is rather surprising. While the basic equation, in its interpretation of potential energy, is not strictly applicable to water and methanol, these substances do not show any marked departure from the other substances.

The Entropy.—Since $(\partial S/\partial T)_V = C_V/T$, it is possible to obtain a formal expression for the entropy of a liquid. The integration of eq. 18 yields

$$\bar{S} = \bar{S}^0 + \frac{1}{\bar{V}^0}\int\frac{1}{T}\left(\frac{\partial a}{\partial T}\right)_V \mathrm{d}T + s(V,n) \qquad (19)$$

Here $\bar{S}^0$ is the entropy due to the translational, vibrational and rotational modes of motion in the ideal gas but does not contain any term involving the concentration. The term $s(V,n)$ is the integration constant and is a function of the volume and the number of moles. Throughout this paper the partition function for the liquid has been considered to be the product of independent partition functions for translational, vibrational, and rotational motion, and for the potential energy. The last two terms of eq. 19 then result from the partition function for the potential energy. Following the suggestion of Eyring and Hirschfelder[29] for this partition function, the integration constant may be written as $-R\ln(n/\mathcal{V})$, so that

$$\bar{S} = \bar{S}^0 + \frac{1}{\bar{V}^0}\int\frac{1}{T}\left(\frac{\partial a}{\partial T}\right)_V \mathrm{d}T - R\ln\frac{n}{\mathcal{V}} \qquad (20)$$

Here $\mathcal{V}$ is a volume which might be called a free volume defined by this equation.

Equation 20 can only be considered as a formal, semi-empirical equation at the present time and the same information would be required for further study as for the energy. Obviously, it means that the coefficients of the separate terms of eq. 12 or 17 are functions of the temperature. It does afford an opportunity, however, of estimating the entropy of mixing for solutions as will be shown in the following paper.

[29] H. Eyring and J. Hirschfelder, *J. Phys. Chem.*, **41**, 249 (1937).

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

The Estimation of the Properties of Solutions from Those of the Pure Components[1,2]

BY SCOTT E. WOOD

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Expressions for the change of the energy and of the entropy on mixing have been developed by a method similar to that of Hildebrand and Scatchard. In this development the interaction parameter a, defined by the equation $\bar{E} = \bar{E}_0 + (a/\bar{V})$, is taken to be a function of the volume and the temperature. The volume is taken as one of the independent variables rather than the pressure, thereby permitting calculations for any chosen change of state, the two most important cases being mixing at constant volume and mixing at constant pressure. It is necessary to assume that the a's are independent of the composition and that a_{12} is determinable from a_{11} and a_{22}. The geometrical mean is used in this paper. Other methods are suggested, but they require more information than is available at the present time. Calculations have been made for the three binary systems composed of benzene, carbon tetrachloride and cyclohexane. The calculations for the energy of mixing show improvement over the Hildebrand–Scatchard equation, although the agreement with the observed values is still not good. Except for the benzene–carbon tetrachloride system, the excess entropy of mixing is positive but smaller than the observed values. The agreement of the excess free energy, while not exact, is surprisingly good because of a cancellation of errors.

The Hildebrand–Scatchard equation[3,4] has attained great prominence for the estimation of the properties of solutions from those of the pure components, but it does have a few outstanding difficulties. The entropy of mixing at constant volume must be assumed to be that of an ideal solution of the same concentration or use must be made of the Flory–Huggins theory expressing the entropy in terms of the volume fraction rather than the mole fraction. Also, the energy of mixing at constant volume is usually much smaller than the observed value. Great progress has been made in the theoretical treatment of solutions by Guggenheim,[5] Kirkwood,[6] Prigogine[7] and many others. Since a complete, theoretical treatment of the problem is so difficult, a method of estimating the properties of solutions from those of the pure components is still important. This paper presents such a method, very similar to that of Hildebrand and Scatchard, but which appears to be a considerable improvement. The estimates of the energy of mixing at constant volume and the heat of mixing at constant pressure are in closer agreement with the observed values. An estimate of the entropy of mixing both at constant volume and at constant pressure is obtained, but with only fair agreement with the observed values. The free energies of mixing at constant pressure are in rather surprising agreement with the observed values for the systems studied. The method is strictly applicable only to non-polar liquids.

The Energy of Mixing.—As in the preceding paper,[8] the energy of n moles of a pure liquid at a given volume and temperature may be expressed as

$$E_i^0 = n_i\bar{E}_{0i} + \frac{n_i^2 a_{ii}'}{\bar{V}^0_i} \qquad (1)$$

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[1] The financial assistance of the National Science Foundation through grant NSF-G579 is gratefully acknowledged.

[2] Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the Dallas meeting, April, 1956.

[3] G. Scatchard, *Chem. Revs.*, **8**, 321 (1931).

[4] J. H. Hildebrand and S. E. Wood, *J. Chem. Phys.*, **1**, 817 (1933).

[5] E. A. Guggenheim, "Mixtures," Oxford University Press, London, 1952.

[6] J. G. Kirkwood and F. P. Buff, *J. Chem. Phys.*, **19**, 774 (1951); Z. W. Salsburg and J. G. Kirkwood, *ibid.*, **20**, 1538 (1952).

[7] I. Prigogine and G. Garikian, *Physica*, **16**, 239 (1950).

[8] S. E. Wood, O. Sandus and S. Weissman, THIS JOURNAL, **79**, 1777 (1957).

where $\bar{E}_{0i}$ is the molar energy of the substance in the ideal gas state at the same temperature, V_i^0 is the volume of n_i moles of liquid and a_i' is a function of the molar volume and temperature and is evaluated at the specified volume and temperature. Similarly, for a binary solution at a given volume and temperature the energy may be expressed as

$$E = n_1\bar{E}_{01} + n_2\bar{E}_{02} + (n_1^2a_{11} + 2n_1n_2a_{12} + n_2^2a_{22})/V \tag{2}$$

where a_{11}, a_{22} and a_{12} are functions of the molar volume and the composition of the solution and of the temperature. It is necessary to distinguish the a's for the pure liquid from those of the solution by means of a prime, because the volumes of the solution and of the pure components are different. It must be emphasized here that the volume is being taken as the independent variable, rather than the pressure, in addition to the temperature and number of moles of each component.

The change of energy on mixing n_1 moles of the first component at a volume V_1^0 and n_2 moles of the second component at a volume V_2^0 at a given temperature to form a solution at the same temperature and a volume V is then

$$\Delta E^{\mathrm{M}} = \frac{n_1^2a_{11} + 2n_1n_2a_{12} + n_2^2a_{22}}{V} - \frac{n_1^2a_{11}'}{v_1^0} - \frac{n_2^2a_{22}'}{V_2^0} \tag{3}$$

The change of energy for this change of state per mole of solution, after conversion to mole fractions and substitution of $x_1(1 - x_2)$ for x_1^2 and $x_2(1 - x_1)$ for x_2^2, is[9]

$$\Delta\bar{E}^M = x_1x_2\left(\frac{2a_{12} - a_{11} - a_{22}}{\bar{V}}\right) + x_1\left(\frac{a_{11}}{\bar{V}} - \frac{a_{11}'}{\bar{V}_1^0}\right) + x_2\left(\frac{a_{22}}{\bar{V}} - \frac{a_{22}'}{\bar{V}_2^0}\right) \tag{4}$$

The extension of this equation to multi-component systems does not present any difficulties.

Since the volume is considered as the independent variable, the molar volumes of the pure components and of the solution may have any values whatsoever. The two most important cases will be mixing at constant volume and mixing at constant pressure. The initial volume in either case will usually be the molar volume of each component at one atmosphere pressure at some specified temperature. For mixing at constant volume the final volume will be the additive volumes of the components so that $\bar{V}_0 = x_1\bar{V}_1^0 + x_2\bar{V}_2^0$ while for mixing at constant pressure the final volume will be that of the solution at one atmosphere pressure at the same initial temperature. In this case, $V = \bar{V}^0 + \Delta\bar{V}^M$ where $\Delta\bar{V}^M$ is the change of the molar volume on mixing at constant pressure. The difference between the change of enthalpy on mixing at constant pressure and the change of energy on mixing at constant pressure is $P\Delta\bar{V}^M$, which is usually negligible, and consequently eq. 4 will give the change of enthalpy on mixing at constant pressure. When $\bar{V}^0 + \Delta\bar{V}^M$ is substituted for $\bar{V}$ in the last two terms of equation 4, the energy of mixing at constant pressure is given by

$$\Delta\bar{E}_p{}^M = \frac{x_1x_2}{\bar{V}}(2a_{12} - a_{11} - a_{22}) + \frac{x_1}{\bar{V}}\left(a_{11} - \frac{a_{11}'\bar{V}^0}{\bar{V}_1^0}\right) + \frac{x_2}{\bar{V}}\left(a_{22} - \frac{a_{22}'\bar{V}^0}{\bar{V}_2^0}\right) - \left(\frac{x_1a_{11}'}{\bar{V}_1^0} + \frac{x_2a_{22}'}{\bar{V}_2^0}\right)\frac{\Delta\bar{V}^M}{\bar{V}} \tag{5}$$

This equation gives a somewhat complicated relation between the volume of mixing and the energy of mixing at constant pressure. It can be simplified for many systems in which $\Delta\bar{V}^M$ is small in comparison to $\bar{V}^0$, because then $\bar{V}$, appearing in the denominator of each term, may be substituted by $\bar{V}^0$.

The work of Prigogine and Mathot[10] predicts, for mixtures of components whose volumes are not too different but whose energies of evaporation are quite different, that $\Delta\bar{V}^M$ may be negative while $\Delta\bar{E}_p{}^M$ is positive. Experimental evidence[11-13] has shown this to be true. While eq. 5 does not predict the volume of mixing independently of the energy of mixing, it is not inconsistent with these predictions. The numerical values of the a's are negative, and thus, for a solution of a given composition, $\Delta\bar{V}^M$ is proportional to the difference between $\Delta\bar{E}_p{}^M$ and the sum of the first three terms on the right-hand side of eq. 5. The first term will be positive unless strong attractive forces occur between the unlike molecules. Of the second and third terms, usually one will be positive and one negative, and if the volumes of the components are not too different, the sum of these terms may be quite small. In such a case the sign of $\Delta\bar{V}^M$ will depend primarily on the difference between $\Delta\bar{E}_p{}^M$ and the first term. There seems to be no *a priori* reason why this difference will always be positive. If the a's are assumed to be constant, independent of the volume and concentration, eq. 5 reduces to

$$\Delta\bar{E}_p{}^M = \frac{x_1x_2\bar{V}_1^0\bar{V}_2^0}{\bar{V}}\left(\frac{2a_{12}}{\bar{V}_1^0\bar{V}_2^0} - \frac{a_{11}}{(\bar{V}_1^0)^2} - \frac{a_{22}}{(\bar{V}_2^0)^2}\right) - \left(\frac{x_1a_{11}}{\bar{V}_1^0} + \frac{x_2a_{22}}{\bar{V}_2^0}\right)\frac{\Delta\bar{V}^M}{\bar{V}} \tag{6}$$

This equation is of the same form as that of Prigogine and Mathot.[10] Experience has shown that, for most binary mixtures of non-polar liquids, $\Delta\bar{E}_p{}^M$ and the first term of eq. 6 are both positive. Consequently, the sign of $\Delta\bar{V}^M$ will depend on the difference between these two terms.

The interaction parameters a_{11}, a_{22} and a_{12} are dependent upon the properties of the solution and not those of the components. But in order to make further progress, the assumption that they are independent of the composition at a fixed volume

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(9) Equation 4 may be transformed into several other expressions based on different concentration variables. Thus, according to this equation, tbe energy of mixing per unit volume is a function of the volume concentrations. In terms of volume fractions, defined as $z_1 = n_1\bar{V}_1/n_1\bar{V}_1 + n_2\bar{V}_2$, the equation becomes

$$\frac{\Delta E^M}{V} = z_1z_2\left(\frac{2a_{12}}{\bar{V}_1\bar{V}_2} - \frac{a_{11}}{\bar{V}_1^2} - \frac{a_{22}}{\bar{V}_2^2}\right) + z_1\left(\frac{a_{11}}{\bar{V}_1^2} - \frac{a_{11}'}{\bar{V}_1\bar{V}_1^0}\right) + z_2\left(\frac{a_{22}}{\bar{V}_2^2} - \frac{a_{22}'}{\bar{V}_2\bar{V}_2^0}\right)$$

Certain processes of mixing may be imputed to the different equations, but the value of the energy of mixing for a given change of state must be independent of the process,

(10) I. Prigogine and V. Mathot, *J. Chem. Phys.*, **20**, 49 (1952); see also Z. W. Salsburg and J. G. Kirkwood, *ibid.*, **21**, 2169 (1953).

(11) V. Mathot and A. Desmyter, *ibid.*, **21**, 782 (1953).

(12) R. Thacker and J. S. Rowlinson, *ibid.*, **21**, 2242 (1953).

(13) P. Meares, *ibid.*, **22**, 955 (1954).

must be made.[14] This means that neither the potential energy between two molecules nor the distribution function, averaged over the position and orientation of all the other molecules, can vary with the composition.[15] Then each a_{ii} may be approximated in terms of the properties of the pure component. From the form of the term $a_{ii}/\bar{V} - a_{ii}'/\bar{V}_i^0$ in eq. 4, it would appear that each a_{ii} should be determined at the molar volume of the solution while each a_{ii}' is determined at the molar volume of each component in the initial state. Moreover, with this assumption, the relation

$$\frac{a_{ii}}{\bar{V}} - \frac{a_{ii}'}{\bar{V}_i^0} = \bar{E}_i(\bar{V},T) - \bar{E}_i(\bar{V}_i^0,T) \qquad (7)$$

is obtained by use of eq. 1. Such quantities then are the change of energy per mole of component on changing the volume from the molar volume of the pure component to the molar volume of the solution at the specified temperature. The process of mixing may be thought of as expanding or compressing each component from its initial molar volume to the molar volume of the solution, and then mixing at *identical* volumes.[16]

The Estimation of a_{12}.—Assumptions concerning a_{12} in addition to its independence of composition must be made in order to estimate the properties of a solution from those of the components. The usual assumption and the one used perforce in this paper is that a_{12} is the geometrical mean of a_{11} and a_{22}. But each a represents the value of a rather complicated integral involving both repulsive and attractive forces and, therefore, this assumption can be very poor. If the liquids are relatively expanded so that the effects of the repulsive forces are small or negligible, this assumption might be valid within our knowledge of the London dispersion forces. If the liquids are relatively compressed, then this assumption may be invalid because of the effect of the repulsive forces. Moreover, when the molar volumes are very different, the geometrical mean can become imaginary. This can occur when, in the calculations which are described later, it is necessary to compress the component having the larger volume to a volume approximately that of the other component. In such a case the a of the first component may become positive while that of the second component remains negative.[17] The geometrical mean is then imaginary.

The a's are actually functions of the volume and a better approximation for a_{12} might be obtained by appropriate combination of the coefficients in equations which express this dependence such as eq. 12 or 17 of the preceding paper.[8] The combination of constants for gas mixtures[18] suggests that C_1 might be combined linearly or by the Lorentz combination and C_2 quadratically. The combination of C_3 cannot be predicted at the present time. Equation 13 of the previous paper[8] or a similar equation affords an alternate method. With this equation, the combination of the three quantities $(\bar{E}_0 - \bar{E}_m)$, $\bar{V}_m^0$ and $\bar{V}^*$, would need to be considered. Probably $(\bar{E}_0 - \bar{E}_m)$ would combine quadratically while $\bar{V}_m^0$ would combine linearly or with the Lorentz combination. For the present the combination of $\bar{V}^*$ can only be guessed although based on the law of corresponding states, it might be assumed that $\bar{V}^*/\bar{V}^0{}_m$ is the same for each non-polar liquid. These suggestions cannot be tested with our present knowledge.

Comparison with Other Equations.—Equation 4 reduces to the Hildebrand–Scatchard equation in the form

$$\Delta\bar{E}_V{}^M = \frac{x_1\bar{V}_1{}^0x_2\bar{V}_2{}^0}{\bar{V}^0}\left(\frac{2a_{12}}{\bar{V}_1{}^0\bar{V}_2{}^0} - \frac{a_{11}}{(\bar{V}_1{}^0)^2} - \frac{a_{22}}{(\bar{V}_2{}^0)^2}\right) \qquad (8)$$

for mixing at constant volume with the two assumptions that the a's are independent of composition and of the volume. Equation 8 reduces to the usual form of the Hildebrand–Scatchard equation with the additional assumption that a_{12} is the geometrical mean of a_{11} and a_{22}. In order to obtain the change of energy on mixing at constant pressure, Simons and Dunlap[19] have already used the method given here with the exception that they have considered the a's to be independent of the volume. Dunlap[20] has extended this work by setting $E = E_0 + k/V^n$. This relation removes the assumption of the constancy of the a's. But with constant n and k, $(\partial a/\partial V)_T$ cannot change sign as suggested in the preceding paper.[8] As used by Dunlap, this relation introduces one parameter into the equation for the change of enthalpy on mixing at constant pressure for each component. Reed[21] has used the same development as Simons and Dunlap,[19] but has avoided the assumption of the geometrical mean for a_{12}. He has evaluated this quantity by use of the $(6 - n)$ law of intermolecular energies and the method of Hildebrand and Wood.[4] Values of the energy of mixing calculated by this method agree much better with the observed values than those calculated by the method of Simons and Dunlap[19] or the simple Hildebrand–Scatchard equation.

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(14) The independent variables are the temperature, the volume and the number of moles of each component. The volume may be a function of the number of moles of each component and is such a function for mixing at constant pressure and at constant volume. Thus, the a's will be functions of the composition indirectly. The intent of this assumption is that the a's are dependent on the composition only through the volume and are independent of the composition otherwise.

(15) This assumption is equivalent to those of Scatchard, *Trans. Faraday Soc.*, **33**,160 (1937), except that the assumption of the independence of the a's on the temperature has been removed.

(16) Other processes of mixing may be considered, but from the derivation of eq. 4 and our present knowledge, it would still appear that each a_{ii} for the solution should be determined at the molar volume of the solution.

(17) Such a situation arises in the calculations for the carbon tetrachloride–methanol and benzene–methanol systems. The molar volume of carbon tetrachloride at 25° and one atmosphere pressure is 97 cc. while that of methanol is 40 cc. For dilute solutions of carbon tetrachloride in methanol, the calculations require a maximum hypothetical compression for carbon tetrachloride from 97 to 40 cc. For such a compression a passes through a minimum at about 73 cc. and then rapidly increases to positive values on further compression. Benzene exhibits similar behavior. The a for methanol remains negative, since in the calculations methanol is always expanded. Therefore, in such incidences, the geometric mean is imaginary. It is recognized that the required change of volume is tremendous for a liquid and that the limited compressibility data cannot be extrapolated so far without possible serious error, nevertheless, a will for any liquid always become positive when the compression (real or hypothetical) is sufficiently large.

(18) J. A. Beattie and W. H. Stockmayer, *J. Chem. Phys.*, **10**, 473 (1942).

(19) J. H. Simons and R. D. Dunlap, *ibid.*, **18**, 335 (1950).

(20) R. D. Dunlap, *ibid.*, **21**, 1293 (1953).

(21) T. M. Reed, III, *J. Phys. Chem.*, **59**, 425 (1955).

The Entropy of Mixing.—An expression for the entropy of one mole of a pure liquid has been given in the preceding paper[8] and for n_i moles it becomes

$$S^0_i = n_i\bar{S}_{i0} + \frac{n_i^2}{V_i^0}b_{ii} - n_iR\ln\frac{n_i}{\mathcal{V}_i^0} \qquad (9)$$

where

$$b_{ii} = \int\frac{1}{T}\frac{\partial a_{ii}}{\partial T}\,\mathrm{d}T$$

The entropy of a binary solution containing n_1 and n_2 moles of the components is given by the equation[22]

$$S = n_1\bar{S}_{10} + n_2\bar{S}_{20} + \frac{n_1^2b_{11} + 2n_1n_2b_{12} + n_2^2b_{22}}{V} - n_1R\ln\frac{n_1}{\mathcal{V}} - n_2R\ln\frac{n_2}{\mathcal{V}} \qquad (10)$$

where $\mathcal{V}$ is a free volume of the solution which may be considered to be defined by this equation. This equation is obtained from eq. 2 by the method used in the preceding paper. The entropy of mixing is then

$$\Delta S^M = \frac{n_1^2b_{11} + 2n_1n_2b_{12} + n_2^2b_{22}}{V} - \frac{n_1^2b'_{11}}{V_1^0} - \frac{n_2^2b'_{22}}{V_2^0} - n_1R\ln\frac{\mathcal{V}_1^0}{\mathcal{V}} - n_2R\ln\frac{\mathcal{V}_2^0}{\mathcal{V}} \qquad (11)$$

and for one mole of solution, after substitution of $x_1(1 - x_2)$ for x_1^2 and $x_2(1 - x_1)$ for x_2^2, is

$$\Delta\bar{S}^M = \frac{x_1x_2}{\bar{V}}(2b_{12} - b_{11} - b_{22}) + x_1\left(\frac{b_{11}}{\bar{V}} - \frac{b'_{11}}{\bar{V}_1^0}\right) + x_2\left(\frac{b_{22}}{\bar{V}} - \frac{b'_{22}}{\bar{V}_2^0}\right) - x_1R\ln\frac{\mathcal{V}_1^0}{\mathcal{V}} - x_2R\ln\frac{\mathcal{V}_2^0}{\mathcal{V}} \qquad (12)$$

Since the b's are derived from the a's, all the assumptions and discussions concerning the a's are applicable to the b's. The terms $\ln\mathcal{V}_1^0/\mathcal{V}$ and $\ln\mathcal{V}_2^0/\mathcal{V}$ need further discussion. Each $\mathcal{V}$ is a free volume defined by eq. 9 or 10 and, as such, is not susceptible to experimental determination. It is not necessarily equal to the experimental volume. But in the interest of estimating the properties of the solution from those of the pure components, the assumption must be made that the ratios of the free volumes are equal to the ratios of the actual volumes. This assumption[23] is probably more accurate than setting each free volume equal to the volume. When this assumption is made, these ratios become the volume fractions, defined as $x_1\bar{V}_1^0/\bar{V}$, rather than $x_1\bar{V}_1^0/\bar{V}^0$. The difference, however, is usually negligible. Thus, the last two terms of eq. 12 yield the Flory–Huggins relation.

Calculations and Comparison with Experiment.—Calculations have been made for the change of energy and the excess entropy on mixing at constant volume and a constant pressure for the three binary systems composed of benzene, carbon tetrachloride and cyclohexane. The initial state has always been chosen as the pure components at 25° and one atmosphere pressure. The volumes of the solutions at one atmosphere pressure have been determined from the volumes of mixing measured by Wood and his co-workers.[24–26] According to eq. 7, the last two terms of eq. 4 involve simply the change of the energy of the pure components for the designated change of volume. The Tait equation was used for these calculations. The values of a_{11} and a_{22}, which were used in the first term of eq. 4, were obtained by means of eq. 7 in which $a'/\bar{V}^0$ is taken to be the negative of the energy of evaporation from the liquid state at 25° and one atmosphere pressure to an ideal gas at 25°. The data referred to in the preceding paper were used.[8] The geometrical mean of a_{11} and a_{22} was used perforce to evaluate a_{12}.

The excess entropy of mixing is defined as

$$\Delta\bar{S}^E = \Delta\bar{S}^M + x_1R\ln x_1 + x_2R\ln x_2 \qquad (13)$$

With substitution of eq. 12 in eq. 13 and of the ratio of volumes for the ratio of free volumes, $\Delta\bar{S}^E$ becomes

$$\Delta\bar{S}^E = \frac{x_1x_2(2b_{12} - b_{11} - b_{22})}{\bar{V}} + x_1\left(\frac{b_{11}}{\bar{V}} - \frac{b'_{11}}{\bar{V}_1^0}\right) + x_2\left(\frac{b_{22}}{\bar{V}} - \frac{b'_{22}}{\bar{V}_1^0}\right) - x_1R\ln\frac{\bar{V}_1^0}{\bar{V}} - x_2R\ln\frac{\bar{V}_2^0}{\bar{V}} \qquad (14)$$

According to eq. 9

$$\bar{S}_1^0(\bar{V},T) - \bar{S}_1^0(\bar{V}_1^0,T) = \frac{b_{ii}}{\bar{V}} - \frac{b'_{ii}}{\bar{V}_1^0} - R\ln\frac{\mathcal{V}_1^0}{\mathcal{V}} \qquad (15)$$

so that the sum of the last four terms of eq. 14 is the change of entropy on expanding or compressing the pure compounds from their volumes in the initial state to the volume of the final state. Again the Tait equation has been used for these calculations. The values of b_{11} and b_{22} in the first term of eq. 14 were determined from b'_{11} and b'_{22} by means of eq. 15. Equation 9 was used to evaluate b'_{11} and b'_{22}. From eq. 9

$$b'_{1i}/\bar{V}_i^0 = (\bar{S}_i^0 - \bar{S}_{i0} - R\ln\mathcal{V}_i^0) \qquad (16)$$

Here, it must be assumed that the free volume is equal to the volume itself. Then $b'_{ii}/\bar{V}_i^0$ is equal to the negative of the change of entropy on evaporating one mole of liquid at the volume $\bar{V}_i^0$ to an ideal gas of the same molar volume as the liquid at the same temperature. Again the same data were used for these calculations as were used in the preceding paper. The value of b_{12} was taken as the geometrical mean of b_{11} and b_{22}.

The results of these calculations are given in Table I for the benzene–carbon tetrachloride system, Table II for the benzene–cyclohexane system, and Table III for the cyclohexane–carbon tetrachloride system. The columns in each table are (1) the mole fraction, (2) the change of energy on mixing at constant volume calculated by the Hildebrand–Scatchard equation, (3) the same quantity calculated by eq. 4, (4) the observed value of this quantity, (5) the change of energy on mixing at constant pressure calculated by eq. 4, (6) the observed value of the change of enthalpy on mixing at constant pressure, (7) and (8) the excess change of entropy on mixing at constant volume calculated according to eq. 14 and the observed value, respectively, (9) and (10) the excess change of entropy on mixing at constant pressure calculated according to eq. 14 and the observed value, respectively, and (11) and (12) the excess change of free energy on mixing at constant pressure, calculated and observed, respectively. All values

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[22] The terms $n_1R\ln n_1$ and $n_2R\ln n_2$ come from the presence of the product $n_1!n_2!$ in the denominator of the partition function.

[23] J. H. Hildebrand, *J. Chem. Phys.*, **15**, 225 (1947).

[24] S. E. Wood and J. P. Brusie, THIS JOURNAL, **65**, 1891 (1943).

[25] S. E. Wood and A. E. Austin, *ibid.*, **67**, 480 (1945).

[26] S. E. Wood and J. A. Gray, III, *ibid.*, **74**, 3729 (1952).

TABLE I

THE THERMODYNAMIC PROPERTIES OF THE BENZENE–CARBON TETRACHLORIDE SYSTEM

X_{CCl_4}	$\Delta\bar{E}_V^M$ H.S.	$\Delta\bar{E}_V^M$ W	$\Delta\bar{E}_V^M$ obsd.	$\Delta\bar{E}_p^M$ W	$\Delta\bar{H}_p^M$ obsd.	$\Delta\bar{S}_V^E$ W	$\Delta\bar{S}_V^E$ obsd.	$\Delta\bar{S}_p^E$ W	$\Delta\bar{S}_p^E$ obsd.	$\Delta\bar{F}_p^E$ W	$\Delta\bar{F}_p^E$ obsd.
0.1	+2.9	+2.5	+10.0	+3.4	+10.9	−0.01	+0.01	−0.01	+0.01	+ 8	+ 7
.2	+5.1	+5.1	+18.3	+6.2	+19.4	− .02	+ .02	− .02	+ .02	+12	+13
.3	+6.7	+7.0	+24.5	+7.9	+25.4	− .03	+ .03	− .02	+ .03	+14	+16
.4	+7.5	+8.1	+28.2	+9.1	+29.0	− .03	+ .03	− .02	+ .03	+16	+19
.5	+7.8	+8.8	+29.4	+9.6	+30.2	− .02	+ .03	− .02	+ .04	+16	+20
.6	+7.5	+8.6	+28.2	+9.5	+28.9	− .02	+ .03	− .02	+ .03	+14	+19
.7	+6.4	+7.6	+24.2	+8.7	+25.3	− .02	+ .03	− .01	+ .03	+13	+16
.8	+4.4	+5.7	+18.0	+6.9	+19.2	− .01	+ .02	− .01	+ .02	+ 9	+12
.9	+2.7	+2.9	+10.1	+3.9	+11.0	− .01	+ .01	− .00	+ .01	+ 5	+ 7

TABLE II

THE THERMODYNAMIC PROPERTIES OF THE BENZENE–CYCLOHEXANE SYSTEM

$X_{C_6H_6}$	$\Delta\bar{E}_V^M$ H.S.	$\Delta\bar{E}_V^M$ W	$\Delta\bar{E}_V^M$ obsd.	$\Delta\bar{E}_p^M$ W	$\Delta\bar{H}_p^M$ obsd.	$\Delta\bar{S}_V^E$ W	$\Delta\bar{S}_V^E$ obsd.	$\Delta\bar{S}_p^E$ W	$\Delta\bar{S}_p^E$ obsd.	$\Delta\bar{F}_p^E$ W	$\Delta\bar{F}_p^E$ obsd.
0.1	+ 8	+29	+ 53	+ 46	+ 71	+0.02	+0.08	+0.08	+0.15	+22	+27
.2	+14	+52	+ 93	+ 84	+127	+ .03	+ .15	+ .14	+ .26	+42	+48
.3	+19	+69	+123	+111	+167	+ .03	+ .20	+ .17	+ .35	+59	+63
.4	+22	+82	+142	+129	+193	+ .02	+ .23	+ .19	+ .40	+73	+73
.5	+23	+86	+150	+137	+203	.00	+ .24	+ .18	+ .42	+83	+77
.6	+23	+85	+146	+132	+197	− .02	+ .24	+ .15	+ .41	+87	+75
.7	+20	+78	+130	+122	+175	− .02	+ .21	+ .13	+ .36	+83	+66
.8	+16	+63	+101	+ 96	+135	− .03	+ .17	+ .09	+ .28	+70	+51
.9	+ 9	+38	+ 58	+ 59	+ 77	− .02	+ .10	+ .05	+ .16	+43	+29

TABLE III

THE THERMODYNAMIC PROPERTIES OF THE CARBON TETRACHLORIDE–CYCLOHEXANE SYSTEM

X_{CCl_4}	$\Delta\bar{E}_V^M$ H.S.	$\Delta\bar{E}_V^M$ W	$\Delta\bar{E}_V^M$ obsd.	$\Delta\bar{E}_p^M$ W	$\Delta\bar{H}_p^M$ obsd.	$\Delta\bar{S}_V^E$ W	$\Delta\bar{S}_V^E$ obsd.	$\Delta\bar{S}_p^E$ W	$\Delta\bar{S}_p^E$ obsd.	$\Delta\bar{F}_p^E$ W	$\Delta\bar{F}_p^E$ obsd.
0.1	+1	+10	+ 9	+14	+13	+0.007	+0.009	+0.02	+0.03	+ 9	+ 6
.2	+2	+19	+15	+26	+24	+ .011	+ .017	+ .03	+ .05	+18	+10
.3	+3	+26	+21	+35	+32	+ .014	+ .022	+ .04	+ .06	+24	+14
.4	+4	+30	+24	+41	+36	+ .014	+ .026	+ .05	+ .07	+28	+16
.5	+4	+32	+25	+44	+38	+ .014	+ .028	+ .05	+ .07	+29	+17
.6	+4	+32	+25	+44	+37	+ .013	+ .028	+ .05	+ .07	+28	+16
.7	+3	+29	+22	+39	+33	+ .010	+ .025	+ .05	+ .06	+25	+14
.8	+3	+23	+17	+31	+25	+ .008	+ .020	+ .04	+ .05	+20	+11
.9	+2	+14	+10	+18	+15	+ .006	+ .011	+ .02	+ .03	+12	+ 6

are molar quantities and are in units of cal. per mole or cal. per mole deg. The observed values are obtained from the work of Wood with Brusie,[23] Austin[24] and Gray[25] based on the work of Scatchard, Wood and Mochel. For the benzene–carbon tetrachloride system, $\Delta\bar{E}_v^M$ calculated here is only a little larger than that calculated by the Hildebrand–Scatchard equation and is much smaller than the observed value. Also $\Delta\bar{E}_p^M$ is smaller than $\Delta\bar{H}_p^M$. Both of the excess entropies are negative and smaller than the observed. The approximate agreement between the free energies is rather surprising. The benzene–cyclohexane system has the greatest deviation from ideality of the three systems. For this system, $\Delta\bar{E}_v^M$ calculated here is considerably larger than the value calculated by the Hildebrand–Scatchard equation and lies about midway between this value and the observed value. $\Delta\bar{E}_p^M$ is smaller than $\Delta\bar{H}_p^M$ but is comparable to it. The excess entropies are both too small; $\Delta\bar{S}_v^E$ (calcd.) has both positive and negative values while $\Delta\bar{S}_p^E$ (calcd.) is entirely positive. Again the agreement between the two free energies is striking; here, however, the calculated values are greater than those observed for cyclohexane-rich solutions. For the carbon tetrachloride–cyclohexane system, all the calculated values, except the two entropies, are greater than the observed values and considerably improved over the Hildebrand–Scatchard equation. Both $\Delta\bar{S}_v^E$ and $\Delta\bar{S}_p^E$ are smaller than the observed values but are comparable to them. The approach of $\Delta\bar{F}_p^E$ (calcd.) to the observed values for each system, in contrast to the other quantities, is probably due to the cancellation of errors in the integral of $(\partial P/\partial T)_V$ which appears in both the energy and the entropy. In all three systems, the difference between $\Delta\bar{E}_p^M$ and $\Delta\bar{E}_v^M$ agrees well with the difference between the observed quantities, $\Delta\bar{H}_p^M$ and $\Delta\bar{E}_v^M$, which has been calculated by the method of Scatchard.[27]

The relative importance of the first term of eq. 4 and 14, and the sum of the remaining terms is obtained by comparing the items of Table IV with the corresponding items of Tables I, II and III. Table IV gives the changes of the energy and the excess changes of the entropies on mixing at constant volume and at constant pressure at half mole fraction on the assumption that the first term in

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[27] G. Scatchard, *Trans. Faraday Soc.*, **33**, 160 (1937).

the eq. 4 and 14 is zero. This assumption requires the use of the arithmetic mean for both a_{12} and b_{12} rather than the geometric mean. The values of the energy of mixing for both constant volume and constant pressure in Table IV range from 70 to 90% of the corresponding values in the other tables. Thus, it seems that the compression or expansion of the pure components largely accounts for the energy of mixing. This is not true of the entropies of mixing, and the value of the first term of eq. 14 is roughly the same as the sum of the other terms.

TABLE IV

VALUES OF THE CHANGE OF ENERGY AND ENTROPY AT HALF MOLE FRACTION USING THE ARITHMETIC MEAN

	C_6H_6–CCl_4	C_6H_6–C_6H_{12}	C_6H_{12}–CCl_4
$\Delta\bar{E}_V{}^M$	8.0	71	23
$\Delta\bar{E}_p{}^M$	8.7	122	34
$\Delta\bar{S}_V{}^E$	−0.04	−0.11	−0.04
$\Delta\bar{S}_p{}^E$	− .03	+ .07	.00

Partial Molal Quantities.—Expressions for the partial molal energies of mixing and the partial molal excess entropies of mixing are readily obtained from eq. 4 and 14. These equations are

$$\Delta\bar{E}_1{}^M = \frac{x_2{}^2\bar{V}_1\bar{V}_2{}^2}{\bar{V}^2}\left(\frac{2a_{12}}{\bar{V}_1\bar{V}_2} - \frac{a_{11}}{\bar{V}_1{}^2} - \frac{a_{22}}{\bar{V}_2{}^2}\right) + \left(\frac{a_{11}}{\bar{V}_1} - \frac{a_{11}'}{\bar{V}_1{}^0}\right) + \frac{x_2(\bar{V}_1 - \bar{V}_2)}{V}\left[x_1{}^2\left(\frac{\partial a_{11}}{\partial\bar{V}}\right)_{T,P,n_2} + 2x_1x_2\left(\frac{\partial a_{12}}{\partial\bar{V}}\right)_{T,P,n_2} + x_2{}^2\left(\frac{\partial a_{22}}{\partial\bar{V}}\right)_{T,P,n_2}\right] \quad (17)$$

and

$$\Delta\bar{S}_1{}^E = \frac{x_2{}^2\bar{V}_1\bar{V}_2{}^2}{\bar{V}^2}\left(\frac{2b_{12}}{\bar{V}_1\bar{V}_2} - \frac{b_{11}}{\bar{V}_1{}^2} - \frac{b_{22}}{\bar{V}_2{}^2}\right) + \left(\frac{b_{11}}{\bar{V}_1} - \frac{b_{11}'}{\bar{V}_1{}^0}\right) + \frac{x_2(\bar{V}_1 - \bar{V}_2)}{\bar{V}}\left[x_1{}^2\left(\frac{\partial b_{11}}{\partial\bar{V}}\right)_{T,P,n_2} + 2x_1x_2\left(\frac{\partial b_{12}}{\partial\bar{V}}\right)_{T,P,n_2} + x_2{}^2\left(\frac{\partial b_{22}}{\partial\bar{V}}\right)_{T,P,n_2}\right] - R\ln\frac{\bar{V}_1{}^0}{\bar{V}} + \frac{x_2R}{\bar{V}}(\bar{V}_1 - \bar{V}_2) \quad (18)$$

The equations for the second component are obtained by interchange of subscripts. Equation 17 reduces to that given by Simons and Dunlap with the assumption that the *a*'s are independent of the volume.

Wood[28] has attempted to correlate the excess entropy of mixing at infinite dilution of one component in the other with the difference between the entropy of vaporization of the component to an ideal gas at an arbitrary concentration and that of argon to the same concentration in the gas phase. Such correlation could only exist if the solvent was considered to be merely an inert diluent, but the effect of the solvent was shown to be very marked. Equation 18 reduces to

$$\Delta\bar{S}_1{}^E = \frac{2b_{12}}{\bar{V}_2{}^0} - \frac{b_{22}\bar{V}_1{}^\infty}{(\bar{V}_2{}^0)^2} - \frac{b_{11}'}{\bar{V}_1{}^0} + \frac{\bar{V}_1{}^\infty - \bar{V}_2{}^0}{\bar{V}_2{}^0}\left(\frac{\partial b_{22}}{\partial\bar{V}}\right)_{T,P,n_2} - R\ln\frac{\bar{V}_1{}^0}{\bar{V}_2{}^0} + R\left(\frac{\bar{V}_1{}^\infty - \bar{V}_2{}^0}{\bar{V}_2{}^0}\right) \quad (19)$$

for the partial molar excess entropy of the first component at infinite dilution in the second component. Here $\bar{V}_1{}^\infty$ is the partial volume of the first component at infinite dilution. The effect of the solvent and the interaction between the unlike molecules is quite apparent. Even under the stringent conditions that the molar volumes are identical and that the volume of the solution is additive in the volume of the components, the three terms $b_{12}/\bar{V}^0$, $b_{22}/\bar{V}^0$ and $b_{11}/\bar{V}^0$ still appear. Only under the additional condition that b_{22} be zero would the partial molar excess entropy of the solute be dependent upon its properties alone.

[28] S. E. Wood, *J. Chem. Phys.*, **15**, 358 (1947).

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE VIRAL AND RICKETTSIAL SECTION, RESEARCH DIVISION, AMERICAN CYANAMID COMPANY]

The Calculation of Reduced Moments of Refractive Index Gradient Curves Obtained in Diffusion Experiments by Means of Rayleigh Fringes

BY RAYMOND A. BROWN, MAURICE C. DAVIES AND MARY E. ENGLERT

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A method has been devised for calculating reduced second and fourth moments of gradient curves obtained in diffusion experiments by means of Rayleigh fringes. Theoretical calculations and experimental data indicate that the reduced second moment can be measured with an accuracy of about 0.1%.

Although the free diffusion of homogeneous substances in liquids has been studied extensively with the Rayleigh method,[1] there is little published work on heterogeneous systems. Baldwin,[2] Dunlop[3] and Akeley[4] have shown that moments of the refractive index gradient curves are useful for measuring average diffusion constants of a heterogeneous system. Baldwin has named D_{2m} and $D^2{}_{4m}$ the reduced second and fourth moments, respectively.

$$D_{2m} \equiv \frac{m_2}{2t} \quad (1)$$

$$D^2{}_{4m} \equiv \frac{m_4}{12t^2} \quad (2)$$

In a non-interacting ($D_{ij} = 0$; $i \neq j$) heterogeneous system in which all the solutes have the same refractive index increment we have

$$D^s{}_{2m} = \overline{D^s} = \Sigma\, x_iD^s{}_i \quad (3)$$

where x_i is the weight fraction of component i.

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[1] (a) L. G. Longsworth, THIS JOURNAL, **75**, 5705 (1953); (b) J. M. Creeth, *ibid.*, **77**, 6428 (1955).

[2] R. L. Baldwin, P. J. Dunlop and L. J. Gosting, *ibid.*, **77**, 5235 (1955).

[3] P. J. Dunlop and L. J. Gosting, *ibid.*, **77**, 5238 (1955).

[4] D. F. Akeley and L. J. Gosting, *ibid.*, **75**, 5685 (1953).