depend on the nature of the other component, the present model requires that the association constant be a property of the alcohol.

Since K is extremely sensitive against experimental errors, only very accurate data can contribute to a test of this conclusion. The data of Benedict *et al.*⁷ were obtained at atmospheric pressure, i.e., at varying temperatures. However, most of the measurements on toluene-methanol ($K=3.8$) were carried out in the neighborhood of 64°, those on heptane-methanol ($K=6.6$) close to 58°.

The association constants for methanol derived at 64° (with toluene) and 35° (with benzene and carbon tetrachloride) lead to the reasonable value of 3300 cal./mole for the heat of association. The value $K=4.4$ resulting for 55° has been used to represent the data obtained by Scatchard, Wood and Mochel¹⁰ at this temperature for the systems with benzene ($B=0.981$; $C=-0.113$) and carbon tetrachloride ($B=1.027$; $C=-0.120$). Here, too, the deviations of the mole fraction of the vapor and of the pressure are of the same order as in the equations of Scatchard *et al.* with three independent coefficients.

The interpolation between 35 and 64° leads to $K=5.1$ at 45° and $K=4.2$ at 58°. The deviations of the values 30 (with hexane) and 6.6 (with

¹⁵ L. D. Roberts and J. E. Mayer, J. Chem. Phys. **9**, 852 (1941).

¹⁶ R. T. Lattey, J. Am. Chem. Soc. **91**, 1959 (1969).

heptane) derived directly from experimental data for these two temperatures are probably due to errors in the measurements.

The best test of the present results would be a comparison of the association constants derived from vapor pressures with values obtained from the intensity of infra-red absorption bands of the hydroxyl group. At present no data are available for this comparison. Further tests could be made in connection with data on dielectric constants (cf. Wilson⁵), the frequencies of the hydroxyl bands (cf. Rasmussen⁵) and with data on heats of mixing.

7. SYSTEMS OF TWO ASSOCIATING COMPOUNDS

If both components associate, one has, in the general case, to consider bonds between molecules of the first component (equilibrium constant K'), between molecules of the second component (K''), from a molecule of the first kind to one of the second (K''') and conversely (K^{iv}). Even with the far-reaching assumptions introduced in the first section, the general case leads to difficulties of such extent that a thorough treatment does not appear to be worth while. But quantitative results can be easily derived for two special cases. They are limiting cases of such nature that the whole field appears to be qualitatively covered.

If the association constants for all four types of bonds are equal, $K' = K'' = K''' = K^{iv}$, no association term at all appears in the free energy. This somewhat surprising result seems to be in satisfactory agreement with data for systems both components of which tend equally to the formation of hydrogen bonds like systems of two alcohols.

The second special case is characterized by the absence of interassociation between the components, $K''' = K^{iv} = 0$. One will expect that this

case is realized only by a kind of association entirely different from that caused by hydrogen bonds. A calculation which runs strictly parallel to the course followed in the third and fourth section of this paper furnishes again Eqs. (37) and (42) with

$$K = K' + K'' + K'K'' \quad (50)$$

In other words, a system of this kind behaves just like a system with a single associating component, except that the "apparent" association constant has a different significance.

The system benzene-cyclohexane appears to be an example of this kind. Scatchard, Wood and Mochel¹⁷ have already interpreted their measurements by means of association. The association is so small in this case that the influence of the volumes as indicated by (38) is still significant. The approximation (46) is valid. The experimental data are satisfactorily represented by (38) with $b_{01} - b_{11} = 0.001133$; $K = 0.244$ (40°C) and $b_{01} - b_{11} = 0.000796$; $K = 0.184$ (70°C).

The results obtained so far indicate a fairly simple general interpretation of the thermodynamic properties on non-electrolyte solutions. The B -term in series (1) is known to represent interaction and the C -term indicates in the simplest cases the influence of the difference of the molal volumes. The D -term indicates the influence of association and is better replaced by the association function A . This interpretation may offer a suitable starting point for a discussion of the coefficients of series (1) in relation with the nature of the components.

The authors wish to express their thanks to Dr. R. W. Millar, Dr. R. S. Rasmussen and Dr. J. N. Wilson for valuable discussions and advice.

¹⁷ G. Scatchard, S. E. Wood, and J. M. Mochel, *J. Phys. Chem.* **43**, 119 (1939).