We can see from Table 2 that if both $y_1 = f_1(T)$ and $y_2 = f_2(T)$ are replaced algebraically in Equation (26) by their respective values as a function of T, the resulting loop will then be represented by Figure 12c. This is a simple loop for which there exists a reciprocal path.

There are no easy manipulations which one can make in order to get a reciprocal path for loop A. Therefore direct substitution techniques for this problem become useless. A graphical representation of

$$x_{3N} = f(x_{3_0}) \tag{34}$$

has been obtained from a digital computer and is shown in Figure 13. The curve is not monotonic and there is a discontinuity at $x_{3_0} = 0.699$. There are two values R_1 and R_2 for which $x_{3_0} = x_{3N}$. On the forward path C convergence is always at R_1. Unfortunately, the solution to the system corresponding to $x_3 = R_1$ has no physical meaning. The reciprocal path is shown as C′ but cannot be realized via iterative computation since inverse flow is not possible for loop A.

A quasilinearization solution of this problem has been carried out. The system has eight nonlinear terms. Depending upon the initial guess for the nonlinear variables, convergence has been obtained on either the real root R_2 or the nonreal root R_1.

As we can see from the study of the last example, a solution by direct substitution loses many of its advantages when nested loops appear. However, the algorithm of Ramirez and Vestal (1972) tends to minimize the number of nested loops required to solve a problem, and therefore nested loops are fairly rare in actual design computations. If they cannot be avoided, the engineer must be very careful when he tries to get an actual solution to his problem. For this type of problem quasilinearization is recommended.

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Determination of Liquid-Mixture Solubility Parameters and Interaction Energy Densities

Integral, isothermal heat-of-condensation values for continuously generated vapors of various constant-composition mixtures, along with the isothermal densities of the condensates, enable the calculation of the cohesive energy densities of solutions. Data for the complete range of composition of the chloroform-acetone system and for a major portion of the chloroform-diethyl ether system at 35°C are reported. From these data, the specific-interaction-energy density for each system is calculated, based upon an extension of the Scatchard-Hildebrand Regular Solution Theory.

The essential equality of the specific-interaction energy-density values for the two systems indicates a preponderance of the same kind of hydrogen bonding (CH- - -O) in each.

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SCOPE

Despite many proposals, no comprehensive theory has evolved to explain the behavior and predict the properties of many classes of solutions. Moreover, testing of various theories has been generally limited because sufficient experimental data to establish valid parameters are not available.

The simplest theory, the Scatchard-Hildebrand Regular Solution Theory, is especially notable for its successful correlation and prediction of nonpolar solution properties. This theory predicts the molar energy of mixing of a two-component, additive-volume system by means of the equation:

$$\Delta U_{\text{mixing}} = \phi_1\phi_2(C_{11} + C_{22} - 2C_{12})V_{\text{mixt.}} \tag{1}$$

The ϕ's represent molal-average volume fractions of the components while C_{11} and C_{22} are their cohesive energy densities (C.E.D.'s) as defined by Hildebrand (1919). Evaluation of the energy density of interaction between the dissimilar molecules C_{12} presents the major difficulty in using this equation. Scatchard (1931) and Hildebrand (1929) made the basic assumptions that solutions in which the molecules are randomly oriented and the volumes are

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additive involve only dispersion forces. They concluded that each such solution has a characteristic interaction energy density equal to the geometric mean of the C.E.D.'s of the pure components.

Although the Regular Solution Theory has been quite successfully used for the study of nonpolar liquids (for which it was derived), Prausnitz (1969) claims its most serious defect is the geometric-mean assumption. For example, when the components are polar or when strong specific interactions are involved, the geometric-mean rule is significantly inadequate.

In the research described below, equipment and procedures were developed to make possible the evaluation of the interaction-energy-density term C_{12} from experimentally determined cohesive energy densities of mixtures. The rationale of these evaluations stems from the original assumption of the Regular Solution Theory that the cohesive energy density of a binary mixture is a quadratic function of the additive-volume fractions, the C.E.D.'s, and the interaction energy density of the components (Hildebrand and Scott, 1950). Thus,

$$C_{\text{mixt.}} = C_{11}\phi_1^2 + 2C_{12}\phi_1\phi_2 + C_2\phi_2^2 \qquad (2)$$

The term $C_{\text{mixt.}}$ is essentially an experimentally determinable quality for all compositions of volatile-component solutions, provided the integral, isothermal heat of vaporization of the binary mixture can be experimentally evaluated, along with the density of the liquid. In 1919, Hildebrand made the assumption that the cohesive energy of a pure liquid was equal to its energy of vaporization, and at low pressures the energy of vaporization of a pure component could be equated to the enthalpy of vaporization minus the work of expansion. Hence, for a mixture, the present research makes the adaptation that

$$C_{\text{mixt.}} = \frac{\Delta U^{\text{vap}}_{\text{mixt.}}}{V_{\text{mixt.}}} = \frac{\Delta H^{\text{vap}}_{\text{mixt.}} - RT}{V_{\text{mixt.}}} \qquad (3)$$

With $C_{\text{mixt.}}$ evaluated from Equation (3), the interaction energy density can be calculated from Equation (2). This provides opportunity for extension of the Regular Solution Theory without the restriction imposed by the geometric-mean rule but including the other assumptions mentioned above.

In essence, the desired data were determined by continuous condensation of constant-composition vapor streams generated by means of an Othmer-type still under various isobaric conditions to obtain constant dew-point temperature. A heat-energy balance over the primary condenser, combined with the determination of the rate of flow of the cooled-condensate in the unit previously used by Shah and Donnelly (1967), enabled the calculation of the integral, isobaric heat of condensation for each particular mixture. The constancy of dew-point temperature for all experimental mixtures enabled calculation of the cohesive energy density for any particular mixture at 35°C.

The values so calculated are not only of significant use for the ultimate determination of the interaction energy density, as mentioned above, but they are of particular value in the explanation of some of the solubility characteristics of mixed solvents used industrially in polymer solution processes (Burrell, 1967).

CONCLUSIONS AND SIGNIFICANCE

In the manner described above, integral isothermal heat-of-condensation values were obtained at 35°C for two binary systems. With corrections for the work of expansion of the vapors, and with experimentally determined composition and density data, the cohesive-energy-density values for selected mixtures over the full range of system compositions were calculated.

Such values provided an experimentally based evaluation of the interaction-energy-density parameter for these systems according to Equation (2). Neglecting the extremes of composition, these interaction-energy-density parameters are shown in Figure 5 to be composition-dependent, but they are satisfactorily representable—within plus or minus 3%—by straight lines of the same general slope. The commonly used geometric-mean values of these parameters would not only be constant over each of the entire systems, but the relative magnitude of the values for the separate systems is reversed from the order indicated by the lines of Figure 5.

These experimentally based parameters also make it possible to test the concepts of Blanks and Prausnitz (1964) for extending the Regular Solution Theory beyond the simple dispersion aspects of the pure-state solubility parameters. Following their procedure and data, the values of C_{12} enabled the calculation of a specific interaction function for each of the two systems. Even with all of the procedures of others used for making these calculations, it is significant that the portion of the interaction energy density representing the specific interaction function of the two separate systems is representable by essentially the same linear curve (Figure 6) when plotted as a function of the proton-donor compound (chloroform).

The method described provides an important tool for the experimental determination of the solubility parameter of volatile liquid mixtures, which are widely employed in the surface coatings industry. Further, it can be concluded from the data obtained by this method that the specific interaction function may be common to other binary systems in which the only type of hydrogen bonding between the components is of the CH- - -O kind. If this conclusion is valid, the research presented in this paper should have significant value in the calculation of mixed-solvent interaction-energy-density parameters when used in conjunction with the concepts of Blanks and Prausnitz (1964) and with the homomorph concepts of Brown et al. (1953) and of Bondi and Simkin (1957).

DETAILED EXPERIMENTAL WORK

The need for better understanding of solution behavior is emphasized by the widespread use of nonideal solvents for extraction and polymeric solution processes in related industries. Hildebrand and Scott (1950) and Prausnitz (1969) provide adequate historical and technical literature review of these developments. Both of these sources discuss the success of the Regular Solution Theory for the handling of nonpolar solutions; they likewise present some of the various modifications proposed to extend the Regular Solution Theory for handling solutions of polar substances. Much of this latter effort has been of analytical nature.

From the standpoint of engineering, the major emphasis must rest on the development of methods for the rapid experimental determination of solubility behavior. In this direction, the work of Shah and Donnelly (1967) provided the means for simple and accurate evaluation of the integral isobaric heats of condensation of binary vapor mixtures. The research of this paper concerns the direct adaptation of that equipment to produce data from which the integral isothermal heats of condensation are obtainable. These data yield for the first time the cohesive-energy-density values for volatile mixtures in accordance with Equation (3) above.

The importance of this development is emphasized by the greatly increased breadth of application of the Regular Solution Theory and its many modifications. Since no work of this nature has been previously reported, the experimental apparatus and procedure are presented in moderate detail in the supplement* to this paper. General statements amplifying the description of the developments indicated in the Scope section are given below.

GENERAL EXPERIMENTAL SYNOPSIS

A modified Othmer still and a Condensate-Return-Unit for determining the rate of circulation have been described by Shah (1965). Additional modifications were made to permit sampling at subatmospheric pressures. Details of these modifications are described in the dissertation by Lui (1970).

In essence, the overall experimental procedure consisted of achieving liquid-vapor equilibrium in the still at the desired temperature, making an enthalpy balance over the condensing stage of the heat exchangers, determining the rate of condensation, and withdrawing samples for composition and density determinations.

The experimental procedure produced condensation under isobaric conditions, within one-half mm of the established point for any run. This isobaric process is simple to accomplish, and complete condensation is obtained by subcooling several degrees. Although the composition of the condensed phase varies with temperature as it progresses through the heat exchanger from its dew-point to below its bubble-point temperatures, steady state operation is assured by constancy of pressure and lack of accumulation of liquid in the cold-trap in the vacuum system. Thus, there is complete assurance that the enthalpy balance over the main condenser, when corrected for the subcooling, produces the integral, isobaric heat of condensation of the vapor being generated. (Calibration runs reproduced literature values for acetone, for example, at three different pressures to within 1%.)

CONVERSION OF DATA

The requirement of isothermal enthalpy values for this phase change makes it necessary to convert the isobaric data for each equilibrium run to the integral, isothermal heat of condensation. Constancy of the dew-point temperature of the vapor at 35°C provides the overall isothermal basis for the condensation process, regardless of the vapor composition. In the systems investigated, the condensate was cooled several degrees below its bubble-point temperature for the pressure of the system during each run, and its temperature was measured at regular intervals by means of a thermocouple in a stilling bulb in the condenser outlet. By neglecting the effect of pressure on the enthalpy of the liquid, the integral, isothermal heat of condensation is equal to the sum of the integral isobaric heat of condensation and the increase in enthalpy of the liquid phase between 35°C and the subcooled-liquid temperature.

For the systems involved in this research, experimentally determined heat-capacity data for mixtures covering the complete range of composition were available in the International Critical Tables (vol. 5, p. 126).

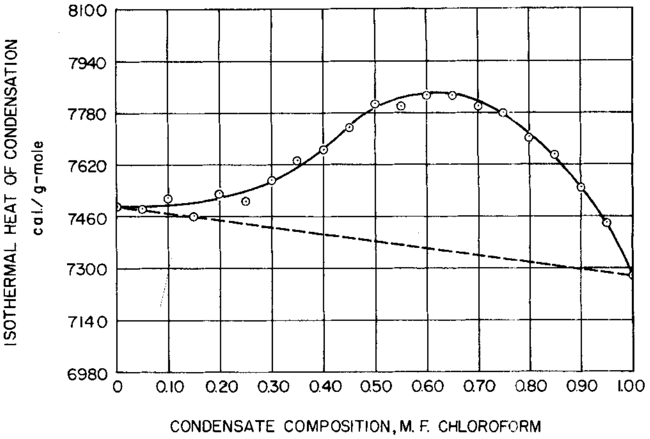

Fig. 1. Isothermal heat of condensation for chloroform-acetone at 35°C.

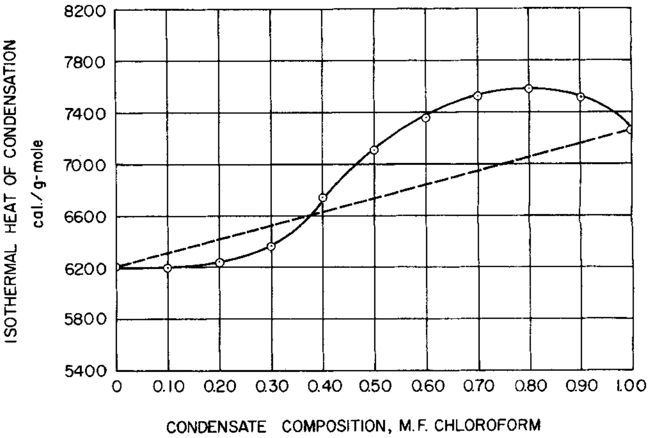

Fig. 2. Isothermal heat of condensation for chloroform-diethyl ether at 35°C.

RESULTS

Experimental data were obtained for two of the pure components and for two binary systems to evaluate the integral, isothermal heats of condensation at 35°C, in accordance with the above procedure. Twelve data points, each representing the average of three or more runs of constant composition, were obtained for the chloroform-acetone system; eight data points of similarly averaged nature were obtained for the chloroform-diethyl ether system, principally in the range of zero to 0.65 mole fraction of the ether. For safety, the ether-rich portion of the system was obtained by extrapolation from 0.65 mole fraction ether to the heat of condensation of pure ether at 35°C, as obtained from the International Critical Tables (vol. 5, p. 138). The values in calories per gram were plotted as a function of composition; then, values calculated on a molar basis from the smoothed curves through these data points were selected at even compositions. These values are presented in the Supplement; the curves representing the systems are shown in Figures 1 and 2.

Analysis and Discussion

From the compositions of the samples of the condensate and their densities, the molar volumes of the mixtures were calculated, and smooth curves representing the molar density as a function of composition of the systems were prepared. In accordance with Equation (3) the cohesive energy densities $C_{\text{mixt.}}$ were calculated at even values of composition for each of the systems and are presented in Figures 3 and 4.

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* The Supplement has been deposited at Document No. 02093 with the National Auxiliary Publications Service (NAPS), c/o Microfiche Publications, 305 E. 46th St., New York 10017 and may be obtained for $1.50 for microfiche and $5.00 for photocopies.

INTERACTION ENERGY DENSITY

From the smooth curves of Figures 3 and 4, the values of $C_{\text{mixt.}}$ enable the calculation of the interaction energy density values for the various compositions by means of Equation (2). The calculations were made for even compositions and are presented in the second and third columns of Table 1. Negligible excess volume was assumed for all mixtures, since any deviation from the molal-average-volume curve is insignificant in comparison with the inaccuracy involved in assuming the applicability of Equation (2) to these polar systems.

The calculated values of C_{12} are plotted in Figure 5 for the two systems. The straight lines drawn over the range of 0.1 to 0.9 mole fraction chloroform for each system seems to be a reasonable approximation of the variation of interaction energy density with composition, neglecting the extremes.

The concentration-dependence of C_{12} shown for each system invites comparison with the geometric-mean constant values of 87.7 and 64.5 for the acetone-chloroform and the ether-chloroform systems, respectively. There is strong indication that the hydrogen-bonding forces in these solution systems make the Regular Solution Theory inapplicable.

The similarity of the slopes of the interaction-energy-density lines, however, lends credence to the assumption that the same specific interaction probably occurs on mixing in each of the two systems. Accordingly, a test indicative of such similarity was made, following the method suggested by Blanks and Prausnitz (1964).

SPECIFIC INTERACTION FUNCTION

In an attempt to extend the concept of interaction energy density (C_{12}) beyond the dispersion-forces-only assumption, Blanks and Prausnitz expressed the quantity in terms of four kinds of interaction functions:

$$C_{12} = F_{\text{disp.}} + F_{(\text{di-p.})(\text{di-p.})} + F_{\text{ind.di-p.}} + F_{\text{spec.int.}} \quad (4)$$

These four functions are respectively representative of dispersion forces, di-pole-di-pole forces, induced di-pole forces, and specific interaction forces such as hydrogen bonding.

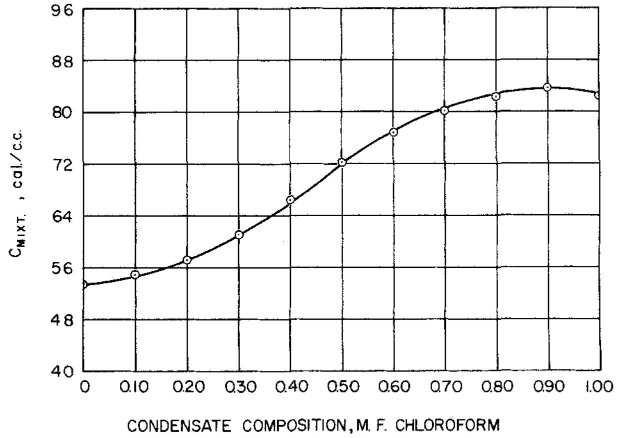

Fig. 4. Smoothed cohesive energy densities of chloroform-diethyl ether at 35°C.

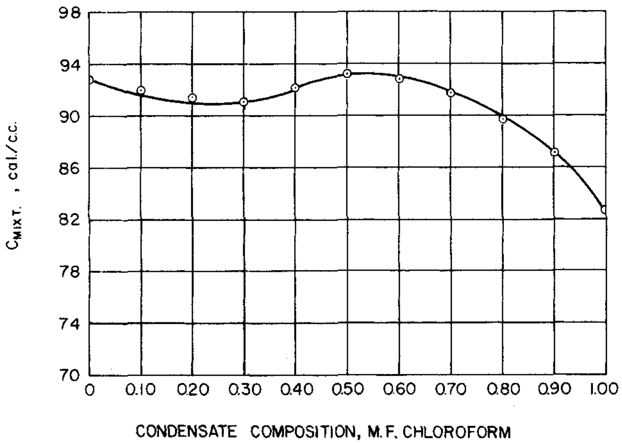

Fig. 3. Smoothed cohesive energy densities of chloroform-acetone at 35°C.

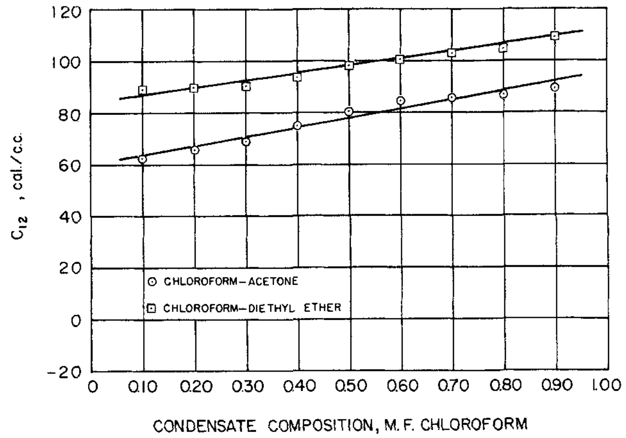

Fig. 5. C_{12} for chloroform-acetone and chloroform-diethyl ether at 35°C.

TABLE 1. CALCULATED VALUES OF C_{12} AND $F_{\text{spec.int}}$ AT 35°C

Composition, m.f. $CHCl_3$	Interaction energy density C_{12}, cal/cc $CHCl_3$-$(CH_3)_2CO$	$CHCl_3$-$(C_2H_5)O$	Specific interaction function $F_{\text{spec.int.}}$, cal/cc $CHCl_3$-$(CH_3)_2CO$	$CHCl_3$-$(C_2H_5)_2O$
0.10	89.66	63.01	1.07	(−)2.64
0.20	90.62	65.71	2.03	0.06
0.30	92.15	69.20	3.56	3.55
0.40	94.93	75.27	6.34	9.62
0.50	98.94	80.41	10.35	14.76
0.60	101.40	83.28	12.81	17.63
0.70	103.39	85.50	14.80	19.85
0.80	104.85	87.26	16.26	21.61
0.90	108.44	89.22	19.85	23.57

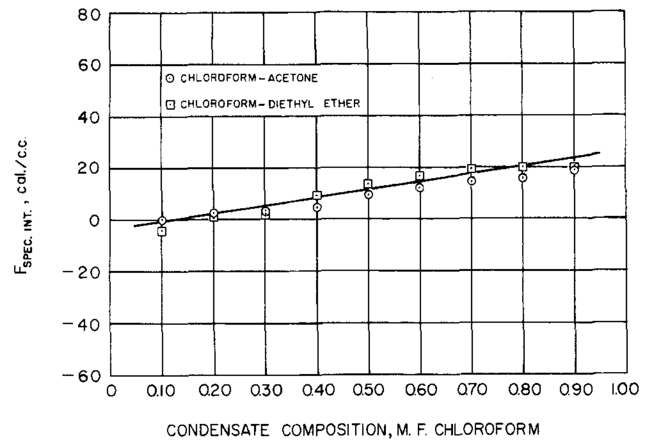

Fig. 6. Specific interaction functions at 35°C for chloroform-acetone and chloroform-diethyl ether.

In a polar-polar binary system, the effects of induced di-poles are considered relatively small; hence, the induced-di-pole function can be neglected. In order to define the other functions, Blanks and Prausnitz used the concept of nonpolar homomorphs set forth by Brown (1953) and by Bondi and Simkin (1957). The cohesive energy density for any simple polar substance can be represented, according to Blanks and Prausnitz, by

$$C_i = (\lambda_i)^2 + (\tau_i)^2 \qquad (5)$$

In this equation, λ is the nonpolar contribution to the solubility parameter, being considered equivalent to the solubility parameter of the nonpolar homomorph. τ is the polar contribution to the solubility parameter.

With these newly defined solubility parameters, the functions in Equation (4) were described in the geometric-mean manner, neglecting the di-pole effect:

$$C_{12} = \lambda_1\lambda_2 + \tau_1\tau_2 + F_{\text{spec.int.}} \qquad (6)$$

Blanks and Prausnitz (1964) presented values for the polar and nonpolar portions of the solubility parameters for pure chloroform, acetone, and diethyl ether at several temperatures; however, for these calculations, the values at 25°C were used to calculate the specific interaction function at 35°C via Equation (6).

The results of these calculations are presented in the last two columns of Table 1 and in Figure 6. Despite the relatively large differences existing between the curves of C_{12} for the individual systems, the values of the specific interaction function are surprisingly close. A single straight line represents the calculated values satisfactorily. The significance of this emerges from the interpretation of Equation (6).

As a term in the evaluation of the interaction-energy-density summation, $F_{\text{spec.int.}}$ is also an energy density function arising from the strong hydrogen bonding known to exist in these systems. It appears that the only type of bonding possible in the systems under consideration is one involving the proton of chloroform with the exposed and slightly charged oxygen atoms of the ketone and the ether. Therefore, the values for the specific interaction energy density may be the exothermic interaction energy density for this CH- - -O type of hydrogen bond.

The assuredly significant conclusion is that the very close values of the specific interaction energy density of these two systems with similar hydrogen-bonding interactions indicate that $F_{\text{spec.int.}}$ may be a function common to other systems involving the same type of hydrogen bonding (CH- - -O). It appears plausible, at least, that the values for $F_{\text{spec.int.}}$ reported here could be applied in reverse fashion for systems containing chloroform and an oxygen atom which is not a part of a hydroxyl group.

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NOTATION

C_i = cohesive energy density, cal/cc
C_{12} = interaction energy density between components 1 and 2, cal/cc
$C_{\text{mixt.}}$ = cohesive energy density of a mixture, cal/cc
C_p = specific heat at constant pressure, cal/g-mole °C
$F_{\text{spec.int.}}$ = specific interaction energy function, cal/cc
$\Delta H_{\text{iso-b}}$ = integral isobaric heat of condensation, cal/g-mole
$\Delta H_{\text{iso-t}}$ = integral isothermal heat of condensation, cal/g-mole
ΔU_{mixing} = energy of mixing, cal/g-mole
$\Delta U^{\text{vap.}}_{\text{mixt.}}$ = energy of vaporization of mixture, cal/g-mole
$V_{\text{mixt.}}$ = molar volume of liquid mixture, cc/g-mole
λ = nonpolar solubility parameter, $(\text{cal/cc})^{1/2}$
τ = polar solubility parameter, $(\text{cal/cc})^{1/2}$
ϕ = molal-average volume fraction of component

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