

various temperatures under such conditions of pressure that the volume is constant at all temperatures. This problem is treated in the following paper.

The cohesive energy density between the unlike molecules has been estimated by the equation

$$a_{12} = (a_{11} + a_{22} + E_{V_{12}}^M / V_{12}^0) / 2 \quad (11)$$

The absolute values of a_{12} are always less than the geometrical mean of a_{11} and a_{22} in agreement with the prediction given by London.¹⁷ The per cent.

(17) F. London, *Z. physik. Chem.*, **B11**, 222 (1930).

decrease increases with the temperature. The values of a_{11} and a_{22} at 25, 40 and 70° used in these equations are -73.88, -69.86 and -63.86 cal. per cc. for carbon tetrachloride and -67.32, -64.11 and -58.15 cal. per cc. for cyclohexane. The values of β in the equation of state for the vapor, $V = (RT/p) + \beta$ at the same temperatures are -2544, -2071 and -1455 cc. for carbon tetrachloride and -2488, -2028 and -1427 cc. for cyclohexane.

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY, AND THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

The Effect of Volume and Temperature on the Energy and Entropy of Mixing at Constant Volume^{1,2}

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The energy of mixing at constant volume and the excess entropy of mixing at constant volume for the benzene-carbon tetrachloride, benzene-cyclohexane and carbon tetrachloride-cyclohexane systems have been calculated at 70° but at the molal volume at 25° and one atmosphere pressure from previously reported data making use of the Tait equation. It is thus possible to compare the effect of temperature at constant volume and the effect of volume at constant temperature on these mixing quantities. It appears that these functions are only slowly varying functions of the temperature but are definitely dependent upon the volume.

In the development of the theory of solutions of non-polar liquids, it was necessary to assume the energy of mixing at constant volume to be independent of the temperature and the excess entropy of mixing, that is, the difference between the entropy of mixing of the solution and that of an ideal solution of the same concentration, under conditions of mixing at constant volume to be zero. However, experimental determinations of the excess entropy of mixing⁴ for the three possible binary systems composed of benzene, cyclohexane and carbon tetrachloride have shown that the excess entropy of mixing at constant volume was positive over the entire range of composition. Measurements on the volume of mixing at various temperatures⁵ have shown that both the energy of mixing at constant volume and the excess entropy of mixing at constant volume appear to be functions of the temperature.

However, it is important to realize that the change of these functions with the temperature has actually been determined under conditions of changing volume. While the process of mixing has taken place under conditions of constant volume, the comparisons with temperature are made

at volumes equal to the additive volumes of the pure components at one atmosphere pressure and the temperature in question. Consequently the volumes of the solution and of the components are changing with the temperature and these two effects actually enter into the apparent change of these thermodynamic quantities with temperature. It is therefore necessary to separate the effects of each of these variables keeping the other constant. This can be accomplished if the volumes of the solutions and of the components are known as a function of the pressure and of the temperature. These data are not available for the solutions but it is possible to estimate the necessary quantities from the data available in order to make the calculations and to obtain an approximate value of the energy of mixing and the excess entropy of mixing, both at constant volume at various temperatures referred to some reference volume independent of the temperature. In particular, the energy of mixing and the excess entropy of mixing at 70° at a constant volume equal to that of the components at 25° and one atmosphere pressure have been calculated from the values of these functions for the process of mixing at a constant volume equal to the additive volume of the components at 70° and one atmosphere pressure. These values are compared to the energy of mixing and the excess entropy of mixing at 25° and one atmosphere pressure. The necessary corrections are small and are somewhat uncertain. However, the results are indicative that the energy of mixing at constant volume and the excess entropy of mixing at constant volume are approximately independent of the temperature or at least slowly varying functions of the temperature for the three systems studied when referred to the same reference

(1) Presented in part before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Atlantic City, N. J., September, 1949.

(2) This contribution contains material taken from a thesis by John A. Gray, III, presented to the Graduate School, Yale University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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(4) (a) G. Scatchard, S. E. Wood and J. M. Mochele, *J. Phys. Chem.*, **43**, 119 (1939); (b) *THIS JOURNAL*, **61**, 3206 (1939); (c) *ibid.*, **62**, 712 (1940).

(5) (a) S. E. Wood and J. P. Brusie, *ibid.*, **65**, 1891 (1943); (b) S. E. Wood and A. E. Austin, *ibid.*, **67**, 480 (1945); (c) S. E. Wood and J. A. Gray, III, *ibid.*, **74**, 3729 (1952).

volume independent of the temperature, but are definitely functions of the volume.

The difference between the energy of mixing at constant volume, E_V^M , at 70° and at the additive volume at 70° and one atmosphere pressure and the same quantity at 70° but at the additive volume at 25° and one atmosphere pressure is calculated as

$$\Delta E_V^M = E_V^M(70^\circ, V_{25^\circ}^0) - E_V^M(70^\circ, V_{70^\circ}^0) \quad (1)$$

But

$$E_V^M(70^\circ, V_{70^\circ}^0) = E(70^\circ, V_{70^\circ}^0) - x_1 E_1(70^\circ, V_{1,70^\circ}^0) - x_2 E_2(70^\circ, V_{2,70^\circ}^0) \quad (2)$$

and

$$E_V^M(70^\circ, V_{25^\circ}^0) = E(70^\circ, V_{25^\circ}^0) - x_1 E_1(70^\circ, V_{1,25^\circ}^0) - x_2 E_2(70^\circ, V_{2,25^\circ}^0) \quad (3)$$

It is then necessary to determine the integral

$$\Delta E = \int_{V_{70^\circ}^0}^{V_{25^\circ}^0} \left(T \frac{\partial P}{\partial T} - P \right) dV$$

for each solution at various concentrations as well as for the pure components since the limits of integration are different in each case and from the value of these integrals to determine ΔE_V^M as indicated in equations (1), (2) and (3). Similarly

$$\Delta S_V^E = S_V^E(70^\circ, V_{25^\circ}^0) - S_V^E(70^\circ, V_{70^\circ}^0) \quad (4)$$

and

$$S_V^E(T, V_T^0) = S(T, V_T^0) - x_1 S_1(T, V_{1,T}^0) - x_2 S_2(T, V_{2,T}^0) + x_1 R \ln x_1 + x_2 R \ln x_2 \quad (5)$$

The change in entropy with volume is

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V \quad (6)$$

and from equations (4), (5) and (6), ΔS_V^E may be evaluated.

It is obvious that some equation of state is necessary in order to carry out the indicated integrations. Gibson and his co-workers⁶ have shown that the Tait equation can be used to express their compressibility data. This equation is

$$\frac{V^0 - V}{V^0} = C \log \frac{B + P}{B} \quad (7)$$

where V^0 is the volume at zero pressure and a given temperature and V the volume at the pressure P and the same temperature; C is a constant independent of the temperature while B is a function of the temperature only. The pressure P may then be expressed as

$$P = B e^{\frac{V^0 - V}{C}} - B \quad (8)$$

Equation (8) has been used to evaluate the integrals previously indicated. The values of C and B for benzene and carbon tetrachloride are those given by Gibson and Kincaid⁷ and by Gibson and Loeffler,⁶ respectively. The value of C for cyclohexane was taken equal to that for benzene since Gibson has pointed out that C is almost the same for many substances. The value of B and its temperature derivative were then obtained from

the compressibility data for cyclohexane given in the Tables Annuelles.⁸ The actual values of C , B and $dB/B dT$, the last two values at 70°, used in the calculations are given in Table I.

TABLE I
CONSTANTS FOR THE TAIT EQUATION

	C ₆ H ₆	C ₆ H ₁₂	CCl ₄
B	662.0	550.0	587.5
C	0.21591	0.21591	0.21290
$dB/B dT$	-0.008837	-0.008326	-0.008845

For the solutions C was assumed to be additive in the volume fractions. This assumption should not be much in error since the various C 's are nearly equal. The B 's for the solutions have been calculated from the values of the pure components by the equation

$$B = B_1^{z_1} B_2^{z_2} e^{-VM/0.4343CV} \quad (9)$$

as suggested by Gibson and Loeffler.⁹ This equation is based on the concept that the components expand on mixing until the same value of B is obtained for both components. There is no information of the effect of pressure on V^M/V^0 and the values at one atmosphere have been used in these calculations. The maximum contribution of the exponential term to B is about 7%, thus making an approximate 7% contribution to ΔE_V^M and ΔS_V^E . It appears then that the dependence of V^M/V^0 on the pressure is of little significance. The results of Gibson and Loeffler show that the values of B determined by this combination are too small for the solutions of aniline with nitrobenzene and chlorobenzene where the volume of mixing is positive. Scatchard,¹⁰ on the other hand, has developed a method of combining the compressibilities of the pure components to obtain the compressibility of the solution. This method is based on the simple theory of non-polar mixtures and is dependent upon the assumptions made in this theory. The values of B determined from these compressibilities are somewhat large for the aniline-nitrobenzene system. For the solutions under consideration in this paper, the contributions to ΔE_V^M and ΔS_V^E using Scatchard's approximation are very small and negative, being in the order of -0.2 cal. for ΔE_V^M and -0.001 cal. per degree for ΔS_V^E for the benzene-carbon tetrachloride system at half mole fraction and -3 cal. for ΔE_V^M and -0.01 cal. per degree for ΔS_V^E for the benzene-cyclohexane system at half mole fraction. The actual values presumably lie between the values calculated by the two methods. The decision to use Gibson and Loeffler's method is arbitrary and the values thus calculated are uncertain to an unknown extent. The rather consistent results, viewed as a whole, for the three systems studied in this paper would appear to partially justify this decision.

The results for the benzene-carbon tetrachloride system are given in Table II. The first column

(8) "Tables Annuelles de Constants et Donnees Numeriques," Vol. VI, p. 16 (1923-1924).

(6) R. E. Gibson and O. H. Loeffler, THIS JOURNAL, **68**, 898 (1941), and earlier paper.

(7) R. E. Gibson and J. F. Kincaid, *ibid.*, **60**, 511 (1938).

(9) R. E. Gibson and O. H. Loeffler, *J. Phys. Chem.*, **43**, 207 (1939).

(10) G. Scatchard, *Trans. Faraday Soc.*, **33**, 160 (1937).

TABLE II

ENERGY OF MIXING AND EXCESS ENTROPY OF MIXING AT CONSTANT VOLUME BENZENE-CARBON TETRACHLORIDE

X_{CCl_4}	$E_v^M(25^\circ, V_{25^\circ}^0)$	E_v^M (obsd.)	E_v^M (calcd.)	$S_v^E(25^\circ, V_{25^\circ}^0)$	S_v^E (obsd.)	S_v^E (calcd.)
0.1	10.0	2.1	2.5	0.011	0.006	0.008
.2	18.3	3.6	3.9	.021	.009	.012
.3	24.5	4.7	4.7	.030	.013	.014
.4	28.2	5.3	5.3	.035	.014	.016
.5	29.4	5.6	5.6	.036	.014	.017
.6	28.0	5.5	5.9	.034	.014	.018
.7	24.2	5.0	5.8	.029	.014	.018
.8	18.0	3.9	5.1	.020	.010	.016
.9	10.1	2.4	3.3	.011	.002	.010

gives the mole fraction of carbon tetrachloride and the second the energy of mixing at 25° and a constant volume equal to the additive volume at 25° and one atmosphere pressure. The third column is the observed difference between the values in the second column and the energy of mixing at 70° and the additive volume at 70° and one atmosphere pressure. The fourth column is the calculated change of the energy of mixing as defined by equation 1. The last three columns give the values for the excess entropy of mixing and the changes in that quantity for the same changes described for the energy of mixing, the last column being defined by equation 4. The differences between the third and fourth column and between the sixth and seventh column give the effect of temperature on the energy of mixing and the entropy of mixing on cooling from 70 to 25° at the constant additive volumes at 25° and one atmosphere pressure. It appears from comparison of these columns that both the energy of mixing and excess entropy of mixing are essentially independent of the temperature when compared at the same volumes but are definitely dependent upon the volume at constant temperature, both decreasing as the volume is increased.

The results for the benzene-cyclohexane system are given in Table III; the arrangement of the columns are the same as that in Table II. Here, however, there is a question of what values of E_v^M at 70 and 25° to use as a basis. Scatchard, Wood and Mochel^{4a} give two equations for the excess free energy of mixing at constant pressure, one of which is linear in respect to the temperature while the other is quadratic. Wood and Austin^{4b} have shown that E_v^M and S_v^E referred to the volumes at one atmosphere pressure at the various temperatures in question increase with the temperature if the linear equation is used while they both markedly decrease when the quadratic equation is used. The results given in Table III are calculated using the quadratic equation. It is again evident that with this equation both E_v^M and S_v^E are essentially independent of the temperature when referred to the same volumes and that they decrease with increase of volume at constant temperature. If the linear equation had been used S_v^E and E_v^M would have increased with temperature even more rapidly when referred to the same reference volumes than those reported by Wood

TABLE III

ENERGY OF MIXING AND EXCESS ENTROPY OF MIXING AT CONSTANT VOLUME BENZENE-CYCLOHEXANE

$X_{C_6H_6}$	$E_v^M(25^\circ, V_{25^\circ}^0)$	E_v^M (obsd.)	E_v^M (calcd.)	$S_v^E(25^\circ, V_{25^\circ}^0)$	S_v^E (obsd.)	S_v^E (calcd.)
0.1	51.7	10.9	10.9	0.083	0.040	0.034
.2	92.7	21.7	19.5	.150	.054	.061
.3	123.0	29.2	26.6	.199	.072	.082
.4	142.2	34.0	29.5	.230	.084	.092
.5	150.0	36.3	31.6	.244	.091	.098
.6	146.0	35.5	31.2	.238	.089	.097
.7	129.7	31.9	28.2	.212	.081	.088
.8	100.6	24.9	22.1	.165	.063	.069
.9	57.7	14.4	12.1	.095	.036	.038

and Austin. Based on the results of the benzene-carbon tetrachloride system and the comparison of the results of the benzene-cyclohexane system using the two equations for the excess free energy, it is believed—but by no means certain—that the quadratic equation is the better equation and that again in this system the energy of mixing at constant volume and the excess entropy of mixing at constant volume are almost independent of the temperature when referred to the same reference volumes.

The results for the cyclohexane-carbon tetrachloride system are given in Table IV. The col-

TABLE IV

ENERGY OF MIXING AND EXCESS ENTROPY OF MIXING AT CONSTANT VOLUME CYCLOHEXANE-CARBON TETRACHLORIDE

X_{CCl_4}	$E_v^M(25^\circ, V_{25^\circ}^0)$	E_v^M (obsd.)	E_v^M (calcd.)	$S_v^E(25^\circ, V_{25^\circ}^0)$	S_v^E (obsd.)	S_v^E (calcd.)
0.1	8.5	1.7	2.4	0.009	0.003	0.007
.2	15.4	3.0	4.5	.017	.006	.014
.3	20.6	4.0	5.9	.022	.007	.018
.4	23.9	4.5	6.8	.026	.008	.021
.5	25.3	4.7	6.9	.028	.009	.022
.6	24.7	4.5	6.8	.028	.009	.021
.7	22.0	4.0	5.3	.025	.008	.017
.8	17.0	3.0	3.6	.020	.006	.012
.9	9.8	1.8	2.2	.011	.003	.007

TABLE V

COHESIVE ENERGY DENSITIES

	70°, $V_{70^\circ}^0$	70°, $V_{25^\circ}^0$	25°, $V_{25^\circ}^0$
Benzene-cyclohexane			
a_{11}	-72.54	-81.63	-84.18
a_{22}	-58.15	-65.92	-67.32
a_{12}	-63.16	-70.81	-72.70
$\sqrt{a_{11} a_{22}}$	-64.95	-73.36	-75.28
$100(a_{12} - \sqrt{a_{11} a_{22}})/a_{12}$	+ 2.83	+ 3.48	+ 3.55
Carbon tetrachloride-benzene			
a_{11}	-63.86	-72.30	-73.88
a_{22}	-72.54	-81.63	-84.18
a_{12}	-67.72	-76.37	-78.40
$\sqrt{a_{11} a_{22}}$	-68.06	-76.82	-78.87
$100(a_{12} - \sqrt{a_{11} a_{22}})/a_{12}$	+ 0.50	+ 0.59	+ 0.60
Carbon tetrachloride-cyclohexane			
a_{11}	-63.86	-72.30	-73.88
a_{22}	-58.15	-65.92	-67.32
a_{12}	-60.62	-68.57	-70.10
$\sqrt{a_{11} a_{22}}$	-60.94	-69.04	-70.52
$100(a_{12} - \sqrt{a_{11} a_{22}})/a_{12}$	+ 0.53	+ 0.69	+ 0.60

umns in the table are identical with those in the previous tables. The values of the energy and excess entropy of mixing used in this table are those calculated in the preceding paper^{5c} and combine the vapor pressure data of Scatchard, Wood and Mochel with the heat of mixing data of Scatchard. The results for this system are very similar to those in the other two systems and tend to indicate that the energy of mixing at constant volume and the excess entropy of mixing at constant volume are relatively independent of temperature when referred to the same constant volume but are dependent upon the volume at constant temperature.

It is also of interest to compare the cohesive energy densities under these various conditions. The values of a_{11} , a_{22} and a_{12} in cal. per cc. for the three systems studied in this paper are given in Table V.

The second column gives these values at 70° and at the volume at 70° and one atmosphere pressure, the third column gives the values at 70° but at the volume at 25° and one atmosphere pressure while the last column gives the values at 25° and at the volume at 25° and one atmosphere pressure. It is again evident that the effect of volume is relatively large while the effect of the temperature is rather small. These same trends are evident also in the percentage differences of a_{12} and the geometric mean of a_{11} and a_{22} .

Similar calculations have been made for the benzene-methanol and carbon tetrachloride-methanol systems but the effects are too small in comparison to the uncertainties in the reported thermodynamic functions to draw any conclusions.

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[CONTRIBUTION FROM IONICS, INCORPORATED]

Electrochemical Properties of Ion Exchange Resins. I. Donnan Equilibria, Membrane Potentials and Conductivities

BY W. JUDA, N. W. ROSENBERG, J. A. MARINSKY AND A. A. KASPER

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Ion-exchange resins have been considered as solid electrolytes. Electrochemical properties of sodium salts, including transport numbers and conductances, have been investigated and correlated with Donnan absorption for two chemically different cross-linked phenolsulfonate resin membranes, PERMIONIC CR-41 and PERMIONIC CR-51. The data are consistent with the assumption that the sodium salt of one of the materials (CR-51) is strongly ionized, whereas the other could be partially associated into ion pairs. Electrical conductivity in the two membranes studied can be considered to be entirely electrolytic in character with a uniform ionic flux across the cross-section.

The recent announcement of homogeneous ion exchange membranes¹ of high exchange capacities, water contents and specific electric conductances has stimulated considerable interest in the electrochemistry of ion exchange resins because the membrane form is well suited for theoretical and applied electrochemical work. A correlation of membrane potentials and conductances with Donnan electrolyte diffusion into the membrane phase is of importance in all cells transferring ions from one solution to another through a membrane. Although each of these properties has been investigated² separately on different materials, including ion exchange granules and insulating membranes made of collodion, clay and polystyrene bonded ion exchange granules, it was impractical to carry out experimental studies of all three either on the same granular exchanger or on the same insulating membrane; it is difficult to make reliable potential and conductance measurements with the granular exchanger and Donnan determinations are not easily obtained with the insulating type membrane.

(1) W. Juda and W. A. McRae, *THIS JOURNAL*, **72**, 1044 (1950). See also T. R. E. Kressman, *Nature*, **165**, 568 (1950).

(2) W. C. Bauman and J. Eichorn, *THIS JOURNAL*, **69**, 2820 (1947); H. Jenny, T. R. Nielsen, N. T. Coleman and D. E. Williams, *Science*, **112**, 164 (1950); K. Sollner, *J. Electrochem. Soc.*, **97**, 139C (1950) and preceding papers; S. K. Mukherjee and C. E. Marshall, *J. Phys. Chem.*, **55**, 61 (1951) and preceding papers; M. R. J. Wyllie and H. W. Patnode, *ibid.*, **54**, 204 (1950); M. R. J. Wyllie, *Science*, **108**, 684 (1948); E. Heymann and I. J. O'Donnell, *J. Colloid Sci.*, **4**, 405 (1949); W. S. Albrink and R. M. Fuoss, *J. Gen. Physiol.*, **32**, 453 (1949).

In this paper, systems involving the sodium salts of two chemically different cross-linked polyphenol-sulfonic acids, identified as Permionic CR-41 and Permionic CR-51, in equilibrium with sodium chloride solutions, were chosen for transport, conductance, and Donnan studies. A univalent cation for which simple theoretical concepts may be tested is required for this initial investigation; sodium ion was selected because of its relatively low mobility (compared to hydrogen or potassium, for example), a property which enhances the sensitivity of membrane potentials to the presence of the mobile counterions (chloride ions) in the solid phase.

Experimental

Conversion to Sodium Form.—A membrane sample, 7.5 cm. long, 1.9 cm. wide and 0.9 mm. thick, in the hydrogen form and in equilibrium with sulfuric acid (sp. gr. 1.30) was immersed in about 100 times its volume of distilled water. After 7 minutes of rapid stirring, this leaching procedure was repeated with fresh portions of distilled water until the water was neutral to methyl orange. (Five washes were sufficient to bring the membranes to the leached hydrogen form.) The sample of membrane was then converted to the sodium form with 4 *N* sodium chloride solution. A 7-minute contact time, with agitation, of five successive portions of this solution effected complete conversion as evidenced by pH measurements of each spent portion. The volume of each portion provided roughly a forty-fold stoichiometric excess over the total equivalents of membrane capacity. The sample was finally leached free from diffused salt by successive washes with distilled water, as described above, until two successive leach waters were free from chloride (silver nitrate test).

Moisture Determination.—A two-gram sample of leached sodium membrane was wiped surface dry, weighed to the