Series expansion of the residual chemical potential leads to

$$(\mu_1 - \mu_1^0)^R = (A^2\alpha_1T/2 + Y_{12})(p_1^*v_1^*/\bar{v}_1)\varphi_2^2 + \{2Y_{12}(1 - s_2/s_1) + [2Y_{12} + (1 - p_2^*T_1^*/p_1^*T_2^*)A] \times (A\alpha_1T) - (6\alpha_1T + 4\alpha_1^2T^2 + 4\alpha_1^3T^3)(A^3/9)\} \times (p_1^*v_1^*/\bar{v}_1)\varphi_2^3 + \ldots \quad (43)$$

where

$$A = (1 - T_1^*/T_2^*)(p_2^*/p_1^*) - (s_2/s_1)(X_{12}/p_1^*) \quad (44)$$

$$Y_{12} = (s_2/s_1)^2(X_{12}/p_1^*) \quad (45)$$

$\alpha_1$ is the thermal expansion coefficient of pure component 1 (see eq. 41). If $s_1 = s_2$, the coefficients simplify in eq. 43–45.

Series expansions for the partial molar enthalpy and entropy may be obtained from eq. 43 by differentiation.

## Concluding Remarks

Adaptation of the reduced partition function expressed by eq. 7 to mixtures and adoption of eq. 20 for the intermolecular energy on the assumption of random mixing underlies the theory developed above.

The expressions derived for the various residual (or excess) properties of a binary mixture involve a single parameter, $X_{12}$, beyond those furnished by the properties of the two pure components. The thermodynamic properties (*e.g.*, $H$, $V$, and $S$) are thus related explicitly to one another in terms of this parameter characterizing the given mixture. Treatment of mixtures of small, nonpolar molecules on this basis is demonstrated in the following paper.[14] Application to polymer solutions will be presented in a future communication.

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# The Thermodynamic Properties of Mixtures of Small, Nonpolar Molecules

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*The excess enthalpies, volumes, and entropies of 23 equimolar binary liquid mixtures for which necessary data are available in the literature are interpreted according to the relationships presented in the preceding paper. Most of the mixtures comprise pairs of small globular molecules from the group c-$C_6H_{12}$, $C_6H_6$, $C(CH_3)_4$, $CCl_4$, $SiCl_4$, $TiCl_4$, and $SnCl_4$ or from the condensed gases $CH_4$, Ar, $O_2$, and $N_2$. Also included are mixtures of $C_6H_6$ and of c-$C_6H_{12}$ with n-hexane and n-heptane, the benzene–diphenyl system, and two hydrocarbon–fluorocarbon mixtures. Previously unaccounted equation of state terms, which depend on properties of the pure components, make important contributions to each of the excess quantities. Through use of pair interaction parameters chosen to achieve agreement with the observed excess enthalpies, excess volumes are calculated which agree in nearly all cases with those observed within limits set by experimental errors. Although excess entropies calculated on the same basis tend to be somewhat lower than those observed, the agreement is favorable for most systems. Exceptions involve benzene as one component or cyclohexane in admixture with n-alkanes. Because account was taken of equation of state contributions, the present interaction parameters differ from those deduced from experimental results by previous procedures. Departures from the Berthelot geometric mean rule are discussed.*

## Introduction

In this paper we present an analysis of the experimental excess thermodynamic functions $V^E$, $H^E$, and $S^E$ for binary liquid mixtures of nonpolar molecules. The systems considered comprise pairs of molecules which (i) are small rather than polymeric, (ii) do not differ greatly in size, and (iii) in general are approximately spherical. The analysis is carried out on the basis of the relationships formulated in the preceding paper[1] and, hence, serves to put to test the theory there set forth.

A preliminary examination of experimental data for several representative systems in the category specified above was presented in a recent communication.[2] The results seemed to warrant an exhaustive investigation of mixtures of globular, nonpolar molecules. A wealth of experimental material is at hand for such systems,[3] and we have accordingly undertaken to include in the present report an account of all of those for which the necessary data are available. Deviations from ideality or from regularity are generally small for such systems, and this fact places greater demands on experimental accuracy and at the same time provides, in some respects, a more stringent test of theory.

Treatment of excess properties according to the theoretical scheme set forth in the preceding paper[1] and elsewhere[4,5] depends first of all on reliable equation of state parameters for the pure liquids. These comprise the molar volume v, the thermal expansion coefficient $\alpha$, and the isothermal compressibility $\kappa$, or,

(1) P. J. Flory, *J. Am. Chem. Soc.*, 87, 1833 (1965).
(2) P. J. Flory and A. Abe, *ibid.*, 86, 3563 (1964).
(3) J. S. Rowlinson, "Liquids and Liquid Mixtures," Butterworth and Co. Ltd., London, 1959.
(4) P. J. Flory, R. A. Orwoll, and A. Vrij, *J. Am. Chem. Soc.*, **86**, 3507 (1964).
(5) P. J. Flory, R. A. Orwoll, and A. Vrij, *ibid.*, **86**, 3515 (1964).

in place of $\kappa$, the thermal pressure coefficiently $\gamma = (\partial p/\partial T)_V = \alpha/\kappa$. They are required to provide the characteristic parameters $v^*$, $T^*$, and $p^*$ for the pure liquids, these being the main ingredients entering the equations for the various excess, or residual,[1] quantities.

### Characteristic Parameters for the Pure Components

The numerical evaluation of parameters for the pure liquids is carried out according to the procedure previously applied to the *n*-alkanes.[4] Starting with the reduced equation of state for zero pressure

$$\tilde{T} = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3} \qquad (1)$$

(see eq. 13* of the preceding paper[1,6]), we obtain

$$\tilde{v}^{1/3} - 1 = (\alpha T/3)/(1 + \alpha T) \qquad (2)$$

where $\alpha$ is the coefficient of thermal expansion at $p = 0$. Thus, from the measured value of $\alpha$, we obtain the reduced volume $\tilde{v}$. Substitution in eq. 1 then yields the reduced temperature $\tilde{T}$. Given the molar volume v at temperature $T$ and at $p = 0$ (or, without appreciable error, at 1 atm.), we obtain the hard-core volume per mole $v^* = v/\tilde{v}$. Similarly, the characteristic temperature $T^* = T/\tilde{T}$.

From the reduced equation of state as expressed by eq. 8* (of the preceding paper[6]) it follows that[1,4]

$$p^* = \gamma T \tilde{v}^2 \qquad (3)$$

where $\gamma = (\partial p/\partial T)_V$ is the thermal pressure coefficient at $p = 0$. Having evaluated the reduced volume $\tilde{v}$ from the thermal expansion coefficient, the calculation of the characteristic parameters $v^*$, $T^*$, and $p^*$ is thus complete.

Experimental values of the molar volumes, v, of the thermal expansion coefficients, $\alpha$, and of the thermal pressure coefficients, $\gamma$, are listed in Table I for the various pure liquids whose binary mixtures are considered. The temperatures chosen are those at which properties of the mixtures have been investigated. All data refer to ordinary pressure and may be considered to hold for zero pressure without appreciable error. Sources are indicated in footnotes to the table.

Limits of error are difficult to ascertain. Thermal expansion coefficients are believed to be accurate in general to about 1%. Thermal pressure coefficients are subject to larger errors. Values reported by different investigators for the same liquid frequently differ by more than the acknowledged limits of error; discrepancies as great as 10% are sometimes found. Quoted values of $\gamma$ determined by static methods are believed to be fairly reliable, with limits of error ranging from $\pm 1\%$ to $\pm 3\%$. Larger uncertainties may apply to some of the $\gamma$ values calculated from the adiabatic compressibilities obtained from sonic measurements.

Thermal pressure coefficients for the first three liquids listed in Table I have been determined by static methods at temperatures from 25 to 70° with extraordinary precision; errors here are certainly less than 1%. Moreover, the $\kappa$ values for all of these liquids were measured by the same investigators, Holder and Whalley,[7] using the same method. Mixtures of these liquids can therefore be treated with the assurance that parameters for the pure components are both accurate and mutually consistent.

The reduced volume $\tilde{v}$, the characteristic volume $v^*$, the characteristic temperature $T^*$, and the characteristic pressure $p^*$, all computed as indicated above, are given in succeeding columns of Table I. Values of the parameter[1] $C = p^* v^*/RT^*$, expressing the effective number of external degrees of freedom per molecule, are included in the last column. They are of incidental interest only and are not required for purposes of the present paper.

The limitations of the equation of state are manifest in the changes of the parameters with temperature. The core volume $v^*$ increases with temperature in all cases. Expressed as $(v^*)^{-1}dv^*/dT$, these increases range from about 5 to 25% of $\alpha$. The simultaneous increase in $T^*$ with temperature is implicitly related to the increase in $v^*$ according to the procedure for calculating both on the basis of eq. 1, as we have had occasion to point out previously.[4] The characteristic pressure $p^*$ decreases with temperature. These observations parallel those for the *n*-alkanes.[4]

In the following applications of these results to mixtures, values of the parameters are taken at the temperature of the solution measurements in each instance. The effects of the shortcomings inherent in the simple equation of state, deliberately chosen for its ease of application to mixtures, are believed to be minimized in this manner.

### Treatment of Data for Mixtures

Most of the systems considered here consist of pairs of component molecules of similar volume. The distinction between "excess" and "residual" thermodynamic quantities introduced in the preceding paper consequently vanishes, and we may revert to conventional terminology within the scope of the present paper. The excess entropy $S^E$, for example, is related to the residual entropy $S^R$ according to

$$S^E = S^R + \Delta S_{comb} - \Delta S_{id} \qquad (4)$$

where $\Delta S_{comb}$ is the combinatorial entropy appropriate for the system concerned, and

$$\Delta S_{id} = -R[N_1 \ln (N_1/N) + N_2 \ln (N_2/N)] \qquad (5)$$

is the ideal entropy of mixing. For most of the mixtures treated below, $\Delta S_{id}$ offers the best available representation for $\Delta S_{comb}$. Hence, for these mixtures $S^E = S^R$. For the benzene–diphenyl system the disparity in molecular sizes justifies use of the expression for mixtures involving chain molecules, namely

$$\Delta S_{comb} = -R[N_1 \ln \varphi_1 + N_2 \ln \varphi_2] \qquad (6)$$

where $\varphi_1$ and $\varphi_2$ are the segment fractions defined in the preceding paper; *i.e.*

$$\varphi_2 = 1 - \varphi_1 = N_2 v_2^*/(N_1 v_1^* + N_2 v_2^*) \qquad (7)$$

*Experimental Excess Quantities.* Principal experimental results and calculations for the systems considered are presented in Table II. Included are the molar enthalpy of mixing $\Delta H_M$, *i.e.*, the excess molar enthalpy $H^E$ as it is here designated, the excess molar volume $v^E$, and the excess molar entropy $s^E$ represented by the product $Ts^E$. All refer to equimolar mixtures, and

(6) Equation numbers referring to the preceding paper are superscripted with an asterisk.
(7) See Table I, ref. *f*.

Table I. Parameters for the Pure Liquids

| Liquid | $T$, °C. | v, cc. mole$^{-1}$ | $\alpha \times 10^3$, deg.$^{-1}$ | $\gamma$, cal. cc.$^{-1}$ deg.$^{-1}$ | $\tilde{v}$ | v*, cc. mole$^{-1}$ | $T^*$, °K. | $p^*$, cal. cc.$^{-1}$ | $C$, molecule$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| $CCl_4$ | 0 | 94.21[a] | 1.191[b] | 0.321[c,d] | 1.2660 | 74.42 | 4571 | 140 | 1.15 |
| | 20 | 96.49[b] | 1.219[b] | 0.277[e] | 1.2869 | 74.97 | 4675 | 134 | 1.08 |
| | 25 | 97.08[b] | 1.229[b] | 0.273[f] | 1.2927 | 75.10 | 4697 | 136 | 1.09 |
| | 40 | 98.91[b] | 1.265[b] | 0.248[f] | 1.3113 | 75.43 | 4752 | 133 | 1.06 |
| | 70 | 102.88[b] | 1.363[b] | 0.205[f] | 1.3536 | 76.00 | 4836 | 129 | 1.02 |
| $c$-$C_6H_{12}$ | 0 | 105.59[b] | 1.145[b] | 0.296[g] | 1.2576 | 83.96 | 4668 | 128 | 1.16 |
| | 20 | 108.10[b] | 1.202[b] | 0.264[g] | 1.2837 | 84.21 | 4708 | 127 | 1.14 |
| | 25 | 108.75[b] | 1.217[b] | 0.255[f] | 1.2905 | 84.27 | 4719 | 127 | 1.14 |
| | 40 | 110.79[b] | 1.264[b] | 0.234[f] | 1.3111 | 84.51 | 4754 | 126 | 1.13 |
| | 70 | 115.25[b] | 1.365[b] | 0.193[f] | 1.3540 | 85.12 | 4834 | 121 | 1.07 |
| $C_6H_6$ | 0 | 86.74[h] | 1.191[h] | 0.354[g] | 1.2660 | 68.52 | 4571 | 155 | 1.17 |
| | 25 | 89.40[h] | 1.223[h] | 0.302[f] | 1.2916 | 69.21 | 4708 | 150 | 1.11 |
| | 40 | 91.07[h] | 1.256[h] | 0.274[f] | 1.3096 | 69.54 | 4768 | 147 | 1.08 |
| | 70 | 94.69[h] | 1.346[h] | 0.228[f] | 1.3503 | 70.13 | 4862 | 142 | 1.03 |
| $C(CH_3)_4$ | 0 | 118.03[a] | 1.811[i] | 0.185[c,d] | 1.3687 | 86.24 | 3762 | 94.7 | 1.09 |
| $n$-$C_6H_{14}$ | 20 | 130.67[j] | 1.352[j] | 0.200[k] | 1.3114 | 99.64 | 4447 | 101 | 1.14 |
| | 25 | 131.57[j] | 1.378[j] | 0.194[k] | 1.3203 | 99.65 | 4448 | 101 | 1.14 |
| | 35 | 133.43[j] | 1.430[j] | 0.181[k] | 1.3380 | 99.72 | 4455 | 100 | 1.13 |
| $n$-$C_7H_{16}$ | 20 | 146.59[j] | 1.238[j] | 0.210[l] | 1.2905 | 113.59 | 4640 | 102 | 1.26 |
| | 25 | 147.51[j] | 1.248[j] | 0.204[l] | 1.2963 | 113.79 | 4661 | 102 | 1.25 |
| $c$-$CH_3 \cdot C_6H_{11}$ | 65 | 134.59[m] | 1.212[m] | 0.180[n] | 1.3197 | 101.99 | 5051 | 106 | 1.08 |
| $(C_6H_5)_2$ | 70 | 155.28[o] | 0.840[o] | 0.297[d,p] | 1.2409 | 125.14 | 6132 | 157 | 1.61 |
| $SiCl_4$ | 20 | 114.64[q] | 1.415[q] | 0.214[e] | 1.3227 | 86.67 | 4354 | 110 | 1.10 |
| | 25 | 115.47[q] | 1.442[q] | 0.208[e] | 1.3317 | 86.71 | 4358 | 110 | 1.10 |
| $TiCl_4$ | 20 | 109.80[q] | 1.026[q] | 0.286[e] | 1.2494 | 87.88 | 5118 | 131 | 1.13 |
| $SnCl_4$ | 20 | 116.92[q] | 1.171[q] | 0.271[e] | 1.2778 | 91.50 | 4771 | 129 | 1.25 |
| Ar | 84(°K.) | 28.20[r] | 4.37[r] | 0.518[d,r] | 1.2933 | 21.81 | 1322 | 72.8 | 0.604 |
| | 91(°K.) | 29.15[r] | 4.62[r] | 0.438[d,r] | 1.3267 | 21.97 | 1345 | 70.3 | 0.578 |
| $CH_4$ | 91(°K.) | 35.47[r] | 2.96[r] | 0.496[d,r] | 1.2280 | 28.88 | 1693 | 68.2 | 0.586 |
| $O_2$ | 77(°K.) | 26.50[r] | 3.96[r] | 0.673[d,r] | 1.2523 | 21.16 | 1334 | 81.3 | 0.649 |
| | 84(°K.) | 27.28[r] | 4.27[r] | 0.601[d,r] | 1.2879 | 21.18 | 1338 | 83.7 | 0.667 |
| $N_2$ | 77(°K.) | 34.62[r] | 5.67[r] | 0.436[d,r] | 1.3357 | 25.92 | 1118 | 59.9 | 0.699 |
| | 84(°K.) | 36.10[r] | 6.32[r] | 0.371[d,r] | 1.3884 | 26.00 | 1126 | 60.1 | 0.698 |
| $n$-$C_6F_{14}$ | 35 | 205.98[s] | 1.876[s] | 0.137[k] | 1.4127 | 145.80 | 4000 | 84.0 | 1.54 |
| $c$-$CF_3 \cdot C_6F_{11}$ | 65 | 209.2[t] | 1.70[t] | 0.129[u] | 1.4111 | 148.3 | 4400 | 86.8 | 1.47 |

[a] V. Mathot and A. Desmyter, *J. Chem. Phys.*, **21**, 782 (1953). [b] S. E. Wood and J. A. Gray, *J. Am. Chem. Soc.*, **74**, 3729 (1952). The thermal expansion coefficient of $CCl_4$ and $c$-$C_6H_{12}$ and the molar volume of $c$-$C_6H_{12}$ at 0° were deduced by extrapolation. [c] J. Jeener, *J. Chem. Phys.*, **25**, 584 (1956). [d] Values of $\gamma$ based on sound velocity measurements. All others have been determined by static methods. [e] J. H. Hildebrand and J. M. Carter, *J. Am. Chem. Soc.*, **54**, 3592 (1932). [f] G. A. Holder and E. Whalley, *Trans. Faraday Soc.*, **58**, 2095 (1962). [g] Estimated by extrapolation of thermal pressure coefficients obtained at higher temperatures as given in the table. [h] S. E. Wood and J. P. Brusie, *J. Am. Chem. Soc.*, **65**, 1891 (1943). The values at 0° were estimated by extrapolation. [i] Estimated from densities given in the American Petroleum Institute compilations: F. D. Rossini, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," API Research Project 44, Carnegie Press, Pittsburgh, Pa., 1953. [j] "International Critical Tables," Vol. 3, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p. 29. [k] R. D. Dunlap and R. L. Scott, *J. Phys. Chem.*, **66**, 631 (1962). [l] W. Westwater, H. W. Franz, and J. H. Hildebrand, *Phys. Rev.*, **31**, 135 (1928). [m] L. Massart, *Bull. soc. chim. Belges*, **45**, 76 (1936). [n] The thermal pressure coefficient at 25° was deduced from the compressibility measurement by K. Shinoda and J. H. Hildebrand, *J. Phys. Chem.*, **65**, 183 (1961). Assuming the same temperature coefficient ($\partial\gamma/\partial T$) as that of cyclohexane, the value at 65° was estimated. [o] Computed from density–temperature data reported by R. W. Bowring and D. A. Garton, United Kingdom Atomic Energy Authority Report A.E.R.E. R/R 2762, Harwell, Didcot, Berkshire, England, 1958. [p] Calculated from sound velocity data by P. R. K. L. Padmini and B. R. Rao, *Indian J. Phys.*, **35**, 346 (1961); *Z. Physik*, **162**, 245 (1961). The heat capacity required in the calculation was taken from H. O. Forrest, E. W. Brugmann, and L. W. T. Cummings, *Ind. Eng. Chem.*, **23**, 37 (1931). [q] From density–temperature data reported by H. Sackmann and H. Arnold, *Z. Elektrochem.*, **63**, 565 (1959). [r] See ref. 3, pp. 47–56. The values were taken from the tables compiled by Rowlinson. The thermal pressure coefficients are mainly based on sound velocity measurements. [s] R. D. Dunlap, C. J. Murphy, Jr., and R. G. Bedford, *J. Am. Chem. Soc.*, **80**, 83 (1958). [t] R. N. Haszeldine and F. Smith, *J. Chem. Soc.*, 603 (1951). [u] Estimated by extrapolation of the thermal pressure coefficient between 13 and 41°, by E. B. Smith and J. H. Hildebrand, *J. Chem. Phys.*, **31**, 145 (1959), and also by extrapolation of the sound velocity reported between 20 and 60° by T. Lagemann, W. E. Woolf, J. S. Evans, and N. Underwood, *J. Am. Chem. Soc.*, **70**, 2994 (1948), with the aid of the heat capacity given by R. M. Yarrington and W. B. Kay, *J. Phys. Chem.*, **61**, 1259 (1957).

they are expressed in appropriate units per mole of mixture. Sources of these experimental results are given in footnotes to the table. Citations in the last column of the table refer to sources of the experimental excess free energies which, in conjunction with the $H^E$ in column five, yielded the quoted values of $TS^E$. Where more than two references are indicated, the mean of the values from these sources is given. Error ranges included in some instances correspond to differences between values from diverse sources, or they represent authors' estimates where these are deemed significant. In general, the excess enthalpies are probably in error by less than ±5 cal. mole$^{-1}$, except as otherwise indicated in Table II; in some cases the range of uncertainty is as small as ±1 cal. mole$^{-1}$. Large excess enthalpies, such as occur for the hydrocarbon–fluorocarbon mixtures, are subject to correspondingly greater errors, of course. Uncertainties in the values given for $TS^E_{obsd}$ are difficult to assess inasmuch as they represent differences between experimental excess enthalpies $H^E_{obsd}$ and excess free energies $G^E_{obsd}$, the two quantities usually having been determined by different investigators. The observed excess volumes are quoted to the last digit believed to be significant.

**Table II.** Comparison of Calculated and Observed Excess Quantities for Equimolar Mixtures

| System 1,2 | $T$, °C. | $r_1/r_2$ | $s_1/s_2$ | $H^E_{obsd}$, cal. mole$^{-1}$ | $v_1^*\theta_2 X_{12}/2\bar{v}_{calcd}$, cal. mole$^{-1}$ | $X_{12}$, cal. cc. | $\bar{v}_{calcd}$ | $\bar{v}_{obsd}$ | $v^E$, cc. mole$^{-1}$ Calcd. | $v^E$, cc. mole$^{-1}$ Obsd. | $-Ts^E$, cal. mole$^{-1}$ Calcd. from $\bar{v}_{calcd}$ | $-Ts^E$, cal. mole$^{-1}$ Calcd. from $\bar{v}_{obsd}$ | $-Ts^E$, cal. mole$^{-1}$ Obsd. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Group A | | | | | | | | | | | | | |
| $CCl_4$, $c$-$C_6H_{12}$ | 25 | 0.891 | 1.04 | 35[a] | 26 | 1.7 | 1.2931 | 1.2936 | 0.12 | 0.16[b,c,d] | 9 | 13 | 18[a,e] |
| | 40 | 0.893 | 1.04 | 34[a] | 24 | 1.6 | 1.3128 | 1.3132 | 0.13 | 0.16[b] | 10 | 12 | 18[a,e] |
| | 70 | 0.893 | 1.04 | 30[a] | 20 | 1.4 | 1.3555 | 1.3559 | 0.14 | 0.17[b] | 10 | 11 | 16[a,e,f] |
| $C_6H_6$, $CCl_4$ | 25 | 0.922 | 1.03 | 27[g,h] | 20 | 1.4 | 1.2933 | 1.2923 | 0.08 | 0.01[i] | 7 | 1 | 7[j] |
| | 40 | 0.922 | 1.03 | 30 (±1)[k,l] | 21 | 1.5 | 1.3119 | 1.3110 | 0.10 | 0.04[i] | 9 | 3 | 11[j] |
| | 70 | 0.923 | 1.03 | (30)[m] | 21 | 1.5 | 1.3538 | 1.3535 | 0.13 | 0.11 (±0.03)[i,n] | 10 | 9 | (12)[j,m] |
| $C_6H_6$, $c$-$C_6H_{12}$ | 25 | 0.821 | 1.07 | 195 (±5)[o] | 142 | 10.0 | 1.2995 | 1.2995 | 0.65 | 0.65 (±0.01)[p,q] | 53 | 53 | 117[r] |
| | 40 | 0.823 | 1.07 | 180 (±10)[o] | 128 | 9.1 | 1.3190 | 1.3190 | 0.66 | 0.66[p] | 52 | 52 | 109[r] |
| | 70 | 0.824 | 1.07 | 155[o] | 105 | 7.7 | 1.3613 | 1.3609 | 0.70 | 0.67[p] | 51 | 48 | 95[r] |
| $CCl_4$, $C(CH_3)_4$ | 0 | 0.863 | 1.05 | 75 (±5)[s] | 61 | 4.1 | 1.3118 | 1.3149 | −0.75 | −0.5[s,t] | 1 | 17 | −1(± 8)[s,t] |
| $c$-$C_6H_{12}$, $C(CH_3)_4$ | 0 | 0.974 | 1.01 | ... | 27[u] | 1.7[u] | 1.3030 | 1.3021 | −0.92 | −1.0[s,t] | ... | ... | ... |
| $C_6H_6$, $C(CH_3)_4$ | 0 | 0.795 | 1.08 | ... | 121[u] | 8.6[u] | 1.3158 | 1.3167 | −0.58 | −0.5[s,t] | ... | ... | .. |
| $CCl_4$, $SiCl_4$ | 20 | 0.865 | 1.05 | 42[v] | 31 | 2.1 | 1.3060 | 1.3067 | −0.01 | 0.05[w] | ... | ... | ... |
| | 25 | 0.866 | 1.05 | 36 (±4)[v,x] | 27 | 1.8 | 1.3130 | 1.3138 | −0.05 | 0.02 (±0.01)[w,y] | 7 | 12 | 16 (± 10)[z] |
| $CCl_4$, $TiCl_4$ | 20 | 0.853 | 1.05 | 42[v] | 33 | 2.1 | 1.2680 | 1.2677 | 0.11 | 0.08[w] | ... | ... | ... |
| $CCl_4$, $SnCl_4$ | 20 | 0.819 | 1.07 | 69[v] | 51 | 3.3 | 1.2847 | 1.2875 | 0.23 | 0.46[w] | ... | ... | ... |
| $SiCl_4$, $TiCl_4$ | 20 | 0.986 | 1.00 | 38[v] | 33 | 1.9 | 1.2824 | 1.2814 | −0.29 | −0.38[w] | ... | ... | ... |
| $SiCl_4$, $SnCl_4$ | 20 | 0.947 | 1.02 | 64[v] | 48 | 2.8 | 1.3000 | 1.3011 | 0.03 | 0.13[w] | ... | ... | ... |
| $TiCl_4$, $SnCl_4$ | 20 | 0.960 | 1.01 | 45[v] | 35 | 2.0 | 1.2650 | 1.2648 | 0.10 | 0.08[w] | ... | ... | ... |
| Ar, $CH_4$ | 91(°K.) | 0.761 | 1.10 | 25[aa] | 20 | 4.2 | 1.2740 | 1.2777 | 0.09 | 0.18[aa] | 2 | 6 | 6[aa] |
| $O_2$, Ar | 84(°K.) | 0.971 | 1.01 | 14[bb,cc] | 10 | 2.5 | 1.2942 | 1.2971 | 0.08 | 0.14[cc] | 4 | 7 | 5[bb,cc] |
| Ar, $N_2$ | 84(°K.) | 0.839 | 1.06 | 12[cc] | 9 | 2.2 | 1.3418 | 1.3375 | −0.08 | −0.18[cc] | 1 | −3 | 4[cc] |
| $O_2$, $N_2$ | 77(°K.) | 0.816 | 1.07 | 11[bb,dd] | 9 | 2.0 | 1.2926 | 1.2893 | −0.13 | −0.21[dd,ee] | 0 | −3 | 1[bb] |
| Group B | | | | | | | | | | | | | |
| $C_6H_6$, $n$-$C_6H_{14}$ | 25 | 0.695 | 0.95 | 205[q] | 147 | 9.3 | 1.3153 | 1.3140 | 0.57 | 0.46[q] | 56 | 49 | 129[ff] |
| $C_6H_6$, $n$-$C_7H_{16}$ | 25 | 0.608 | 0.98 | 225 (±5)[h,gg] | 163 | 9.8 | 1.3036 | 1.3013 | 0.83 | 0.62 ±(0.02)[q,hh,ii] | 61 | 47 | 142[hh] |
| $c$-$C_6H_{12}$, $n$-$C_6H_{14}$ | 20 | 0.845 | 0.89 | 51 (±1)[q,jj] | 37 | 2.0 | 1.2992 | 1.3004 | 0.04 | 0.15[q,kk,ll] | 12 | 19 | 34[jj] |
| $c$-$C_6H_{12}$, $n$-$C_7H_{16}$ | 20 | 0.741 | 0.91 | 64 (±4)[h,gg,mm] | 47 | 2.4 | 1.2898 | 1.2906 | 0.21 | 0.30 (±0.05)[q,ii] | 17 | 23 | 64[mm] |
| Group C | | | | | | | | | | | | | |
| $C_6H_6$, $(C_6H_5)_2$ | 70 | 0.560 | 1.17 | 34[nn] | 38 | 2.3 | 1.2753 | 1.2771 | −0.48 | −0.30[oo] | 0 | 16 | 15[pp,qq] |
| Group D | | | | | | | | | | | | | |
| $n$-$C_6H_{14}$, $n$-$C_6F_{14}$ | 35 | 0.684 | 1.16 | 516[rr] | 335 | 17.0 | 1.4099 | 1.4262 | 3.37 | 5.38[ss] | 171 | 257 | 200[rr,tt] |
| $c$-$CH_3 \cdot C_6H_{11}$, $c$-$CF_3 \cdot C_6F_{11}$ | 65 | 0.688 | 1.13 | 670[uu] | 439 | 21.5 | 1.4052 | 1.4322 | 3.9 | 7.3[uu] | 214 | 362 | 340[uu] |

[a] D. S. Adcock and M. L. McGlashan, *Proc. Roy. Soc.* (London), **A226**, 266 (1954). The empirical equation derived between 10 and 55° was extrapolated to estimate the heat of mixing at 70°. [b] See Table I, ref. *b*. [c] A. Bellemans, *Bull. soc. chim. Belges*, **66**, 636 (1957). [d] M. D. Peña and M. L. McGlashan, *Trans. Faraday Soc.*, **57**, 1511 (1961). [e] G. Scatchard, S. E. Wood, and J. M. Mochel, *J. Am. Chem. Soc.*, **61**, 3206 (1939). [f] I. Brown and A. H. Ewald, *Australian J. Sci. Res.*, **A3**, 306 (1950). [g] J. A. Larkin and M. L. McGlashan, *J. Chem. Soc.*, 3425 (1961). [h] G. W. Lundberg, *J. Chem. Eng. Data*, **9**, 193 (1964). [i] See Table I, ref. *h*. [j] G. Scatchard, S. E. Wood, and J. M. Mochel, *J. Am. Chem. Soc.*, **62**, 712 (1940). [k] Ch. G. Boissonnas and M. Cruchaud, *Helv. Chim. Acta*, **27**, 994 (1944). [l] J. R. Goates, R. J. Sullivan, and J. Bevan, *J. Phys. Chem.*, **63**, 589 (1959). [m] The heat of mixing observed at 40° was used in this instance. [n] L. A. K. Staveley, W. I. Tupman, and K. R. Hart, *Trans. Faraday Soc.*, **51**, 323 (1955). [o] Estimated graphically from the heats of mixing at various temperatures between 15 and 90° as reported in the following references: G. Scatchard, L. B. Ticknor, J. R. Goates, and E. R. McCartney, *J. Am. Chem. Soc.*, **74**, 372 (1952); R. Thacker and J. S. Rowlinson, *Trans. Faraday Soc.*, **50**, 1036 (1954); C. P. Brown, A. R. Mathieson, and J. C. J. Thynne, *J. Chem. Soc.*, 4141 (1955); W. R. Moore and G. E. Styan, *Trans. Faraday Soc.*, **52**, 1556 (1956); R. M. A. Noordtzij, *Helv. Chim. Acta*, **39**, 637 (1956); D. E. Nicholson, *J. Chem. Eng. Data*, **6**, 5 (1961); see also ref. *h* and *l* of this table. [p] S. E. Wood and A. E. Austin, *J. Am. Chem. Soc.*, **67**, 480 (1945). [q] A. R. Mathieson and J. C. J. Thynne, *J. Chem. Soc.*, 3708 (1956). [r] G. Scatchard, S. E. Wood, and J. M. Mochel, *J. Phys. Chem.*, **43**, 119 (1939). [s] A. Englert-Chwoles, *J. Chem. Phys.*, **23**, 1168 (1955). [t] See Table I, ref. *a*. [u] Since no heat of mixing data have been reported for these systems, the values of $X_{12}$ indicated were so chosen as to match the experimental excess free energies as follows: 44 cal. mole$^{-1}$ for cyclohexane–neopentane and 135 cal. mole$^{-1}$ for benzene–neopentane. (See Table I, ref. *a*, and ref. *s* of this table.) [v] A. Kolbe and H. Sackmann, *Z. physik. Chem.*, **31**, 281 (1962). [w] See Table I, ref. *q*. [x] R. D. Vold, *J. Am. Chem. Soc.*, **59**, 1515 (1937). [y] See Table I, ref. *e*. [z] S. E. Wood, *J. Am. Chem. Soc.*, **59**, 1510 (1937). [aa] M. Lambert and M. Simon, *Physica*, **28**, 1191 (1962). [bb] C. M. Knobler, R. J. J. Van Heijningen, and J. J. M. Beenakker, *ibid.*, **27**, 296 (1961). [cc] R. A. H. Pool, G. Saville, T. M. Herrington, B. D. C. Shields, and L. A. K. Staveley, *Trans. Faraday Soc.*, **58**, 1692 (1962). [dd] C. M. Knobler, H. F. P. Knaap, and J. J. M. Beenakker, *Physica*, **26**, 142 (1960). [ee] H. F. P. Knaap, M. Knoester, and J. J. M. Beenakker, *ibid.*, **27**, 309 (1961). [ff] See ref. 3, Chapter 4, p. 147. [gg] C. P. Brown, A. R. Mathieson, and J. C. J. Thynne, *J. Chem. Soc.*, 4141 (1955). [hh] I. Brown and A. H. Ewald, *Australian J. Sci. Res.*, **A4**, 198 (1951). The excess free energy at 25° was estimated by linear extrapolation of the data reported at 60 and 80°. [ii] F. Danusso, *Atti accad. nazl. Lincei*, **13**, 131 (1952). [jj] V. Mathot, *Bull. soc. chim. Belges*, **59**, 111 (1950). [kk] H. Klapproth, *Nova Acta Leopoldina*, **9**, 305 (1940). [ll] J. Gómez-Ibáñez and C.-T. Liu, *J. Phys. Chem.*, **65**, 2148 (1961). [mm] J. L. Crützen, R. Haase, and L. Sieg, *Z. Naturforsch.*, **5a**, 600 (1950). [nn] G. Kortüm, G. Dreesen, and H.-J. Freier, *ibid.*, **8a**, 546 (1953). [oo] J. Marechal, *Bull. soc. chim. Belges*, **61**, 149 (1952). [pp] J. H. Baxandale and B. V. Enüstün, *Phil. Trans. Roy. Soc. London*, **A243**, 169 (1951). [qq] D. H. Everett and M. F. Penney, *Proc. Roy. Soc.* (London), **A212**, 164 (1952). [rr] A. G. Williamson and R. L. Scott, *J. Phys. Chem.*, **65**, 275 (1961). [ss] R. G. Bedford and R. D. Dunlap, *J. Am. Chem. Soc.*, **80**, 282 (1958). [tt] R. D. Dunlap, R. G. Bedford, J. C. Woodbrey, and S. D. Furrow, *ibid.*, **81**, 2927 (1959). [uu] D. E. L. Dyke, J. S. Rowlinson, and R. Thacker, *Trans. Faraday Soc.*, **55**, 903 (1959).

Analysis of the dependence of the various excess quantities on composition has not been undertaken for the reason that comparison of theoretical prediction with the observed compositional dependence would be indecisive for the mixtures of nonpolar, small molecules considered. Hence, results are quoted only for the equimolar mixture, interpolated where necessary from observations at other compositions.

The mixtures are arranged in four groups. The largest of these, group A, comprises binary mixtures of molecules which are approximately spherical. Group B consists of mixtures of cyclic hydrocarbons with *n*-alkanes. The respective components in these mixtures differ in form, and also to some degree in size. The benzene–diphenyl system, designated as the single member of group C, is of special interest on account of the homologous (monomer–dimer) relationship of its two components. The disparity in molecular size for the components of this mixture is greater than for any other system considered here. Reserved for group D are the hydrocarbon–perfluorocarbon systems; their special properties obviously call for separate classification.

*Calculations.* As inspection of the relationships in the preceding paper will show, explicit definition of the segment or element having the core volume $v^* = \mathrm{v}_1^*/r_1 = \mathrm{v}_2^*/r_2$ is unnecessary. It suffices to specify the ratio $r_1/r_2 = \mathrm{v}_1^*/\mathrm{v}_2^*$ of the molar core volumes and similarly the ratio $s_1/s_2$ of the surface contact sites per segment for the respective components. These ratios are given in the third and fourth columns, respectively, of Table II, the latter having been calculated as explained below. This ratio, $s_1/s_2$, finds use in the calculations associated with Table II only for the purpose of separating the interaction parameter $X_{12}$ presented in column seven from the quantity given in column six. The site fraction $\theta_2$ required to effect this separation depends on $s_1/s_2$ (see eq. 16*). Succeeding calculations summarized in Table II involve the product $\theta_2 X_{12}$ (column six) and not $X_{12}$ alone. The latter quantity will be needed, however, for testing the Berthelot relationship (Table IV). For completeness, we include here an account of the methods used for calculating $s_1/s_2$ although the values obtained have no effect on the comparisons of observed and calculated results which it is the main purpose of Table II to present.

For the molecules of the A group and for methylcyclohexane and perfluoromethylcyclohexane of group D, we take the number of sites $r_i s_i$ per molecule to be proportional to the surface area of a sphere of the same core volume. Thus

$$r_1 s_1/r_2 s_2 = (\mathrm{v}_1^*/\mathrm{v}_2^*)^{2/3}$$

$$s_1/s_2 = (r_1/r_2)^{-1/3} = (\mathrm{v}_1^*/\mathrm{v}_2^*)^{-1/3} \tag{8}$$

The molecular surface areas for the *n*-alkanes and perfluoro-*n*-hexane have been calculated by ascribing to them the form of right cylinders having lengths given by $L^* = 1.27(n + 1.05)$ in Å. where $n$ is the number of carbon atoms in the molecule. The factor 1.27 Å. corresponds to the projection of the C–C bond on the molecular axis of the planar form; the constant 1.05 establishes consistency with the relationship[4] $\mathrm{v}^* = 14.15(n + 1.05)$ cc. mole$^{-1}$ for the molar volumes of the *n*-alkanes at 25°. Diphenyl has been treated as a cylinder capped with hemispherical ends, the radii being equated to that for benzene treated as a sphere and the length being chosen to match the volume $\mathrm{v}^*$ for diphenyl.

By use of the relationships given in the preceding paper,[1] all excess quantities for the binary mixture may be calculated from the sets of characteristic parameters for the respective pure components together with the additional parameter $X_{12}$ (or $\theta_2 X_{12}$) for the particular pair. Conversely, values of $X_{12}$ (or $\theta_2 X_{12}$) could be calculated from each of the excess quantities $\mathrm{H^E}$, $\mathrm{V^E}$, and $\mathrm{S^E}$ for a given mixture. We have chosen to test the theoretical relationships by first calculating $X_{12}$ from the observed excess enthalpy for the given mixture and then calculating the other excess quantities from the value of $X_{12}$ thus obtained.

According to the preceding paper, the excess enthalpy $\mathrm{H^E} = \Delta H_\mathrm{M}/N$ depends explicitly on $X_{12}$ as expressed by the last term of eq. 34′* and implicitly on $X_{12}$ through the reduced volume $\tilde{v}$ for the mixture. The connection between $X_{12}$ and $\tilde{v}$ rests on eq. 27* for $T^*$ for the mixture, which for purposes at hand may be transcribed to express the reduced temperature as

$$\tilde{T} = T/T^* = \left(\frac{\varphi_1 p_1^* \tilde{T}_1 + \varphi_2 p_2^* \tilde{T}_2}{\varphi_1 p_1^* + \varphi_2 p_2^*}\right) \times \left(1 - \frac{\varphi_1 \theta_2 X_{12}}{\varphi_1 p_1^* + \varphi_2 p_2^*}\right)^{-1} \tag{9}$$

The reduced temperature for the mixture, calculated according to eq. 9 from the composition, the parameters for the pure components, and the chosen value of $\theta_2 X_{12}$, is substituted in the reduced equation of state, (1), to obtain the calculated reduced volume.[8] Substitution of $\tilde{v}$, thus calculated, together with $\theta_2 X_{12}$ into eq. 34* or 34′*, yields the corresponding value of $\mathrm{H^E}$. Values of $\theta_2 X_{12}$ which reproduce the experimental excess enthalpies have been determined through solution by trial in this manner. Results of these calculations, expressed as $\mathrm{v}_1^* \theta_2 X_{12}/2\tilde{v}$, are tabulated in the sixth column of Table II. The corresponding $X_{12}$ are given in the following column, and the reduced volumes $\tilde{v}_{\mathrm{calcd}}$ calculated from the chosen $\theta_2 X_{12}$ are given in column eight. Shown for comparison are the observed reduced volumes $\tilde{v}_{\mathrm{obsd}}$ computed from the experimental molar volumes $\mathrm{v}_{\mathrm{obsd}}$ according to the relationship

$$\tilde{v} = \mathrm{v}/(x_1 \mathrm{v}_1^* + x_2 \mathrm{v}_2^*) \tag{10}$$

where $x_1$ and $x_2$ are the mole fractions equal to 0.500 for the mixtures considered. Calculated and observed excess molar volumes $\mathrm{V^E}$ are tabulated in the tenth and eleventh columns of the table. These are related to the reduced volumes as

$$\tilde{v} - \tilde{v}^\circ = \tilde{v}^\mathrm{E} = \mathrm{V^E}/(x_1 \mathrm{v}_1^* + x_2 \mathrm{v}_2^*) \tag{11}$$

where

$$\tilde{v}^\circ = \varphi_1 \tilde{v}_1 + \varphi_2 \tilde{v}_2 \tag{12}$$

is the "ideal" reduced volume which would obtain if additivity of volumes prevailed.

The excess entropies represented by the $T\mathrm{S^E}$ in the third from last column of Table II complete the set of excess quantities calculated from the values of $\theta_2 X_{12}$

(8) Since eq. 1 is not explicitly solvable for $\tilde{v}$, the calculation of $\tilde{v}$ from $\tilde{T}$ is advantageously carried out as follows.[5] By eq. 1, find $\tilde{T}^\circ$ corresponding to $\tilde{v}^\circ$, the "ideal" reduced volume according to eq. 12. Then, with a usually negligible approximation, the excess reduced volume is given by

$$\tilde{v}^\mathrm{E} = (\partial \tilde{v}/\partial \tilde{T})(\tilde{T} - \tilde{T}^\circ) = (\tilde{v}^\circ)^{7/3}[4/3 - (\tilde{v}^\circ)^{1/3}]^{-1}(\tilde{T} - \tilde{T}^\circ)$$

from which $\tilde{v} = \tilde{v}^\circ + \tilde{v}^\mathrm{E}$ may be calculated.

(column six) selected on the basis of the excess enthalpies. These have been calculated from the $\tilde{v}_{calcd}$ according to eq. 38* for $s^R$, with $s^E$ equated to $s^R$ (see eq. 4) for all mixtures except benzene–diphenyl. For this system the difference between the combinatory and ideal entropy calculated from eq. 6 and 5, respectively, yields $T(\Delta s_{comb} - \Delta s_{id}) = 28$ cal. mole$^{-1}$, which has been combined with $Ts^R$ according to eq. 4 to obtain the value of $Ts^E$ given in the table. Shown for comparison in the next to last column are the values of $Ts^E$ similarly calculated for the various systems according to eq. 38* using the experimental reduced volumes $\tilde{v}_{obsd}$ instead of $\tilde{v}_{calcd}$. Inasmuch as $X_{12}$ is not explicitly represented in eq. 38*, this calculation depends only on the reduced volume $\tilde{v}_{obsd}$ or on the excess molar volume $v^E{}_{obsd}$ to which it is directly related; it is independent of the measured excess enthalpy.

## Results

*The Excess Enthalpy.* The quantity $v_1^*\theta_2X_{12}/2\tilde{v}$ given in the sixth column of Table II may be identified through eq. 34'* as the "contact interaction" contribution to the enthalpy of mixing. The difference between $H^E{}_{obsd}$ (column five) and the contact term (column six) represents the "equation of state" contribution to the enthalpy, as expressed by other terms in this equation. This contribution depends[1,5] (see eq. 34'*) not only on the reduced volume of the mixture, and therefore on the excess volume, but also on the difference between the reduced volumes $\tilde{v}_1$ and $\tilde{v}_2$ of the pure components.

The equation of state contribution is positive for all systems considered save one. These observations should not be generalized, however. This contribution tends to be negative for mixtures of components with very different reduced volumes. Mixtures of *n*-alkanes differing considerably in chain length (*e.g.*, *n*-hexane with *n*-hexadecane) are illustrative.[5,9] For these the equation of state terms may dominate the contact term, thereby rendering the enthalpy of mixing negative[5] and setting the stage for emergence of separation into two phases at elevated temperatures.[5,10] Systems of this character are not included within the scope of the present study. Although the equation of state terms are dominated by the contact terms for most of the systems included in Table II, the former will be seen to be significant in the majority of cases.

*The Excess Volume.* A direct test of the theory is afforded by comparison of the excess volumes $v^E{}_{calcd}$ and $v^E{}_{obsd}$ given in columns 10 and 11 of Table II. The former having been calculated from the parameter $\theta_2X_{12}$ chosen to match the observed excess enthalpy, the comparison relates the excess volume to the mixing enthalpy. The agreement is remarkably good. Negative as well as positive values occur, and the sign is predicted unerringly for systems whose excess volumes depart significantly from zero. Only the hydrocarbon–fluorocarbon systems of group D show large discrepancies between observed and calculated excess volumes. The calculated values are large and positive but not as large as those reported.

(9) Th. Holleman, *Physica*, **29**, 274 (1963).
(10) A. J. Davenport and J. S. Rowlinson, *Trans. Faraday Soc.*, **59**, 78 (1963); J. S. Rowlinson and P. I. Freeman, *Pure Appl. Chem.*, **2**, 329 (1961); P. I. Freeman and J. S. Rowlinson, *Polymer*, **1**, 20 (1960).

For all other systems the standard deviation is 0.11 cc. mole$^{-1}$; for systems of group A it is 0.09 cc. mole$^{-1}$. Positive and negative deviations occur with about equal frequency. The algebraic average deviation is +0.02 cc. mole$^{-1}$ (group D excluded), which is scarcely significant. It will be apparent from inspection of the table that a simple correlation of the excess volume with $H^E$ does not exist. Equation of state considerations assume foremost importance except in those cases where $X_{12}$ is large.

A clue to the factors affecting $v^E$ is afforded by eq. 9 for $\tilde{T}$ considered in conjunction with eq. 1. If the characteristic temperatures $T_1^*$ and $T_2^*$ for the pure components should be equal, and this will be seen from Table I to be very nearly the case for $CCl_4$, $c$-$C_6H_{12}$, and $C_6H_6$, then the first of the two factors comprising the right-hand member of eq. 9 simplifies to $\tilde{T}_1$ or $\tilde{T}_2$. If also $X_{12} = 0$, then $\tilde{v} = \tilde{v}_1 = \tilde{v}_2 = \tilde{v}°$ and $v^E = 0$. A positive value of $X_{12}$ increases $\tilde{T}$ for the mixture, thus making $\tilde{v} > \tilde{v}°$; hence, $v^E > 0$, and its magnitude depends exclusively on $\theta_2X_{12}$ relative to $\varphi_1p_1^* + \varphi_2p_2^*$. Excess volumes for the various systems consisting of binary combinations from the aforementioned set of components are readily rationalized on this basis. Another mixture conforming approximately to this description is $O_2$–Ar.

If the characteristic temperatures of the components differ considerably but $p_1^* = p_2^*$ and $X_{12} = 0$, then the reduced temperature for the mixture will be given by $\varphi_1\tilde{T}_1 + \varphi_2\tilde{T}_2$; *i.e.*, $\tilde{T}$ is the linear interpolation of $\tilde{T}_1$ and $\tilde{T}_2$ with the segment fraction composition. In this respect it partakes of the same character as $\tilde{v}°$ of eq. 12. Owing, however, to the pronounced upward curvature[5] of $\tilde{v}$ with $\tilde{T}$ which is manifest in the reduced equation of state, the reduced volume $\tilde{v}$ of a mixture having the linearly interpolated $\tilde{T}$ must fall below $\tilde{v}°$ given by eq. 12. Accordingly, $\tilde{v}^E$ and $v^E$ are negative, with magnitudes which increase rapidly with the difference between $T_2^*$ and $T_1^*$. Examples closely following this description are benzene–diphenyl and mixtures of *n*-alkanes treated in a previous paper.[5] In each of these instances the negative excess volume is moderated to some extent by a small, positive interaction parameter $X_{12}$.

Usually the component with the larger $T^*$ will also have the larger $p^*$. Inspection of eq. 9 shows that if $T_2^* \neq T_1^*$, the expected inequality of the $p^*$ values will reduce $\tilde{T}$ below its value for $p_1^* = p_2^*$. By extension of the argument of the preceding paragraph, therefore, $v^E$ must be rendered more negative by $p_2^* < p_1^*$ given that $T_2^* < T_1^*$. Examples are provided by group A mixtures of neopentane with $CCl_4$, with $c$-$C_6H_{12}$, and with $C_6H_6$, respectively, and also by the $O_2$–$N_2$ mixture.

Of the several mixtures of the tetrahalides of group IV elements investigated by Sackmann and coworkers,[11] one of them, $SiCl_4$–$TiCl_4$, appears at first sight to be anomalous in being characterized by a rather large negative excess volume. Explanation is readily found, however, in the parameters for the component liquids. $T^*$ for $TiCl_4$ is considerably larger than that for $SiCl_4$ and indeed larger than for any of the other tetrahalides. (This relates directly, of course, to the low thermal expansion coefficient for

(11) (a) See Table I, ref. *q*; (b) see Table II, ref. *v*.

$TiCl_4$.) The negative excess volume resulting from this difference is enhanced by the difference between the $p^*$ values for the two components; it is diminished somewhat by the small positive value of $X_{12}$. The observed result is in substantial agreement with that calculated by the present method.

As will be apparent from the equations involved, the primary determinant of the excess volume resides in the difference between the thermal expansion coefficients for the two components. These coefficients fix $T_1^*$ and $T_2^*$. The inequality of $p_1^*$ and $p_2^*$ and the value of $X_{12}$ may be important also, but their effects usually are secondary.

The calculated excess volumes are subject to vitiation by errors in $T^*$ and $p^*$ for the pure components. The former parameter depends on the thermal expansion coefficient $\alpha$; the latter is principally determined by the thermal pressure coefficient $\gamma$. It is readily found from the foregoing relationships that

$$\partial \bar{v}^E/\partial \ln \alpha_2 \cong [(p_2^* - p_1^*)/2(p_1^* + p_2^*)] \times \bar{v}_2^{2/3}\alpha_2 T/(\alpha_2 T + 1)^2 \quad (13)$$

in first approximation. Thus, the effect on $v^E_{calcd}$ of an error in $\alpha_2$ is approximately proportional to $(p_2^* - p_1^*)/(p_1^* + p_2^*)$. Among systems of Table II for which this quantity is large (*e.g.*, for benzene–neopentane or benzene–*n*-hexane) an error of 2% in one of the $\alpha$'s would alter $v^E$ by about 0.05 cc. mole$^{-1}$. In other systems the effect would be substantially less. Thus, errors contributed by the experimental expansion coefficients are generally small but not necessarily negligible in all cases.

Errors in the thermal pressure coefficients undoubtedly are more serious. We find, again in first approximation and assuming $X_{12}$ to be small, that

$$\partial \bar{v}^E/\partial \ln \gamma_2 \cong (\tilde{T}_2 - \tilde{T}_1)[p_1^* p_2^*/(p_1^* + p_2^*)^2] \times 3\bar{v}^{7/3}/(4 - 3\bar{v}^{1/3}) \quad (14)$$

The sensitivity of $v^E$ to $\gamma_2$ is approximately proportional to the difference $\tilde{T}_2 - \tilde{T}_1$. For the maximum value of *ca.* 0.015 for this quantity (*e.g.*, for $CCl_4$–$C(CH_3)_4$ or for $C_6H_6$–$(C_6H_5)_2$), an error of 5% in $\gamma_2$ would alter $v^E$ by about 0.15 cc. mole$^{-1}$. For other systems characterized by smaller reduced temperature differences, the sensitivity to $\gamma_1$ and $\gamma_2$ is correspondingly diminished.

In light of these considerations, most of the differences between $\bar{v}_{calcd}$ and $\bar{v}_{obsd}$ in Table II appear to be within the limits of error in the former quantity accruing from errors in the equation of state data for the pure components, assuming the errors to range up to 2% in $\alpha$ and up to 5% in $\gamma$. Discrepancies unaccountable in this manner occur only for the group D systems and for $CCl_4$–$SnCl_4$. For the latter mixture, differences between $T_2^* - T_1^*$ and $p_2^* - p_1^*$ are small, hence the calculated excess volume should be relatively insensitive to both the $\gamma$ and the $\alpha$ for the pure components.

*The Excess Entropy.* Comparison of the two columns of calculated values for $Ts^E$ in Table II illustrates the sensitivity of the calculated excess entropy to the excess volume of the mixture, other parameters being fixed. The effects of errors in the $\alpha$ and the $\gamma$ for the pure components may be analyzed by procedures paralleling those applied above to the excess volume. An error of 2% in $\alpha_1$ affects $Ts^E$ by a maximum of 3 cal. mole$^{-1}$ in the most sensitive situations encountered in Table II. The effect of an error in $\gamma$ for one of the components depends on the difference between $\bar{v}$ and $\bar{v}_i$, as will be apparent from eq. 38*. When this difference is large, as for the $CCl_4$–$C(CH_3)_4$ mixtures, a 5% error in $\gamma_2$ would alter $Ts^E$ by about 7 cal. mole$^{-1}$.

Examination of the calculated and observed results presented in the last three columns of Table II leads to the following conclusions: (1) the sign of the calculated excess entropy is positive in nearly all cases, and this accords with observation; (2) the calculated excess entropy is generally less than the value observed; (3) the disparity between calculated and observed values is large for mixtures of benzene with aliphatic hydrocarbons, including cyclohexane; (4) mixtures of cyclohexane with *n*-hexane and *n*-heptane show similar discrepancies though of much smaller magnitude; (5) agreement for most of the other systems of group A, including the condensed gases, is satisfactory; (6) the benzene–diphenyl and the hydrocarbon–fluorocarbon systems (group D) display agreement within probable limits of uncertainty in the various experimental quantities involved, including the possible error in the value of $\gamma$ for diphenyl; (7) the two columns of calculated $Ts^E$ correlate about equally well with the experimental results.

Inequality of molecular sizes for the two components suggests itself as a possible factor augmenting the excess entropy. Only for the benzene–diphenyl system has this difference been taken into account in the calculations. For several of the other systems in Table II the difference between the core volumes of the two components, indicated by the ratio $r_1/r_2$, approaches that for the benzene–diphenyl pair. This fact might suggest that eq. 6 should be adopted for the combinatorial entropy in preference to the ideal entropy, eq. 5, for other mixtures as well. However, *both* molecular species in systems other than benzene–diphenyl are globular in form, and for mixtures of such molecules eq. 6 overestimates $\Delta s_{comb}$ considerably.[12] Moreover, $T(\Delta s_{comb} - \Delta s_{id})$ calculated according to eq. 5 and 6 converges rapidly to zero as $r_1/r_2$ approaches unity.[13] For these reasons, we have refrained from introducing corrections for the disparity of molecular sizes in other systems. This is not to deny the possible importance of the difference between the sizes of the components of a mixture of molecules of globular form.

The large excess entropies for benzene–cyclohexane (group A) and for the benzene–*n*-alkane mixtures (group B) suggest an ordered arrangement in pure benzene which is dissipated by mixing. In keeping with this explanation, the observed excess entropy for the former mixture diminishes with temperature. On the other hand, the absence of a similar anomaly in the $C_6H_6$–$CCl_4$ system indicates that its occurrence depends on the character of the second component as well.

Judgment of the lesser discrepancies between observation and calculation for other systems, insofar as

(12) J. H. Hildebrand and R. L. Scott, "Regular Solutions," Prentice-Hall, Englewood Cliffs, N. J., 1962, p. 29.

(13) For an equimolar mixture at 25° $T(\Delta s_{comb} - \Delta s_{id})$ calculated in this way is about 19 cal. mole$^{-1}$ for $r_1/r_2 = 0.60$ and about 3.7 cal. mole$^{-1}$ for $r_1/r_2 = 0.80$.

these discrepancies exceed the combined effects of incident experimental errors, should be tempered by the realization that the ideal entropy mixing law is indeed an idealization and therefore approximate when applied to real systems. A small departure from its prescribed value of 410 cal. mole$^{-1}$ for $Ts$ for an equimolar mixture at 25° would affect the observed result significantly. The fact that the observed excess entropy generally exceeds the calculated value suggests, of course, that mixing of dissimilar species tends to introduce disorder beyond the mere randomization of positions of the centers of the component molecules or segments, which alone is taken into account by the usual combinatory expressions. This is not implausible. It is noteworthy, however, that related deviations are not apparent in the excess volumes.

*The Excess Compressibility and Thermal Pressure Coefficients.* Calculated values of the equation of state parameters $\alpha$, $\gamma$, and $\kappa = \alpha/\gamma$ are fixed by the value of $X_{12}$ in conjunction with the reduced equation of state, eq. 8*, and its corollaries. Experimental values for some of these quantities provide further tests of the theory. The comparisons are conveniently carried out in terms of corresponding excess quantities.

The excess compressibility for the mixture, defined by

$$\kappa^E = -v^{-1}(\partial v^E/\partial p)_T = -\bar{v}^{-1}(\partial \bar{v}^E/\partial p)_T \tag{15}$$

can be expressed as follows on the basis of eq. 11 and 12

$$\kappa^E = \kappa - (\varphi_1\bar{v}_1\kappa_1 + \varphi_2\bar{v}_2\kappa_2)\bar{v}^{-1} \tag{16}$$

Evaluating the compressibility $\kappa$ using eq. 8* and setting $p = 0$, we find

$$\kappa^E = 3\bar{v}^2/p^*[(\bar{v}^{1/3} - 1)^{-1} - 3] - (\varphi_1\bar{v}_1\kappa_1 + \varphi_2\bar{v}_2\kappa_2)\bar{v}^{-1} \tag{17}$$

Excess compressibilities calculated from the $\bar{v}_{calcd}$ given in Table II using this equation are compared in Table III with experimental results for several systems. In order to provide a basis for judging the significance of differences between calculated and observed results given in the last two columns, the mean compressibilities for the mixtures have been assembled in the third column of the table. The agreement on the whole is quite satisfactory. The largest discrepancies between calculated and observed results are again exhibited by the benzene–cyclohexane system.

An excess thermal pressure coefficient may be defined similarly as the deviation from the additive value, *i.e.*

$$\gamma^E = \gamma - (x_1\gamma_1 + x_2\gamma_2) \tag{18}$$

The calculated thermal pressure coefficient $\gamma$ may be obtained from $p^*$ for the solution, as given by eq. 25*, by resort to eq. 3. Substitution in eq. 18 gives $\gamma^E_{calcd}$. We thus find $\gamma^E_{calcd} = -0.017$ cal. cc.$^{-1}$ deg.$^{-1}$ for the equimolar mixture of *n*-hexane with perfluoro-*n*-hexane at 35°, in exact agreement with $\gamma^E_{obsd}$ found by Dunlap and Scott[14] for this system.

*The Berthelot Relationship.* According to the Berthelot geometric mean rule as expressed by eq. 28* of the preceding paper

$$\Delta\eta/\eta_{11} = [1 - (\eta_{22}/\eta_{11})^{1/2}]^2 \tag{19}$$

(14) See Table I, ref. *k*.

**Table III.** Excess Compressibilities for Equimolar Mixtures

| System | $T$, °C. | $\kappa \times 10^3$, cc. cal.$^{-1}$ | $-\kappa^E \times 10^3$, cc. cal.$^{-1}$ Calcd. | Obsd. |
|---|---|---|---|---|
| $C_6H_6$, $CCl_4$ | 25 | 4.29 | 0.03 | 0.04[a] |
| | 40 | 4.85 | 0.05 | 0.04[a] |
| | 70 | 6.29 | 0.07 | 0.05[a] |
| $C_6H_6$, $c$-$C_6H_{12}$ | 25 | 4.42 | 0.30 | 0.14[a] |
| | 40 | 5.00 | 0.33 | 0.17[a] |
| | 70 | 6.51 | 0.41 | 0.24[a] |
| $CCl_4$, $C(CH_3)_4$ | 0 | 7.12 | −1.18 | −0.94[b] |
| $CCl_4$, $SiCl_4$ | 20 | 5.60 | −0.12 | −0.02[c] |
| $CCl_4$, $TiCl_4$ | 20 | 3.96 | 0.04 | −0.03[c] |
| $CCl_4$, $SnCl_4$ | 20 | 4.34 | 0.12 | 0.06[c] |
| $SiCl_4$, $TiCl_4$ | 20 | 5.15 | −0.35 | −0.48[c] |
| $SiCl_4$, $SnCl_4$ | 20 | 5.45 | −0.09 | −0.12[c] |
| $TiCl_4$, $SnCl_4$ | 20 | 3.97 | 0.04 | −0.01[c] |

[a] Estimated from the data reported by G. A. Holder and E. Whalley, *Trans. Faraday Soc.*, **58**, 2108 (1962). [b] See Table I, ref. *c*. [c] H. Sackmann and A. Boczek, *Z. physik. Chem.*, **29**, 329 (1961).

With the aid of eq. 11* and 23*, this equation yields the following relationship between $X_{12}$ and parameters for the pure components

$$X_{12}/p_1^* = [1 - (s_1/s_2)^{1/2}(p_2^*/p_1^*)^{1/2}]^2 \tag{20}$$

The experimental value of the ratio occurring in the right-hand members of eq. 19 and 20 and given in the third column of Table IV has been calculated from

**Table IV.** Comparison of Interaction Parameters Calculated from the Berthelot Relation with Those Observed

| System | $T$, °C. | $\eta_{22}/\eta_{11} = (s_1p_2^*/s_2p_1^*)$ | $\Delta\eta/\eta_{11} = X_{12}/p_1^*$ Calcd. $\times 10^3$ | Obsd. $\times 10^3$ | $\eta_{12}$(obsd.)/$\eta_{12}$(calcd.) |
|---|---|---|---|---|---|
| $CCl_4$, $c$-$C_6H_{12}$ | 25 | 0.97 | 0 | 13 | 0.99 |
| $C_6H_6$, $CCl_4$ | 25 | 0.93 | 1 | 9 | 1.00 |
| $C_6H_6$, $c$-$C_6H_{12}$ | 25 | 0.90 | 2 | 67 | 0.97 |
| $CCl_4$, $C(CH_3)_4$ | 0 | 0.71 | 25 | 29 | 1.00 |
| $c$-$C_6H_{12}$, $C(CH_3)_4$ | 0 | 0.75 | 18 | 13 | 1.00 |
| $C_6H_6$, $C(CH_3)_4$ | 0 | 0.66 | 35 | 56 | 0.99 |
| $CCl_4$, $SiCl_4$ | 20 | 0.86 | 5 | 15 | 0.99 |
| $CCl_4$, $TiCl_4$ | 20 | 1.03 | 0 | 16 | 0.99 |
| $CCl_4$, $SnCl_4$ | 20 | 1.03 | 0 | 25 | 0.99 |
| $SiCl_4$, $TiCl_4$ | 20 | 1.20 | 9 | 18 | 1.00 |
| $SiCl_4$, $SnCl_4$ | 20 | 1.19 | 9 | 26 | 0.99 |
| $TiCl_4$, $SnCl_4$ | 20 | 1.00 | 0 | 15 | 0.99 |
| Ar, $CH_4$ | 91(°K.) | 1.06 | 1 | 60 | 0.97 |
| $O_2$, Ar | 84(°K.) | 0.88 | 4 | 30 | 0.99 |
| Ar, $N_2$ | 84(°K.) | 0.88 | 4 | 30 | 0.99 |
| $O_2$, $N_2$ | 77(°K.) | 0.79 | 13 | 24 | 0.99 |
| $C_6H_6$, $n$-$C_6H_{14}$ | 25 | 0.64 | 40 | 62 | 0.99 |
| $C_6H_6$, $n$-$C_7H_{16}$ | 25 | 0.66 | 34 | 65 | 0.98 |
| $c$-$C_6H_{12}$, $n$-$C_6H_{14}$ | 20 | 0.71 | 26 | 16 | 1.01 |
| $c$-$C_6H_{12}$, $n$-$C_7H_{16}$ | 20 | 0.73 | 21 | 19 | 1.00 |
| $C_6H_6$, $(C_6H_5)_2$ | 70 | 1.30 | 19 | 16 | 1.00 |
| $n$-$C_6H_{14}$, $n$-$C_6F_{14}$ | 35 | 0.97 | 0 | 170 | 0.91 |
| $c$-$CH_3 \cdot C_6H_{11}$, $c$-$CF_3 \cdot C_6F_{11}$ | 65 | 0.93 | 1 | 203 | 0.90 |

data assembled in Tables I and II. Calculated and observed values of $X_{12}/p_1^*$ are compared in the fourth and fifth columns of Table IV. The former have been obtained according to eq. 20 in the Berthelot approximation; the latter are ratios of $X_{12}$ and $p_1^*$ values taken from Tables II and I, respectively. The very large discrepancies demonstrate the futility of resort to the Berthelot relation as a means of securing the interaction parameter $X_{12}$ from properties of the pure components alone. Inaccuracies in $p_1^*$ and $p_2^*$ (*i.e.*, in the experimental $\gamma_1$ and $\gamma_2$) and perhaps also in the estimates of $s_1/s_2$ may in part be responsible for the poor correspondence between the two columns of figures. The calculated value is obviously very sensitive to $s_1p_2^*/s_2p_1^*$ when this quantity is near unity, and discrepancies are greatest when this is the case. The prevalence of observed values in excess of those calculated suggests, however, that experimental errors are not alone responsible for the differences but that the Berthelot relationship is itself insufficiently reliable for the purpose.[15]

From a different standpoint, the geometric mean rule appears to succeed quite well in predicting the value of the parameter $\eta_{12}$ characterizing the interaction energy between a pair of unlike molecules. The ratio of the "observed" $\eta_{12} = \eta_{11}X_{12}/p_1^*$ to its value $\eta_{12} = \eta_{11}(\eta_{22}/\eta_{11})^{1/2}$ calculated according to this rule is shown in the last column of Table IV. If the hydrocarbon–fluorocarbon systems are excepted, the mean deviation of the two quantities is only 1% although the observed values are lower than those calculated according to the geometric mean rule in most cases. For the purpose at hand, however, a much higher order of accuracy in $\eta_{12}/\eta_{11}$ is required, as will be apparent from examination of the relevant equations. The much larger departures of hydrocarbon–fluorocarbon mixtures from the Berthelot relation has been noted and discussed by Scott.[15]

## Concluding Remarks

Perhaps the most serious shortcoming of the analysis of experimental data presented above occurs in the equation of state for the pure liquids, as is evidenced by the changes of the characteristic parameters with temperature (Table I). The effect of this deficiency on the analysis of results for mixtures obviously cannot have been eliminated altogether by the device of choosing those values of the parameters for the pure components corresponding to the temperature applicable to the data for the given mixture. Thus, a theory which would better represent the equation of state for the pure liquids could be expected to afford the basis for improvement in the treatment of mixtures. Obvious refinements, such as representation of the energy (see eq. 6*) as depending on an arbitrary inverse power of the volume differing from unity (*i.e.*, on $1/v^m$), treatment of $v^*$ as temperature dependent, or allowance for change of $c$ with temperature, have failed to afford a more satisfactory representation of the experimental equation of state covering changes in both pressure and temperature. More drastic revision of the simple partition function adopted in preceding papers[1,4,5] of this series appears to be required in order to achieve significant improvement. Whether such refinement is possible without inordinate sacrifice in simplicity of application to mixtures seems questionable.

Whatever the nature of refinements which may be forthcoming in the future, the analysis of experimental results presented in this paper serves to demonstrate the importance of equation of state contributions to the excess properties of mixtures. These contributions may, of course, be treated in other ways by more elaborate schemes, but the reality of their importance can scarcely be questioned.

Pending the appearance of a more elegant and possibly more satisfactory theory of liquid mixtures, it is perhaps noteworthy that the present one pushes available experimental data to the limits of their accuracy and, in some cases, beyond these limits. The kinds of experimental results needed should be more clearly apparent from the investigations presented in this paper and in its predecessors.

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(15) For a critical discussion of the Berthelot geometric mean approximation, see R. L. Scott, *J. Phys. Chem.*, **62**, 136 (1958).