VOLUME CHANGES ON MIXING FOR BINARY MIXTURES OF LIQUIDS

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Contents

I. Introduction

"Of the various thermodynamic functions for the mixing process, the volume change on mixing at constant pressure . . . is one of the most interesting, yet certainly still one of the least understood." Hildebrand and Scott[1] wrote this (1962) at a time when the subject of this review was entering a phase of renewed interest and development. This renewed interest is closely tied to the advances in the theories of solutions which were made in the 1960's. For a long time the precision attainable on measuring volume changes on mixing was several orders of magnitude better than theory could calculate. The first breakthrough in the corresponding states theories was in predicting accurately the *sign* of the volume change on mixing. Current theories of solution are much more accurate with respect to sign and magnitude, and this has spawned a vigorous expansion in techniques and measurement. Although the subject of this review is narrowly restricted to volume changes on mixing, the theories discussed and the subject, itself, cannot be separated from the other excess thermodynamic properties of solutions. The subject will continue to be of interest in the 1970's simply because the experiments are relatively easy to perform with great precision and because the volume change on mixing is a sensitive indicator to the accuracy of theories of solution.

There have been a number of short reviews and compilations on volume changes on mixing. These include surveys in the relevant volumes of the *Annual Review of Physical Chemistry*, a survey[2] for simple systems both in the gaseous and liquid states, and a short review by Gomel.[3] One early survey[4] cited data for 28 systems, another[5] cited data for 46 systems, and a third[6] cited qualitative data of pharmaceutical interest for some 66 systems (45 aqueous and 21 tinctures). Markgraf and Nikuradse[7] report data for 29 mixtures at 20°, and Rodger, Hsu, and Furter[8] report data for mixtures of CCl_4 with 23 hydrocarbons at 20°. Millero[9] has written a review on the partial molal volumes of electrolytes in aqueous solutions which includes a compilation of partial molal volumes at infinite dilution.

Our search of the literature was restricted to volume changes on mixing at constant pressure for binary mixtures of liquids. We interpreted this to include mixtures of liquefied gases and gas–gas mixtures near atmospheric pressure. (For convenience we shall use the term "liquefied gas" to apply to measurements on liquid–liquid systems whose components are gaseous at 1 atm and 25°.) *Chemical Abstracts* was searched from Volume 49 (1955) through 69 (1968) since Timmermans[10] covers all of the earlier literature on binary systems. We have on file copies of almost all of the papers cited and have included references to those papers cited by Timmermans which were especially relevant with respect to apparatus, precision, systems reported, or theory. In general, we have only considered data sufficiently precise for this review where the density was determined to four decimal places (*ca.* ±0.0002 g cm^{-3}) or the volume change

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(1) J. H. Hildebrand and R. L. Scott, "Regular Solutions," Prentice-Hall, Englewood Cliffs, N. J., 1962, Chapter 8.

(2) J. J. M. Beenakker and H. F. P. Knaap, *Progr. Low Temp. Phys.*, **5**, 287 (1967).

(3) M. Gomel, *J. Chim. Phys. Physicochim. Biol.*, **65**, 1915 (1968).

(4) J. B. Peel, W. M. Madgin, and H. V. A. Briscoe, *J. Phys. Chem.*, **32**, 285 (1928).

(5) H. Hirobe, *J. Fac. Sci., Univ. Tokyo, Sect. 1*, **1**, 155 (1926).

(6) K. H. Ludde, *Pharm. Prax. Beilage Pharmazie*, **6**, 61 (1958).

(7) H.-G. Markgraf and A. Nikuradse, *Z. Naturforsch.*, **9a**, 27 (1954); *Chem. Abstr.*, **49**, 39*i* (1955).

(8) A. J. Rodger, C. C. Hsu, and W. F. Furter, *J. Chem. Eng. Data*, **14**, 362 (1969).

(9) F. J. Millero, "Structure and Transport Processes in Water and Aqueous Solutions," R. A. Horne, Ed., Wiley Interscience, New York, N. Y., 1970, Chapter 15.

(10) J. Timmermans, "The Physico-Chemical Constants of Binary Systems in Concentrated Solutions," Interscience, New York, N. Y.: Vol. 1, 2, 1959; Vol. 3, 4, 1960.

on mixing determined to two decimal places (*ca.* ±0.02 $cm^3 mol^{-1}$).

II. Symbols

The system of notation used in this review follows. Some specialized symbols which apply to a particular approach, and where we wished to use the author's own notation for clarity, are defined where they are used. The bar over a symbol ($\bar{X}$) denotes a partial molar property, the tilde ($\tilde{X}$) a molar property, and the superscript zero (X^0) the property of the pure components.

	Upper Case Symbols
A	Helmholtz free energy
A, B, C	arbitrary constants
B	second virial coefficient
E	energy
ΔE^V	energy of vaporization
G	Gibbs free energy
H	enthalpy
M	molarity
$\tilde{N}$	Avogadro's number
P	pressure
T, T_c	temperature (°K); critical solution temperature or critical temperature
$V, \tilde{V}$	volume, molar volume
$\bar{V}$	partial molar volume
$\tilde{V}_i^0$	molar volume of *i*th pure component
V^0	additive volume of pure components, *i.e.*, $\Sigma_i n_i \tilde{V}_i^0$
$V^E, \Delta V^M$	excess volume, volume change on mixing

	Lower Case Symbols
a, b, c, a', b', c'	arbitrary constants
d	density
k	Boltzmann's constant
m	molal
m	mixture (as subscript)
n_i	number of moles of *i*th component
t	temperature (°C)
x_i	mole fraction of *i*th component
z_i	volume fraction of *i*th component

	Greek Letter Symbols
α	coefficient of thermal expansion
β	isothermal coefficient of compressibility
γ	thermal pressure coefficient
δ	Hildebrand solubility parameter
$-\epsilon$	energy of a molecular pair at its equilibrium distance
ρ	density
σ	collision diameter

III. Methods and Apparatus

A. SOME GENERAL CONSIDERATIONS

Volume changes on mixing have been determined *via* two principal methods: directly *via* mixing the liquids and observing volume changes in dilatometers, and indirectly by measuring the density of liquid mixtures. The best single source for general information on the determination of density (*via* pycnometers, dilatometers, and other diverse methods) is the article by Bauer and Lewin.[11] In general, the following discussion will be limited to recent developments.

There are many factors which affect the precision and accuracy of measuring volume changes on mixing. The following remarks all refer to attaining an accuracy of about ±0.00002 $g cm^{-3}$ in density and about ±0.002 $cm^3 mol^{-1}$ in direct measurements.

The average coefficient of expansion of organic solvents with temperature is such that thermostat temperatures should be controlled to ±0.01° to determine the density to ±0.00001 $g cm^{-3}$. It should be noted that about one-fifth less temperature control is required for calibrations done with water and mercury, assuming that these materials are sufficiently pure. For room-temperature measurements water need not be degassed. (Caution: the density of degassed *vs.* aerated organic solvents can differ by as much as 0.0003 $g cm^{-3}$ and precautions should be taken to ensure that the mixtures are thoroughly degassed *or* aerated, and this fact should be stated explicitly.) Procedures should be designed such that evaporation into vapor spaces and evaporation losses will not change compositions beyond the capability of correcting for these effects.

Compositions of mixtures are determined by weighing each component (taking into account buoyancy corrections) or by measuring the volume of each component. In measurements where only the volume change on mixing is of interest, the precision in the composition need be no greater than the precision in the volume change. If compositions are to be determined from the densities of mixtures, then the precision in the composition is related directly to the difference in the densities of the two components and the precision in the density. A difference of 0.1 $g cm^{-3}$ between the density of pure components corresponds for fifth place density measurements to an error of about ±0.0001 in the mole fraction. When V^E is determined directly, the purity of the components is not very critical. For example, McLure and Swinton[12] found no detectable change in V^E (determined to ±0.003 $cm^3 mol^{-1}$) for mixtures with cyclohexane of 99.7 *vs.* 99.99 mol % purity. When V^E is determined by density measurements, the purity of the components is again not very critical as long as the density of the individual components is determined to the same precision as the density of the mixture. The previous comments with respect to purity, of course, must be hedged by knowledge of the extent and nature of the impurities. Adequate mixing of the components must be assured.

Timmermans[10] cites a great many measurements made early in the present century and, indeed, some measurements made much earlier. It is therefore relevant to note that the presently used density values of water are based on the measurements of Chappuis[13] (1907) and Thiesen, *et al.*[14] (1900), measurements which were made on "pure" water before isotopes had been discovered. Kell[15] has summarized recent

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(11) N. Bauer and S. Z. Lewin, "Physical Methods of Organic Chemistry," Vol. I, Part 1, 3rd ed, A. Weissberger, Ed., Interscience, New York, N. Y., 1959, pp 131–190.

(12) I. A. McLure and F. L. Swinton, *Trans. Faraday Soc.*, **61**, 421 (1965).

(13) P. Chappuis, *Trav. Mem. Bur. Intern. Poids Mesures*, 13 D1 (1907).

(14) M. Thiesen, K. Scheel, and H. Diesselhorst, *Wiss. Abhandl. Physik.-Tech. Reichsanst.*, **3**, 1 (1900).

(15) G. S. Kell, *J. Chem. Eng. Data*, **12**, 66 (1967).

measurements[16,17] and older ones[13,14] to give a precise representation of the volume properties of water at 1 atm. This equation is reproduced here for convenience (eq 1). Note

$$\rho(\text{g ml}^{-1}) = [0.9998396 + (18.224944 \times 10^{-3})t - (7.922210 \times 10^{-6})t^2 - (55.44846 \times 10^{-9})t^3 + (149.7562 \times 10^{-12})t^4 - (393.2952 \times 10^{-15})t^5]/[1 + (18.159725 \times 10^{-3})t] \quad (1)$$

that $\rho(\text{g ml}^{-1}) \times 0.999972 = \rho(\text{g cm}^{-3})$. Kell[15] also gives a table for the density of water at 1° intervals from −20 to 110° and equations for the density of $H_2{}^{18}O$, $D_2{}^{18}O$, D_2O, and T_2O. The reader is also referred to the careful enumeration of factors involved in making precision density measurements by Wade and Merriman[18] in 1909. Physical chemistry laboratory manuals[19,20] give directions for the easy (if not very precise) determination of the density of liquid mixtures.

One aspect of high-precision density measurements that has received much interest is the existence or nonexistence of "kinks" in the properties of pure components (the liquid of greatest concern has been water) and mixtures. Falk and Kell[21] have tabulated reports of discontinuities in the thermal properties of water and have carefully evaluated these reports. We, therefore, quote their conclusions:

> "The pattern common to all reports that we have examined, including those we have not discussed in detail, is that the size of the supposed discontinuity is comparable to the degree of accuracy of the measurement. Experimenters commonly overestimate their degree of accuracy, and errors often produce odd points that do not fit a smooth plot. Accordingly, we believe that the discontinuities so far reported in the properties of liquid water are artifacts. The wide scatter of temperatures at which discontinuities have been reported strongly supports this conclusion. The balance of evidence is that the physical properties of water *do* vary continuously with temperature."

In support of their conclusions we can cite our own investigation of the results reported by Wajahat Ali and Bhatti[22] on dilute aqueous ethanol solutions using the dilatometer described by Qurashi and Wajahat Ali.[23] By using large-scale graphs and least-squares fits of their[22] data, we did find "kinks" but they corresponded roughly with the emptyings and fillings of the dilatometer every 10 or 12°. We suspect that their main source of error lay in not applying stem corrections for the exposed section of capillary—we estimate these corrections to be five to ten times larger than their[23] estimated error. Korson, Drost-Hansen, and Millero,[24] who recently determined the viscosity of water with high precision in the range 8–70°, found that their results suggest no evidence for thermal anomalies, and they suggest that the reported anomalies may have arisen from structural transitions in ordered water structures near interfaces.

We agree with the suggestion by Powell and Swinton[25] that the system benzene–cyclohexane be used as a test system for measurements of V^E. This system has been carefully measured by a number of other workers.[26–29] Powell and Swinton's results are in excellent agreement with Watson, *et al.*;[28] both groups used dilatometers. The highly precise values of Wood and Austin[29] obtained by a density method were consistently higher, differing by +0.025 cm³ mol⁻¹ (for V^E = 0.639 cm³ mol⁻¹) for an equimolar mixture. Powell and Swinton state that for equimolar mixtures of benzene–cyclohexane an error of as little as ±3 × 10^{-6} in density measurements would give rise to an uncertainty of 2% (±0.013 cm³ mol⁻¹) in V^E. In general, the dilatometric method is capable of higher precision than the density method, but this leaves unexplained the unusual precision in V^E (±0.002 cm³ mol⁻¹) in Wood and Austin's measurements. For convenience we reproduce here Powell and Swinton's equation for $\bar{V}^E$ for the benzene–cyclohexane system at 25° (eq 2). The subscript 1 refers to benzene and the precision

$$\bar{V}^E = x_1x_2[2.5564 - 0.0577(x_1 - x_2) + 0.0267(x_1 - x_2)^2] \quad (2)$$

(standard deviation) of the fit to their experimental values is 0.0005.

B. DENSITY MEASUREMENTS ON MIXTURES

1. Pycnometers

Many types of pycnometers and their characteristics and handling are discussed by Bauer and Lewin.[11] The author has had much experience with the single-arm pycnometer described by Wood and Brusie[30] and used earlier by Scatchard, Wood, and Mochel.[31] This pycnometer is depicted in Figure 1 and can be used for fifth-place density measurements. The bulb has an 11-cm³ capacity and the 1-mm i.d. precision bore capillary has 11 lines lightly etched all around the stem and spaced 1 mm apart. The pycnometer is filled using a hypodermic syringe and cannula. Corrections for buoyancy and vapor space are readily applied.[30,32] Other pycnometers capable of fifth-decimal-place accuracy have been described recently.[33–36]

In the process of determining densities by pycnometric techniques, it is important to be able to also determine the composition of the mixtures with precision. Many workers have simply weighed the two components into the pycnometer. This procedure is open to many uncertainties concerning adequacy of mixing, evaporation losses, and composition of the vapor space. A better technique is to use a mixing bottle of the type described by Wood and Brusie[30] or an improved version of this described by Battino.[37] Kohler

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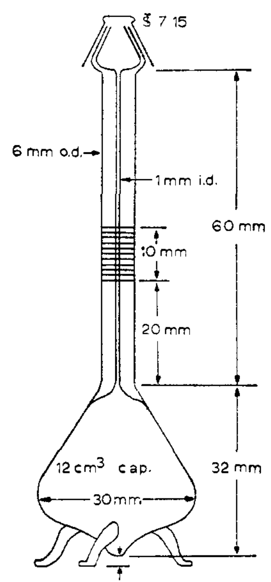

Figure 1. Single-arm pycnometer of Wood and Brusie.[30]

and Rott[33] and Ruiter[35] reported other good designs of mixing bottles.

2. Dilatometers

The basic weight dilatometer, wherein a mixture (or pure liquid) is confined by mercury and volume changes (which occur upon change of temperature) are determined by the weight of mercury expelled or added to the dilatometer, was described by Neubeck[38] in 1887. Improved versions of this have been reported by Burlew,[39] Wood and Brusie,[30] and most recently by Wirth and LoSourdo.[40] The double-arm dilatometer described by Hildebrand and Carter[41] was used for both direct measurements of volume changes on mixing and their temperature dependence (25–35°). Washington and Battino[42] describe a dilatometer convenient to use, accurate to ±0.003 cm^3 mol^{-1} in V^E, and useful over the temperature range 10–80°.

3. Magnetic Float and Other Methods

The magnetic float method has been used recently for fifth- and sixth-place density measurements on mixtures. Benjamin's apparatus[43] has a sensitivity of ±0.001%. Franks and Smith[44] describe a magnetic float technique with a sensitivity of ±0.0001% for a cell with a 600-cm^3 capacity. They give a detailed description of the method and an excellent analysis of errors. Millero[45] surveyed the earlier literature on magnetic float densitometers and described a highly versatile new apparatus with a precision of ±0.0002%, a capacity of about 32 cm^3, and a useful temperature range greater than from 20 to 50°. Drost-Hansen, *et al.*,[46] give details on a magnetic float densitometer, and Masterton and Seiler[47] fully describe their apparatus which has a reproducibility of 3 ppm.

Wirth[48] described a sinker method which is accurate to ±0.0002% for determining density differences. Klotz and Eckert[49] used a similar method.

C. DIRECT MEASUREMENT OF V^E

Apparatus for the direct measurement of V^E have been designed in two basic styles: (1) for one composition per loading of the apparatus at a single temperature; and (2) for a number of compositions per loading at a single temperature. Although it is theoretically possible to use some of the designs discussed herein to obtain the temperature dependence of V^E on a single loading, in practice most workers have not done this. [The dilatometers discussed in section III.B.2 measure the temperature variation of V^E for a single loading (composition).]

1. One Composition per Loading

The apparatus of Keyes and Hildebrand[50] (K–H) shown in Figure 2 has gone through many variations. The apparatus is basically a U-tube with mercury at the bottom to separate the two components, and with graduated capillaries on the ends of the tubes to record volumes before and after mixing. Composition is determined directly by weighing. Mixing is accomplished by rocking the apparatus, and the canted design permits ease of mixing while maintaining the ends of the capillary above the fluid level of the thermostat. The two liquids were aerated, and at the end of mixing the arms

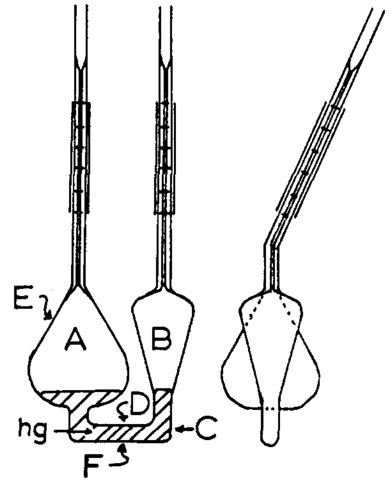

Figure 2. Double-arm pycnometer of Keyes and Hildebrand.[50] Copyright 1917 by the American Chemical Society. Reprinted by permission of the copyright owner.

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(38) F. Neubeck, *Z. Phys. Chem.*, 1, 649 (1887).

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had to be opened to the atomsphere to equalize the pressure in each arm and to prevent outgassing. The adequacy of the mixing is tested by extra rockings and checkings of the liquid levels until they remain constant. The precision attainable depends on the capacity of A and B and the capillary bore. K-H's apparatus had a precision of *ca.* ±0.003 cm^3 mol^{-1}.

Bellemans'[51] apparatus was similar to that of K-H's but used very small samples (*ca.* 1 cm^3 of each component) and had a precision of ±0.002 cm^3 mol^{-1}. The liquids are degassed in place (see Figure 3), and then the tubes are sealed under vacuum at E and E′. By letting air in through D the vapor space disappears. Mixing is accomplished by rotating the apparatus 180° with the mixture collecting in C.

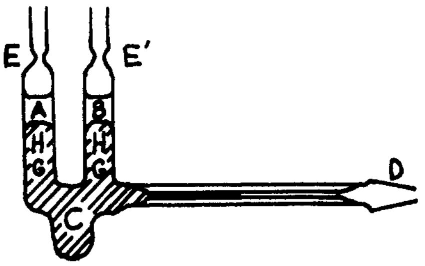

Figure 3. Bellemans'[51] dilatometer. Reprinted by permission of the author and the *Bulletin des Societes Chimiques Belges.*

Brown and Smith[52] use a ground-glass stopper on a chamber similar to A (Figure 2) and a 1.4-mm i.d. capillary attached to chamber B. The total capacity was 25 ml and the apparatus had a precision of ±0.003 cm^3 mol^{-1}. It is easier to fill and handle than the K-H apparatus. Kehlen and Sackmann[53] used a similar arrangement to measure V^{E} for mixtures of cyclohexane with several tetrachlorides. In the apparatus used by Diaz Pena and Haya,[54] chambers A and B can be reproducibly capped for ease of filling, and the capillary to determine the volume change is attached at point D (Figure 2). Their apparatus had a precision of ±0.01 cm^3 mol^{-1}. Rastogi and Nath[55] used ground-glass stoppers on A and B (Figure 2) and attached a capillary arm at E. This apparatus had the advantages of using degassed solvents, ease of filling, and a precision of ±0.001 cm^3 mol^{-1}.

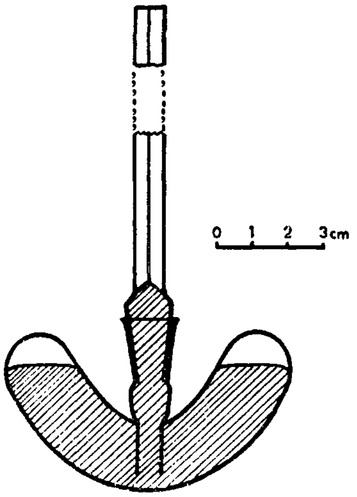

Figure 4. Dilatometer of Duncan, Sheridan, and Swinton.[56] Reprinted by permission of the authors and the Faraday Society.

In Figure 4 we see the apparatus of Duncan, Sheridan, and Swinton.[56] This apparatus requires 0.2–0.8 cm^3 of each liquid (degassed) and has the added flexibility of changeable capillaries (they used i.d.'s of 0.2–1.0 mm) to accommodate different magnitudes of change. A minor disadvantage is that the pressure before and after mixing is not the same, but this is negligible in most cases. The precision attainable is about ±0.002 cm^3 mol^{-1} or ±0.5% in V^{E}.

Wirth and Mills[57] have designed a variation of K-H's apparatus for measuring volume changes on mixing aqueous solutions of inorganic salts. In this apparatus A and B (140-ml capacity each) are closed by stopcocks, the lower portion of each tube is calibrated, and a capillary for the confining mercury is connected at point F. Volume changes as small as 2×10^{-4} cm^3 are detectable. Staveley and Spice[58] designed a one-arm apparatus specifically to determine V^{E} for very small concentrations. They measured V^{E} for primary alcohols (alcohol mole fractions in the range 0.005–0.035) in benzene, heptane, and cyclohexane.

Rasper and Kauzman[59] used the "Carlsberg" dilatometer (see ref 59 for pertinent references) for measuring V^{E} for protein solutions upon mixing with acid or alkali. The dilatometer is in the form of an inverted "V" with each solution placed in a leg of the "V" and purified kerosene confining the solutions and extending up into a capillary attached to the apex of the "V." The total volume is about 12 cm^3 and changes of *ca.* 10^{-5} cm^3 can be detected. This apparatus is a variation of that of K-H for the condition where it is possible to use a confining immiscible liquid whose density is *less* than that of the components. Garrod and Herrington[60] describe an improved version of an earlier dilatometer[61] used for measuring the apparent molar volumes and V^{E} for dilute aqueous solutions. A capsule (*ca.* 11 cm^3) containing the solute is opened with a magnet while immersed in water in a flask to which a single calibrated capillary is attached. Volume changes of 1–10 parts in 10^8 are detectable.

The dilatometer described by Holleman[62] (earlier version, ref 63) is a particularly ingenious variation of the basic principle in that it permits four compositions to be measured on a single loading. The apparatus is shown in Figure 5 where it is noted that a critical selection of angles and chamber sizes permits four successive dilutions. The apparatus has been used to determine $\bar{V}^{\mathrm{E}}$ to 1–2% for mixtures of alkanes in the range 51–126°.

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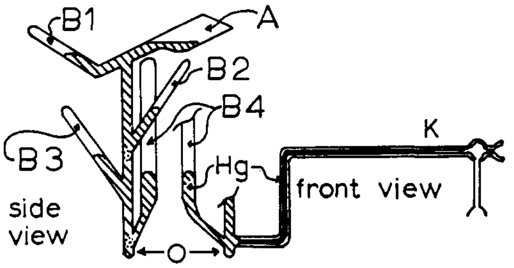

Figure 5. Holleman's[62] dilatometer for four compositions. Reprinted by permission of the North-Holland Publishing Co., Amsterdam.

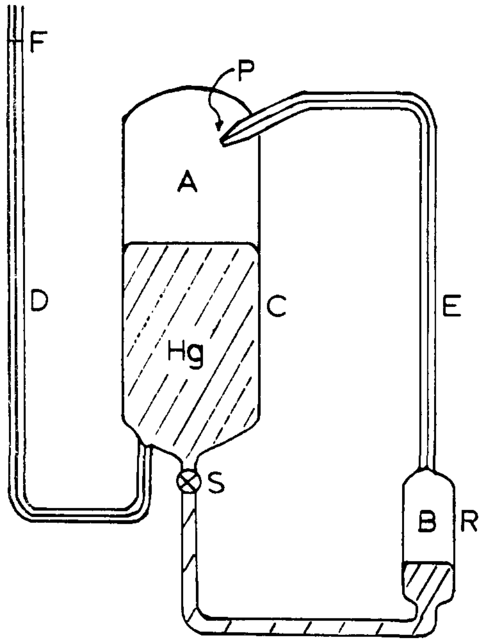

Figure 6. Principle of operation of the apparatus of Geffcken, Kruis, and Solana.[64]

2. Many Compositions per Loading

The dilatometer designed by Geffcken, Kruis, and Solana[64] has been used and modified by many workers.[12,28,65–70] The principle of operation is depicted schematically in Figure 6. The mixing chamber C is initially loaded with pure component A and mercury. Stopcock S leads to reservoir R where pure component B is confined over mercury. The mercury level in the calibrated capillary D is read with respect to a fiduciary mark F. Some provision is made for stirring the contents of C, and the entire apparatus is thermostated. When S is opened mercury from C forces some of component B into C *via* the connecting tube E. S is closed, mixing begins, and the change in level of the mercury in capillary D is noted. Successive increments of B are added in a similar way to directly determine V^E as a function of composition at one temperature. Different designs have employed different methods for determining the amount of A initially present and the incremental amounts of B added. Some designs have incorporated interchangeable capillaries at D. The main differences between the various designs is in the method of separation of the two components at point P.

The recent design of Pflug and Benson[68] utilizes a small mercury cup into which the capillary at point P extends. Their apparatus is capable of very high precision: for a $\bar{V}^E$ at one-half mole fraction of 0.2 cm^3 mol^{-1} the error was $\pm 0.5\%$, and for 0.002 cm^3 mol^{-1} the error was $\pm 5\%$. Pflug and Benson's apparatus incorporated a provision for maintaining the pressure on the system constant; although this is a small effect, it is not negligible in high precision work. Care must be taken to avoid entrapping air bubbles on filling the apparatus. However, Pflug and Benson found no difference in V^E using aerated and partially degassed samples. As a check on their dilatometer they also determined V^E by using a 10-cm^3 twin-stemmed pycnometer and the dilatometer of Duncan, *et al.*,[56] and found good agreement between the three methods while noting that it is inherent in the continuous dilution method for the results to show less scatter than the other methods.

The apparatus designed by Beath, *et al.*,[70] is shown in Figure 7. Solvents are weighed separately into bulbs A (30 cm^3) and B (50 cm^3) and are confined by mercury which is in capillaries C and D and connecting capillary S. These capillaries are all calibrated. By applying suction to G some solvent in A is added to B. Readjusting levels and reading heights on the capillaries provides all of the necessary information for determining V^E at one temperature as a function of concentration. The precision the authors obtained in determining V^E for eight ethers with CCl_4 and $CHCl_3$ at 25° was 0.005 cm^3 mol^{-1}, and their test run on the benzene +

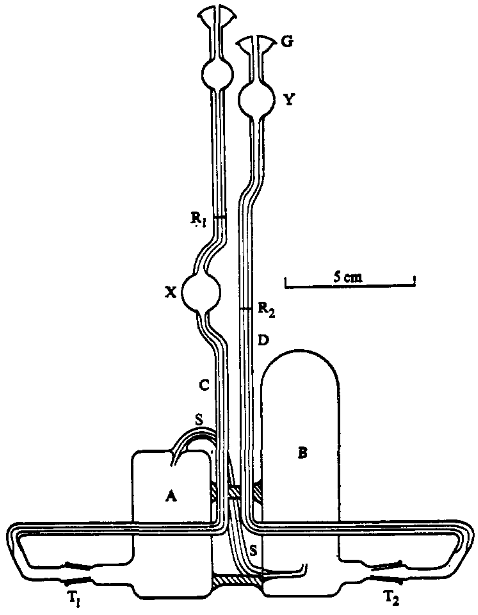

Figure 7. The apparatus of Beath, *et al.*[70] Reprinted by permission of the authors and the *Journal of Chemical Thermodynamics.*

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cyclohexane system gave a standard deviation of 0.0055 $cm^3\ mol^{-1}$. The apparatus appears simple in design and use. By using smaller bore capillaries the precision should be readily improvable.

The apparatus of Geffcken, *et al.*,[64] had a mixing chamber capacity of 250 cm^3, could reproducibly detect volume changes of 0.0002 cm^3, and was used for the determination of volume changes on successive dilutions of aqueous salt solutions. Desmyter and van der Waals' apparatus[65] had provision for degassing the components, a capacity of 25 cm^3 for the combined components, and an error of about ±1% for a $\tilde{V}^E$ of about 0.5 $cm^3\ mol^{-1}$. Wirth, *et al.*,[66] used their apparatus with a mixing chamber capacity of 350 cm^3 (volume changes determinable to ±0.0001 cm^3) for determining volume changes on mixing electrolyte solutions. Van Ness and coworkers[71-74] used the dilatometer described by Pardo[67] which has a mixing chamber capacity of 200 cm^3, a provision for degassing the components, and a reproducibility of about 1% in $\tilde{V}^E$ (ranging from 9.1 to 0.6 $cm^3\ mol^{-1}$). Pasfield[69] describes a similar dilatometer of 600 cm^3 capacity for determining partial molar volumes in dilute solutions.

D. MEASUREMENT OF V^E FOR MIXTURES OF LIQUEFIED GASES AND GASES

1. V^E for Mixtures of Liquefied Gases

The desire to study mixtures of simple substances in the liquid state has led in very recent times to the intense study of the properties of mixtures of liquefied gases, *i.e.*, for substances which are gaseous at 1 atm and 25°. Staveley and coworkers[75] described an apparatus for measuring the following properties of mixtures of liquefied gases: (a) the total vapor pressure, (b) the dew-point pressure, (c) the volume change on mixing, (d) the virial coefficients of the gases at the temperature of the other measurements. They tested their apparatus with mixtures of carbon monoxide and methane at 90.67°K. V^E was determined to a precision of ±0.01 $cm^3\ mol^{-1}$ by measuring the densities of the pure components and the mixtures. An improved version[76] of this apparatus was used to determine V^E (to ±0.002 $cm^3\ mol^{-1}$) for the following liquid systems: $Ar + O_2$, $Ar + N_2$, $O_2 + N_2$, $CO + N_2$, and $Ar + CO$ at temperatures between 84 and 90°K. Staveley and coworkers[77] recently described a variation of the above apparatus to measure the vapor pressure and density of liquefied gases up to about 15 atm. For the system $Ar + Kr$ it was necessary to go to elevated pressure to maintain the liquid phase over a sufficient range of compositions.

Jeener[78] described an apparatus based on the calorimeter of Cheeseman and Whittaker[79] which could be used for both measurements of H^E and V^E at low temperatures. The apparatus was tested on mixtures of argon and methane at 91°K and has a precision of about 1% in $\tilde{V}^E$. Davenport, Rowlinson, and Saville's[80] apparatus was used to determine the volumes of mixing at saturation pressure of mixtures of methane with isopentane and 2-methylpentane from 115 to 155°K. These are not strictly excess volumes since the pressure is changing with composition at constant temperature, but both systems show substantial contractions (1–4 $cm^3\ mol^{-1}$). Fuks, Legros, and Bellemans[81] describe an apparatus to measure the density of liquefied gases to ±0.02% at temperatures from 70 to 300°K. The apparatus of Shana'a and Canfield[82] was designed to measure the density of cryogenic liquids and mixtures in the range 77–273°K with a precision of ±0.00008 $g\ cm^{-3}$. Schneider and Engels[83] described an apparatus for the direct measurement of V^E between 20 and 150° and up to 3000 atm with an accuracy exceeding ±0.005 $cm^3\ mol^{-1}$.

The apparatus of Knaap, Knoester, and Beenakker[84] was used for measuring the volume change on mixing of liquids at constant pressure for the systems $O_2 + N_2$, $O_2 + Ar$, $n\text{-}H_2 + p\text{-}H_2$, and $n\text{-}D_2 + o\text{-}D_2$ at temperatures ranging from 20.4 to 90°K. The overall accuracy in V^E is about ±0.003 $cm^3\ mol^{-1}$. With reference to Figure 8, P_1 and P_2 are used for purification and storage of the components. The liquid from P_1 is distilled into the measuring vessel V, and then the separator S is positioned by the magnets M at the surface of the first liquid. The second liquid is then condensed on to the top of S until V is completely filled. Condensation of the second liquid in the capillary C is carefully controlled by the vacuum jacket E. The liquid level in the capillary is measured at equilibrium. Stirring is accomplished by moving the separator S (with M) which has a narrow slit in it. Volume changes are read directly on the capillary by adding pure

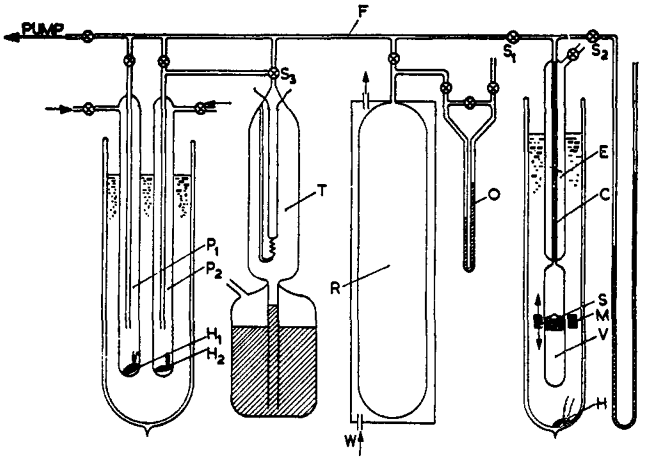

Figure 8. Low-temperature dilatometer of Knaap, Knoester, and Beenakker.[84] Reprinted by permission of the North-Holland Publishing Co., Amsterdam.

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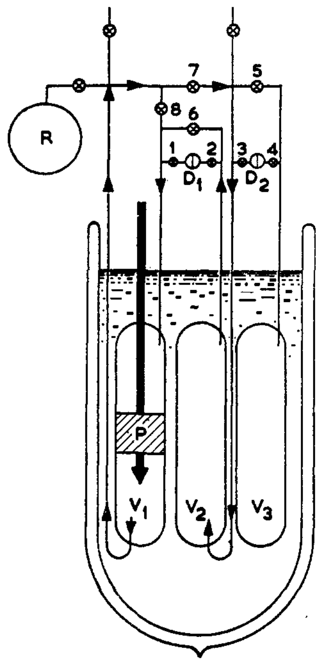

Figure 9. Apparatus of Zandbergen and Beenakker[93] for the determination of $\bar{V}^E$ for mixtures of gases. Reprinted by permission of the North-Holland Publishing Co., Amsterdam.

gas in the case of a volume contraction so that the liquid again came into the capillary, or in the case of a volume expansion a small amount of liquid was evaporated into the Toepler pump before mixing.

2. V^E *for Mixtures of Gases*

Although we had no difficulty at all with the idea of incorporating in this review references to mixtures of liquefied gases, we did have some initial qualms about including mixtures of gases. They are certainly both mixtures of fluids, and in the circumstance of elevated pressures gases do approach densities we normally attribute to liquids. Basically, PVT measurements done on mixtures of gases may be analyzed to retrieve V^E for the mixtures at constant pressure. We choose to give brief reference to PVT work and more weight to mixtures of gases around atmospheric pressure.

Bartlett[85] determined the compressibility isotherms for mixtures of nitrogen and hydrogen at 0° from 1 to 1000 atm. This paper describes the apparatus used, and in two subsequent papers[86,87] the work on $H_2 + N_2$ was extended to a greater temperature range. Wiebe and Gaddy[88] also studied $H_2 + N_2$ mixtures and give a full description of their modified Bartlett[85] apparatus which they used in the ranges 25–1000 atm and 0–300°. Lentz and Franck[89] describe an apparatus for determining the pressure and temperature as functions of the volume and composition for conditions up to 400° and 3000 atm. They studied the system water + argon.

We next take up mixtures of gases around atmospheric pressure with the work of Edwards and Roseveare[90] who studied volume changes on mixing to determine the second virial coefficients of gaseous mixtures. They carried out their experiments at 25° on nine binary mixtures selected from H_2, N_2, He, O_2, CO_2, and C_2H_4 at pressures of 380 and 760 mm with an error of about ± 0.08 cm^3 mol^{-1}. Michels and Boerboom[91] described an apparatus for determining V^E at 1 atm and 25° with an error of ± 0.5 cm^3 mol^{-1} for 12 binary mixtures of the following: H_2, He, N_2, Ar, CO, CO_2, CH_3F, C_2H_4, and C_3H_6. They were also interested in the second virial coefficients of the mixtures. The gas-expansion method for determining PVT data on gases and mixtures of gases is described in detail by Streett and Staveley.[92]

Zandbergen and Beenakker's[93] apparatus is for the precise (about $\pm 2\%$ in $\bar{V}^E$) determination of V^E at constant pressure for gaseous $N_2 + H_2$, $Ar + H_2$, and $Ar + N_2$ between 170 and 292°K and up to 100 atm. The apparatus was briefly described earlier[94] and is based on the design of Knobler, *et al.*[95] Figure 9 is a schematic diagram of the apparatus which consists of the metal vessels V_1 containing gas A and close-fitting piston for stirring, V_2 containing gas B, and V_3 which is the pressure reference vessel also containing gas B. D_1 and D_2 are differential manometers. After mixing, the pressure of the mixture is compared with that in V_2 and the pressure reduced (for positive V^E) to the reference pressure by bleeding out excess gas in two steps to the previously evacuated vessel R. By precisely knowing the volumes of each vessel, the pressure in each vessel, and the equations of state for the pure components, it is comparatively easy to calculate $\bar{V}^E$. R is also thermostated and different volumes are used (80, 1000, or 3000 cm^3) depending on the expected volume change. The volumes V_1 and V_2 are of the order of 50 cm^3. By changing the size of V_2 and interchanging the gases a variety of compositions may be obtained. Second virial coefficients obtained in this manner agree very well with those obtained by other techniques. Knobler[96] described a variation of this apparatus which can be used for the determination of interaction virial coefficients (and the calculation of V^E) for systems containing condensables. This apparatus was used[97] for fluorocarbon mixtures at 50 and 100°, and for the 15 binary mixtures of the normal alkanes (methane through hexane) at 25, 50, 75, and 100°.[98]

E. SUMMARY

In this section we have attempted to provide a key to the several methods which have been used to determine V^E. Details are given in the original papers. The simplest precise

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method for mixtures of liquids at ambient temperatures is the dilatometer used by Duncan, *et al.*[56] Next, we would recommend Pflug and Benson's design[68] for high-precision and multiple compositions in a single run.

IV. Relation of V^E to Thermodynamic Properties

A. GENERAL CONSIDERATIONS

Volume changes on mixing have been of interest for several reasons: (1) to test theories of solution; (2) to convert thermodynamic properties determined at constant pressure to the condition of mixing at constant volume; (3) to determine the second virial cross coefficient; and (4) for the practical purpose of determining composition from density measurements. Reason 2 will be discussed in section IV.B, reasons 1 and 3 will be taken up in subsequent sections, and reason 4 was discussed earlier.

There is no volume change on mixing two liquids to form a thermodynamically ideal solution at constant temperature and pressure. Thus, $\Delta V^M = 0 = V^E$ for thermodynamically ideal mixtures (we shall use V^E rather than ΔV^M from here on).

For a binary mixture of real liquids the change of state for a volume change on mixing (under isothermal but *nonisobaric* conditions) is

$$n_1A(T,P_A) + n_2B(T,P_B) \rightarrow (n_1 + n_2)M(T,P_M) \qquad (3a)$$

and

$$n_1A(T,\tilde{V}_1^0) + n_2B(T,\tilde{V}_2^0) \rightarrow (n_1 + n_2)M(T,\tilde{V}) \qquad (3b)$$

where $\tilde{V}$ is the molar volume of the mixture M. Here $\tilde{V}$, $\tilde{V}_1^0$, and $\tilde{V}_2^0$ are independent variables and may be given any reasonable values. In general, then, the volume change on mixing is given by

$$\tilde{V}^E = \tilde{V} - x_1\tilde{V}_1^0 - x_2\tilde{V}_2^0 = \tilde{V} - \tilde{V}^0 \qquad (4)$$

and can be given any value since the pressure P is a dependent variable in each case. However, in order to fix a value of $\tilde{V}^E$, it is the usual practice to make $P_A = P_B = P_M = 1$ atm, so that the mixing takes place under conditions of constant pressure.

In general in terms of partial molar volumes we have

$$\tilde{V}(T,P) = x_1\tilde{V}_1(T,P) + x_2\tilde{V}_2(T,P) \qquad (5a)$$

so that

$$\tilde{V}^E = x_1[\tilde{V}_1(T,P) - \tilde{V}_1^0(T,P_A)] + x_2[\tilde{V}_2(T,P) - \tilde{V}_2^0(T,P_B)] \qquad (5b)$$

Again, it is usual practice to make $P = P_A = P_B = 1$ atm so that

$$\tilde{V} = x_1\tilde{V}_1 + x_2\tilde{V}_2 \qquad (6a)$$

and

$$\tilde{V}^E = x_1(\tilde{V}_1 - \tilde{V}_1^0) + x_2(\tilde{V}_2 - \tilde{V}_2^0) \qquad (6b)$$

The partial molar volume is defined as

$$\tilde{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j\neq i}} \qquad (7)$$

For purposes of expressing V^E as a function of composition the following expressions have been used for the left-hand side of the equation: $\tilde{V}^E$, V^E/V^0, $100V^E/V^0$, and any of the following for the right-hand side of the equation

$$x_1x_2[a + b(x_1 - x_2) + c(x_1 - x_2)^2 + \ldots]$$

$$x_1x_2[a' + b'(x_1) + c'(x_1)^2 + \ldots]$$

and the preceding two forms with volume fractions, z, replacing mole fractions, x. In general, the volume fraction yields slightly better fits than the mole fraction. Mikhailov[99,100] emphasizes the advantage of using volume fractions rather than mole fractions to relate composition to density isotherms. Duboc[101] has developed a polynomial method of representing d^E and V^E/V. (Caution: Since the volume fraction, z_k, may be defined as $n_k\tilde{V}_k^0/\Sigma_i n_i\tilde{V}_i^0$ or $n_k\tilde{V}_k^0/V$ or $n_k\tilde{V}_k/V$, it is important to define this term. We use the first definition.) When V^E is known both as a function of temperature and composition, the constants a, b, and c (or a', b', and c') are fit as polynomials in terms of the temperature, *e.g.*, $a = A + Bt + Ct^2 + \ldots$. When using V^E to determine composition from density measurements, the following form for fitting V^E is recommended.

$$V_E/V^0 = z_1z_2(a + bz_1 + cz_1^2 + \ldots)$$

because the following convenient relations apply

$$d = \frac{d_2 + (d_1 - d_2)z_1}{1 + (V^E/V^0)} \qquad (8)$$

$$x_1 = \frac{z_1\tilde{V}_2^0}{\tilde{V}_1^0 - z_1(\tilde{V}_1^0 - \tilde{V}_2^0)} \qquad (9)$$

For the graphical representation of V^E, plotting $\tilde{V}^E$ *vs.* x_1 is the most convenient form, but plotting $\tilde{V}^E/z_1z_2$ *vs.* z_1 is the easiest to interpret in terms of evaluating the precision of the data, although this latter plot does not give proper weighting to the points for a least-squares fitting of the data.

B. CONSTANT VOLUME *vs.* CONSTANT PRESSURE PROPERTIES

Thermodynamic properties of mixtures are most readily determined by experiments carried out under conditions of constant pressure. Yet, most theories of solutions yield thermodynamic properties at constant volume. The conversion from one set of conditions to the other utilizes the volume change on mixing. Methods for doing this were first developed by Scatchard[102] and have been extensively discussed by other workers.[103-108] Several different processes for mixing at "constant volume" are possible, and Scott[108] gives a rather complete treatment of them. However, the change of state of practical interest is

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Table I

Difference in Excess Thermodynamic Properties at Constant Volume for Two Systems

	Benzene + 2,2,4-trimethylpentane[a]	*n*-C_6F_{14} + *n*-C_6H_{14}[b]
Temp (°C)	40	25
x_1[c]	0.6	0.5
$\tilde{V}^E$ (cm^3)	0.50	4.84
$\tilde{A}_V{}^E - \tilde{G}_p{}^E$ (cal)	90.4 − 90.2 = 0.2	329 − 323 = 6
$\tilde{S}_V{}^E - \tilde{S}_p{}^E$ (cal deg^{-1})	0.426 − 0.535 = −0.109	−0.161 − 0.647 = −0.808
$\tilde{E}_V{}^E - \tilde{H}_p{}^E$ (cal)	224 − 258 = −34	281 − 516 = −235

[a] Reference 109. [b] References 108, 110, 111. [c] Mole fraction of first-named component.

$$n_1A(T,\tilde{V}_1{}^0, 1\ \text{atm}) + n_2B(T,\tilde{V}_2{}^0, 1\ \text{atm}) \rightarrow (n_1 + n_2)M(T,\tilde{V},P) \quad (10)$$

where P is chosen so that $V^E = 0$. For this process on a molar basis, *i.e.*, $\tilde{V} = x_1\tilde{V}_1{}^0 + x_2\tilde{V}_2{}^0$ (where the left-hand and right-hand terms are at different pressures), we have the following set of relations[1] (also see ref 103).

$$\Delta A_V{}^E - \Delta\tilde{G}_p{}^E = (\tilde{V}^E)^2/2\tilde{V}_m\beta_m + \ldots \quad (11)$$

$$\Delta\tilde{S}_V{}^E - \Delta\tilde{S}_p{}^E = -\left(\frac{\alpha_m}{\beta_m}\right)\tilde{V}^E + \frac{1}{2\tilde{V}_m\beta_m}\left[\frac{d\ln\beta_m}{dT} + \frac{\alpha_m}{\beta_m}\left(\frac{d\ln\beta_m}{dP}\right)\right](V^E)^2 + \ldots \quad (12)$$

$$\Delta\tilde{E}_V{}^E - \Delta\tilde{H}_p{}^E = -T\left(\frac{\alpha_m}{\beta_m}\right)\tilde{V}^E + \frac{1}{2\tilde{V}_m\beta_m}\left[\frac{d\ln\beta_m}{d\ln T} + \frac{\alpha_m T}{\beta_m}\left(\frac{d\ln\beta_m}{dP}\right) + 1\right](\tilde{V}^E)^2 + \ldots \quad (13)$$

In these equations the subscript m refers to the mixture. Except for the cases where $\tilde{V}^E$ is large (greater than 1 cm^3 mol^{-1}) the terms in $(\tilde{V}^E)^2$ can usually be neglected. The difference between the constant pressure and the constant volume properties is much greater for the entropy, enthalpy, and energy than it is for the free energies. Table I gives values for these differences for two systems.

V. Theories of Solution Pertaining to Volume Changes on Mixing

A. REGULAR SOLUTIONS

In an early definition Hildebrand[112] described a regular solution as one "involving no entropy change when a small amount of one of its components is transferred to it from an ideal solution of the same composition, the total volume remaining unchanged." By making the following assumptions[1]: (1) $\tilde{S}_V{}^E = 0$; (2) n (where n is the ratio of the internal pressure to the cohesive energy density, *i.e.*, $n = [(\partial E/\partial V)_T/(\Delta\tilde{E}^V/\tilde{V})]$ is essentially the same for the unmixed and mixed components; and (3) $\tilde{S}_V{}^E = 0$, $\tilde{E}_V{}^E = \tilde{G}_p{}^E$; it is possible to derive

$$\tilde{V}^E = n\beta\tilde{E}_V{}^E = n\beta\tilde{G}_p{}^E \quad (14)$$

For many normal liquids $n \sim 1$ which simplifies eq 14. An equation equivalent to (14) derived by Longuet-Higgins[113] from first-order conformal solution theory results in the equation

$$\tilde{V}^E = \alpha T\tilde{G}_p{}^E/\delta^2 \quad (15)$$

In eq 14 and 15 α and β apply to the mixture and are strictly additive in terms of the volume fractions of the pure components although simple averages have been used. δ is also for the mixture and is calculated as a simple average, *i.e.*, $\delta = (\delta_1 + \delta_2)/2$. Croll and Scott[114] compared $\alpha T/\delta^2$ and $\tilde{V}^E/\tilde{G}_p{}^E$ (eq 15) for five mixtures of fluorocarbons with hydrocarbons (CF_4 + CH_4, 107°K; *n*-C_4F_{10} + *n*-C_4H_{10}, 233°K; *n*-C_5F_{12} + *n*-C_5H_{12}, 266°K; *n*-C_6F_{14} + *n*-C_6H_{14}, 298°K; *n*-C_7H_{16} + *n*-C_7F_{16}, 323°K) and found that the latter term was greater than the former in all cases by about 50%. The anomalous behavior of fluorocarbon solutions has been discussed in detail by Scott.[115] Battino and coworkers[87,42,116] found in applying eq 15 to binary mixtures of cyclohexane and carbon tetrachloride that much better correlations were obtained with experimental $\tilde{V}^E$ by using the experimentally determined values of $\tilde{G}_p{}^E$ rather than those calculated from regular solution equations. Meares[117] used eq 14 with experimental values of $\tilde{E}_V{}^E$ and $n = 1$ to calculate $\tilde{V}^E$ for mixtures of 19 esters with 1,3-butanediol diacetate, and the average deviation between calculated[117] and experimental[118] $\tilde{V}^E$ was ±0.08 cm^3 for data of precision ±0.03 cm^3 mol^{-1}, but eight systems had $\tilde{V}^E$ of 0.08 cm^3 or less and the average value (absolute) of $\tilde{V}^E$ for the 19 systems was 0.15 cm^3.

Hildebrand and Scott[1] present the following equation derived by Scott which is more exact and is also free from the approximations cited earlier.

$$\left.\begin{aligned}\tilde{V}^E = n_m\beta_u\tilde{G}_p{}^E & \quad \text{(i)}\\ - T(\partial\tilde{S}_V{}^E/\partial P)_T & \quad \text{(ii)}\\ + (n_m\beta_u\tilde{E}_u - x_1n_1\beta_1\tilde{E}_1 - x_2n_2\beta_2\tilde{E}_2) & \quad \text{(iii)}\\ + n_m\beta_uT\tilde{S}_V{}^E & \quad \text{(iv)}\end{aligned}\right\} \quad (16)$$

The subscript u refers to the unmixed initial state of the system and m refers to the mixture, *e.g.*, $\beta_u = z_1\beta_1 + z_2\beta_2$. Equation 16 cannot be used for *a priori* calculations but can be used to back-calculate to assess for the contributions of the various terms in eq 16 which correspond to the assumptions listed for eq 14. Table II gives numerical values

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Table II[a]

Terms of Eq 16 for Four Systems

System	*Temp,* *°C*	*Terms in eq 16* *(i)*	*(ii)*	*(iii)*	*(iv)*	$\tilde{V}^E$ *(obsd)*
$CCl_4 + SiCl_4$	25	0.18	−1.35	1.17	0.01	0.01
$C_6H_6 + C_2H_4Cl_2$	25	0.03	0.18	0.09	−0.06	0.24
$CCl_4 + C(CH_3)_4$	0	0.63	4.5	−6.0	0.27	−0.52
n-C_6F_{14} + n-C_6H_{14}	25	3.9	−6.4	6.7	0.2	4.84

[a] See ref 1.

for the four terms in eq 16 for four systems. To quote Hildebrand and Scott,[1] "We suspect that any agreement between eq 14 and experimental data is, for small volume changes, fortuitous, but for large volume changes the approximate cancellation of (ii) and (iii) is such as to leave term (i) (eq 14) the dominant factor in determining the magnitude of volume (change)."

As pointed out by McGlashan[119] and Hildebrand and Scott[1] among others, the most serious shortcoming of eq 14 is its failure to allow $\tilde{V}^E$ and $\tilde{G}_p{}^E$ to have opposite signs. One of the first systems found to exhibit this behavior was the carbon tetrachloride–neopentane system[120] at 0° for which $\tilde{V}^E = -0.55$ cm^3 mol^{-1} and $\tilde{G}_p{}^E = 80$ cal mol^{-1} for an equimolar mixture. There are few systems which satisfy the conditions for this behavior, namely, that the substances are sufficiently alike to follow the same law of corresponding states (see next section), and that the substances are very nearly the same in intrinsic size (*i.e.*, $\sigma_{11} = \sigma_{22}$).

Wood[121] derived equations relating the volume change on mixing to the energy of mixing at constant pressure. He found no *a priori* reason from his equations for $\tilde{V}^E$ and $\tilde{E}_p{}^M$ to have the same or opposite signs. Fernandez-Garcia, *et al.*,[122] did some regular solution calculations at 20° on mixtures of n-hexadecane and the isomers of hexane. Mathieson[123] derived equations for binary liquid mixtures relating the heat of mixing to the excess volume and compressibility, and the excess compressibility to the excess volume and vapor pressure. Rowlinson and Mathieson[124] presented a shorter derivation of Mathieson's key equation, an equation similar to one derived earlier by Scatchard[102] and tested by Meares.[117]

B. CORRESPONDING STATES APPROACHES

Pitzer[125] has usually been credited with the formulation of the corresponding states approach in terms of molecular interactions. The following workers applied the molecular corresponding states equations to liquid mixtures: Longuet-Higgins,[113] Brown,[126] Scott,[127] Prigogine and coworkers,[125,128–134] Wojtowicz, *et al.*,[135] and Bellemans and coworkers.[136–139] The Longuet-Higgins[113] conformal solution equations for volume changes on mixing reduce in the first order to the regular solution equations (for $n = 1$, see eq 15). Recent developments in the average potential model, especially as related to mixtures of gases and liquefied gases, will be treated later in this section, as will Balescu's[140] extension to molecules with small dipole moments. The one- and two-fluid van der Waals approximation developed by Leland, *et al.*,[141,142] will be discussed later in this section. Rowlinson[143] gives an excellent survey of applicable theories of solutions.

The basic assumption of any corresponding states theory is that the intermolecular potential energy is due to central forces only and has the same form for all pair interactions. The theory is characterized by parameters, $-\epsilon$, the energy of a molecular pair at its equilibrium distance, and σ, the collision diameter. For substances which obey the principle of corresponding states, a plot of reduced volume ($V/N\sigma^3$) against the reduced temperature (kT/ϵ) at a fixed and arbitrary value of the reduced pressure ($P\sigma^3/\epsilon$) should give the same curve not only for the pure substances A and B, but also for all A–B mixtures, each of which has suitably averaged ϵ and σ values appropriate to its composition. Usually the Lennard-Jones 6–12 interaction potential is used along with the Lorentz–Berthelot combining rules for the A–B interactions, *i.e.*

$$\sigma_{AB} = (1/2)(\sigma_{AA} + \sigma_{BB}) \text{ and } \epsilon_{AB} = (\epsilon_{AA}\epsilon_{BB})^{1/2} \qquad (17)$$

Kohler[144] does not use the geometric mean rule but develops an equation based on the London dispersion-forces formula but which does not require a knowledge of ionization potentials. For systems with components of similar electronic structure, *e.g.*, aliphatic–aliphatic or aromatic–aromatic interactions, there is little difference between the interaction energies given by Kohler's equation and the geometric mean. For some systems Kohler's equation has a pronounced advantage over the geometric mean.

Scott[127] proposed three models for averaging the intermolecular energy parameters for mixtures and they are called the "single-liquid," "two-liquid," and "three-liquid" models. The first two models correspond to Prigogine's[134] "crude approximation" and "refined average potential," respectively. For performing the calculations one of the two components is taken as a reference substance, and ϵ and σ along with experimental PVT data for this substance are used to establish a basic reduced equation of state which is then assumed

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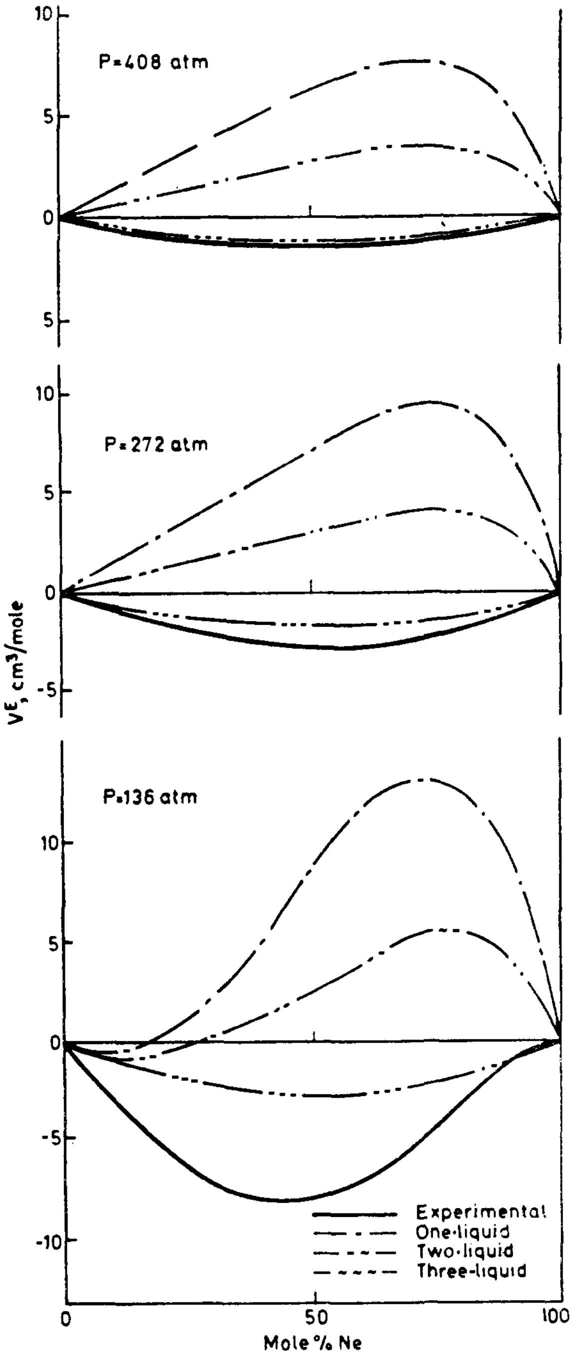

Figure 10. Comparison of experimental and predicted values of excess volume for the system Ne–N_2 at high pressures.[146] Reprinted by permission of *Cryogenics*, a publication of Iliffe Science and Technology Publications, Ltd.

to fit the pure component and all mixtures. Mixture volumes, V_m, are calculated from this equation of state using the averaged ϵ and σ values appropriate to each of the three models. The following are the three models used in averaging the intermolecular energy parameters: (1) the one-liquid model behaves as a single liquid with an effective interaction which is the average of the separate pair interactions; (2) in the "two-liquid" model the mixture is effectively regarded as a mixture of the appropriate amounts of an A-centered liquid with parameters $\langle\epsilon\rangle_A$ and $\langle\sigma\rangle_A$, and a B-centered liquid with parameters $\langle\epsilon\rangle_B$ and $\langle\sigma\rangle_B$; (3) the "three-liquid" model is sometimes called the "separate interaction" model. This model is strictly applicable to a slightly imperfect gas. The mixture can be thought of as consisting of three independent liquids in appropriate amounts, pure A, pure B, and an imaginary liquid with intermolecular energy parameters ϵ_{AB} and σ_{AB}. Streett and Staveley[145] present the equations commonly used at "zero" pressure, and Streett[146] give the equations used at high pressures.

Streett[146] applied the theory to neon–nitrogen mixtures at pressures up to 544 atm and at 100.78°K. Figure 10 shows his results for 136 atm for the experimental $\bar{V}^E$ and those calculated on the basis of the three models. It is a necessity for the model used for these calculations that $\bar{V}^E{}_{\rm I} > \bar{V}^E{}_{\rm II} > \bar{V}^E{}_{\rm III}$. The principal qualitative difference between the results for the different models is to be found in the concentration dependence which is symmetric for the "three-liquid" model as contrasted with the results for the "one-liquid" and "two-liquid" models. This is evident in Figure 10 and was also found by Zandbergen and Beenakker[93,147] for several mixtures of supercritical gases for all three models. Table III summarizes the results of Streett and Staveley[145] for several systems for all three models in the columns marked "one-liquid," "two-liquid," and "three-liquid." (The remaining columns are discussed below.) Upon examining the table there appears very little one can say with respect to correlations between the three models and the experimental results. Even in theoretically favorable cases like Ar–Kr and Ar–CH_4 the discrepancies are rather large.

Several workers have commented on the use of these three models. Streett and Staveley[145] make several points: (1) all three models predict $\bar{V}^E$ will be negative if the two components have molecules of the same size (a consequence of the unsymmetrical nature of the intermolecular potential energy curve for a pair of molecules); (2) the calculated $\bar{V}^E$ values are in general more sensitive to the ratio of the σ parameters than the ϵ parameters; (3) however, the calculated values of $\bar{V}^E$ are not so sensitive to the ratio of the σ and ϵ parameters that uncertainties in selecting intermolecular energy parameters can be held responsible for the lack of agreement between theory and experiment; (4) the "three-liquid" model necessarily requires a symmetrical dependence of $\bar{V}^E$ on mole fraction, but the other two models are capable of predicting rather asymmetric $\bar{V}^E$ curves; and (5) departures from the combining rules (eq 17) may be a possible contributory factor to the disagreement between theory and experiment. Bellemans, Mathot, and Simon[186] in a thorough discussion of the average potential model (APM) and particularly the "two-liquid" model have examined the adjustment which must be made to the values of ϵ_{AB} and σ_{AB} derived from the combining rules (eq 17) to bring the calculated and observed values of $\bar{V}^E$ in line. They give a detailed analysis of the average potential model ("two-liquid") for the excess properties of the following five mixtures: CO–CH_4, Ar–CH_4, N_2–O_2, N_2–Ar, and O_2–Ar. Bellemans and Vilcu[187] compared the experimental and calculated (APM) excess free energies and volumes for the five additional liquid mixtures: CH_4–Kr, N_2–CH_4, Ar–Kr, N_2–CO, and CO–Ar. Some of the conclusions that Bellemans and coworkers[186,187] draw are: (1) the APM is valuable for predicting the *sign*

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Table III[a]

Calculated and Experimental Values of $\tilde{V}^E$ (cm^3) for Equimolar Mixtures[b]

System	*Temp (°K)*	*"Single-liquid"*	*"Two-liquid"*	*"Three-liquid"*	*"One-liquid" vdW*[c]	*"Two-liquid" vdW*[c]	*Exptl*
Ar–Kr	115.8	0.4	0.05	−0.1	−0.78	−0.53	−0.50
Ar–CH_4	91	1.5	0.6	−0.1	−0.31	−0.23	0.18
Ar–O_2	83.8	∼0	∼0	∼0	−0.00	0	0.136
Ar–N_2	83.8	0.4	∼0	−0.2	−0.32	−0.26	−0.18
Ar–CO	83.8	0.4	0.1	−0.15	−0.20	−0.17	0.10
CO–N_2	83.8	∼0	∼0	∼0	−0.03	−0.01	0.13
O_2–N_2	83.8	0.4	∼0	−0.2	. . .	. . .	−0.31
O_2–N_2	78	. . .	. . .	. . .	−0.32	−0.25	−0.21
CO–CH_4	90.7	∼0	∼0	−0.05	−0.84	−0.60	−0.33
N_2–CH_4	91	. . .	. . .	. . .	. . .	−0.82	−0.21
CH_4–CF_4	111	13.9	7.1	. . .	0.90	. . .	0.88

[a] See ref 141, 142, and 145, for sources of data and details of calculations. [b] The entry ∼0 means <0.05. [c] These columns refer to the van der Waals approximation used in ref 141 and 142.

of the main excess functions of mixtures of roughly spherical molecules (italics added); (2) the average interactions which are evaluated assuming a random distribution of the A and B molecules in space when corrected as applied to the excess functions have corrections of the order of 5–10%; (3) the most readily evaluated restriction on the pair potentials $\epsilon_{AA}(r)$, $\epsilon_{AB}(r)$, and $\epsilon_{BB}(r)$ in the development of the APM is the values of n and m in the Lennard-Jones potential—and they found in the worst case they investigated a variation of 50% in the excess functions in going from a 6–12 to a 7–14 potential. Fuks and Bellemans[138] found that their experimental results on $\tilde{V}^E$ for the two simple binary liquid mixtures of CH_4 + Kr and CH_4 + N_2 confirm the fact that the APM is still able to predict semiquantitatively the excess properties of simple mixtures. Vilcu and Bellemans[139] extended the APM to systems to moderate pressures and as an illustration discussed the theoretical excess volumes of the systems Ar + CH_4 and CO + CH_4. Wheeler and Smith[148] point out that there are four points of flexibility in present molecular formulations of the corresponding states idea, and that at these points the procedure followed on the numerical values used can be tailored to give better agreement between experiment and theory without violation of physical principles. These four points are the exponent values used in the pair-potential function, the averaging procedure used to obtain an effective mixture pair-potential function, the combination rule for unlike-pair parameters, and the selection of a reference substance. Wheeler and Smith made use of the first two flexibilities to show that the conformal-parameter equations can correlate excess free energy and activity coefficient data of highly nonideal liquid mixtures.

Eckert, *et al.*,[149] using the equations developed by Renon, *et al.*,[150] based on Scott's "two-liquid" theory coupled with a three-parameter theorem of corresponding states, together with additional information provided by another mixture property such as the cross second virial coefficient, B_{12}, found improved agreement between calculated and experimental values of $\tilde{V}^E$ for mixtures of simple liquids. For the following systems the average deviation between experimental and calculated values of $\tilde{V}^E$ was 0.14 cm^3: Ar–N_2, Ar–O_2, O_2–N_2, CH_4–Ar, CH_4–CF_4, CH_4–N_2, CH_4–CO, and N_2–CO. It is of interest to see if their calculated values of $\tilde{V}^E$ for the following systems will be corroborated by experiment: Kr–Ar, Kr–CH_4, Kr–CF_4, Kr–O_2, CH_4–C_2H_6, C_2H_4–C_2H_6, Ar–C_2H_6, N_2–CF_4, and CH_4–C_3H_8. They proposed the following

$$\epsilon_{ij} = (1 - k_{ij})(\epsilon_{ii}\epsilon_{jj})^{1/2} \tag{18}$$

rather than the usual mixing rule for the energy parameter ϵ. In eq 18 k_{ij} is an essentially empirical factor to correct for deviations from the geometric mean. Using London's formula for molecules having the same ionization potentials but a 20% difference in their molecular diameters, the predicted value of k_{ij} is 0.025. It was pointed out that a deviation of this magnitude can have a large effect on the excess properties, especially on the excess volume and the excess entropy.

Throop and Bearman[151] using the Percus–Yevick equation and the Lennard-Jones 6–12 potential for the noble gases calculated the thermodynamic functions for a number of binary mixtures for supercritical isotherms and at densities up to twice the critical density. They also calculated the excess functions along the isotherms as a function of density for mixing at constant volume and for mixing at constant pressure. For the constant-pressure process they found that the excess energy, volume, and Gibbs free energy were positive at low densities, increased with increasing density to a maximum, and then decreased to small positive or negative values at higher densities. The mixtures investigated *corresponded* to Ar–Kr, Ar–Xe, Ne–Kr, and Ne–Xe.

A significant contribution based on the Percus–Yevick equation was made by Leland, Rowlinson, and Sather[141] in a paper in which they deal with the statistical thermodynamics of mixtures of molecules of different sizes. Their paper gives an excellent review of theories of solution and clearly indicates where their work fits in. Since a central aspect is based on an approximation for mixtures of a type originally suggested by van der Waals, the approach here used may be called the "one-fluid van der Waals" approach. In his theory of mixtures van der Waals assumed that the parameters of his equation of state, a_x and b_x, were quadratic sums of $a_{\alpha\beta}$ and $b_{\alpha\beta}$ or

$$a_x = \sum_{\alpha}\sum_{\beta} x_\alpha x_\beta a_{\alpha\beta}, \quad b_x = \sum_{\alpha}\sum_{\beta} x_\alpha x_\beta b_{\alpha\beta} \tag{19}$$

This quadratic form is used by Leland, *et al.*, although the

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developed equations are not tied to the van der Waals equation of state, but do apply to any fluid mixture with conformal potentials. In the past few years work on pure fluids has shown that even at low temperatures the structure is determined primarily by the repulsive forces, and that the attractive forces merely provide the so-called "internal pressure" which maintains the high fluid density. This observation provides the basis for considering the Percus–Yevick result for mixtures of hard spheres to be equally relevant to mixtures of real molecules. Their calculations show that the van der Waals approximation avoids the false large positive contributions to $\tilde{G}^E$ and $\tilde{H}^E$ of earlier theories. The column in Table III headed "one-liquid" vdW gives the results for $\tilde{V}^E$ for a variety of systems and for the assumption that the Lorentz–Berthelot combining rules hold. The agreement is obviously better than that found for the non-van der Waals approach. This is especially the case for the system CH_4–CF_4 for which there is a great difference in molecular size and for which the cross-parameters are known from the virial coefficients.

In a second paper Leland, *et al.*,[142] extended the van der Waals' approximation to a two-fluid model which takes into account the departures from a random distribution induced by differences of intermolecular energy. Their treatment was also extended to mixtures of molecules of different shapes. The two-fluid van der Waals model has the advantages of (a) leading to results similar to those of the one-fluid van der Waals model for molecules that differ only in size (which avoids the basic fault of the random mixing approximation); (b) leading to the same degree of order in mixtures that differ only in energy as the two-fluid modification of the random mixing approximation (*i.e.*, the average potential model); and (c) having the reference substance which is used as the source of the free energy not necessarily the same for each component. If all components and reference substances form a strictly conformal family, then the calculated properties of the mixture are independent of the choices of the reference substances. Table III gives the results of the calculations for the "two-fluid" van der Waals approximation assuming the geometric mean rule. The original paper also presents results for adjusted values of the cross-term in the energies and for taking into account the "shape" factors. The results of using the van der Waals approximation are significantly better than the random mixing approximation. The authors also discuss the recent strong evidence that the geometric mean rule give values slightly higher than those obtained from measurements yielding the cross second virial coefficient.

The systems which have been under discussion so far in this section have all involved "simple" liquids. The determination of $\tilde{V}^E$ for mixtures of gases at low and high pressures has been used to determine the cross second virial coefficient B_{12}. Experimental work and equations for this have been carried out by many workers.[90,91,98,147,152] Until the work of Zandbergen and Beenakker[98] the requisite precision in measuring $\tilde{V}^E$ to obtain good values of B_{12} was not attained.

A particularly valuable test of Prigogine's theory was made by Kohler and Rott[88] who determined $\tilde{V}^E$ at 15 and 25° for the following three systems with essentially equal molar volumes ($\tilde{V}^0$ in parentheses at 25° in cm^3): *n*-hexane (131.50)–1,2,4-trichlorobenzene (125.31); mesitylene (139.67)–triethylamine (139.98); and bromobenzene (105.49)–cyclohexane (108.77). For the first two systems the calculated values were incorrect by a factor of 2 and the wrong sign was predicted for the third system. Kohler[144,153] reworked Prigogine's approach and for six mixtures involving benzene, cyclohexane, neopentane, and carbon tetrachloride found rather good agreement between experimental and calculated values of $\tilde{V}^E$. Mathot and Desmyter[86] applied the cell model to $\tilde{V}^E$ for the following binary systems made up of (roughly) spherical molecules: neopentane plus CCl_4, C_6H_6, C_6H_{12} (see Figure 11); and CCl_4 plus $CCl(Me)_3$, $CCl_2(Me)_2$, $CCl_3(Me)$, and $C(Me)_3OH$ (see Figure 11). They found reasonable agreement between experiment and theory in these essentially favorable systems. Holleman[68] used a variation of Prigogine's average potential model to calculate $\tilde{V}^E$ at 70° for the benzene–biphenyl system ($\tilde{V}^E{}_{calcd} = -0.1\ cm^3$, $\tilde{V}^E{}_{exptl} = -0.3\ cm^3$). Diaz Pena and McGlashan[154] made calculations for $\tilde{V}^E$ for the system carbon tetrachloride + cyclohexane and confirmed Prigogine's conclusion that for this pair of substances it made little difference as to which of the two components was chosen as the reference component. Their calculated values of $\tilde{V}^E$ were in fair agreement with experiment, but their calculated values of $\partial\tilde{V}^E/\partial P$ were in excellent agreement with experiment. Knapp, Knoester, and Beenakker[84] determined $\tilde{V}^E$ for the following systems at 90, 77, and 20.4°K: O_2–N_2, O_2–Ar, *n*-H_2–*n*-D_2, *n*-H_2–*p*-H_2, and *n*-D_2–*o*-D_2. They found that in using Prigogine's theory the results depended very much on the set of potential parameters chosen and also on the choice of the reference liquid. Similar conclusions were drawn by Pool and Staveley[155] for the system (liquid) methane–carbon monoxide. Pool *et al.*,[76] found similar results for the liquid systems Ar–D_2, Ar–N_2, N_2–O_2, N_2–CO, and Ar–CO. Diaz Pena and Cavero[156] studied the systems C_6H_6–

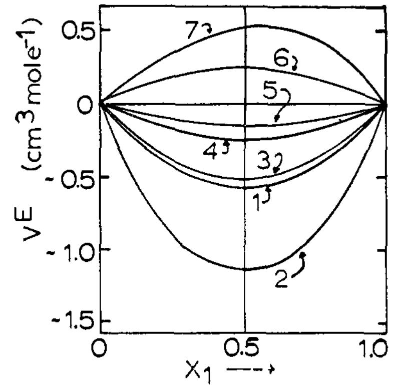

Figure 11. Volume changes on mixing for systems involving spherical molecules.[86] The first-named component is x_1, temperature in parentheses: (1) tetramethylmethane + carbon tetrachloride (0°); (2) tetramethylmethane + cyclohexane (0°); (3) tetramethylmethane + benzene (0°); (4) 2-chloro-2-methylpropane + carbon tetrachloride (0°); (5) 2,2-dichloropropane + carbon tetrachloride (0°); (6) 1,1,1-trichloroethane + carbon tetrachloride (0°); (7) 2-methylpropanol-2 + carbon tetrachloride (25°).

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(152) S. Glasstone, "Textbook of Physical Chemistry," 2nd ed, Van Nostrand, New York, N. Y., 1946, pp 305–307.

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C_6H_{12}, C_6H_6–CCl_4, C_6H_6–$CHCl_3$, CCl_4–$CHCl_3$, and C_6H_{12}–$CHCl_3$ and found for the average potential theory good agreement for the systems with nonpolar components, but only qualitative agreement for the systems involving $CHCl_3$. McLure and Swinton[12] used the Prigogine treatment for monomer plus polymer mixtures of cyclohexane (as the reference component) with *tert*-butylcyclohexane, bicyclohexyl, dicyclohexylmethane, 1,2-dicyclohexylmethane, and 1,3-dicyclohexylpropane at 20 and 40°. They found poor quantitative agreement between theory and experiment for both $\tilde{V}^E$ and $d\tilde{V}^E/dT$ and attributed this to the tendency of the theory to overemphasize the contribution of differing molecular size to the excess functions even when the series of mixtures they studied obeyed the theorem of corresponding states to a high degree of precision with respect to molar volume. Lal and Swinton[157] determined the excess enthalpy of mixing as a function of composition and the equimolar excess volume of mixing at 30° for the two binary systems benzene + benzene-d_6 and cyclohexane + cyclohexane-d_{12}. For these systems, respectively, $\tilde{V}^E$ was 0.0004 and 0.0032 $cm^3\ mol^{-1}$ (both ± 0.0002). They found that the results were in reasonable agreement with APM with the assumption that the energy of the unlike interactions is slightly weaker than the value predicted by the geometric mean rule. Lal and Swinton[158] determined $\tilde{H}^E$ (30 and 70°) and $\tilde{V}^E$ ($-0.053\ cm^3\ mol^{-1}$ at 30° for an equimolar mixture) for the system *cis*-decalin + *trans*-decalin. They compared values calculated from conformal solution theory (Longuet-Higgins), Prigogine's theory, and Flory's theory with experimental results and found that all three theories gave the correct sign for $\tilde{V}^E$ but about one-fourth the experimental value. Benson and coworkers[159] measured $\tilde{H}^E$ and $\tilde{V}^E$ at 25° for solutions of benzene and toluene with cyclopentane, *n*-hexane, *n*-heptane, and *n*-octane and applied the Scatchard–Hildebrand equation and average potential model to their results. The quantitative agreement was poor although they felt that their study did yield useful information about the molecular interactions. Kozdon[160] derived a general expression for $\tilde{V}^E$ as a function of the analytical mole fraction based upon chemical treatment of associated solutions. Duncan and Staveley[161] studied the liquid systems Ar–CO, O_2–N_2, and CO–N_2 and found poor agreement with theory. Rastogi, Nath, and Misra[162] in studying the thermodynamics of weak interactions in liquid mixtures measured $\tilde{V}^E$ for solutions of CCl_4 and benzene with *o*- and *m*-xylene. They found poor agreement with Prigogine's refined model and attributed this partly to the fact that the theory does not take into account the specific interaction between CCl_4 and the aromatics. Rastogi and Varma[163] found that the Prigogine theory does yield the inversion in sign for $\tilde{V}^E$ for the cyclohexane–cyclohexanol system as a function of composition. Also, size effects contribute to the disparity. Davies, *et al.*,[77] discussed the "two-liquid" and "three-liquid" models as applied to the Ar–Kr system. Duboc[101] applied the Prigogine theory to mixtures of CCl_4 and 2-butanol, 2-methyl-2-propanol, and 2-methyl-2-butanol.

Balescu[140] extended the Prigogine theory to solutions of molecules of different sizes and different central interactions. He discussed binary solutions with pure dipolar interactions and inductive forces for the case of one polar constituent and found excellent agreement for the system CCl_4–$CHCl_3$. Rowlinson,[148] among others, pointed out that Balescu's treatment suffers from a faulty averaging of the direct dipole–dipole term. One of the major difficulties with the theory is to find a mixture of spherical or near-spherical molecules in which the excess functions are determined mainly by the dipole–dipole interactions. In the almost ideal system of CCl_4–$CHCl_3$ about one-third of the excess functions are a consequence of the dipole–dipole energy of the $CHCl_3$ molecules.

In an extension of Balescu's treatment (with corrected averaging) as applied to binary solutions of chlorobenzene with cyclohexane and carbon tetrachloride, Anantaraman, *et al.*,[164] found that a departure from the combination rule used in the theory gave good agreement. Their development of the relations for the calculation of $\tilde{V}^E$ was broken up into the three contributions: those due to central forces only, pure dipolar, and polarizability. Their analysis showed that the two systems studied should be treated as a mixture of polarizable-polar and polarizable-nonpolar molecules not obeying the usual approximation of dispersion forces. In a second paper[165] the same authors studied binary mixtures of chlorobenzene with benzene and toluene and applying the same methods as the first paper came to similar conclusions for these systems. Anantaraman, *et al.*,[166] found Balescu's theory did not apply to the systems benzene + fluorobenzene and carbon tetrachloride + fluorobenzene. However, they found using their modified approach excellent agreement for the system cyclohexane + fluorobenzene.[167]

Deshpande and Pandya[168] applied Balescu's treatment of $\tilde{V}^E$ and $\tilde{H}^E$ for binary solutions of aniline with benzene, chlorobenzene, and carbon tetrachloride. They found that calculated values of $\tilde{V}^E$ were extremely sensitive to slight changes in the values of δ and θ $\{(1 + \delta) = \epsilon_{BB}^*/\epsilon_{AA}^*; \theta = (1/\epsilon_{AA}^*) \cdot [\epsilon_{AB}^* - 0.5(\epsilon_{AA}^* + \epsilon_{BB}^*)]\}$. Deshpande and Pandya[169] extended Balescu's equations to systems where both components have permanent dipole moments. However, their calculations on the aniline + toluene and the aniline + chlorobenzene systems showed that the Balescu approach does not work for these systems. The toluene + fluorobenzene system at 25° had a negative $\tilde{H}^E$ ($-55.0\ J\ mol^{-1}$) and a positive $\tilde{V}^E$ ($0.028\ cm^3\ mol^{-1}$) for the equimolar mixture.[170] A modified Balescu treatment[164] gave good results including the correct signs. Bhattacharyya[171] combined nonpolar central forces and noncentral forces of both weak dipolar and structural origin into a single potential. By neglecting higher order terms the excess thermodynamic functions of a mixture of nonpolar globular molecules and

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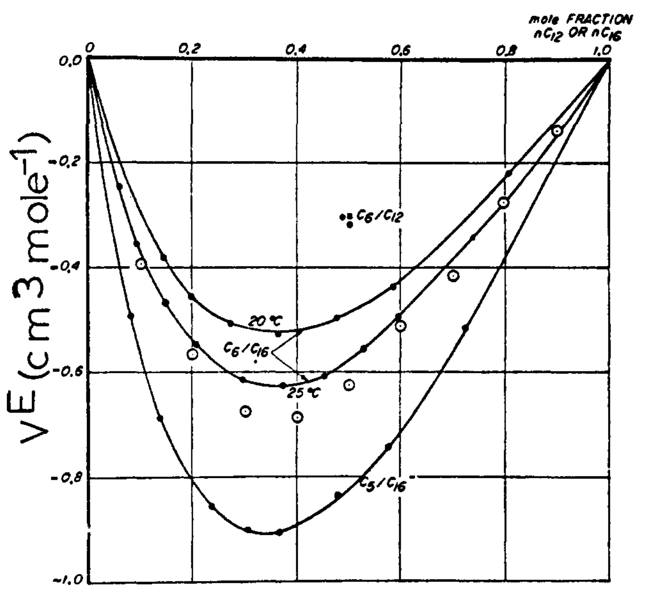

Figure 12. Volume changes on mixing for three *n*-alkane systems.[65] Reprinted by permission of the authors and *Recueil.*

weakly dipolar globular molecules were found to consist of four terms: pure nonpolar, pure dipolar, polarizabilities, and structural. Predicted values of $\bar{G}^E$, $\bar{H}^E$, and $\bar{V}^E$ for fluorobenzene with benzene, carbon tetrachloride, or cyclohexane agreed satisfactorily with exeprimental data. $\bar{V}^E$ was determined at 30° for four binary solutions with dioxane by Chand and Ramakrishna.[172] They found good agreement by using APM and Balescu's adjustable parameter θ but questioned the highly idealized assumptions of the Balescu theory.

C. PRINCIPLE OF CONGRUENCE

According to Brønsted and Koefoed's principle of congruence,[173] the activity coefficient of a given component in a liquid mixture of *n*-alkanes is determined by the average number, *n*, of carbon atoms per molecule, defined as

$$n = \sum_i n_i x_i \tag{20}$$

where x_i is the mole fraction in the mixture of an *n*-alkane having n_i carbon atoms. Desmyter and van der Waals[65] extended this by assuming that the volume of a mixture of *n*-alkanes also depends on the average number of carbon atoms per molecule only and proposed the relation

$$\bar{V}^E = \bar{V}_n{}^0 - x_1\bar{V}_{n_1}{}^0 - x_2\bar{V}_{n_2}{}^0 \tag{21}$$

where $\bar{V}_{n_1}{}^0$, $\bar{V}_{n_2}{}^0$, and $\bar{V}_n{}^0$ are the molar volumes of *n*-alkanes having n_1, n_2, and $n = x_1n_1 + x_2n_2$ carbon atoms per molecule, respectively. They checked this for six mixtures of *n*-alkanes ($C_5 + C_{16}$, $C_6 + C_{16}$, $C_7 + C_{16}$, $C_8 + C_{16}$, $C_{10} + C_{16}$, and $C_6 + C_{12}$) with an average error of 0.035 cm^3 mol^{-1} (relative to $\bar{V}^E$ of -0.5 cm^3). Desmyter and van der Waals also found that the excess volumes of equimolar mixtures at 20° for their systems was proportional to $[1/(n_1 + 1) - 1/(n_2 + 1)]^2$. This is shown in Figure 12. Hijmans[174] found by plotting the $\bar{V}^E$ data of Desmyter and van der Waals[65] on one graph that the data were mutually consistent from the standpoint of the principle of congruence. For the $\bar{V}_n{}^0$ terms in eq 21 McGlashan[175] proposed an expansion of the type

$$\bar{V}(n) = \sum_{i=0}^{s} A_i n^i \tag{22}$$

whereas Hijmans and Holleman[176] proposed an expansion in descending powers of $n - 2$ or

$$\bar{V}(n) = a_1(n - 2) + a_0 + \frac{a_{-1}}{(n - 2)} + \frac{a_{-2}}{(n - 2)^2} + \ldots \tag{23}$$

Equation 23 has superior characteristics to eq 22 and is recommended since, among other features, it requires only two constants (*vs.* four for eq 22) to fit the data of Desmyter and van der Waals to ±0.003 cm^3 mol^{-1}. This is so because the first two terms (a_1 and a_0) in eq 23 do not contribute to $\bar{V}^E$. Holleman[62] verified the principle of congruence with binary mixtures of *n*-alkanes in the range C_6 to C_{62} and for temperatures from 51 to 126°. He found the data to be mutually consistent by using a similar graphing procedure as that of Hijmans[174] and fit the data within experimental accuracy (±0.02 cm^3 mol^{-1}) using the following equation (based on eq 23).

$$\bar{V}^E(n_1,n_2,n,T) = \left[\frac{-(n - n_1)(n_2 - n)}{(n_1 - 2)(n_2 - 2)(n - 2)}\right]\left[a_{-1}(T) + a_{-2}(T)\left(\frac{1}{n_1 - 2} + \frac{1}{n_2 - 2} + \frac{1}{n - 2}\right)\right] \tag{24}$$

Table IV gives Holleman's values for a_{-1} and a_{-2}.

Table IV

Values of a_{-1} and a_{-2} for Eq 24 for *n*-Alkanes[a]

Temp (°C)	a_{-1} *(cm^3 mol^{-1})*	a_{-2} *(cm^3 mol^{-1})*
20	11.48	−3.93
51	17.57	−2.21
76	24.29	2.74
96	32.29	4.85
106	35.46	10.00
126	48.00	11.68

[a] Taken from ref 62.

Pflug and Benson[68] tested the principle of congruence on $\bar{V}^E$ at 25° for 11 binary mixtures of the normal alcohols C_1, C_2, C_3, C_4, C_6, C_8, and C_{10} containing either 1-butanol or 1-octanol as one component. For $\bar{V}(n)$ they used the function

$$\bar{V}(n) = \sum_{i=0}^{P} A_i n^{-(i+1)} \tag{25}$$

and found that deviations of $\bar{V}^E$ from congruence were similar to those they had found earlier[177] for $\bar{H}^E$ for the same systems. The constants in eq 25 for the 11 systems studied are:

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(177) A. E. Pope, H. D. Pflug, B. Dacre, and G. C. Benson, *Can. J. Chem.*, **45**, 2665 (1967).

$A_0 = -6.75$, $A_1 = 14.48$, $A_2 = -15.04$, and $A_3 = 5.74$. Bhattacharyya, *et al.*,[178] applied the principle of corresponding states and the principle of congruence to literature data on the (*n*-alkane) $C_6 + C_{16}$ system and found that their corresponding states results gave poorer results than Brønsted's principle of congruence. $\bar{V}^E$'s for the binary *n*-alkane systems $C_{10} + C_{12}$, $C_{12} + C_{14}$, and $C_{12} + C_{16}$ at 45, 55, and 65° and $C_{10} + C_{14}$ and $C_{10} + C_{16}$ at 55 and 65° were measured by Sims and Winnick.[179] Their data reaffirm the principle of congruence and its application to the form $\bar{V}(n)$ (eq 23) proposed by Hijmans and Holleman.[176] Deviations from this correlation averaged 0.004 cm^3 mol^{-1}. Shana'a and Canfield[180] determined the liquid densities of methane, ethane, and propane, of binary mixtures containing methane, ethane, propane, and *n*-butane, and of ternary mixtures of methane, ethane, and propane at −165°. They found that, although the principle of congruence is in good accord with experimental data for the *n*-alkanes above *n*-butane, their results show it to be inadequate for the light hydrocarbons.

Brzostowski[181] developed a principle of corresponding volumes for liquid mixtures which correlates molar volumes with excess thermodynamic properties. This principle was subsequently satisfactorily applied to the system cyclohexane + pyridine.[182]

Dantzler and Knobler[97] found that the principle of congruence was approximately valid for binary dilute gas mixtures of the normal perfluorocarbons, perfluoromethane through perfluorohexane, at 50 and 100° for both $\bar{V}^E$ and $\bar{H}^E$. The excess volumes in the fluorocarbon systems were nearly identical with those in the hydrocarbon systems.[98] The excess volumes were calculated from the excess second virial coefficient and interaction second virial coefficients.

D. THE APPROACH USED BY FLORY AND COWORKERS

Flory and coworkers have developed an approach (we shall adhere to their notation in this section) which relates the excess properties of the mixture to measurable macroscopic properties of the pure liquid components. The equation of state parameters they use to characterize the pure components are the specific volume v, the thermal expansion coefficient $\alpha = v^{-1}(\partial v/\partial T)_p$, and the thermal pressure coefficient $\gamma = (\partial P/\partial T)_v = \alpha/\beta$, where β is the coefficient of compressibility and α and γ are evaluated at nominal pressure. The properties of the mixture are related to those of the pure components by a partition function of such simplicity that it has been shown to be applicable generally to mixtures including those comprising component molecules which are disparate in size and shape. We will first present the equations for Flory's approach and then discuss the applications.

Flory, Orwoll, and Vrij[183] first developed the theory for normal paraffin hydrocarbons.[184] Flory and Abe[185] briefly extended the treatment to mixtures of small molecules. Then Flory[186] developed the equations for liquid mixtures, and Abe and Flory[187] applied the theory to the thermodynamic properties of mixtures of small nonpolar molecules. Abe and Flory[188] extended the treatment to liquid–liquid phase equilibria. Orwoll and Flory[189] used the theory for equation of state parameters for normal alkanes and then treated[190] the thermodynamic properties of binary mixtures of normal alkanes.

Starting with the reduced equation of state and using Flory's notation

$$\bar{p}\bar{v}/T = \bar{v}^{1/3}(v^{1/3} - 1)^{-1} - (\bar{v}\tilde{T})^{-1} \tag{26}$$

we obtain

$$p/\bar{p}_i = p_i^* = \gamma_i T\tilde{v}_i^2 \qquad (27$$

which at zero pressure gives

$$\tilde{T}_i = T/T_i^* = (\bar{v}_i^{1/3} - 1)\bar{v}_i^{-4/3} \tag{28}$$

$$v_i^{1/3} - 1 = (\alpha_i T/3)(1 + \alpha_i T)^{-1} \tag{29}$$

where $\bar{p}$, $\bar{v}$, and $\tilde{T}$ are the reduced variables and p^*, T^*, and V^* (equal to $V^0/\bar{v}$ where V^0 is the molar volume of the pure component) are the characteristic parameters for each of the pure components. For a mixture of two components the following are obtained

$$\tilde{T} = T/T^* = (\phi_1 p_1^*\tilde{T}_1 + \phi_2 p_2^*\tilde{T}_2)(\phi_1 p_1^* + \phi_2 p_2^* - \phi_1\theta_2 X_{12})^{-1} \tag{30}$$

where ϕ_1 and ϕ_2 are the segment fractions, or

$$\phi_2 = 1 - \phi_1 = x_1V_1^0\bar{v}_1^{-1} + (x_1V_1^0\bar{v}_1^{-1} + x_2V_2^0\bar{v}_2^{-1}) \tag{31}$$

and θ_2 is the site fraction or

$$\theta_2 = 1 - \theta_1 = s_2\phi_2/(s_1\phi_1 + s_2\phi_2) \tag{32}$$

with $s_1/s_2 = (V_1^*/V_2^*)^{-1/3}$ for spherical molecules.[187] The interaction parameter X_{12} is the only adjustable quantity in the theory and is used so by Flory and coworkers and others, although some workers[87, 42, 116] have calculated it from[186]

$$X_{12} = p_1^*[1 - (s_2/s_1)^{1/2}(p_2^*/p_1^*)^{1/2}]^2 \tag{33}$$

The reduced excess volume is given approximately[187] by

$$\bar{v}^E = (\bar{v}^0)^{7/3}[{}^4/_3 - ({}^0\tilde{v})^{1/3}]^{-1}(\tilde{T} - \tilde{T}^0) \tag{34}$$

where

$$\bar{v}^0 = \phi_1\bar{v}_1 + \phi_2\bar{v}_2 \tag{35}$$

is the reduced volume which would obtain if mixing occurred without change in volume, and $\tilde{T}^0$ is related to $\bar{v}^0$ according to the form of eq 28. The excess molar volume is then given by

$$\bar{V}^E = (x_1V_1^* + x_2V_2^*)\bar{v}^E \tag{36}$$

Flory, Orwoll, and Vrij[184] applied the thoery to the (*n*-alkane) C_6–C_{16} system with excellent results at both 20 and 50°. Flory and Abe[185] briefly treated some mixtures of small

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(190) R. A. Orwoll and P. J. Flory, *ibid.*, **89**, 6822 (1967).

(191) M. C. Chowdary and V. R. Krishnan, *Aust. J. Chem.*, **20**, 2761 (1967).

nonpolar molecules and this was expanded by Abe and Flory[187] to some 23 mixtures classed in four groups: (a) mixtures of approximately spherical molecules; (b) *n*-alkanes plus cyclic hydrocarbons; (c) benzene plus biphenyl; and (d) hydrocarbons plus fluorocarbons. The agreement between calculated and experimental values of $\bar{V}^{E}$ is very good and is perhaps the strongest point of Flory's approach. Only in one case (CCl_4–$SiCl_4$) was the sign incorrectly predicted and even here the difference was almost within experimental error. Abe and Flory[187] critically discussed their results and the limitations and strengths of their approach to calculating excess properties (the theory is also used for calculating excess enthalpies and Gibbs free energies). Abe and Flory[188] extended the treatment to liquid–liquid phase equilibria evaluating X_{12} from observed critical solution temperature (UCST) of mixtures of hydrocarbons and fluorocarbons. They found that $\bar{H}^{E}$ and $\bar{G}_{p}^{E}$ were fairly well reproduced by theory, and they found excellent agreement between observed and calculated $\bar{H}^{E}$ and $\bar{G}_{p}^{E}$ by using observed values rather than those calculated according to theory. Orwoll and Flory[190] applied the theory to 17 mixtures of *n*-alkanes (C_6 to C_{62}) and the calculated values were slightly more negative than the negative observed $\bar{V}^{E}$ for all cases. The average deviation was 0.09 $cm^3\ mol^{-1}$; $\bar{V}^{E}$ is comparatively insensitive to X_{12}; and the small discrepancies appear to be attributable to limitations inherent in the formal scheme of interpretation rather than to the particular values chosen for the parameters used in the calculation.

Battino and coworker[87,42,116] used the Flory theory to calculate $\bar{V}^{E}$ for binary mixtures of 2,2,4-trimethylpentane with CCl_4 and c-C_6H_{12} and found good agreement. They did not use X_{12} as an adjustable parameter in their calculations. Rastogi, Nath, and Misra[192] investigated the thermodynamics of weak interactions in liquid mixtures by measuring $\bar{V}^{E}$ and $\bar{H}^{E}$ for the binary mixtures of C_6H_6 and CCl_4 with toluene and *p*-xylene (10 to 35°). They found that only Flory's theory (others tested: lattice model, conformal solution, Prigogine's refined model) correctly predicted sign and magnitude with an average percentage deviation of 60%. Rastogi, Nath, and Misra[162] in a second paper investigated binary mixtures of CCl_4 and C_6H_6 with *o*-xylene and *m*-xylene. The various theories of solutions tested (including Flory's) gave much poorer results here mostly attributable to the specific interaction between CCl_4 and the aromatics, which is not taken into account in the theories. Hocker and Flory[193] got rather good results for calculations on $\bar{V}^{E}$ for liquid mixtures of Ar and Kr. Although the difference between calculated and experimental $\bar{V}^{E}$ was about 0.2 $cm^3\ mol^{-1}$, the sign and skewed shape of the composition dependence of $\bar{V}^{E}$ were correct. Benson and Singh[194] used the Flory theory to analyze $\bar{H}^{E}$ and $\bar{V}^{E}$ for a number of aromatic–alicyclic systems (*cf.* ref 28 and 159). They did an analysis of the effect on $\bar{V}^{E}$ and $\bar{H}^{E}$ of the way in which X_{12} was calculated. For the eight systems studied they found an average deviation in $\bar{V}^{E}$ of ±0.065 $cm^3\ mol^{-1}$ for X_{12} fit to $\bar{H}^{E}$ and ±0.015 $cm^3\ mole^{-1}$ for X_{12} fit to $\bar{V}^{E}$. Nigam and Singh[195] determined $\bar{V}^{E}$ for eight binary mixtures (35–45°) taken from benzene, toluene, cyclohexane, carbon tetrachloride, chloroform, bromobenzene, and chlorobenzene and examined their results in terms of both APM and Flory's theory. They found that the Flory theory gave reasonable quantitative agreement and the correct sign of the excess functions. When Flory's theory is applied to polar mixtures the contributions as well as the deviation from the geometric mean law must be taken into account. Singh, Pflug, and Benson[196] applied the theories of Barker and Flory to their measurements of $\bar{H}^{E}$ and $\bar{V}^{E}$ at 25° on binary mixtures of benzene with *o*-, *m*-, and *p*-xylene. Both theories indicated an increase in the aromatic–aliphatic interaction energy in the benzene solutions of *o*- and *m*-xylene as compared to those of *p*-xylene. However, the Flory theory furnished an independent estimate of $\bar{V}^{E}$ which was of the correct magnitude, whereas similar corroboration of the quasi-lattice theory was not possible. $\bar{H}^{E}$ and $\bar{V}^{E}$ at 25° for the systems benzene + toluene and toluene + *p*-xylene, *o*-xylene, and *m*-xylene were measured by Murakami, Lam, and Benson.[197] The results for these systems and the benzene + isomeric xylene systems were analyzed in terms of the Barker and Flory theories. Both theories gave reasonable correlations; *e.g.*, the Flory theory calculation for these seven systems showed errors of less than 24% for $\bar{V}^{E}$. Benson and coworkers[198] determined the excess functions for the cyclopentane + carbon tetrachloride system at 250°. Neither the theories of Prigogine nor Flory gave satisfactory estimates of $\bar{V}^{E}$, although the Flory theory gave reasonable estimates for the cyclohexane + carbon tetrachloride system. Sims and Winnick[179] found that the Flory theory correctly predicted $\bar{V}^{E}$ for the *n*-alkane systems they studied to a deviation of ±0.012 $cm^3\ mol^{-1}$ (experimental error of 0.007 $cm^3\ mol^{-1}$).

VI. V^{E} and $\bar{V}$ in Dilute Solutions

Partial molar volumes and excess volumes in highly dilute solutions have been of interest primarily because in these solutions the solute molecules are essentially isolated from each other and the principal interactions are solute–solvent and solvent–solvent. Staveley and Spice[58] measured the volume changes at 20° for mixing the first six primary alcohols and 1-octanol and 1-decanol with benzene, *n*-heptane, and cyclohexane for mole fractions of the alcohols between 0.005 and 0.035. They extrapolated their results to obtain partial molar volumes of the alcohols at infinite dilution, $\bar{V}_{\infty}$. In heptane the values of $\bar{V}_{\infty}$ increase by almost constant increments in going from ethanol to 1-decanol; the increments, however, show an alternation in benzene and cyclohexane. Their results suggest that from 1-pentanol onwards in benzene and cyclohexane the monomeric alcohol molecules tend to coil into a cyclic configuration. The evidence points to association of the alcohols as trimers in all three solvents with the possibility that association starts as tetramers or higher aggregates in benzene, although recent work does not suggest the predominance of any particular polymers.

Friedman and Scheraga[199] determined partial molar volumes at 1–50° of solutions (2 wt % and less) of methanol,

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(192) R. P. Rastogi, J. Nath, and J. Misra, *J. Phys. Chem.*, 71, 1277 (1967).

(193) H. Hocker and P. J. Flory, *Trans. Faraday Soc.*, 64, 1188 (1968).

(194) G. C. Benson and J. Singh, *J. Phys. Chem.*, 72, 1345 (1968).

195) R. K. Nigam and P. P. Singh, *Trans. Faraday Soc.*, 65, 950 1969).

(196) J. Singh, H. D. Pflug, and G. C. Benson, *J. Phys. Chem.*, 72, 1939 (1968).

(197) S. Murakami, V. T. Lam, and G. C. Benson, *J. Chem. Thermodyn.*, 1, 397 (1969).

(198) T. Boublik, V. T. Lam, S. Murakami, and G. C. Benson, *J. Phys. Chem.*, 73, 2356 (1969).

(199) M. E. Friedman and H. A. Scheraga, *ibid.*, 69, 3795 (1965).

ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 2-butanol, 1-pentanol, and benzyl alcohol in water. They extrapolated their results to infinite dilution to see if there were additive contributions from the polar and nonpolar portions of the alcohol molecules and to check equations derived by Nemethy and Scheraga.[200,201] Their results provide a qualitative verification of their theory since their model[201] assumes a decrease in volume when hydrocarbon is transferred to water because the hydrocarbon fills the ice-like partial cages (in water) quite efficiently. This volume decrease is observed experimentally. Franks and Quickenden[202] made similar studies at 25° of the partial molar volumes of 1,4-dioxane, 1-butanol, tetrahydrofuran, and tetrahydropyran in dilute (with results extrapolated to infinite dilution) aqueous solutions. Franks and Smith[203] reported on the precision density of dilute (0.003–0.2 *m*) aqueous solutions of isomeric butanols (0.5–40°). Armitage, *et al.*,[204] discuss partial molar volumes and maximum density effects in alcohol–water mixtures. Franks and Ives[205] in an extensive review article discuss and illustrate that the volumetric behavior of dilute aqueous solutions can provide information about solute–water interactions and the influence of the solutes on the intermolecular structure of liquid water. Nakanishi[206] and coworkers[207] studied the volume change on mixing (with some results extrapolated to infinite dilution) of the butanols, 1-pentanol, and five glycols in water. They confirmed the generally observed negative excess volumes found for liquid mixtures containing water, alcohols, or other associated liquids as one or both components. Sircar and Palit[208] proposed a method for the determination of the partial specific volume or the partial molar volume at infinite dilution from refraction measurements only and without solution density measurements at all. Their calculated values agreed to within ±0.6–1.0 cm^3 mol^{-1} with experimental values, and they suggested that their method would be helpful in estimating the partial specific volume of proteins and similar compounds.

Differentiation of eq 15 in the limit as $x_2 \rightarrow 0$ gives

$$\tilde{V}_2^{\mathrm{E}} = \tilde{V}_2 - \tilde{V}_2^0 = n_1\beta_1\tilde{G}_2^{\mathrm{E}} = n_1\beta_1 RT\ln\gamma_2 = \alpha_1 T\tilde{G}_2^{\mathrm{E}}/\delta_1^2 \quad (37)$$

Since for regular solutions $\tilde{G}_2^{\mathrm{E}} = \tilde{V}_2^0(\delta_1 - \delta_2)^2$, we may rearrange eq 37 to give

$$\left(\frac{\tilde{V}_2 - \tilde{V}_2^0}{\tilde{V}_2^0}\right)^{1/2} = \pm(n_1\beta_1)^{1/2}(\delta_2 - \delta_1) \quad (38)$$

This equation suggests that a plot of the left-hand side of eq 38 should be proportional to $\pm(\delta_2 - \delta_1)$. That this was roughly the case was shown by Hildebrand and coworkers[1,209] for a variety of solutes in CS_2, CCl_4, and *n*-C_7H_{16}.

Hildebrand and Dymond[210] proposed the following equation as preferable to eq 38.

$$(\tilde{V}_2 - \tilde{V}_2^0)\left(\frac{\partial E_1}{\partial V}\right)_T = \tilde{V}_2^0(\delta_1 - \delta_2)^2 \quad (39)$$

A comparison was made between the left-hand and right-hand sides of eq 39 for 19 cases for energies up to 2.5 kcal and expansion up to 20%, and remarkably good agreement was found. Equation 39 is certainly better than eq 38, but there are still many systems (*e.g.*, those involving isooctane) for which it does not hold.

Shinoda and Hildebrand[211] reported on the partial molar volumes of iodine in 25 complexing and noncomplexing solvents at 25° and mole fractions less than 0.002. They described a rather simple technique for these measurements which had an uncertainty of about 0.3 cm^3 in the partial molar volume of iodine. Masterton and Seiler[47] determined the apparent and partial molar volumes of water (at water concentrations up to 0.1 *M*) in benzene, carbon tetrachloride, 1,1,1-trichloroethane, and 1,2-dichloroethane. In no case was there any evidence of a decrease in the apparent molar volume with increasing concentration, as would be required if the water were extensively polymerized.

VII. Additional Contributions of Note

In this section we briefly note additional contributions to theory and other interesting observations.

Diaz Pena and Cavero[26] measured $\tilde{V}^{\mathrm{E}}$ and $\mathrm{d}\tilde{V}^{\mathrm{E}}/\mathrm{d}P$ for binary mixtures of chloroform with benzene, cyclohexane, and CCl_4, and benzene with cyclohexane and CCl_4. They subsequently[156] discussed their results as compared with lattice theory and average potential theory. Pardo and Van Ness[74] determined $\tilde{V}^{\mathrm{E}}$ at 25 and 45° for binary solutions or ethanol with cyclohexane, toluene, *o*-xylene, *p*-xylene, and *m*-xylene. All systems (except EtOH + C_6H_{12} which is positive only) show both positive and negative values of $\tilde{V}^{\mathrm{E}}$ as a function of composition. Some of the measurements were made at mole fractions down to 0.005. Van Ness and Machado[72] measured $\tilde{V}^{\mathrm{E}}$ for the systems acetone + CCl_4, $CHCl_3$, and CH_2Cl_2 and for CH_2Cl_2 + methyl acetate. The first two systems show positive and negative values of $\tilde{V}^{\mathrm{E}}$ as a function of composition. Brown and Smith[52] determined $\tilde{V}^{\mathrm{E}}$ at 25, 35, and 45° for binary mixtures of benzene with ten alcohols. All systems show positive $\tilde{V}^{\mathrm{E}}$ except those with MeOH, EtOH, and PrOH which show both positive and negative values (Figure 13). Brown and Smith[212] measured $\tilde{V}^{\mathrm{E}}$ at 25, 35, and 45° for binary mixtures of benzene and CCl_4 with acetone, acetonitrile, and nitromethane. They suggested that the complex behavior shown by these systems indicated that dipole interaction was not the only cause of the deviations and that the electron donor and acceptor properties of the components also played an important part (Figure 14). Brown, Fock, and Smith[213] compared the thermodynamic properties of the normal alcohols in benzene and *n*-hexane solutions with the corresponding properties of the branched alcohol solutions. Since alcohols are strongly associated by hydrogen bonding, it has been found useful to consider

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(200) G. Nemethy and H. A. Scheraga, *J. Phys. Chem.*, **66**, 1773 (1962); 67, 2888 (1963).

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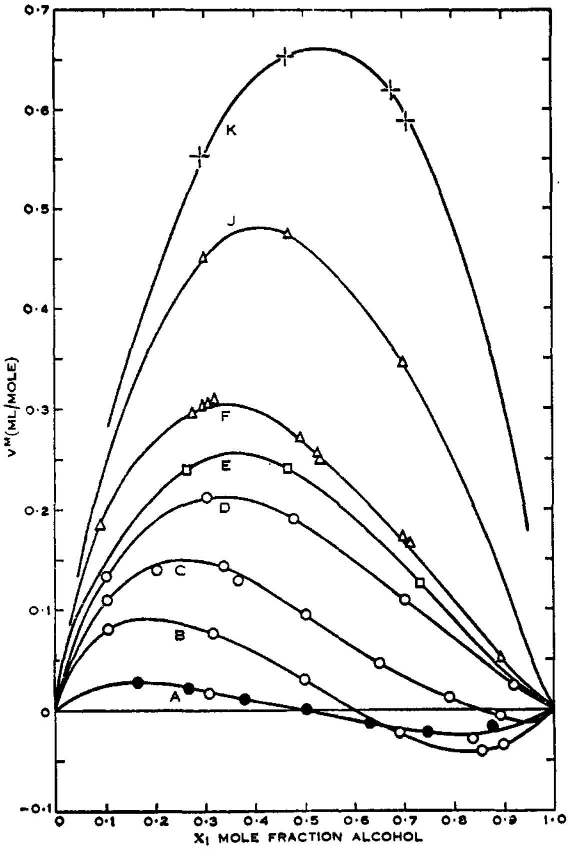

Figure 13. All systems at 25° with benzene as second component. System A from ref 31, all others from ref 52: (A) methanol, (B) ethanol, (C) 1-propanol, (D) 1-butanol, (E) 2-methyl-1-propanol, (F) 2-propanol, (J) 2-butanol, (K) 2-methyl-2-propanol (K at 27°). Reprinted by permission of the authors and the *Australian Journal of Chemistry*.

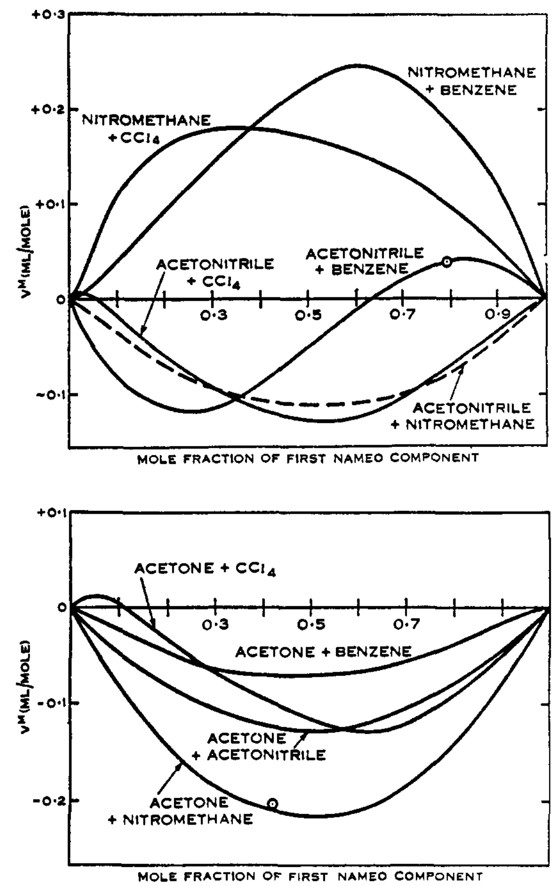

Figure 14. Volume changes on mixing at 25°.[212] Reprinted by permission of the authors and the *Australian Journal of Chemistry*.

changes in the thermodynamic functions which occur on diluting an alcohol with a nonpolar solvent as consisting of a part due to the breaking of hydrogen bonds and another part due to the mixing of the alcohol homomorph with the solvent. The systems discussed in detail are: normal alcohols + normal alkanes, normal alcohols + benzene, branched alcohols + normal alkanes, and branched alcohols + benzene. Figure 15 shows (from ref 213) an excellent summary of $\bar{V}^{E}$ for equimolar mixtures at 25° as a function of the number of carbon atoms per molecule for a variety of systems. Duncan, Sheridan, and Swinton[56] measured $\bar{V}^{E}$ at 40° for binary mixtures of hexafluorobenzene with cyclohexane, cyclohexene, 1,3-cyclohexadiene, benzene, toluene, *p*-xylene, mesitylene, and cumene. Their results (Figure 16) indicated that hexafluorobenzene forms complexes with the hydrocarbons to an increasing extent as the electron-donating power of the hydrocarbon is increased. Munn,[214] using a formula derived by Kohler[144] which is based on the London dispersion forces formula but which does not require knowledge of the ionization potentials, estimated the unlike interaction energies in various perfluorocarbon–hydrocarbon and hydrocarbon–hydrocarbon mixtures. The agreement for thermodynamic excess functions for perfluorocarbon–hydrocarbon systems was good with the exception of the excess volumes.

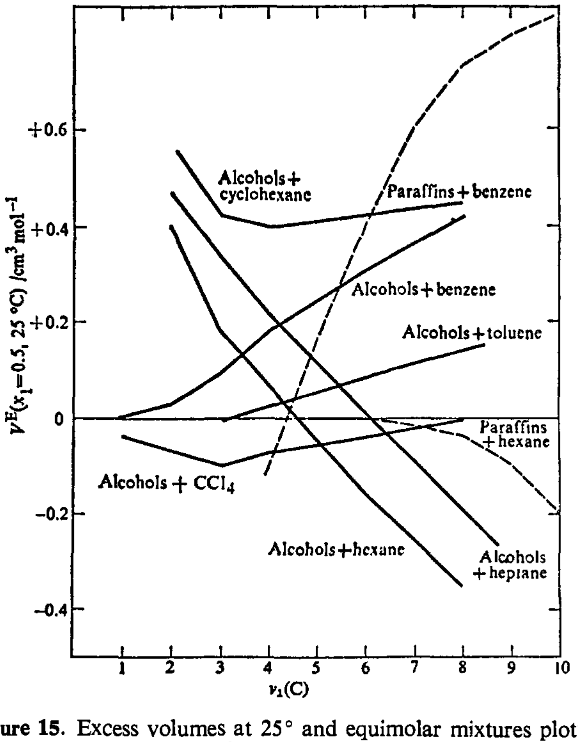

Figure 15. Excess volumes at 25° and equimolar mixtures plotted against the number ν_1(C) of carbon atoms per molecule of the first-named substance.[213] Reprinted by permission of the authors and the *Journal of Chemical Thermodynamics*.

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Eyring and coworkers[215,216] have applied the significant structure theory of liquids to binary liquid mixtures. This theory as applied by Eyring and coworkers gave outstanding results for the excess thermodynamic functions (including $\tilde{V}^E$) for the CCl_4-c-C_6H_{12} system,[215] and for the CCl_4-C_6H_6 and C_6H_6-c-C_6H_{12} systems.[216]

Barriol and Boule[217] related $\tilde{V}^E$ for mixtures of polar and nonpolar liquids to the compressibilities of the liquids. Boule[218] discussed the effect of hydrogen bonding on the molar volume of polar liquid mixtures and found that the formation of complexes *via* hydrogen bonding is accompanied by a decrease in volume which is characteristic of the extent of the bonding. Fialkov[219] gave deviation functions from additivity for 100 binary mixtures for density, molar volumes, and atomic concentrations. Lutskii and Obukhova[220] give an equation relating the density of binary mixtures to size, shape, polarizability, mass, and dipole moment of the components. The benzene + carbon tetrachloride system has been studied by a number of workers.[30,55,221] This system (see Figure 17) shows an unusual double maximum as the temperature decreases. Giguere, *et al.*,[222] determined $\tilde{V}^E$ for $D_2O + D_2O_2$ at 0 and 20° and presented a table of $\tilde{V}^E$ for the $H_2O + H_2O_2$ system from −10 to −50°. The maximum in the $\tilde{V}^E$ curves is presumably related to the formation of the compound $H_2O_2 \cdot 2H_2O$. Excess volumes of binary mixtures of cyclohexane with phenol, *o*-, *m*-, and *p*-cresol, and *o*- and *p*-chlorophenol were measured by Raman, *et al.*,[223] to indicate the relative strengths of hydrogen bonding in phenol and substituted phenols. Schoenert[224] developed a theory relating $\tilde{V}^E$ to the extent of hydration for aqueous solutions of nonelectrolytes. In addition to data on the binary systems involved, Heric and Brewer[225] determined $\tilde{V}^E$ for 11 ternary systems at 25° from among the components n-C_6H_{14}, n-$C_{14}H_{30}$, n-$C_{16}H_{34}$, CCl_4, C_6H_6, 2-bromobutane, and 4-methylcyclohexanone. Campbell, *et al.*,[226] measured $\tilde{V}^E$ for the ternary system acetic acid–chloroform–water and the two binary systems acetic acid + water and + chloroform at 25°. $\tilde{V}^E$ for four systems involving diketones was measured at 25° by Nakanishi, *et al.*[227] The partially miscible system aniline + n-hexane at 25° showed a negative $\tilde{V}^E$ except for solutions rich in n-hexane. This behavior is unusual for partially miscible systems with positive $\bar{H}^E$ and positive deviations from Raoult's law. No evidence of compound formation was found, but there was evidence of association in aniline due to hydrogen bonding. Bhattacharyya, *et al.*,[228] examined their data on the excess functions of the systems toluene + fluorobenzene and methylcyclohexane + fluorobenzene from the viewpoint of a generalized quasi-

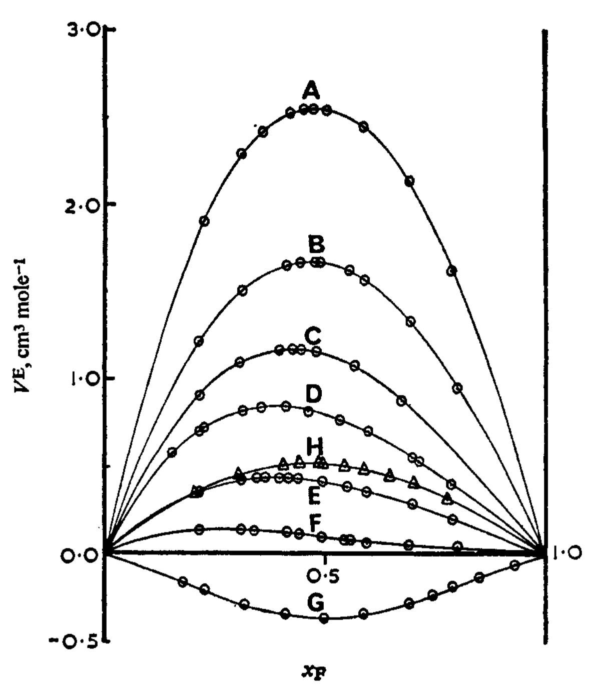

Figure 16. Volume changes on mixing at 40° with hexafluorobenzene (x_F):[56] (A) cyclohexane, (B) cyclohexene, (C) 1,3-cyclohexadiene, (D) benzene, (E) toluene, (F) *p*-xylene, (G) mesitylene, and (H) cumene. Reprinted by permission of the authors and the Faraday Society.

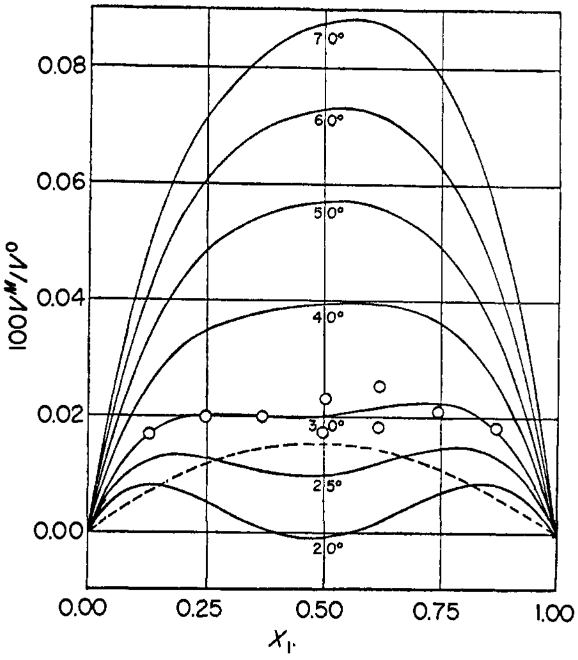

Figure 17. The carbon tetrachloride (x_1)–benzene system.[30] The dashed line is from Scatchard, Wood, and Mochel[221] at 25°. Reprinted by permission of the copyright owner, the American Chemical Society.

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lattice treatment. They discuss some of the drawbacks of the theory but conclude that, although the approach does not provide an independent estimate of $\tilde{H}^E$ and $\tilde{G}^E$, it is nevertheless possible to predict the excess functions in terms of various molecular interaction pairs once these have been obtained uniquely from the analysis of data of other carefully chosen allied binary systems. Kershaw and Malcolm[229] determined $\tilde{H}^E$ and $\tilde{V}^E$ at 5.5° for solutions of polypropylene oxide in chloroform and carbon tetrachloride. The chloroform solutions were treated adequately using the "xeroth approximation" in the lattice theory, and the Flory theory predicted the behavior of the carbon tetrachloride solutions within experimental error. Deshpande and Bhatgadde[230] related free volume to excess volumes, finding the magnitude of the excess free volume to be much smaller than the excess volume. They studied solutions in aniline.

Scott and coworkers[231] related $\tilde{V}^E$ and upper critical solution temperatures and discussed the effect of pressure on liquid miscibility. In the critical region the following approximation holds.

$$\frac{dT_c}{dP} = T_c\left(\frac{\tilde{V}^E}{\tilde{H}^E}\right)_{X_c,T_c} \tag{40}$$

This equation could be tested experimentally and was done so for four systems with reasonable agreement. Data for dT_c/dP are presented for nine systems. Dunlap and Furrow[232] determined the partial molar volumes for the perfluoro-*n*-heptane + 2,2,4-trimethylpentane system at several concentrations through the critical solution region and at infinite dilution. A plot of $(\partial^2\tilde{V}^E/\partial x^2)_{T,P}$ *vs.* composition shows that the third derivative, *i.e.*, $(\partial^3\tilde{V}^E/\partial x^3)_{T_c,P}$, vanishes in the neighborhood of the critical solution point. Scott and coworkers[233] studied the 1-hydro-*n*-perfluoroheptane + acetone system determining $\tilde{G}^E$ at 0°, $\tilde{V}^E$ at 20°, and $\tilde{H}^E$ in the range 0–35°. Volume changes for this system ($\tilde{V}^E_{max}$ = 1.83 cm^3 at x(acetone) = 0.70) are less positive than those observed for fluorocarbon + hydrocarbon systems. Davenport, Rowlinson, and Saville[80] determined the excess volumes of methane with isopentane and 2-methylpentane at 115–155°K, but, strictly speaking, these are not excess volumes since the pressure is changing with composition at constant temperature. Both systems show negative $\tilde{V}^E$, but the contraction is so severe that the apparent partial molar volume of methane is negative at high temperatures and infinite dilution. They suggest that this phenomenon must be fairly common in other systems in which the LCST is near the gas–liquid critical point of the pure solvent.

Strictly speaking, binary systems in which one of the components can exist in two or more conformational isomers or is able to form dimers, trimers, etc., cannot be treated as binary mixtures by the simple theories of binary mixtures outlined in the previous pages. An example of the former type is the system benzene + 1,3-dichloroethane,[234] and of the latter type is the system carbon tetrachloride + acetic acid.[235] The 1,2-dichloroethane may exist in a trans or gauche (skewed) form, and acetic acid is extensively dimerized. Wilhelm, *et al.*,[236] discuss the 1,2-dichloroethane and 1,2-dibromoethane with benzene or cyclohexane systems.

Woycicki and Sadowska in a series of six papers[237–242] systematically studied the excess heats and volumes in 32 binary systems formed from cyclohexane, benzene, pyridine, piperidine, and their methyl derivatives. The choice of these substances enabled them to study the effect of the methyl group upon excess functions and, in particular, the effect when the methyl group is the neighbor of an electron donor. They were thus able to assess the influence of the CH_3 group upon interactions of the π–π, π–n, N–H···π, and N–H···N types. Woycicki[243] defined a kind of pseudo-binary system being constituted from two pseudo-individual liquids. For example, a mixture of cyclohexane and ethylcyclohexane is a pseudo-individual liquid for methylcyclohexane. Mixing two "identical" pseudo-individual liquids should result in both $\tilde{H}^E$ and $\tilde{V}^E$ being close to zero. That this is qualitatively so is shown in Table V for six systems.

Table V

Excess Heats and Volumes for Pseudo-Binary Systems at 25° [a]

x_1	*Component 1*	*Component 2*	$\tilde{H}^E$ (*J*)	$\tilde{V}^E$ (*cm*^{3})
0.487	Cyclohexane	Cyclohexane + ethylcyclohexane	18.3	0.040[b]
0.492	Methylcyclohexane	Cyclohexane + ethylcyclohexane	−4.2	0.008
0.501	Ethylcyclohexane	Cyclohexane + ethylcyclohexane	10.7	0.030
0.491	Benzene	Benzene + ethylbenzene	35.0	0.015
0.495	Toluene	Benzene + ethylbenzene	2.8	−0.035
0.489	Ethylbenzene	Benzene + ethylbenzene	21.2	0.030

[a] From ref 243. [b] All $\tilde{V}^E$ read from graph in ref 243.

Winnick and Powers[244] determined the *P–V–x* behavior of the liquid system acetone + carbon disulfide at 0° and pressures up to 100,000 psi. They give experimental details on the apparatus used. Their results are shown in Figure 18 where it is seen that $\tilde{V}^E$ decreases from a maximum of about 1 cm^3 at atmospheric pressure to about 0.4 cm^3 at 100,000 psi. The maximum also shifts to higher mole fractions of acetone. In a second paper[245] the same authors use their

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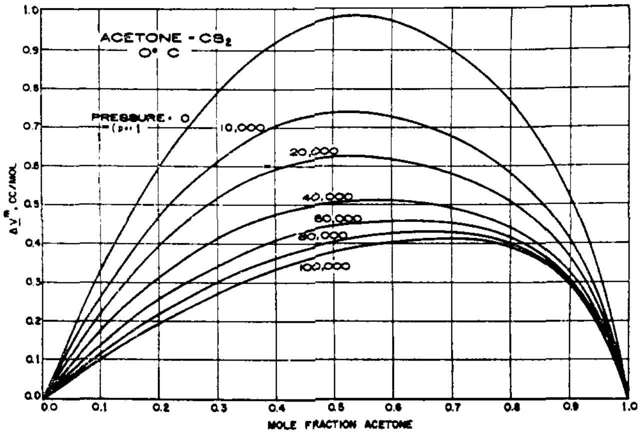

Figure 18. The acetone + carbon disulfide system[244] at high pressures. Reprinted by permission of the authors.

$\bar{V}^E$ data to calculate Gibbs free energies needed to predict the pressure of isothermal liquid–liquid phase separation.

Schneider[246–248] examined the behavior of binary liquid systems at high pressures. In a rather comprehensive paper[248] he assembled and discussed results on the pressure dependence of demixing phenomena in liquid systems. In particular he presents a table giving the sign of various thermodynamic functions for liquid mixtures at high pressures for a variety of conditions. Schneider and Engels[88] developed an apparatus for the direct measurement of $\bar{V}^E$ between 20 and 150° and up to 3000 atm with an accuracy of better than ± 0.005 $cm^3\ mol^{-1}$. The importance of going to high pressures to determine $\bar{V}^E$ is that the pressure dependence of $\bar{G}^E$, $\bar{S}^E$, $\bar{H}^E$, and $\bar{C}_p{}^E$ may be obtained from accurate measurements of $\bar{V}^E$ as a function of temperature, pressure, and concentration. Figure 19 shows Schneider and Engels' results for the 3-methylpyridine + water system. The pressure dependence of the critical solution temperatures suggested that $\bar{V}^E$ should change its sign from minus to plus with increasing pressure. This prediction was confirmed experimentally.

VIII. Volume Changes on Mixing Data

This section contains three tables presenting citations and data for volume changes on mixing for binary systems. Table VI lists all of the post-Timmermans[10] systems for which we found usable data. The listing of systems follows the organization that Timmermans used. The first-named component in column one is component 1. The second column indicates the temperature range of measurement in °C unless otherwise specified. The temperature in column two following the semicolon is the temperature for which the excess volume is reported in column three. A second line in column two indicates the pressure range (if any) of the measurements. Column three presents the excess volume in $cm^3\ mol^{-1}$ for an *equimolar* mixture. Curve A in Figure 20 shows the representative shape for most systems (note that plus signs are not used in the table). Curve B is skewed to the left. This is indicated in the table by a capital L following the data in column three. A capital R indicates a skew to the right. A curve was considered skewed if the

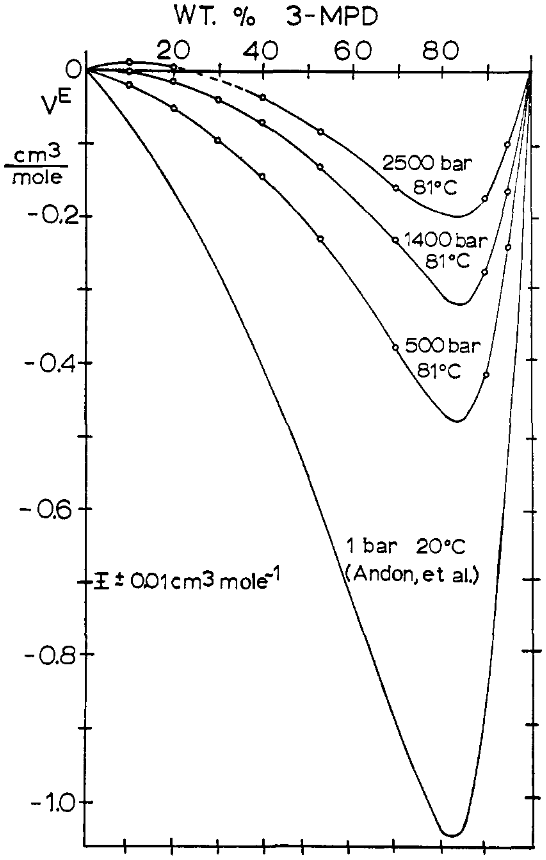

Figure 19. Excess volume of the 3-methylpyridine + water system[88] as a function of pressure. Reprinted by permission of Professor G. M. Schneider.

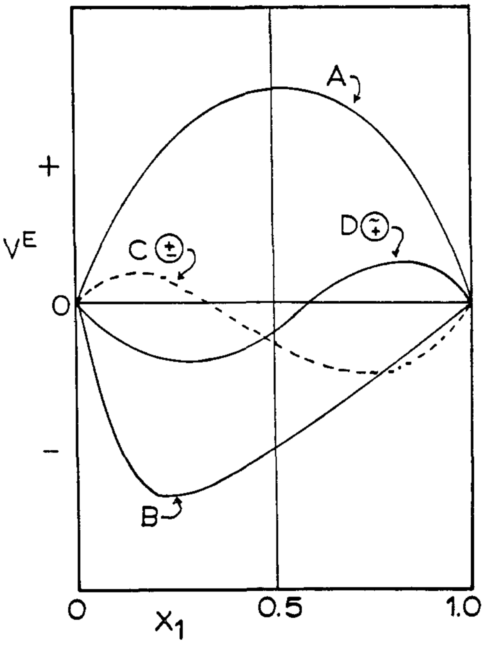

Figure 20. Representative curves for excess volumes. See text for explanation of key to tables.

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maximum was at a mole fraction less than 0.4 or greater than 0.6. (The skew of an experimental curve for a system is not indicated in all cases where it may occur because it was overly time-consuming to extract this information from the literature.) A system which shows both positive and negative excess volumes will have the data followed by ± (curve C) or ∓ (curve D). The letter P following the data indicates that phase separation took place in the system. The letter G indicates that the data was read from graphs. In many cases the excess volume at one-half mole fraction was calculated from density–composition data by interpolation assuming a linear relation in the range used. A second line under the excess volume indicates the pressure for which the excess volume is reported. The precision of the data is indicated in column four in two ways. The symbol DV3 means that the data were reported as excess volumes and that the precision for $\bar{V}^E$ is *three* decimal places or ±0.002 cm^3 mol^{-1}. DV2 refers to *two* decimal places or ±0.02 cm^3 mol^{-1}. If a minus sign follows the DV symbol, then the precision was estimated to be poorer; *i.e.*, DV3− means ±0.005 cm^3 mol^{-1}. If the data were reported as densities, then the precision is indicated numerically as to the number of decimal places, *i.e.*, 5 means density data with a precision of ±0.00002 g cm^{-3} and 4− means ±0.0005 g cm^{-3}. Finally, column five is the literature citation.

Table VII contains excess volume data and information for binary systems where both components are in the gas state (or would be in the gas state at 298°K and 1 atm). The meaning of the columns is the same as in Table VI.

Table VIII lists the partial molar volume at infinite dilution of the second-named component in the first-named component. The partial molar volumes are in cm^3 mol^{-1}. The precision of the data is indicated by the numbers 1 and 2 which correspond to the number of decimal places. For example, $\bar{V}_i^\infty$ of 142.13 ± 0.02 cm^3 mol^{-1} would have a precision of 2. A precision of 2− means ±0.05 cm^3 mol^{-1}.

The author has on file copies of essentially all of the papers cited in Tables VI, VII, and VIII.

Table VI

Volume Changes on Mixing for Liquid + Liquid Systems

System	*Temp range (°C)*	$\bar{V}^E$	*Precision*	*Ref*
	A. Mixtures of Two Hydrocarbons			
I. Paraffins + other hydrocarbons				
Methane + ethane	108°K	−0.506R	DV3−	180
Methane + propane	108°K	−0.731	DV3−	180
Methane + 2-methylbutane	115–155°K; 115°K Pres	−1.2R Pres	DV1	80
Methane + 2-methylpentane	115–155°K; 115°K Pres	−1.2R Pres	DV1	80
Ethane + propane	108°K	−0.384R	DV3−	180
n-Pentane + n-hexadecane	20	−0.82L	DV3−	65
n-Pentane + o-xylene	25	−0.87G	DV2	249
n-Pentane + ethylbenzene	25	−0.63G	DV2	249
2,2-Dimethylpropane + cyclohexane	0	−1.16	DV2	36
2,2-Dimethylpropane + benzene	0	−0.52	DV2	36
n-Hexane + n-dodecane	25–35; 25	−0.23	4	250
n-Hexane + n-dodecane	25–40; 25	−0.31	DV2	251
n-Hexane + n-dodecane	20	−0.31	DV3−	65
n-Hexane + n-tetradecane	25	−0.52	DV2	252
n-Hexane + n-hexadecane	25	−0.56	DV2	252
n-Hexane + n-hexadecane	51	−0.82	DV2	62
n-Hexane + n-hexadecane	20–25; 25	−0.58R	DV3−	65
n-Hexane + n-hexadecane	20–60; 20	−0.484R	DV3	253
n-Hexane + n-C$_{24}$H$_{50}$	51	−1.19	DV2	62
n-Hexane + cyclohexane	15–35; 25	0.150L	DV3	254
n-Hexane + cyclohexane	25	0.043	DV3−	255
n-Hexane + cyclohexane	25	0.20	DV2	27
n-Hexane + cyclohexane	22	0.10L	DV2	256
n-Hexane + benzene	25	0.253	DV3−	255
n-Hexane + benzene	30–40; 30	0.40	DV2	257
n-Hexane + benzene	25	0.42	DV2	27
n-Hexane + benzene	25	0.45	DV2	252
n-Hexane + benzene	25–40; 25	0.48	DV2	258
n-Hexane + toluene	25	0.57G	DV2	249
n-Hexane + ethylbenzene	25	−0.18G	DV2	249
2-Methylpentane + n-hexadecane	20	−0.633	DV3−	122
3-Methylpentane + n-hexadecane	20	−0.457	DV3−	122
2,2-Dimethylbutane + n-hexadecane	20	−0.732	DV3−	122
2,3-Dimethylbutane + n-hexadecane	20	−0.532	DV3−	122
n-Heptane + 2,2,4-trimethylpentane	30	0.00	4	259

Table VI (Continued)

System	*Temp range (°C)*	$\tilde{V}^E$	*Precision*	*Ref*
n-Heptane + *n*-hexadecane	30	0.03	4−	260
n-Heptane + *n*-hexadecane	22	0.03	DV2	261
n-Heptane + *n*-hexadecane	76	−0.77	DV2	62
n-Heptane + *n*-hexadecane	20–40; 25	−0.34R	DV3−	65
n-Heptane + *n*-$C_{24}H_{50}$	76	−1.22	DV2	62
n-Heptane + *n*-$C_{36}H_{74}$	76	−1.59	DV2	62
n-Heptane + cyclohexane	30	0.33	4	260
n-Heptane + cyclohexane	25	0.27	DV2	27
n-Heptane + benzene	30	0.58	4	260
n-Heptane + benzene	25	0.51	DV2	27
n-Heptane + benzene	25–40; 25	0.64	DV2	257
n-Heptane + benzene	25	0.536	DV3	262
n-Heptane + toluene	25	0.23	DV2	27
n-Heptane + decalin	30	−0.64	4	260
n-Heptane + *trans*-decalin	15–40; 25	−0.644	DV3	263
2,4-Dimethylpentane + cyclohexane	28	0.000	DV3−	264
n-Octane + *n*-hexadecane	51–106; 51	−0.32	DV2	62
n-Octane + *n*-hexadecane	20–50; 20	−0.19L	DV3−	65
n-Octane + *n*-$C_{24}H_{50}$	106	−1.34	DV2	62
n-Octane + *n*-$C_{32}H_{66}$	96–106; 96	−1.49	DV2	62
n-Octane + *n*-$C_{36}H_{74}$	96–106; 96	−1.20	DV2	62
n-Octane + toluene	30–95; 30	0.01	4−	265
2,2,4-Trimethylpentane + *n*-dodecane	30	−0.32	DV2	266
2,2,4-Trimethylpentane + *n*-hexadecane	30	−0.57	4	259
2,2,4-Trimethylpentane + *n*-hexadecane	25	−0.50L	DV3−	65
2,2,4-Trimethylpentane + benzene	30	0.58	4	259
2,2,4-Trimethylpentane + benzene	20–75; 25	0.522	DV3	267
2,2,4-Trimethylpentane + cyclohexane	30	0.00	4	259
2,2,4-Trimethylpentane + cyclohexane	25	0.027∓	DV3	37
2,2,4-Trimethylpentane + toluene	28–90; 28	0.085	DV3−	264
2,2,4-Trimethylpentane + decalin	30	−0.78	4	259
n-Nonane + *n*-hexadecane	126	−0.61	DV2	62
n-Nonane + *n*-$C_{24}H_{50}$	51–126; 51	−0.43	DV2	62
n-Nonane + *n*-$C_{32}H_{66}$	96	−1.14	DV2	62
n-Nonane + *n*-$C_{36}H_{74}$	96–126; 96	−1.25	DV2	62
n-Nonane + *n*-$C_{62}H_{126}$	126	−2.51	DV2	62
n-Nonane + *trans*-decalin	25–40; 25	−0.337	DV3	263
n-Decane + *n*-dodecane	45–65; 45	−0.029	DV3−	179
n-Decane + *n*-dodecane	25–35; 25	−0.008	DV3	268
n-Decane + *n*-tetradecane	55–65; 55	−0.081	DV3−	179
n-Decane + *n*-tetradecane	25–45; 25	−0.041	DV3	268
n-Decane + *n*-hexadecane	20–30; 20	−0.07	DV3−	65
n-Decane + *n*-hexadecane	55–65; 55	−0.142	DV3−	179
n-Decane + *n*-hexadecane	25–45; 25	−0.075	DV3	268
n-Undecane + benzene	25–40; 25	0.95L	DV2	257
n-Dodecane + *n*-tetradecane	45–65; 45	−0.012	DV3−	179
n-Dodecane + *n*-tetradecane	25–35; 25	−0.012	DV3	268
n-Dodecane + *n*-hexadecane	45–65; 45	−0.033	DV3−	179
n-Dodecane + *n*-hexadecane	25–35; 25	−0.024	DV3	268
n-Dodecane + benzene	25–40; 25	0.93	DV2	258
n-Dodecane + cyclohexane	15–35; 25	0.506L	DV3	254
n-Dodecane + *trans*-decalin	25	−0.102	DV3	263
n-Dodecane + *n*-hexylcyclohexane	25	−0.02	DV2	269
n-Dodecane + *n*-hexylbenzene	25	0.21	DV2	269
n-Dodecane + *n*-heptylcyclohexane	25	0.00	DV2	269
n-Dodecane + phenylcyclohexane	25	0.00	DV2	269
n-Dodecane + bicyclohexyl	25	−0.22	DV2	269
n-Tetradecane + *n*-hexadecane	25	0.05±	DV2	252
n-Tetradecane + benzene	30–40; 30	0.97L	DV2	257
n-Hexadecane + benzene	30	1.02L	4	260
n-Hexadecane + benzene	25	1.03L	DV2	252
n-Hexadecane + cyclohexane	30	0.60R	4	260
n-Hexadecane + decalin	30	0.10	4	260
n-Hexadecane + *trans*-decalin	25	0.035	DV3	263
II. Two hydrocarbons but no paraffins				
Cyclopentane + cyclohexane	25	0.04	DV2	270
Cyclopentane + cyclohexane	25	0.042	DV3	51

Table VI (Continued)

System	*Temp range (°C)*	$\tilde{V}^E$	*Precision*	*Ref*
Cyclopentane + benzene	22	0.308	DV3	256
Cyclohexane + deuteriocyclohexane	30	0.0032	DV4	157
Cyclohexane + benzene	28	0.64	DV2−	271
Cyclohexane + benzene	30	0.68	4	260
Cyclohexane + benzene	22	0.66	DV2	256
Cyclohexane + benzene	25	0.62	DV2	272
Cyclohexane + benzene	25–40; 25	0.64	DV2	237
Cyclohexane + benzene	25	0.64	DV2	27
Cyclohexane + benzene	20	0.641	DV3−	26
Cyclohexane + benzene	25	0.595	DV3−	255
Cyclohexane + benzene	30	0.650	DV3	273
Cyclohexane + benzene	35–45; 35	0.649	DV3	195
Cyclohexane + benzene	35–45; 35	0.756	DV3	123
Cyclohexane + benzene	15–75; 25	0.653	DV3	29
Cyclohexane + benzene	25–40; 25	0.6391	DV4−	25
Cyclohexane + toluene	33	0.52	DV2−	271
Cyclohexane + toluene	25	0.55	DV2	27
Cyclohexane + *o*-xylene	35	0.52	DV2−	271
Cyclohexane + *m*-xylene	34	0.70	DV2−	271
Cyclohexane + *p*-xylene	33	0.45	DV2−	271
Cyclohexane + *tert*-butylcyclohexane	20–40; 20	0.075	DV3−	12
Cyclohexane + methylcyclohexane	25	0.02	DV2	270
Cyclohexane + 1,2,3,4-tetrahydronaphthalene	30	0.23	DV2−	271
Cyclohexane + decalin	30	0.06	4	260
Cyclohexane + *trans*-decalin	25	−0.060R	DV3	263
Cyclohexane + dicyclohexyl	20–40; 20	−0.021L	DV3−	12
Cyclohexane + dicyclohexylmethane	20–40; 20	−0.100	DV3−	12
Cyclohexane + 1,2-dicyclohexylethane	20–40; 20	−0.065L	DV3−	12
Cyclohexane + 1,3-dicyclohexylpropane	20–40; 20	−0.063L	DV3−	12
Methylcyclohexane + toluene	25–40; 25	0.37	DV2	237
Benzene + deuteriobenzene	30	0.0004	DV4	157
Benzene + toluene	20–40; 20	0.12	4	274
Benzene + toluene	20–70; 20	0.34	4	275
Benzene + toluene	30	0.00	DV2	163
Benzene + toluene	25	0.15	DV2	27
Benzene + toluene	30	0.050	DV3−	276
Benzene + toluene	10–30; 25	0.065	DV3	192
Benzene + toluene	25	0.088	DV3	197
Benzene + toluene	35–45; 35	0.073	DV3	195
Benzene + ethylbenzene	20–70; 20	0.16	4	275
Benzene + xylene	20–40; 20	0.28	4	274
Benzene + *o*-xylene	0–80; 20	0.36	4	275
Benzene + *o*-xylene	30	0.28	DV2	163
Benzene + *o*-xylene	30	0.220	DV3−	276
Benzene + *o*-xylene	25	0.249	DV3	196
Benzene + *o*-xylene	30	0.224	DV3	162
Benzene + *m*-xylene	30	0.19	DV2	163
Benzene + *m*-xylene	30	0.265	DV3−	276
Benzene + *m*-xylene	25	0.293	DV3	196
Benzene + *m*-xylene	30	0.269	DV3	162
Benzene + *p*-xylene	10–80; 20	0.15	4	275
Benzene + *p*-xylene	30	0.00	DV2	163
Benzene + *p*-xylene	30	0.189	DV3−	276
Benzene + *p*-xylene	25	0.207	DV3	196
Benzene + *p*-xylene	15–30; 25	0.197	DV3	192
Benzene + cumene	10–70; 20	0.13	4	275
Benzene + decalin	30	0.28L	4	260
Benzene + biphenyl	70	−0.30R	DV2	277
Benzene + biphenyl	45–72; 60	−0.121R	DV3	63
Benzene + diphenylmethane	35	−0.13	DV2	278
Benzene + diphenylmethane	30–80; 30	−0.61	DV2	279
Benzene + diphenylmethane	30–50; 30	−0.219	DV3	25
Benzene + diphenylethyne	60	−0.62	DV2	277
Benzene + 1,8-diphenyloctane	25	0.00	DV2	277
Benzene + bibenzyl	60	−0.38	DV2	277
Toluene + xylene	20–40; 20	0.02	4	274
Toluene + *o*-xylene	−20–80; 20	0.02	4	275

Table VI (Continued)

System	*Temp range (°C)*	$\bar{V}^E$	*Precision*	*Ref*
Toluene + *o*-xylene	25	0.0422	DV4−	197
Toluene + *m*-xylene	25	0.0512	DV4−	197
Toluene + *p*-xylene	10–80; 20	0.10	4	275
Toluene + *p*-xylene	25	0.0175	DV4−	197
Toluene + ethylbenzene	−20–80; 20	0.18	4	275
Toluene + cumene	−20–80; 20	0.16	4	275
o-Xylene + *p*-xylene	30	0.00	DV2	163
cis-Decalin + *trans*-decalin	30	−0.055	DV3−	158
Kerosine(NBS 62) + kerosine(NBS 72)	25	. . .	DV2	269
	B. Mixtures with Halogen Derivatives			
III. Hydrocarbons + halogen derivatives				
n-Butane + perfluoro-*n*-butane	233–260°K; 260°K	3.46	4	280
n-Pentane + perfluoro-*n*-pentane	258–293°K; 20	5.02	4	281
Neopentane + carbon tetrachloride	24 0–400 atm	−1.0 1 atm	DV1	282
2,2-Dimethylpropane + carbon tetrachloride	0	−0.55	DV2	120
2,2-Dimethylpropane + carbon tetrachloride	0	−0.59	DV2	36
n-Hexane + carbon tetrachloride	25	0.14	DV2	252
n-Hexane + 2-bromobutane	25	0.13	DV2	252
n-Hexane + perfluoro-*n*-hexane	25–55; 25	4.84	DV2	283
n-Hexane + 1,2-dichlorohexafluorocyclopentene	25–45; 25	1.18R	DV2	284
n-Hexane + 1,2,4-trichlorobenzene	15–25; 25	−0.919	DV3	33
n-Heptane + carbon tetrachloride	22	0.230	DV3	261
2,2,4-Trimethylpentane + perfluoro-*n*-heptane	24	4.7	DV1	285
2,2,4-Trimethylpentane + perfluoro-*n*-heptane	25–45; 25	4.97R	DV2	284
2,2,4-Trimethylpentane + perfluoro-*n*-heptane	30	6.21	DV2	286
2,2,4-Trimethylpentane + 1,2-dichlorohexafluorocyclopentene	25–45; 25	1.33	DV2	284
n-Tetradecane + 2-bromobutane	25	0.51	DV2	252
n-Hexadecane + carbon tetrachloride	25	0.62L	DV2	252
n-Hexadecane + 2-bromobutane	25	0.51	DV2	252
Cyclopentane + carbon tetrachloride	25	−0.0351	DV4−	198
Cyclopentane + carbon tetrachloride	25	−0.026	DV3	51
Cyclohexane + dichloromethane	20	1.03	DV2	7
Cyclohexane + chloroform	20	0.58	DV2	7
Cyclohexane + chloroform	20	0.505	DV3−	26
Cyclohexane + carbon tetrachloride	30	0.17	DV2−	271
Cyclohexane + carbon tetrachloride	30	0.17	DV3−	65
Cyclohexane + carbon tetrachloride	10–40; 20	0.165	DV3	53
Cyclohexane + carbon tetrachloride	25	0.125	DV3	287
Cyclohexane + carbon tetrachloride	25	0.158	DV3	154
Cyclohexane + carbon tetrachloride	25	0.163	DV3	51
Cyclohexane + carbon tetrachloride	15–75; 25	0.164	DV3	288
Cyclohexane + carbon tetrachloride	25	0.171	DV3	289
Cyclohexane + 1,1,2-trichloroethylene	20	0.56	DV2	7
Cyclohexane + fluorobenzene	40	0.712	DV3	167
Cyclohexane + chlorobenzene	40	0.387	DV3−	164
Cyclohexane + bromobenzene	35	−0.16	DV2	290
Cyclohexane + bromobenzene	15–25; 25	0.281	DV3	33
Cyclohexane + hexafluorobenzene	40	2.657	DV3	56
Methylcyclohexane + perfluoromethylcyclohexane	65	7.3G	DV1	291
Methylcyclohexane + fluorobenzene	40	0.59	DV2	292
Cyclohexene + hexafluorobenzene	40	1.670	DV3	56
1,3-Cyclohexadiene + hexafluorobenzene	40	1.146	DV3	56
IV. Aromatic hydrocarbons + halogen derivatives				
Benzene + chloroform	25	0.12	4	293
Benzene + chloroform	25	0.18	DV2	272
Benzene + chloroform	20	0.176	DV3−	26
Benzene + chloroform	25	0.150	DV3	294
Benzene + carbon tetrachloride	25	0.04	DV2	252
Benzene + carbon tetrachloride	70	0.14	DV2	107
Benzene + carbon tetrachloride	25	0.010	5	295
Benzene + carbon tetrachloride	20–40; 25	0.041	5	34
Benzene + carbon tetrachloride	20	0.000	DV3−	26

Table VI (Continued)

System	*Temp range (°C)*	$\bar{V}^E$	*Precision*	*Ref*
Benzene + carbon tetrachloride	15–35; 25	0.001	DV3	55
Benzene + carbon tetrachloride	15–35; 25	0.002	DV3	296
Benzene + carbon tetrachloride	20–40; 25	0.010	DV3	297
Benzene + carbon tetrachloride	25	0.014	DV3	221
Benzene + carbon tetrachloride	15-75; 30	0.019LR	DV3	30
Benzene + ethylene dichloride	70	0.24	DV2	107
Benzene + 1,2-dichloroethane	20–50; 20	0.25	DV2	35
Benzene + 1,2-dichloroethane	20	0.247	5	298
Benzene + 1,2-dichloroethane	20–40; 20	0.275	DV3	234
Benzene + ethylene chlorohydrin	30–75; 30	0.14	4−	265
Benzene + 1,2-dibromoethane	20	0.276	DV3−	299
Benzene + 1,2-dibromoethane	20–40; 20	0.257	DV3	234
Benzene + fluorobenzene	40	0.079	DV3	166
Benzene + chlorobenzene	40	0.00	DV2	165
Benzene + chlorobenzene	20–40; 25	0.058	5	34
Benzene + chlorobenzene	20–40; 25	0.032	DV3	297
Benzene + chlorobenzene	35–50; 35	0.010	DV3	195
Benzene + bromobenzene	35	−0.07	DV2	290
Benzene + bromobenzene	25	−0.000	DV3	300
Benzene + bromobenzene	35–45; 35	−0.027	DV3	195
Benzene + hexafluorobenzene	40	0.801	DV3	56
Toluene + carbon tetrachloride	10–30; 20	−0.048	DV3−	276
Toluene + carbon tetrachloride	10–30; 25	−0.045	DV3	192
Toluene + fluorobenzene	25	0.028	DV3	170
Toluene + chlorobenzene	20–60; 20	−0.09	4	301
Toluene + chlorobenzene	40	−0.09	DV2	165
Toluene + chlorobenzene	35–45; 35	−0.102	DV3	195
Toluene + bromobenzene	20–60; 20	−0.23	4	301
Toluene + bromobenzene	20	−0.15	DV2	302
Toluene + bromobenzene	35–45; 35	−0.148	DV3	195
Toluene + hexafluorobenzene	40	0.416R	DV3	56
o-Xylene + carbon tetrachloride	10–30; 20	−0.010∓	DV3−	276
o-Xylene + carbon tetrachloride	10–30; 25	−0.001∓	DV3	162
m-Xylene + carbon tetrachloride	10–30; 20	0.099	DV3−	276
m-Xylene + carbon tetrachloride	10–30; 25	0.102	DV3	162
p-Xylene + carbon tetrachloride	15–30; 20	0.024	DV3−	276
p-Xylene + carbon tetrachloride	15–30; 25	0.025	DV3	192
p-Xylene + *p*-difluorobenzene	30	0.17	DV2	303
p-Xylene + hexafluorobenzene	40	0.086R	DV3	56
Mesitylene + hexafluorobenzene	40	−0.357	DV3	56
Cumene + hexafluorobenzene	40	0.516	DV3	56
V. Two halogen derivatives				
Methyl iodide + carbon tetrachloride	25	0.118	DV3−	304
Difluoromethane + pentafluoromonochloroethane	−32–58; 25	. . .	4−	305
Dichloromethane + methyl iodide	25	0.259	DV3−	304
Dichloromethane + dibromomethane	30	−0.38	DV2	306
Dichloromethane + diiodomethane	30	−0.69	DV2	306
Dichloromethane + chloroform	20	−0.05	DV2	7
Dichloromethane + chloroform	30	−0.06	DV2	306
Dichloromethane + bromoform	30	−0.60	DV2	306
Dichloromethane + carbon tetrachloride	20	0.26	DV2	7
Chloroform + methyl iodide	25	0.023±	DV3−	304
Chloroform + carbon tetrachloride	20	0.14	DV2	307
Chloroform + carbon tetrachloride	20	0.162	DV3−	26
Chloroform + carbon tetrachloride	25	0.173	DV3	308
Chloroform + carbon tetrachloride	35–45; 35	0.165	DV3	195
Carbon tetrachloride + 1,1,1-trichloroethane	0	0.25	DV2	36
Carbon tetrachloride + tetrachloroethylene	25	0.029	5	309
Carbon tetrachloride + 2-chloro-2-methylpropane	0	−0.26	DV2	36
Carbon tetrachloride + 2,2-dichloropropane	0	−0.16	DV2	36
Carbon tetrachloride + fluorobenzene	40	0.073	DV3	166
Carbon tetrachloride + chlorobenzene	40	−0.153	DV3−	164
Carbon tetrachloride + chlorobenzene	20–40; 25	−0.153	5	34
Carbon tetrachloride + chlorobenzene	20–40; 25	−0.131	DV3	297
1,1,2,2-Tetrabromoethane + 1-bromododecane	25–40; 25	0.13	4	310
2,2,3-Trichloroheptafluorobutane + 1,2-dichlorohexafluorocyclopentene	25–45; 25	0.04	DV2	284

Table VI (Continued)

System	*Temp range (°C)*	$\tilde{V}^E$	*Precision*	*Ref*
1,2-Dichlorohexafluorocyclopentene + *n*-perfluoroheptane	25–45; 25	0.76	DV2	284
Chlorobenzene + bromobenzene	35–45; 35	0.038	DV3	195
C. Hydrocarbons + Oxygen Derivatives (excluding hydroxyl ones)				
VI. Hydrocarbons + CO, CO_2, CS_2, etc.				
Cyclohexane + carbon disulfide	29	0.74	DV2−	271
VII. Hydrocarbons of the fatty and polymethylene series + oxygen derivatives				
n-Hexane + acetone	25	0.39	DV2−	311
n-Hexane + acetone	35	1.26	DV2	307
n-Hexane + perfluorocyclic oxide	25–45; 25	P	DV2	284
n-Hexane + 4-methylcyclohexanone	25	−0.39	DV2	252
2,4-Dimethylpentane + 1,4-dioxane	28–70; 28	0.405R	DV3−	264
2,2,4-Trimethylpentane + perfluorocyclic oxide	25–45; 25	4.29R	DV2	284
n-Decane + tributyl phosphate	25	1.2	DV1	312
n-Tetradecane + 4-methylcyclohexanone	25	0.56	DV2	252
n-Hexadecane + 4-methylcyclohexanone	25	0.70	DV2	252
n-Hexadecane + octamethylcyclotetrasiloxane	30	0.22	DV2	313
Cyclopentane + tetrahydrofuran	25	0.31	DV2	270
Cyclopentane + tetrahydropyran	25	0.15	DV2	270
Cyclohexane + methyl acetate	20	1.50	DV2	7
Cyclohexane + diethyl ether	20	0.28	DV2	7
Cyclohexane + *n*-dibutyl ether	20	0.40	DV2	7
Cyclohexane + acetone	20	1.13	DV2	7
Cyclohexane + cyclohexanone	30	0.165R	DV3−	54
Cyclohexane + tetrahydrofuran	25	0.52	DV2	314
Cyclohexane + tetrahydrofuran	25	0.59	DV2	270
Cyclohexane + tetrahydropyran	25	0.33	DV2	270
Cyclohexane + dioxane	35	1.02	DV2−	271
Cyclohexane + dioxane	25	1.00	DV2	270
Cyclohexane + 1,4-dioxane	35	0.91R	DV2	315
Cyclohexane + 1,4-dioxane	28–70; 28	0.979	DV3−	264
Cyclohexane + dioxane	22	0.433∓	DV3	256
VIII. Aromatic hydrocarbons + oxygen derivatives				
Benzene + methyl acetate	25	0.34	4	293
Benzene + tributyl phosphate	25	−0.1	DV1	312
Benzene + diethyl ether	20	−0.62	DV2	7
Benzene + acetone	25–45; 25	−0.07	DV2	212
Benzene + acetone	20–70; 25	−0.075	5−	316
Benzene + acetone	25	−0.070±	DV3	294
Benzene + diisobutyl ketone	25	0.061R	DV3	317
Benzene + acetophenone	25	−0.099R	DV3	317
Benzene + dioxane	20	−0.09	DV2	7
Benzene + 1,4-dioxane	35	−0.11L	DV2	315
Benzene + dimethyl sulfoxide	25	−0.257	DV3	317
Benzene + dimethyl sulfoxide	25	−0.308	DV3	318
Benzene + thiophene	20	0.014	5	298
Benzene + octamethylcyclotetrasiloxane	25–60; 25	−0.008R	DV3	319
Toluene + dioxane	30	−0.048	DV3	172
Toluene + dimethyl sulfoxide	25–45; 25	−0.31R	DV2	320
Xylene + dioxane	30	0.216	DV3	172
Soybean oil + 10 solvents	30	. . .	DV2	321
D. Hydrocarbons + Nitrogen Derivatives				
IX. Hydrocarbons + nitriles and amines				
n-Hexane + aniline	40	±	DV2	50
n-Hexane + aniline	25–65; 25	P	DV3	322
Cyclopentane + *N*-methylpyrrolidine	25	0.13	DV2	270
Cyclohexane + pyridine	25	0.54	DV2	182
Cyclohexane + pyridine	25–40; 25	0.52R	DV2	237
Cyclohexane + pyrrole	25	0.59	DV2	270
Cyclohexane + *N*-methylpyrrole	25	0.89	DV2	270
Cyclohexane + piperidine	25	0.31	DV2	270
Cyclohexane + piperidine	25–40; 25	0.34	DV2	239
Cyclohexane + *N*-methylpiperidine	25	0.16	DV2	270
Cyclohexane + *N*-methylpiperidine	25–40; 25	0.15	DV2	241
Cyclohexane + pyrrolidine	25	0.50	DV2	270

Table VI (Continued)

System	*Temp range (°C)*	$\bar{V}^E$	*Precision*	*Ref*
Cyclohexane + *N*-methylpyrrolidine	25	0.35	DV2	270
Cyclohexane + *o*-toluidine	30	0.47	4	191
Cyclohexane + *m*-toluidine	30	0.46	4	191
Cyclohexane + α-picoline	25–40; 25	0.69	DV2	237
Cyclohexane + α-pipecoline	25–40; 25	0.50	DV2	239
Methylcyclohexane + pyridine	25–40; 25	0.37	DV2	237
Methylcyclohexane + piperidine	25–40; 25	0.21	DV2	239
Methylcyclohexane + *N*-methylpiperidine	25–40; 25	−0.24	DV2	241
Methylcyclohexane + α-picoline	25–40; 25	0.40R	DV2	237
Methylcyclohexane + α-pipecoline	25–40; 25	0.38	DV2	239
Benzene + acetonitrile	25–45; 25	−0.05±	DV2	212
Benzene + aniline	25–45; 25	−0.24	DV2	230
Benzene + aniline	20–30; 25	−0.242	DV3	168
Benzene + pyridine	20–60; 20	−0.19	4	301
Benzene + pyridine	25–40; 25	−0.18R	DV2	238
Benzene + *o*-toluidine	30	−0.15	4	191
Benzene + *m*-toluidine	30	−0.12	4	191
Benzene + piperidine	25–40; 25	0.16L	DV2	240
Benzene + *N*-methylpiperidine	25–40; 25	0.13	DV2	241
Benzene + α-picoline	25–40; 25	−0.03	DV2	238
Benzene + α-pipecoline	25–40; 25	0.32	DV2	240
Toluene + aniline	25–45; 25	−0.19	DV2	230
Toluene + pyridine	25–40; 25	−0.16	DV2	238
Toluene + 2-methylpyridine	20–60; 20	−0.15	4	301
Toluene + piperidine	25–40; 25	0.16L	DV2	240
Toluene + *N*-methylpiperidine	25–40; 25	−0.00	DV2	241
Toluene + α-picoline	25–40; 25	−0.10	DV2	238
Toluene + α-pipecoline	25–40; 25	0.20	DV2	240
Mesitylene + triethylamine	15–25; 25	−0.300	DV3	33
Cumene + trimethylphenylamine	20–60; 20	0.34	4	301
X. Hydrocarbons + oxygen–nitrogen derivatives				
n-Hexane + nitroethane	25	0.273R	DV3	317
n-Hexane + nitrobenzene	21–25; 25	−0.967	DV3−	323
1-Hexene + nitroethane	25	−0.125∓	DV3	317
1,5-Hexadiene + nitroethane	25	−0.458	DV3	317
1-Hexyne + nitroethane	25	−0.347	DV3	317
Cyclohexane + nitrobenzene	22	0.30	DV2	256
Cyclohexane + nitrobenzene	20	0.333	DV3	324
Benzene + nitromethane	25–50; 25	0.21	4	325
Benzene + nitromethane	25–45; 25	0.22L	DV2	212
Benzene + dimethylformamide	25–40; 25	−0.265	DV3−	326
Benzene + β,β'-oxydipropionitrile	25	−0.502R	DV3	317
E. Halogen + Oxygen and Nitrogen Derivatives				
XI. Halogen + oxygen derivatives				
Methyl iodide + acetone	253–308°K; 20	0.56	4	327
Dichloromethane + acetone	20	0.18	DV2	7
Dichloromethane + acetone	25–30; 25	0.128	DV3	72
Dichloromethane + methyl acetate	20	0.34	DV2	7
Dichloromethane + methyl acetate	25–30; 25	0.317	DV3	72
Dichloromethane + diethyl ether	20	−0.76	DV2	7
Chloroform + acetone	20	−0.02±	DV2	307
Chloroform + acetone	25–50; 25	−0.13±	DV2	107
Chloroform + acetone	25	−0.120±	DV3	294
Chloroform + butanal	20	−0.17	DV2	7
Chloroform + methyl acetate	25	0.13	4	293
Chloroform + methyl acetate	20	0.16L	DV2	7
Chloroform + diethyl ether	20	−1.37L	DV2	7
Chloroform + diethyl ether	25	−1.335	DV3	70
Chloroform + di-*n*-propyl ether	25	−0.868	DV3	70
Chloroform + diisopropyl ether	25	−1.684	DV3	70
Chloroform + di-*n*-butyl ether	25	−0.588	DV3	70
Chloroform + di-*tert*-butyl ether	25	−1.200	DV3−	70
Chloroform + di-*n*-pentyl ether	25	−0.466	DV3	70
Chloroform + diisopentyl ether	25	−0.465	DV3	70

Table VI (Continued)

System	*Temp range (°C)*	$\tilde{V}^E$	*Precision*	*Ref*
Chloroform + di-*n*-hexyl ether	25	−0.396	DV3	70
Chloroform + polypropylene oxide	6	−0.0104	. . .	229
	Vol frac	$cm^3\ cm^{-3}$		
Chloroform + 7,14-dioxaeicosane	6	−1.66	DV2−	328
Bromoform + acetone	25	−0.25	DV2	329
Carbon tetrachloride + polypropylene oxide	6	−0.0028	. . .	229
	Vol frac	$cm^3\ cm^{-3}$		
Carbon tetrachloride + octamethylcyclotetrasiloxane	25–60; 25	−0.254	DV3	319
Carbon tetrachloride + 7,14-dioxaeicosane	6	−0.23	DV2−	328
Carbon tetrachloride + acetone	20	−0.19	DV2	7
Carbon tetrachloride + acetone	25–45; 25	−0.12∓	DV2	212
Carbon tetrachloride + methyl acetate	20	0.20	DV2	7
Carbon tetrachloride + tributyl phosphate	25	−0.4	DV1	312
Carbon tetrachloride + diethyl ether	20	−0.97	DV2	7
Carbon tetrachloride + diethyl ether	25	−0.712	DV3	70
Carbon tetrachloride + di-*n*-propyl ether	25	−0.335	DV3	70
Carbon tetrachloride + diisopropyl ether	25	−0.493	DV3	70
Carbon tetrachloride + di-*n*-butyl ether	20	−0.13	DV2	7
Carbon tetrachloride + di-*n*-butyl ether	25	−0.166	DV3	70
Carbon tetrachloride + di-*tert*-butyl ether	25	−0.079	DV3	70
Carbon tetrachloride + di-*n*-pentyl ether	25	−0.033∓	DV3	70
Carbon tetrachloride + diisopentyl ether	25	−0.040	DV3	70
Carbon tetrachloride + di-*n*-hexyl ether	25	0.018∓	DV3	70
Carbon tetrachloride + 1,4-dioxane	35	−0.26	DV2	315
1,1,2-Trichloroethylene + acetone	20	−0.21R	DV2	7
1,1,2-Trichloroethylene + diethyl ether	20	−1.50	DV2	7
1,1,2-Trichloroethylene + cyclohexanone	20	−0.20	DV2	7
2,2,3-Trichloroheptafluorobutane + perfluorocyclic oxide	25–45; 25	0.88	DV2	284
1-Hydro-*n*-perfluoroheptane + acetone	20	1.65L	DV2	233
1-Hydropentadecafluoro-*n*-heptane + 1,4-dioxane	36–50; 36	1.58L	DV2	330
n-Perfluoroheptane + perfluorocyclic oxide	25–45; 25	0.09R	DV2	284
1,2-Dichlorohexafluorocyclopentene + perfluorocyclic oxide	25–45; 25	0.92	DV2	284
Fluorobenzene + dioxane	35	−0.14	DV2	290
Chlorobenzene + dioxane	35	0.01	DV2	290
Chlorobenzene + dioxane	30	−0.080	DV3	172
Chlorobenzene + dimethyl sulfoxide	25–45; 25	−0.08R	DV2	320
Bromobenzene + dioxane	35	−0.01	DV2	290
o-Chlorophenol + dioxane	35	−1.35	DV2	331
p-Chlorophenol + dioxane	35	−0.59	DV2	331
o-Chloroaniline + dioxane	35	−0.72	DV2	331
m-Chloroaniline + dioxane	35	−0.65	DV2	331
XII. Halogen + nitrogen derivatives				
Carbon tetrachloride + hexamethyldisilizane	30	0.06∓	DV2	313
Carbon tetrachloride + octamethylcyclotetrasiloxane	30	−0.05∓	DV2	313
Carbon tetrachloride + nitromethane	25–45; 25	0.17R	DV2	212
Carbon tetrachloride + nitromethane	30–45; 30	0.12R	DV2	332
Carbon tetrachloride + nitromethane	25	0.171	5	333
Carbon tetrachloride + nitroethane	30–45; 30	−0.01∓	DV2	332
Carbon tetrachloride + acetonitrile	25–45; 25	−0.13∓	DV2	212
Carbon tetrachloride + dimethylformamide	25–40; 25	−0.583	DV3−	334
Carbon tetrachloride + aniline	25–45; 25	−0.31	DV2	230
Carbon tetrachloride + aniline	20–30; 25	−0.320	DV3	168
Chlorobenzene + aniline	20	0.005	4	335
Chlorobenzene + aniline	25–45; 25	0.14	DV2	230
Chlorobenzene + aniline	20–30; 25	0.130	DV3	168
Chlorobenzene + *m*-chloroaniline	20	−0.044	4	335
Bromobenzene + 2-methylpyridine	20–60; 20	0.00	4	301
XIII. Halogen derivative + CO, CO_2, CS_2, etc.				
Carbon disulfide + dichloromethane	20	0.71	DV2	7
Carbon disulfide + chloroform	20	0.44	DV2	7
Carbon disulfide + carbon tetrachloride	20	0.30	DV2	7
Carbon disulfide + carbon tetrachloride	22	0.312	DV3	261

Table VI (Continued)

System	*Temp range (°C)*	$\bar{V}^E$	*Precision*	*Ref*
F. One Oxygen Derivative + Another Derivative				
XIV. Two oxygen derivatives				
2-Ethoxyethanol + butyl acetate	25	0.19	4	336
Acetone + dimethyl sulfoxide	25–40; 25	−0.41	4	337
Acetone + dimethyl sulfoxide	30	−0.42R	DV2	338
Acetone + acetylacetone	25	−0.220	DV3	227
Acetone + acetonylacetone	25	−0.461L	DV3	227
Benzaldehyde + dimethyl sulfoxide	25–45; 25	0.07	DV2	320
Dioxane + dimethyl sulfoxide	25–40; 25	−0.11	4	337
1,3-Butanediol diacetate + 19 esters	20	. . .	4	118
Ethyl acetate + 20 esters	20	. . .	4	118
XV. CO, CO_2, $COCl_2$, CS_2, etc., + oxygen and nitrogen derivatives				
Carbon disulfide + acetone	0	0.98	DV2	244
Carbon disulfide + acetone	0	0.37L	DV2	244
	1–6805 atm	6805 atm		
Carbon disulfide + acetone	35	1.06	DV2	107
XVI. Oxygen + nitrogen derivatives				
Tetrahydrofuran + *N*-methylpyrrole	25	−0.04	DV2	339
Tetrahydrofuran + *N*-methylpyrrolidine	25	0.03∓	DV2	339
Tetrahydrofuran + *N*-methylpiperidine	25	0.01	DV2	339
Tetrahydropyran + *N*-methylpyrrole	25	−0.19	DV2	339
Tetrahydropyran + *N*-methylpyrrolidine	25	0.00∓	DV2	339
Tetrahydropyran + *N*-methylpiperidine	25	0.02	DV2	339
Acetone + acetonitrile	25–45; 25	−0.13	DV2	212
Acetone + aniline	25–45; 25	−1.16	DV2	230
Dioxane + acetonitrile	25	−0.30	DV2	340
Dioxane + aniline	25–45; 25	−0.44	DV2	230
Dioxane + aniline	22	−0.508	DV3	256
Dioxane + aniline	30	−0.581	DV3	172
Dioxane + *o*-toluidine	30	−0.55	4	191
Dioxane + *m*-toluidine	30	−0.44	4	191
Dioxane + *N*-methylpyrrole	25	−0.08	DV2	339
Dioxane + *N*-methylpyrrolidine	25	0.20	DV2	339
Dioxane + *N*-methylpiperidine	25	0.34	DV2	339
Dimethyl sulfoxide + aniline	25–45; 25	−0.63	DV2	320
XVII. Oxygen + oxygen–nitrogen derivatives				
Acetone + nitromethane	25–45; 25	−0.22	DV2	212
Acetone + nitromethane	25	−0.211	5	341
Dioxane + formamide	25–40; 25	−0.347	DV3−	342
Dioxane + dimethylformamide	25–40; 25	0.067	DV3−	343
1,4-Dioxane + *N*-methyl-2-pyrrolidone	20–40; 20	0.00	DV2	344
Acetone + formamide	25	−0.82	DV2	345
Dimethyl sulfoxide + nitrobenzene	25–45; 25	0.25	DV2	320
G. Two Nitrogen Derivatives				
XVIII. Two nitriles or amines				
Hydrazine + dimethylhydrazine	20–25; 25	−0.83	DV2	346
Hydrazine + 1,1-dimethylhydrazine	5–30; 30	−0.64R	DV2	347
Pyridine + piperidine	25–40; 25	0.04	DV2	242
Pyridine + α-picoline	25–40; 25	0.03	DV2	238
Pyridine + α-pipecoline	25–40; 25	0.18L	DV2	242
Pyridine + *N*-methylpiperidine	25–40; 25	−0.09	DV2	242
Piperidine + α-pipecoline	25	−0.03	DV2	239
Piperidine + α-picoline	25–40; 25	0.10	DV2	242
Piperidine + *N*-methylpiperidine	25–40; 25	−0.10L	DV2	241
α-Picoline + α-pipecoline	25–40; 25	0.13	DV2	242
α-Picoline + *N*-methylpiperidine	25–40; 25	−0.16	DV2	242
N-Methylpiperidine + α-pipecoline	25–40; 25	−0.09L	DV2	241
XIX. Nitrogen + oxygen–nitrogen derivatives				
Acetonitrile + nitromethane	25–45; 25	−0.11	DV2	212
Dimethylformamide + methyl formate	15–30; 30	−0.35	DV2	348
H. Hydrocarbons + Hydroxyl Derivatives				
XXI. Hydrocarbons + alcohols				
n-Hexane + ethanol	35	0.35	DV2	307
n-Hexane + ethanol	22	0.40R	DV2	256
n-Hexane + 1-propanol	25	0.179R	DV3	213

Table VI (Continued)

System	*Temp range (°C)*	$\tilde{V}^E$	*Precision*	*Ref*
n-Hexane + 2-propanol	22	0.49R	DV2	256
n-Heptane + ethanol	25–45; 25	0.465	DV3−	73
n-Heptane + 1-propanol	25	0.31	DV2	349
n-Heptane + 1-propanol	25	0.31R	DV2	71
n-Heptane + 2-propanol	25	0.59	DV2	349
n-Heptane + 2-propanol	25	0.59	DV2	71
2,2,4-Trimethylpentane + ethanol	0–50; 25	0.421L	DV3	350
Cyclopentane + cyclopentanol	22	0.020∓	DV3	256
Cyclopentane + cyclohexanol	22	−0.403∓	DV3	256
Cyclohexane + methanol	6–30; 30	P	DV3	351
Cyclohexane + ethanol	22	0.57	DV2	256
Cyclohexane + ethanol	25–45; 25	0.566	DV3	74
Cyclohexane + ethanol	27	0.570	DV3	352
Cyclohexane + ethanol	6–30; 30	0.577	DV3	351
Cyclohexane + 1-propanol	50–70; 50	0.39	DV2	353
Cyclohexane + 1-propanol	22	0.400	DV3	351
Cyclohexane + 1-butanol	22	0.390R	DV3	351
Cyclohexane + 2-methyl-2-propanol	30–50; 30	0.78	DV2	354
Cyclohexane + 1-octanol	22	0.450	DV3	351
Cyclohexane + cyclohexanol	30	0.11∓	DV2	163
Cyclohexane + cyclohexanol	27–45; 27	−0.03∓	DV2	355
Cyclohexane + cyclohexanol	30	−0.046∓	DV3−	54
Cyclohexane + cyclohexanol	30	−0.043∓	DV3	256
Cyclohexane + β-ethylhexanol	22	0.500	DV3	351
Methylcyclohexane + ethanol	25	0.343	5	356
XXII. Aromatic hydrocarbons + oximes and alcohols				
Benzene + methanol	20–40; 30	0.05	4	357
Benzene + methanol	25–45; 25	0.00∓	DV2	52
Benzene + methanol	25	0.02±	DV2	358
Benzene + methanol	25	−0.005±	5	295
Benzene + methanol	25	−0.003∓	DV3	31
Benzene + methanol	6–30; 30	−0.016∓	DV3	351
Benzene + ethanol	25	0.00±	DV2	358
Benzene + ethanol	22	0.03∓	DV2	256
Benzene + ethanol	25–45; 25	0.03∓	DV2	52
Benzene + ethanol	6–30; 30	0.038∓	DV3	351
Benzene + 90% ethanol	25	0.19	DV2	358
Benzene + 1-propanol	25–45; 25	0.09R∓	DV2	52
Benzene + 1-propanol	22	0.094∓	DV3	351
Benzene + 2-propanol	25	0.38	DV2	358
Benzene + 2-propanol	25–45; 25	0.26R	DV2	52
Benzene + 2-propanol	22	0.246R	DV3	256
Benzene + 1-butanol	25	0.18	4	359
Benzene + 1-butanol	25–45; 25	0.18R	DV2	52
Benzene + 1-butanol	25–55; 25	0.223	DV3−	360
Benzene + 1-butanol	22	0.193R	DV3	351
Benzene + 2-butanol	25–45; 25	0.46	DV2	52
Benzene + 2-butanol	25–55; 25	0.625	DV3−	360
Benzene + 2-methyl-1-propanol	25–45; 25	0.23R	DV2	52
Benzene + 2-methyl-1-propanol	22	0.202R	DV3	351
Benzene + 2-methyl-2-propanol	25–45; 27	0.66	DV2	52
Benzene + 2-methyl-2-propanol	30–50; 30	0.65	DV2	361
Benzene + 2-methyl-2-propanol	25–55; 25	0.637	DV3−	360
Benzene + 1-pentanol	25	0.21	4	359
Benzene + 1-hexanol	25	0.25	4	359
Benzene + 1-hexanol	25–45; 25	0.32 (x_1 = 0.7)	DV2	52
Benzene + 1-hexanol	22	0.306R	DV3	256
Benzene + 1-hexanol	22	0.309R	DV3	351
Benzene + 2-methyl-1-pentanol	22	0.439	DV3	351
Benzene + 1-octanol	25–45; 25	0.43 (x_1 = 0.7)	DV2	52
Benzene + 2,2,3,3-tetrafluoro-1-propanol	25	1.300	DV3−	362
Toluene + methanol	20–40; 30	−0.07	4	357
Toluene + methanol	25	−0.15	DV2	358
Toluene + ethanol	25	−0.07∓	DV2	358

Table VI (Continued)

System	*Temp range (°C)*	$\tilde{V}^E$	*Precision*	*Ref*
Toluene + ethanol	25	−0.063∓	DV3	363
Toluene + ethanol	25–45; 25	−0.070∓	DV3	74
Toluene + 2-propanol	25	0.26	DV2	358
o-Xylene + ethanol	25–45; 25	−0.037∓	DV3	74
m-Xylene + ethanol	25–45; 25	0.024∓	DV3	74
p-Xylene + ethanol	25–45; 25	−0.027∓	DV3	74
XXIII. Hydrocarbons + phenols				
Cyclohexane + phenol	30	0.21	DV2	223
Cyclohexane + *o*-chlorophenol	30	0.31	DV2	223
Cyclohexane + *p*-chlorophenol	30	0.02	DV2	223
Cyclohexane + *o*-cresol	30	0.32	DV2	223
Cyclohexane + *m*-cresol	30	0.38	DV2	223
Cyclohexane + *p*-cresol	30	0.37	DV2	223
XXIV. Hydrocarbons + acids				
n-Hexane + propionic acid	15	0.490	DV3	256
Cyclohexane + acetic acid	20–40; 20	1.53G	DV2	235
Benzene + acetic acid	20–40; 20	0.82G	DV2	235
Benzene + 1-butanoic acid	25	0.22	4	359
Benzene + 1-pentanoic acid	25	0.19	4	359
Benzene + 1-hexanoic acid	25	0.30	4	359
Benzene + 1-heptanoic acid	25	0.30	4	359
Benzene + 1-octanoic acid	25	0.34	4	359
I. Halogen Derivatives, CO, CO_2, CS_2, etc., + Hydroxyl Derivatives				
XXV. Halogen derivatives + alcohols				
Dichloromethane + 2,2,3,3-tetrafluoro-1-propanol	25	0.972	DV3−	362
Chloroform + ethanol	35	0.14	DV2	307
Chloroform + 2,2,3,3-tetrafluoro-1-propanol	25	1.100	DV3−	362
Carbon tetrachloride + methanol	25	−0.22	4	359
Carbon tetrachloride + methanol	25	G	DV2	364
Carbon tetrachloride + methanol	25	−0.041∓	DV3−	365
Carbon tetrachloride + methanol	25	−0.043	5	295
Carbon tetrachloride + methanol	25	−0.032∓	DV3	366
Carbon tetrachloride + ethanol	25	−0.45	4	359
Carbon tetrachloride + ethanol	25	G	DV2	364
Carbon tetrachloride + 1-propanol	30–75; 30	3.00	4−	265
Carbon tetrachloride + 1-propanol	25	−0.64	4−	359
Carbon tetrachloride + 1-propanol	25	G	DV2	364
Carbon tetrachloride + 1-propanol	25	−0.100∓	DV3−	365
Carbon tetrachloride + 2-propanol	25	G	DV2	364
Carbon tetrachloride + 2-propanol	22	0.210∓	DV3−	256
Carbon tetrachloride + 1-butanol	25	−0.70	4−	359
Carbon tetrachloride + 1-butanol	26	G	DV2	364
Carbon tetrachloride + 1-butanol	25	−0.070∓	DV3−	365
Carbon tetrachloride + 1-butanol	25–55; 25	0.142	DV3−	360
Carbon tetrachloride + 2-methyl-1-propanol	26	G	DV2	364
Carbon tetrachloride + 2-butanol	26	G	DV2	364
Carbon tetrachloride + 2-butanol	26	0.45	DV2	101
Carbon tetrachloride + 2-butanol	25–55; 25	0.215	DV3−	360
Carbon tetrachloride + 2-methyl-2-propanol	26	G	DV2	364
Carbon tetrachloride + 2-methyl-2-propanol	26	−0.80	DV2	101
Carbon tetrachloride + 2-methyl-2-propanol	25	0.53	DV2	36
Carbon tetrachloride + 2-methyl-2-propanol	25–55; 25	0.761	DV3−	360
Carbon tetrachloride + 1-pentanol	25	G	DV2	364
Carbon tetrachloride + 1-pentanol	25	0.43	DV2	367
Carbon tetrachloride + 3-pentanol	25	G	DV2	364
Carbon tetrachloride + 2-methyl-1-butanol	25	G	DV2	364
Carbon tetrachloride + 2-methyl-1-butanol	25	0.32	DV2	367
Carbon tetrachloride + 3-methyl-1-butanol	25	G	DV2	364
Carbon tetrachloride + 3-methyl-1-butanol	25	0.33	DV2	367
Carbon tetrachloride + 2-methyl-2-butanol	25	0.62	DV2	367
Carbon tetrachloride + 2-methyl-2-butanol	25	−0.66	DV2	101
Carbon tetrachloride + 1-hexanol	25	−0.30	4	359
Carbon tetrachloride + 1-heptanol	25	−0.09	4	359
Carbon tetrachloride + 1-heptanol	25	G	DV2	364
Carbon tetrachloride + 1-octanol	25	−0.07	4	359
Carbon tetrachloride + 1-octanol	25	G	DV2	364

Table VI (Continued)

System	*Temp range (°C)*	$\tilde{V}^E$	*Precision*	*Ref*
Carbon tetrachloride + 1-octanol	25	−0.003∓	DV3−	365
Carbon tetrachloride + 1-decanol	25	−0.30	4	359
1,2-Dichloroethane + 1-butanol	40	0.36	4	368
XXVI. Halogen derivatives + phenols and acids				
Dichloromethane + propionic acid	20	0.46	DV2	7
Chloroform + acetic acid	20	0.41	DV2	307
Chloroform + acetic acid	25	0.50	DV2	226
Chloroform + propionic acid	20	0.08	DV2	7
Carbon tetrachloride + phenol	45–50; 45	−0.37	DV2	355
Carbon tetrachloride + acetic acid	25	0.56	4	359
Carbon tetrachloride + acetic acid	20–40; 20	0.72G	DV2	235
Carbon tetrachloride + 1-butanoic acid	25	0.10	4	359
Carbon tetrachloride + 1-hexanoic acid	25	0.22	4	359
Carbon tetrachloride + 1-heptanoic acid	25	0.15	4	359
Carbon tetrachloride + 1-octanoic acid	25	0.11	4	359
J. Oxygen Derivatives + Hydroxyl Derivatives				
XXVIII. Ether oxides + hydroxyl derivatives				
Diethyl ether + methanol	25	−0.80	DV2	369
Tetrahydrofuran + 1,2-ethanediol	22	−0.403	DV3	256
1,4-Dioxane + methanol	30–75; 30	0.12	4−	265
Dioxane + methanol	22	−0.269R	DV3	351
1,4-Dioxane + ethanol	30–75; 30	−0.19	4−	265
Dioxane + ethanol	22	−0.03±	DV2	256
Dioxane + ethanol	30	−0.016±	DV3	351
Dioxane + 1,2-ethanediol	30	−0.198	DV3	256
Dioxane + 1,2-ethanediol	22–30; 30	−0.200	DV3	351
Dioxane + 1,4-butanediol	15–30; 30	−0.153	DV3	351
Dioxane + 1,2,3-propanetriol	15–30; 30	P	DV3	351
XXIX. Ketone + hydroxyl derivatives				
Acetone + methanol	20–35; 20	−0.31	DV2	307
Acetone + 1-propanol	25	−0.06	DV2−	311
Acetone + 1-butanol	30–75; 30	−1.03	4−	265
Acetone + acetic acid	20	−0.73	DV2	307
Acetone + acetic acid	20–91; 25	−0.647	5−	316
Acetonylacetone + 2-propanol	25	0.184	DV3	227
4-Methyl-2-pentanone + ethanol	25	−0.07	4	370
4-Methyl-2-pentanone + 1-propanol	25	−0.00	4	370
4-Methyl-2-pentanone + 1-pentanol	25	−0.02	4	370
4-Methyl-2-pentanone + 2,2,2-trifluoroethanol	25	1.11	4	370
4-Methyl-2-pentanone + 2,2,3,3-tetrafluoropropanol	25	0.35	4	370
4-Methyl-2-pentanone + 2,2,3,3,4,4,5,5-octafluoropentanol	25	1.34	4	370
Cyclohexanone + cyclohexanol	30	0.266	DV3−	54
XXX. Anhydrides and esters + hydroxyl derivatives				
Ethyl acetate + methanol	25	−0.38	DV2	272
K. Nitrogen Derivatives + Hydroxyl Derivatives				
XXXI. Nitrogen derivatives + alcohols				
Triethylamine + methanol	25	−2.23	DV2	371
Triethylamine + ethanol	25	−1.92	DV2	371
Triethylamine + 1-propanol	25	−2.02	DV2	371
Triethylamine + 1-butanol	25	−2.06	DV2	371
Aniline + methanol	20–40; 30	−1.07	4	357
Pyridine + ethanol	25	−0.37	DV2	372
Pyridine + 1-propanol	25	−0.29	DV2	372
Pyridine + 1-butanol	25	−0.19	DV2	372
L. Mixed Oxygen–Nitrogen Derivatives + Hydroxyl Derivatives				
XXXIV. Oxygen–nitrogen derivatives + alcohols				
Formamide + methanol	25	−0.51R	DV2	345
o-Nitrotoluene + methanol	25	−0.21	4	373
N-Methyl-2-pyrrolidone + ethanol	20–40; 20	−0.43	DV2	344
N-Methyl-2-pyrrolidone + dimethyl sulfoxide	20–40; 20	0.03	DV2	344
XXXVI. Oxygen–nitrogen derivatives + acids				
N-Methyl-2-pyrrolidone + acetic acid	20–40; 20	−1.09R	DV2	344

Table VI (Continued)

System	*Temp range (°C)*	$\bar{V}^{E}$	*Precision*	*Ref*
M. Two Hydroxyl Derivatives				
XXXVII. Two hydroxyl derivatives of different species				
Methanol + phenol	20–40; 30	−0.97	4	357
XXXVIII. Two alcohols and two phenols				
Methanol + 1-butanol	25	0.0738R	DV4	68
Methanol + 1-octanol	25	0.1563R	DV4−	68
Methanol + 1,2-ethanediol	25	−0.64	DV2	374
Ethanol + 1-butanol	25	0.0121R	DV4	68
Ethanol + 1-octanol	25	0.0600R	DV4	68
Ethanol + 2,2,2-trifluoroethanol	25	0.44	4−	375
1-Propanol + 1-butanol	25	−0.0019	DV4	68
1-Propanol + 1-octanol	25	0.0513	DV4	68
2-Propanol + 1,2,3-propanetriol	25	−1.13	4	376
1-Butanol + 1-hexanol	25	0.0115	DV4	68
1-Butanol + 1-octanol	25	0.0413	DV4	68
1-Butanol + 1-decanol	25	0.0778	DV4	68
1-Hexanol + 1-octanol	25	0.0098	DV4	68
1-Octanol + 1-decanol	25	0.0076	DV4	68
R. Water + Hydrocarbons and Halogen and Oxygen Derivatives				
LVIII. Water + organic substances (excepting hydroxyl derivatives)				
Water + benzene	340 200–2000 atm	30R 200 atm	DV1−	377
Water + tetrahydrofuran	22	−0.838	DV3	256
Water + 1,3-dioxolane	5–45; 25	−0.507R	DV3	378
Water + dioxane	20–40; 25	−0.61	4	379
Water + dioxane	25	G	DV2	380
Water + 1,4-dioxane	25	−0.521	5	381
Water + dioxane	15–30; 30	−0.600R	DV3	351
Water + dioxane	30	−0.598R	DV3	256
Water + acetone	25	−1.44	DV2	272
Water + dimethyl sulfoxide	25–65; 25	−0.93	4	382
Water + dimethyl sulfoxide	25	−0.83	4	383
LIX. Water + nitrogen derivatives				
Water + methyl cyanide	6–25; 25	−0.503R	DV3	384
Water + acetonitrile	25	−0.55	DV2	272
Water + diethylenetriamine	25	−2.03	4	385
Water + triethylenetetramine	25	−2.10	4	385
Water + tetraethylenepentamine	25	−2.21	4	385
LX. Water + oxygen–nitrogen derivatives				
Water + formamide	25	−0.13	4	386
Water + dimethylformamide	25	−1.17L	4	387
Water + *N,N*-diethylformamide	25	−1.05R	DV2	388
Water + *N*-methylacetamide	30	−1.03	DV2	388
Water + *N*-ethylacetamide	25	−1.35	DV2	388
Water + *N,N*-dimethylacetamide	25	−1.39	DV2	388
Water + *N,N*-diethylacetamide	25	−1.31R	DV2	388
Water + *N,N*-di-*n*-propylacetamide	25	−0.95R	DV2	388
Water + *N,N*-diisopropylacetamide	25	−1.02	DV2	388
Water + *N,N*-diethylpropionamide	25	−1.25	DV2	388
Water + *N*-methylpyrrolidone	25	−1.11	DV2	388
Water + *N*-*tert*-butylpyrrolidone	25	−0.97	DV2	388
Water + *N*-methyl-2-pyrrolidone	20–60; 20	−1.15R	DV2	389
Water + *N*-methylcaprolactam	25	−0.95	DV2	388
S. Water + Alcohols				
LXI. Water + methyl and ethyl alcohols				
Water + methanol	25–50; 25	−0.98	4	390
Water + methanol	30	−1.10L	DV2	163
Water + 2,2,2-trifluoroethanol	25–50; 25	−0.59	DV2	391
LXII. Water + other alcohols				
Water + 1,2-ethanediol	20	−0.339	DV3	206
Water + 1-propanol	30–95; 30	−0.53	4−	265
Water + 1-propanol	25	−0.58	4	392
Water + 1-propanol	25–50; 25	−0.65	4	393
Water + 2-propanol	25	−0.86	4	392

Table VI (Continued)

System	*Temp range (°C)*	$\bar{V}^E$	*Precision*	*Ref*
Water + 1,2-propanediol	25	−0.633R	5	207
Water + 1,3-propanediol	25	−0.404R	5	207
Water + 1,1,1,3,3,3-hexafluoro-2-propanol	25–50; 25	−0.60	DV2	394
Water + 1-butanol	30–95; 30	P	4−	265
Water + 1-butanol	20	−0.345	DV3	206
Water + 2-butanol	20	−0.584	DV3	206
Water + 2-methyl-2-propanol	25	-0.789R	5	207
Water + 2-methyl-2-propanol	20	−0.781	DV3	206
Water + 1,3-butanediol	30	−0.662	5	207
Water + 1,4-butanediol	25	−0.549	5	207
Water + 2-methyl-2-butanol	30	−0.741P	5	207
Water + *n*-butyl glycol	27	−0.707	DV3	395
Water + dipropylene glycol	25	−1.01	4	396
Water + triethylene glycol	25	−0.69	4	396
Water + hexylene glycol	25	−1.24	4	396
Water + polypropylene glycol (400)	50	G	DV2	380
Water + polyethylene glycol (500)	65	G	DV2	380
Water + ethylene glycol dimethyl ether	25	−1.58	4−	397
Water + diethylene glycol dimethyl ether	25	−1.25	4−	398
Water + diethylene glycol monomethyl ether	25	−0.89	4	399
Water + diethylene glycol monoethyl ether	25	−0.82	4	399
Water + diethylene glycol monobutyl ether	25	−0.87	4	399
Water + triethylene glycol dimethyl ether	25	−1.40	4−	400
Water + 2-methoxyethanol	25	−0.37	4	401
Water + 2-ethoxyethanol	25	−1.00	4	401
Water + 2-butoxyethanol	25	−0.69	4	401
Water + 2-(β-methoxyethoxy)ethanol	25	−0.75	4	402
Water + 2-(β-ethoxyethoxy)ethanol	25	−0.84	4	402
T. Waters + Sugars, Phenols, and Organic Acids				
LXV. Water + organic acids				
Water + acetic acid	25	−1.15	DV2	226
U. Water + Inorganic and Nonmetallic Substances				
LXVI. Water + elements and hydrides				
Water + argon	400 300–3000 atm	45 300 atm	DV0	89
Water + heavy water	25	0.009	4	403
Water + hydrogen peroxide	−50–96; −10	−0.390L	DV3	222
$D_2O + D_2O_2$	0–20; 20	−0.222L	DV3	222
Water + dimethyl sulfoxide	25	−0.928	5	404
Water + sulfolane	30–60; 30	−0.10	DV2	405
LXVII. Water + anhydrides and acids				
Water + phosphoric acid	15–80; 25	−0.31	4	406
V. Nonmetallic Inorganic Substances + Organic Substances				
LXX. Hydrides and halogenides + organic compounds				
Silicon tetrachloride + cyclohexane	10–20; 20	0.207	DV3	53
Silicon tetrachloride + carbon tetrachloride	−30–20; 20	0.05	DV2	407
Silicon tetrachloride + carbon tetrachloride	25	0.015	DV3	41
Silicon tetrabromide + carbon tetrachloride	25	0.206	DV3	41
Titanium tetrachloride + cyclohexane	10–20; 20	0.215	DV3	53
Titanium tetrachloride + carbon tetrachloride	−20–20; 20	0.08	DV2	407
Titanium tetrachloride + carbon tetrachloride	25	0.086	DV3	41
Tin tetrachloride + cyclohexane	10–20; 20	0.915	DV3	53
Tin tetrachloride + carbon tetrachloride	−30–20; 20	0.46	DV2	407
Tin tetrachloride + carbon tetrachloride	25	0.438	DV3	41
Tin tetrabromide + carbon tetrachloride	35	0.254	DV3	41
W. Two Inorganic Nonmetallic Substances				
LXXIII. Two inorganic compounds				
Silicon tetrachloride + titanium tetrachloride	−20–20; 20	−0.38	DV2	407
Silicon tetrachloride + tin tetrachloride	−37–20; 20	0.13	DV2	407
Silicon tetrachloride + tin tetrabromide	35	0.138	DV3	41
Silicon tetrabromide + tin tetrabromide	35	0.130	DV3	41
Titanium tetrachloride + tin tetrachloride	20–60; 20	0.00	4	301
Titanium tetrachloride + tin tetrachloride	−20–20; 20	0.08	DV2	407

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Table VII

Volume Changes on Mixing for Gas + Gas Systems

System	*Temp range (°C)*	$\tilde{V}^E$	*Precision*	*Ref*
Methane + ethane	108°K	−0.506R	DV3−	180
Methane + propane	108°K	−0.731	DV3−	180
Ethane + propane	108°K	−0.384R	DV3−	180
Methane + tetrafluoromethane	107°K	0.88	DV2	114
Methane + carbon monoxide	91°K	−0.32	DV2	75
Hydrogen + ethane	25	105.2	DV1−	91
Hydrogen + ethene	25	33.0	DV1−	91
Hydrogen + ethene	25	10.89	DV2−	90
Nitrogen + methane	91°K	−0.21	DV2	138
Nitrogen + methane	90°K	−0.42±	DV2	408
Nitrogen + ethene	25	8.90	DV2−	90
Nitrogen + fluoromethane	25	34.0	DV1−	91
Argon + methane	91°K	0.55%	DV1−	78
Argon + methane	87°K	0.16	DV2−	409
Argon + methane	91°K	0.18	DV2	410
Argon + methane	90°K	0.13	DV2	408
Krypton + methane	116°K	−0.01	DV2	411
Krypton + methane	116°K	0.02	DV2	412
Carbon monoxide + methane	91°K	−0.33	DV2	413
Carbon monoxide + methane	91°K	−0.34	DV2	410
Carbon monoxide + fluoromethane	25	30.1	DV1−	91
Carbon dioxide + ethene	25	1.83	DV2−	90
Carbon dioxide + fluoromethane	25	8.3	DV1−	91
Propane + sulfur hexafluoride	30–80; 30	110	DV0	414
Hydrogen + para-hydrogen	20°K	0.018	DV3	84
Ortho-hydrogen + para-hydrogen	20°K	0.03	DV1	415
Hydrogen + deuterium	20°K	−0.3	DV1	416

Table VII (Continued)

System	*Temp range (°C)*	$\bar{V}^{E}$	*Precision*	*Ref*
Hydrogen + deuterium	14–20°K; 20°K	−0.04	DV2	417
Hydrogen + deuterium	20°K	−0.24	DV2	415
Hydrogen + deuterium	20°K	−0.142	DV3	84
Hydrogen + nitrogen	25	4.2	DV1−	91
Hydrogen + nitrogen	0–300	. . .	4	418
Hydrogen + nitrogen	170–293°K; 170°K	8.0	DV1	94
Hydrogen + nitrogen	77°K	. . .	DV1	419
	12 atm	12 atm		
Hydrogen + nitrogen	25	4.50	DV2−	90
Hydrogen + nitrogen	171–293°K; 171°K	8.84	DV2	93
Hydrogen + nitrogen	203–248°K; 203°K	6.67	DV2	86
Hydrogen + nitrogen	0–20; 20	4.00	DV2	85
Hydrogen + nitrogen	0–100; 25	3.47	DV2	88
Hydrogen + argon	170–293°K; 170°K	9.0	DV1	94
Hydrogen + argon	171–293°K; 171°K	9.31	DV2	93
Hydrogen + carbon monoxide	25	4.9	DV1−	91
Hydrogen + carbon dioxide	25	26.9	DV1−	91
Hydrogen + carbon dioxide	25	7.83	DV2−	90
Deuterium + ortho-deuterium	20°K	0.003	DV3	84
Deuterium + tritium	20–24°K; 21°K	0.16	DV1	420
Helium + argon	25	10.8	DV1−	91
Helium + nitrogen	25	4.47	DV2−	90
Helium + carbon dioxide	25	7.84	DV2−	90
Neon + nitrogen	101°K	−8.4	DV1	146
		136 atm		
Nitrogen + oxygen	30	0.3	DV1	421
Nitrogen + oxygen	65–80°K; 80°K	−0.34	DV2	422
Nitrogen + oxygen	77°K	−0.20	DV2	423
Nitrogen + oxygen	84°K	−0.314	DV3	76
Nitrogen + oxygen	77°K	−0.212	DV3	84
Nitrogen + argon	170–293°K; 170°K	0.0	DV1	94
Nitrogen + argon	171–293°K; 171°K	−0.04	DV2	93
Nitrogen + argon	84°K	−0.180	DV3	424
Nitrogen + argon	84°K	−0.180	DV3	76
Nitrogen + carbon monoxide	25	−0.2	DV1−	91
Nitrogen + carbon monoxide	84°K	0.127	DV3	76
Nitrogen + carbon dioxide	25	11.3	DV1−	91
Nitrogen + carbon dioxide	30	11.0	DV1	421
Nitrogen + carbon dioxide	25	6.79	DV2−	90
Oxygen + argon	72–90°K; 85°K	0.14L	DV2	422
Oxygen + argon	84–90°K; 84°K	0.136	DV3	76
Oxygen + argon	90°K	0.130	DV3	84
Oxygen + argon	84–90°K; 90°K	0.136	DV3	424
Oxygen + carbon dioxide	30	13.4	DV1	421
Oxygen + carbon dioxide	25	6.27	DV2−	90
Argon + carbon monoxide	84°K	0.099	DV3	76
Argon + krypton	116°K	−0.50	DV2	425
Argon + krypton	116°K	−0.518R	DV3	77
Carbon monoxide + carbon dioxide	25	11.5	DV1−	91

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Table VIII

Partial Molar Volumes at Infinite Dilution

System	*Temp range (°C)*	$\bar{V}_i^\infty$	*Precision*	*Ref*
N-Methylpropionamide + benzene	15–40; 25	88.1	1	426
N-Methylpropionamide + pyridine	15–40; 25	31.3	1	426
n-Heptane + methanol	20	48.15	1	58
n-Heptane + ethanol	20	66.25	1	58
n-Heptane + 1-propanol	20	82.15	1	58
n-Heptane + 1-butanol	20	98.0	1	58
n-Heptane + 1-pentanol	20	114.2	1	58
n-Heptane + 1-hexanol	20	130.55	1	58
n-Heptane + 1-octanol	20	162.0	1	58
n-Heptane + 1-decanol	20	193.7	1	58
Cyclohexane + methanol	20	44.25	1	58
Cyclohexane + ethanol	20	66.5	1	58
Cyclohexane + 1-propanol	20	81.45	1	58
Cyclohexane + 1-butanol	20	99.0	1	58
Cyclohexane + 1-pentanol	20	114.7	1	58
Cyclohexane + 1-hexanol	20	131.8	1	58
Cyclohexane + 1-octanol	20	164.95	1	58
Cyclohexane + 1-decanol	20	198.4	1	58
Benzene + methanol	20	41.3	1	58
Benzene + ethanol	20	60.95	1	58
Benzene + 1-propanol	20	76.9	1	58
Benzene + 1-butanol	20	94.15	1	58
Benzene + 1-pentanol	20	111.0	1	58
Benzene + 1-hexanol	20	128.1	1	58
Benzene + 1-octanol	20	161.75	1	58
Benzene + 1-decanol	20	195.4	1	58
Carbon tetrachloride + water	25	31.6	1	47
1,2-Dichloroethane + water	25	20.1	1	47
1,1,1-Trichloroethane + water	25	22.3	1	47
Benzene + water	25	22.1	1	47
Water + tetrahydrofuran	25	76.9	1	202
Water + tetrahydropyran	25	91.8	1	202
Water + 1,4-dioxane	25	81.1	1	202
Water + *N*-methylacetamide	30	72.9	1	388
Water + *N*-ethylacetamide	25	85.5	1	388
Water + *N*-methylpyrrolidone	25	90.4	1	388
Water + *N*,*N*-dimethylacetamide	25	88.9	1	388
Water + *N*,*N*-diethylacetamide	25	121.2	1	388
Water + *N*,*N*-di-*n*-propylacetamide	25	152.4	1	388
Water + *N*,*N*-diisopropylacetamide	25	152.0	1	388
Water + *N*,*N*-diethylformamide	25	106.2	1	388
Water + *N*,*N*-diethylpropionamide	25	135.3	1	388
Water + methanol	0–60; 25	38.68	2–	427
Water + methanol	1–50; 20	38.05	2	199
Water + ethanol	10–40; 25	55.08	2–	427
Water + ethanol	1–50; 20	54.97	2	199
Water + 1-propanol	0–60; 25	70.66	2–	427
Water + 1-propanol	1–50;20	70.20	2	199
Water + 2-propanol	1–50; 20	71.73	2	199
Water + 1,3-propanediol	0–60; 20	71.44	2–	427
Water + 1-butanol	0–60; 20	86.3	1	427
Water + 1-butanol	30	87.0	1	69
Water + 1-butanol	1–40; 1	85.90	2	203
Water + 1-butanol	1–50; 20	85.77	2	199
Water + 2-methyl-1-propanol	1–40; 1	86.15	2	203
Water + 2-methyl-1-propanol	1–50; 20	86.42	2	199
Water + 2-butanol	1–40; 1	86.33	2	203
Water + 2-butanol	1–50; 20	86.63	2	199
Water + 2-methyl-2-propanol	1–40; 1	87.95	2	203
Water + 1-pentanol	0–60; 20	101.80	2–	427
Water + 1-pentanol	1–50; 20	101.92	2	199
Water + benzyl alcohol	1–50; 20	100.82	2	199