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Publisher *Taylor & Francis*

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Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646857>

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To cite this Article Brostow, Witold(1972) 'Equilibrium properties in the liquid state from interactions of walks', *Physics and Chemistry of Liquids*, 3: 2, 91 – 113

To link to this Article: DOI: 10.1080/00319107208084091

URL: <http://dx.doi.org/10.1080/00319107208084091>

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Equilibrium Properties in the Liquid State from Interactions of Walks

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Received November 16, 1971

Abstract—When molecules of chemical compounds are represented by graphs, thermodynamic properties may be connected with numbers of certain classes of walks on graphs. The basic proposition of summing up contributions resulting from interactions of walks is related to fluid distribution functions. The principle of corresponding volumes and structural schemes are discussed. Exemplary calculations for normal alkanes and their binary mixtures give in many cases values within limits of the experimental accuracy.

1. Introduction

Consider an assembly of molecules other than monoatomic. From the point of view of combinatorial contributions to thermodynamic functions, dividing molecules into segments enables an approximate but straightforward treatment of effects of molecular size and shape. From the point of view of interactions, dealing with intersegmental rather than with intermolecular relations also represents an improvement. In theories of thermodynamic properties of homolog liquids and their mixtures, reviewed by Williamson and Scott,⁽¹⁾ considerable use is made of the notion of segments. In approaches to the liquid state based on the principle of corresponding states, as reviewed by Patterson and Delmas,⁽²⁾ the same notion is of importance.

Starting from the segment approach, we shall be particularly concerned with effects of neighboring segments within a molecule upon external interactions of a given segment. A convenient way to do this consists in utilizing the notion of walks; a walk would correspond to a specified number of segments taken together and treated as a single unit. Segments in the customary sense would

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then feature in the lowest approximation—walks of length zero. In the next approximation, i.e. walks of length one, each non-end segment would constitute a part (an end point) of at least two walks; longer walks may be built similarly. It is reasonable to expect that introducing correlations between segments in such a way should improve the agreement of calculations with experiment. In principle, any desired degree of accuracy may be obtained by considering walks of any desired length.

Certain properties accessible at least in principle to macroscopic determination—such as the potential energy—are related somehow automatically to intermolecular interactions. We would like to represent also some other macroscopic properties—such as volume and its derivatives—in terms of pair interactions. It can be shown both by an algebraic argument and by considering radial distribution functions that, say, molar volume of a liquid mixture may be obtained (as it turns out, more accurately) by summing up contributions coming from interactions of specified units rather than contributions of volumes of segments themselves. Pair-type relations describing a number of thermodynamic properties will be formulated for an unlimited number of species present (even if in exemplary calculations we intend to take advantage of a series of homologs, i.e. of a small number of species).

In a way, we have contrasted above “energetic” and “volumetric” properties. We would like also to explore somehow, not only qualitative interrelations between the two kinds of functions, but also feasibility of actual calculations of quantities such as the excess heat of mixing H^E from volumetric properties.

2. Molecules as Graphs. Interesting Walks

A molecule of a chemical compound may be represented by a graph. According to the exact definition,⁽³⁾ a graph consists of a finite nonempty set Z of r points together with a prescribed set X of q unordered pairs of distinct points of Z ; each member of X is called a line. An alternating sequence of points and lines, beginning and ending with points, in which each line is incident with the two points immediately preceding and following it, is called a walk. The length l of a walk is the number of occurrences of lines in it. Thus,

for a given molecule one can assume e.g. that the set Z consists of all atoms, while the respective set X consists of bonds (whether single or multiple) between atoms.

With the above few definitions, we make the following proposition: assume that thermodynamic properties of substances and mixtures in the liquid state may be calculated by summing up contributions resulting from interactions of walks in molecules represented by graphs. Our basic assumption might, and in fact does apply to some physical properties which are not thermodynamic; in the present paper, however, we shall not deal with these. Walks of a single specified length only will be taken into account at a time. We have also confined ourselves to liquids and solutions, leaving open the problem of extending our treatment to other phases.

To apply our basic proposition, we need numbers of walks of given length. For each graph the respective numbers might be obtained by certain known operations on adjacency matrices.⁽³⁾ A number so obtained, however, is the total number of walks of length l in the given graph. Apart of distinguishing between certain kinds of walks (depending e.g. on the kinds of atoms in the underlying molecule) the total number of walks obtained from the adjacency matrix might include some physically redundant walks. For $l > 1$ we have closed walks such as—denoting points by letters—a walk $abca$ which we call uninteresting and eliminate by assumption. Moreover, from the point of view of interactions, two or more interesting walks may represent the same physical situation, so as e.g. two 4-walks (i.e. walks with $l = 4$) involving a 3-cycle: $abcdb$ and $abdc b$; clearly only one of them ought to be included in calculations. To be exact, we have to count not single walks but equivalence classes of interesting walks. Interesting walks of length l in a graph are defined in⁽⁴⁾; the formulas for numbers of appropriate equivalence classes Γ_l for $l \leq 5$ are obtained in the same paper. For our purpose of obtaining equations describing interactions it is sufficient to know that the formulas for Γ_l exist.

3. Interactions and Probability Distributions

Consider a closed system of interacting units, containing N_a units of type a , N_b units of type b , etc. Generally, interacting units may

be whole molecules, atoms, polymer segments, groups of atoms, or—of a particular interest here—walks of specified length and kind on graphs representing molecules. Denote the total number of such units by N :

$$N = \sum_y N_y; \quad y = a, b, \dots p \quad (1)$$

Introduce mole fractions $x_y = N_y/N$. Assume that thermodynamic properties are obtained by summing up contributions from single units and also from interactions of pairs of units:

$$f = \sum_y x_y f_y^* + \sum_y \sum_{y'} x_y x_{y'} f_{yy'}^* \quad (2)$$

where f is a thermodynamic quantity per unit. Representing the pair parameter $f_{yy'}^*$ by

$$f_{yy'}^* = f_{yy'} - 0.5(f_y^* - f_{y'}^*) \quad (3)$$

we can rewrite (2) as

$$f = \sum_y \sum_{y'} x_y x_{y'} f_{yy'} \quad (4)$$

Thus, the basic proposition of Sec. 1 is equivalent to dealing simultaneously with both single and binary terms.

Consider now the problem from the point of view of statistical mechanics, and make the following so called usual assumptions: (i) classical statistical mechanics applies; (ii) non-interactional degrees of freedom of a unit are unaffected by the presence of other units; (iii) the configurational energy of the system U^C depends on the relative positions of interacting units, but not on their relative orientation; (iv) according to the basic proposition outlined above, U^C is obtained by summing up interactions of pairs only, so that all contributions of higher orders are contained in the effective binary interactions. The partition function of the system is

$$Q = Q^D Q^M Q^C \quad (5)$$

where the r.h.s. terms represent respectively internal, momentum or kinetic, and configurational or interactional contributions.

Configurational energy of such a system is (cf. e.g. Ref. 5):

$$U^C = 0.5 \sum_y \sum_{y'} N_y N_{y'} V^{-1} \int u_{(yy')}(R) g_{yy'}(R) 4\pi R^2 dR; \quad (6)$$

V is the volume of the system; $u_{(yy')}$ is the energy of interaction of a y type unit with a y' type unit; R represents distance between two units and $g_{yy'}$ is the radial distribution function. In the above

relation the integration range is of some interest. We could, for instance, confine ourselves to values of R including nearest neighbors only. This would, however, not only disagree with experimental evidence concerning $g(R)$ —cf. e.g. the discussion of coordination shells by Mikolaj and Pings⁽⁶⁾—but also affect adversely our predictions of values of thermodynamic functions; Kohler⁽⁷⁾ has found that introduction of “stretched contacts” i.e. of interactions beyond the closest neighbors improves visibly the agreement of calculations with the experiment for argon. The opposite assumption would be to have R extending over the entire volume; this would but be equivalent to saying that a pair of units in the liquid phase does interact at all separations, even arbitrarily large. Clearly the real situation lies somewhere between these two extreme cases. Fortunately, as we shall see below, the precise knowledge of the integration range is not necessary for meaningful calculations of thermodynamic functions.

Introduce now the average value $\overline{u_{yy'}}$ for all pairs yy' as

$$\overline{u_{yy'}} = \frac{\int u_{(yy')}(R)g_{yy'}(R)R^2 dR}{\int g_{yy'}(R)R^2 dR} \quad (7)$$

Thus:

$$UC = \sum_y \sum_{y'} N_y N_{y'} \frac{\overline{u_{yy'}}}{2} \frac{\int g_{yy'}(R)4\pi R^2 dR}{V} \quad (8)$$

The expression $V^{-1}\int g_{yy'}4\pi R^2 dR$ represents the fraction of the total volume of the system in which interaction of an unit of type y with an unit of type y' leads to a non-zero contribution to configurational energy.

Another way of looking at the energy expression is by introducing

$$z_{yy'} = N_{y'} V^{-1} \int g_{yy'}(R)4\pi R^2 dR \quad (9)$$

so that

$$UC = \sum_y \sum_{y'} N_y 0.5z_{yy'} \overline{u_{yy'}} \quad (10)$$

Clearly $z_{yy'}$ (in general $\neq z_{y'y}$) represents the number of y' type units which interact with a given y type unit with non-zero interaction energy. This resembles somewhat the lattice model, but there, values of $z = 6$ or 8 in a liquid phase are taken as realistic; the well known fact that $z > 12$ or even the procedure of letting $z \rightarrow \infty$ give reasonable values for thermodynamic functions is understandable in

terms of the present approach. Moreover, in the lattice theory a single value of z , independent of kinds of interacting units and usually also of concentration is used.

Eventually in the most concise form, with N_A the Avogadro number, we have per mole of units :

$$\frac{N_A}{N} UC = \sum_{\nu} \sum_{\nu'} x_{\nu} x_{\nu'} U_{\nu\nu'} \quad (11)$$

where

$$U_{\nu\nu'} = NN_A \frac{\overline{u_{\nu\nu'}}}{2} \frac{\int g_{\nu\nu'}(R) 4\pi R^2 dR}{V} \quad (12)$$

We proceed to consider volume. The relevant formula for pressure is

$$P = \frac{NkT}{V} - \sum_{\nu} \sum_{\nu'} \frac{N_{\nu} N_{\nu'}}{6V^2} \int R \frac{du_{(\nu\nu')}(R)}{dR} g_{\nu\nu'}(R) 4\pi R^2 dR \quad (13)$$

Confine further considerations to pressures of few atmospheres, in thermodynamic units let us say to

$$P < 1 \text{ J cm}^{-3} \quad (14)$$

As pressure is a difference of two large quantities on the r.h.s. of (13) we can now neglect it altogether. Therefore

$$V = \frac{1}{6NkT} \sum_{\nu} \sum_{\nu'} N_{\nu} N_{\nu'} \int R \frac{du_{(\nu\nu')}(R)}{dR} g_{\nu\nu'}(R) 4\pi R^2 dR \quad (15)$$

Denoting

$$V_{\nu\nu'} = \frac{2\pi N_A}{3kT} \int \frac{du_{(\nu\nu')}(R)}{dR} g_{\nu\nu'}(R) R^3 dR \quad (16)$$

we have per mole of units

$$\frac{N_A V}{N} = \sum_{\nu} \sum_{\nu'} x_{\nu} x_{\nu'} V_{\nu\nu'} \quad (17)$$

We have used $V_{\nu\nu'} = N_A v_{\nu\nu'}$, and similarly $U_{\nu\nu'} = N_A u_{\nu\nu'}$. Thus both (11) and (17) are of the general form (4). Specifically for the two functions under consideration we can now restate the basic proposition of Sec. 1 by saying that all $u_{\nu\nu'}$ and $v_{\nu\nu'}$ are composition independent at a given temperature and pressure.

Consider now interrelations between configurational energy and volume. There are essentially two ways of doing it. One is to postulate a model of a liquid and to find out $U(V)$ behavior corresponding

to a given set of assumptions. This has been done by Snider⁽⁸⁾ who, for one-component systems considered in turn the lattice gas and some hard-core models with attractive terms added. For the latter, potential energy was found to be a function of density alone; the first term was linear in density, but the overall relation was not linear and contained still an integral involving $g(R)$. Evaluation of the integral was possible only when some further specific assumptions were made.

The second approach is to express the relationship by $U \sim V^n$ and to attempt to find the exponent n from some experimental data. The idea is due to Frank⁽⁹⁾ and was considered since by a number of authors; the most recent contribution to the subject is by Bagley and his collaborators.⁽¹⁰⁾ We follow this second route, assuming for our units

$$U_{vv'} = \frac{-\epsilon_{vv'}}{V^{n_{vv'}}} \quad (18)$$

where $\epsilon_{vv'}$ is a constant. Then by pure thermodynamics (see the next section) we can evaluate $\epsilon_{vv'}$ and $n_{vv'}$.

4. Thermodynamic Relations

Consider some further thermodynamic functions. Define in turn : isobaric expansivity

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{P,N} \quad (19)$$

isothermal compressibility

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{T,N} \quad (20)$$

isochoric exertion

$$\gamma = \left(\frac{\partial P}{\partial T} \right)_{V,N} \quad (21)$$

and configurational heat capacity at constant volume

$$C_V^c = \left(\frac{\partial U^c}{\partial T} \right)_{V,N} \quad (22)$$

The subscript N denotes differentiation at constant concentration. Now Eqs. (11) and (17) tell us, that formulas of the general form (4)

may be used for αV , κV , or C_V^G ; for α and κ we remember that assumption (14) has been made.

The approach described at the end of Sec. 3 may also be applied to a quantity such as one mole of molecules of a substance i .

Then

$$U_{ii}^G = \frac{-E_{ii}}{V_{ii}^{n_{ii}}} \quad (23)$$

Consequently

$$U_{ii}^G = -\frac{V_{ii}}{n_{ii}} (T\gamma_{ii} - P) \quad (24)$$

We take that (23) with the same numerical values of the coefficients n_{ii} applies also the gas phase. As we have limited ourselves to pressures specified by (14), it should be sufficient to write for the vapor

$$PV_V = NkT - BP \quad (25)$$

where B is the second virial coefficient. Introduce the enthalpy of vaporization $H_{ii}^{\text{vap}} = U_{V_{ii}}^G - U_{L_{ii}}^G - P(V_{V_{ii}} - V_{L_{ii}})$, with the subscripts V and L distinguishing phases. Now

$$n_{ii} = \frac{V_{ii}(T\gamma_{ii} - P) - P(B_{ii}P/Nk - T)dB/dT}{H_{ii}^{\text{vap}} - P(NkT/P - B_{ii} - V_{ii})} \quad (26)$$

with V_{ii} and γ_{ii} referring to the liquid phase.

The last relation with $B = 0$ has been used by previous authors to obtain a rounded value of n ; thus for hydrocarbons considered by Bagley *et al.*⁽¹⁰⁾ is $n = 1 \pm 0.2$. Our aim, however, is to substitute n from (26) into (24); from the resulting values of U_{ii}^G one should be able to calculate the excess energy of mixing U^E and related quantities.

Once we have at disposal quantities like U_{ii}^G and V_{ii} we can obtain parameters $U_{yy'}$, $V_{yy'}$, and $\gamma_{yy'} = \alpha_{yy'}/\kappa_{yy'}$. Values of the latter kind depend on the particular type of units considered (e.g. 2-walks). It is not our intention to write out here relations for various possible cases; at a given T and P , relations of the form $F_{yy'} = F_{yy'}(F_{ii}, F_{jj}, \dots)$ contain only concentrations as independent variables. From (18)

$$n_{yy'} = -\frac{V_{yy'}}{U_{yy'}^G} (T\gamma_{yy'} - P) \quad (27)$$

From the definition (20) we have

$$\left(\frac{\partial^2 U}{\partial V^2}\right)_{T,N} = \frac{1}{\kappa V} + \frac{1}{\kappa^2 V} \left[\left(\frac{\partial \kappa}{\partial T}\right)_{P,N} + \gamma \left(\frac{\partial \kappa}{\partial P}\right)_{T,N} \right] \quad (28)$$

We are thus able to complete specification of the parameters in (18) i.e. in (11):

$$\epsilon_{yy'} = - \frac{V^{n_{yy'}+1}}{N_A n_{yy'} (n_{yy'} + 1) \kappa_{yy'}} \left\{ 1 + \frac{T'}{\kappa_{yy'}} \left[\left(\frac{\partial \kappa_{yy'}}{\partial T'}\right)_{P,N} + \gamma_{yy'} \left(\frac{\partial \kappa_{yy'}}{\partial P}\right)_{T,N} \right] \right\} \quad (29)$$

5. Principle of Corresponding Volumes. Structural Schemes

In terms of the present approach we would like to comment on the previously formulated principle of corresponding volumes for liquids and their mixtures.⁽¹¹⁾ One of the ways of restating the principle is the following. Consider a group L of chemically similar substances L_i such as a series of homologs; at a specified temperature and pressure a thermodynamic property F is the same for all mixtures of L_i such that the mixture molar volume is the same. Thus, whatever the number of components in the mixture, including the case of pure substances, and whatever their relative concentrations, the molar value of F depends only on the resulting value of V per mole. The principle was intended for equilibrium properties, but it seems also to apply to transport properties. Thus, e.g. viscosity η of an ethanol + butanol mixture is the same as η of an ethanol + propanol solution which has the same molar volume as the first mixture.⁽¹¹⁾

The intuitive argument which led to proposing the principle of corresponding volumes was, that the value of any thermodynamic property F necessarily reflects both interactions and structural relationships in the respective system. Therefore, "horizontal" relations between various F 's might be simpler than "vertical" between any F and the basic structure-interaction parameters. Obviously, any thermodynamic quantity could serve as the reference, and volume was chosen because of its experimental accessibility and relative physical perspicuity.

We are now able to discuss the mechanism due to which the principle of corresponding volumes is confirmed by experiment.

The point is, that a uniquely specified set of numbers N_v of interacting units corresponds to a chosen molar volume. On the other hand, the desired single set of N_v may be realized by a number of different mixtures of molecules belonging to the class L , with various L_i containing the respective interacting units in various proportions.

As for excess functions of mixing, consider the particular case of homogeneous molecules, i.e. such that each molecule contains only one kind of interacting units. With the further specific assumption that—for a given l —is Γ_l the same for all components, from (4) we have per mole of interacting units

$$F^E = \sum_v \sum_{v'} x_v x_{v'} F_{vv'} - \sum_v x_v (1 - x_v) F_{vv} \quad (30)$$

Thus, for a binary mixture $a + b$, with e.g. $F = U, V$ is in such a case

$$U^E = \frac{2U_{ab} - U_{aa} - U_{bb}}{2V_{ab} - V_{aa} - V_{bb}} V^E \quad (31)$$

with the proportionality factor independent of composition. Some other sets of specific assumptions might also lead to relations such as (31).

We shall consider briefly the so called structural schemes. These include the best known schemes for parachor, refractivity and polarizability. More than two dozen papers and two monographs have been written on structural schemes by Tatevskii and his colleagues.⁽¹²⁾ A number of thermochemical schemes was successfully generalized by Somayajulu and Zwolinski,⁽¹³⁾ who relate their treatment to the linear combination of bond orbitals (LCBO) method of Brown.⁽¹⁴⁾ The group solution model for equilibrium and transport properties developed by Ratcliff *et al.*⁽¹⁵⁾ also makes use of a structural scheme. In terms of graph theory the structural schemes and the LCBO approximation represent summing up contributions of walks on molecules. In most of the cases only walks which are paths i.e. these in which all points are distinct, have been considered.

The main reason for invoking now structural schemes is the following. Our treatment may easily be reduced to the generalized structural scheme, i.e. to the no-external-interactions situation: it is sufficient to assume in Eq. (3) that all

$$f_{vv'} = 0.5(f_v^* + f_{v'}^*) \quad (32)$$

Thus our pair approach represents the second step in a chain. The consecutive better approximation—triplets of walks—should become increasingly useful along with the improvement of present accuracy of experiments.

6. Exemplary Calculations (Normal Alkanes)

For the first calculations we have chosen normal alkanes and their mixtures. Relatively very large amount of data concerning various thermodynamic quantities is here available. Accuracy of experiments appears to be higher for alkanes than for most of other substances and mixtures. Many measurements have been made at the room temperature, where the series is represented by 11 members in the liquid state. In fact, all reasons why alkanes are—apart of argon—the favorite choice of liquid state theorists apply to our case, plus the fact that dealing with walks is here particularly clear.

We take that the set Z consists of carbon atoms. This is the customary assumption; even if hydrogen atoms are included in Z , as end-points they are usually left unlabelled—the fact which led to recent studies of connected graphs with unlabelled end-points.⁽¹⁶⁾ By definition $\Gamma_0 = r$. For any length l denote an entry in the adjacency matrix⁽³⁾ by a_{ij}^l and the matrix itself by M^l , i.e. $M^l = \{a_{ij}^l\}$. Introduce further

$$a_i = \sum_{j=1}^r a_{ij}^l \quad \text{and} \quad a^l = \sum_{i=1}^r a_i^l.$$

Then⁽⁴⁾

$$\Gamma_1 = 0.5 a^1 = 0.5 \operatorname{tr} M^2 \quad (33)$$

$$\Gamma_2 = 0.5(a^2 - \operatorname{tr} M^2) \quad (34)$$

$$\Gamma_3 = 0.5(a^3 - a^1 - \operatorname{tr} M^3) \quad (35)$$

In the following we shall not need Γ_l for $l > 3$. Graphs of n -alkanes are the simplest possible trees, so that values of Γ_l might be obtained almost by inspection. The relations (33)–(35), however, are general—applicable to graphs of any complexity, including graphs containing cycles.

Further advantages of the graph approach may be seen e.g. if we reconsider the well-known problem of division of n -alkane molecules into segments. One possibility is to take CH_3 and CH_2 as segments,

the other choice being CH_3 and CH_2CH_2 . The alternatives have been discussed essentially in terms of volumes corresponding to segments in various cases. From the point of view of graphs the problem is solved immediately, once we notice that CH_3 and CH_2 represents walks of the same length, while CH_3 and CH_2CH_2 are of different length; in our approach there is clearly no requirement of equal volumes of segments.

The first thermodynamic property to be considered is the molar volume.

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We assume two kinds of interacting units in an alkane molecule: terminal ones involving a CH_3 group—to be denoted by subscript e , and middle ones labelled by subscript m . For $l = 0$ (when according to our assumptions the end unit is the methyl group itself) and for a molar thermodynamic property F to which the Eq. (4) applies we now have specifically

$$F = \frac{(r - r_e)^2}{2r} F_{mm} + \frac{r_e^2}{2r} F_{ee} + \frac{(r - r_e)r_e}{r} F_{em} \quad (36a)$$

The above relation is valid for pure substances as well as for mixtures. The relations between x_m , x_e and various molecular concentrations x_i are obvious, once we remember that for a s -component mixture is

$$r = \sum_{i=1}^s x_i r_i;$$

similarly r_m and r_e represent concentration averages, always with $r = r_m + r_e$.

Numerical calculations described in this paragraph are all for 293.15 K. We have taken a set of molar volumes for $r = 6, 8$ and 16 and solved 3 Eqs. (36a) to obtain values of V_{mm} , V_{ee} and V_{em} . From the latter we have calculated excess volume for the equimolar mixture of hexane with hexadecane as $V^E = -0.52 \text{ cm}^3 \text{ mol}^{-1}$.

For $l = 1$ the formula replacing (36a) is

$$F = \frac{(r - r_e - 1)^2}{2(r - 1)} F_{mm} + \frac{r_e^2}{2(r - 1)} F_{ee} + \frac{(r - r_e - 1)r_e}{r - 1} F_{em} \quad (36b)$$

as for any alkane (with or without branches) Eq. (33) gives $\Gamma_1 = r - 1$.

We have made calculations in the same way as before and obtained $V_{6+16}^E (x=0.5) = -0.50 \text{ cm}^3 \text{ mol}^{-1}$.

For $l = 2$ correspondingly

$$F = \frac{(r - r_e - 2)^2}{2(r - 2)} F_{mm} + \frac{r_e^2}{2(r - 2)} F_{ee} + \frac{(r - r_e - 2)r_e}{r - 2} F_{em}$$

as for any n -alkane Eq. (34) gives $\Gamma_2 = r - 2$. Analogous calculations gave $V_{6+16}^E (x=0.5) = -0.48 \text{ cm}^3 \text{ mol}^{-1}$. Diaz Peña and Benitez de Soto⁽¹⁷⁾ determined experimentally V_{6+16}^E for a number of concentrations and temperatures and described their results by a series in powers of $x_i - x_j$ and of temperature; the respective value resulting from their expansion is $-0.487 \text{ cm}^3 \text{ mol}^{-1}$.

The same V_{vy} parameters which predicted V_{6+16}^E values were not equally satisfactory for describing molar volumes of other hydrocarbons. Instead of basing on 3 experimental values (with arbitrariness involved in choosing a particular value among available experimental data for a given hydrocarbon) we have therefore combined different molar volumes for alkanes—including alternative data for the same substances—to obtain V_{vy} parameters. The resulting values for $l = 0, 1$ and 2 are listed in Table 1. Molar

TABLE 1 V_{vy} Parameters for n -alkanes at 293.15 K

	$\frac{V_{mm}}{\text{cm}^3 \text{ mol}^{-1}}$	$\frac{V_{ee}}{\text{cm}^3 \text{ mol}^{-1}}$	$\frac{V_{em}}{\text{cm}^3 \text{ mol}^{-1}}$
$l = 0$	32.965	73.062	46.782
$l = 1$	32.866	86.325	55.481
$l = 2$	32.758	100.427	64.095

volumes obtained therefrom are given in Table 2 within $\pm 0.001 \text{ cm}^3 \text{ mol}^{-1}$ so as to show more clearly the effect of varying l . Experimental data which have been taken into consideration are listed in the same table. Further, using exactly the same sets of V_{vy} parameters we have calculated V^E values for these equimolar binary mixtures for which experimental values were available and also for hexane + hexadecane mixtures at 0.1 concentration intervals. The results of calculations and the respective experimental values (within 0.001, even if accuracy of a particular measurement might be e.g. ± 0.02) are given in Table 3.

TABLE 2 Molar Volumes of *n*-alkanes at 293.15 K

<i>r</i>	$\frac{V}{\text{cm}^3\text{mol}^{-1}}$			
	Experimental	<i>l</i> = 0	<i>l</i> = 1	<i>l</i> = 2
5	115.19 ^a 115.20 ^c	115.032	115.076	115.141
6	130.67 ^{a,d} 130.68 ^{b,e} 130.95 ^c	130.684	130.686	130.688
7	146.56 ^c 146.59 ^a	146.573	146.570	146.567
8	162.59 ^c 162.64 ^a 162.65 ^b	162.611	162.611	162.613
9	178.68 ^a 178.71 ^c	178.747	178.750	178.755
10	194.87 ^a 194.93 ^c	194.953	194.954	194.955
11	211.14 ^a 211.17 ^c	211.209	211.204	211.195
12	227.42 ^a 227.46 ^e 227.48 ^c	227.503	227.487	227.463
13	243.65 ^a 243.82 ^c	243.825	243.795	243.752
14	260.09 ^a 259.81 ^e	260.171	260.122	260.055
15	276.39 ^a	276.535	276.465	276.370
16	292.72 ^e 292.74 ^d 292.81 ^a 292.86 ^b	292.914	292.819	292.694

(a) R. A. Orwoll and P. J. Flory, *J. Am. Chem. Soc.*, **89**, 6814 (1967) Table V; (b) *ibid.*, Table 1; (c) Ref. 12b; (d) Ref. 17; (e) G. H. Findenegg, *Monatsh.*, **101**, 1081 (1970).

TABLE 3 Excess Molar Volumes of *n*-alkanes at 293.15 K

r_i	r_j	x_i	$\frac{VE}{\text{cm}^3\text{mol}^{-1}}$			
			Experimental	$l=0$	$l=1$	$l=2$
5	16	0.5	0.82 ^a 0.827 ^{b,c}	0.898	0.874	0.846
7	16	0.5	0.31 ^a	0.392	0.353	0.304
8	16	0.5	0.19 ^{a,c}	0.259	0.228	0.191
10	16	0.5	0.73 ^{b,c} 0.70 ^a 0.40 ^c	0.108	0.092	0.073
6	12	0.5	0.31 ^{a,c}	0.346	0.336	0.320
5	10	0.5	0.418 ^{b,c}	0.415	0.440	0.473
6	10	0.5	0.200 ^{b,c}	0.208	0.208	0.208
6	16	0.1	0.113 ^d 0.121 ^e	0.156	0.141	0.123
6	16	0.2	0.227 ^d 0.228 ^e	0.297	0.270	0.238
6	16	0.3	0.332 ^d 0.326 ^e	0.420	0.384	0.340
6	16	0.4	0.420 ^d 0.413 ^e	0.519	0.479	0.429
6	16	0.5	0.493 ^c 0.487 ^{c,d,e}	0.590	0.548	0.496
6	16	0.6	0.524 ^d 0.526 ^e	0.623	0.585	0.535
6	16	0.7	0.520 ^d 0.524 ^e	0.606	0.576	0.535
6	16	0.8	0.453 ^d 0.455 ^e	0.519	0.502	0.476
6	16	0.9	0.294 ^d 0.291 ^e	0.334	0.329	0.322

(a) A. Desmyter and J. H. van der Waals, *Recueil Trav. Chim. Pays-Bas*, **77**, 53 (1958); (b) M. L. McGlashan and K. W. Morcom, *Trans. Faraday Soc.*, **57**, 907 (1961); (c) As compiled by Stoeckli *et al.* in Ref. 19 on the basis of literature data and some their own measurements; (d) M. L. McGlashan, K. W. Morcom and A. G. Williamson, *Trans. Faraday Soc.*, **57**, 601 (1961); (e) Ref. 17.

We could have made the next step to $l = 3$, with the total number Γ_3 of equivalence classes of interesting walks for any molecule (for such short and open walks as we consider, an equivalence class contains exactly one element) given by Eq. (35). Qualitatively, however, the situation would change, because we would have to consider more kinds of walks. For a n -pentane molecule, denoting consecutive segments as e, m_1, m_2, m_3 and e , we have walks $em_1m_2m_3$, $em_1m_2m_1$, $m_1em_1m_2$ and $m_1m_2m_3m_2$, and consequently 10 types of pair interactions. For longer molecules the number of parameters to be considered would be still higher. This is why we have confined ourselves to $l = 0, 1$ and 2 , when the assessment of improvement caused by increasing l is particularly clear.

Our results should contrast favorably with structural schemes, as we know of no reason why Eq. (32) should hold. Williamson and Scott⁽¹⁾ used what amounts to a structural scheme (additive contributions of carbon atoms) to describe molar volumes of n -alkanes at 298.15 K; the standard deviation of calculated values from experimental ones for what they call the best equation is 0.38 cm³mol⁻¹. For pure components our standard deviations from averages of the experimental values (disregarding the highest value for hexane and the lower for tetradecane) for $l = 0, 1$ and 2 are respectively 0.087, 0.054 and 0.042 cm³mol⁻¹. A no-external-interactions treatment, has, moreover, a basic defect: all excess functions of mixing are automatically zero (unless of course, non-linear terms are introduced).

Main conclusions from inspection of Tables 2 and 3 are the following. Firstly, for given l using a set of 3 parameters (obtainable basically from 3 exact measurements) it is possible to calculate molar volumes of n -alkanes, molar volumes of their mixtures of any number of components and composition, and in consequence also volumes of mixing. Secondly, accuracy of the description increases along with l ; values for the smallest molecule i.e. n -pentane in Table 2 are particularly indicative in this respect. For $l = 2$ the calculated values (except for n -pentane and the 5 + 10 mixture) are clearly within limits of the experimental accuracy.

EXPANSIVITIES

We performed similar calculations using Eq. (36) with $F = \alpha V$

at 293.15 K, confining ourselves to $l = 0$ in view of limited accuracy of experimental data. The respective parameters are $(\alpha V)_{mm} = 0.02415 \text{ cm}^3 \text{ K}^{-1} \text{ mol}^{-1}$, $(\alpha V)_{ee} = 0.25416 \text{ cm}^3 \text{ K}^{-1} \text{ mol}^{-1}$ and $(\alpha V)_{em} = 0.04631 \text{ cm}^3 \text{ K}^{-1} \text{ mol}^{-1}$. Values of isobaric expansivities calculated therefrom along with the respective experimental data are given in Table 4.

TABLE 4 Isobaric Expansivities of *n*-alkanes at 293.15 K

<i>r</i>	$10^3 \alpha$ K^{-1}	
	Experimental	$l = 0$
5	1.59 ^a	1.556
6	1.35 ^a 1.364 ^b 1.366 ^e 1.367 ^c 1.369 ^d	1.367
7	1.23 ^a 1.243 ^b	1.241
8	1.146 ^c 1.15 ^a 1.151 ^b	1.153
9	1.085 ^b	1.087
10	1.04 ^a 1.045 ^b	1.037
11	1.006 ^b	0.998
12	0.967 ^d 0.974 ^b	0.967
13	—	0.943
14	0.914 ^b 0.930 ^d	0.924
15	0.901	0.907
16	0.878 ^b 0.885 ^a 0.890 ^e 0.893 ^d 0.897 ^c	0.890

(a) estimated within about 3% from earlier literature data by M. L. McGlashan and K. W. Morcom, *Trans. Faraday Soc.*, **57**, 907 (1961); (b) As footnote (a), Table 2, (c) As footnote (b), Table 2; (d) As footnote (e), Table 2; (e) Ref. 17.

Using the same set of parameters, for mixtures of hexane with hexadecane we have calculated excess expansivities α^E defined exactly as

$$\alpha^E = \frac{1}{\bar{V}} \left(\frac{\partial V^E}{\partial T} \right)_{P,N} - \frac{V^E}{\bar{V}^I} (V_{ii} \alpha_{ii} + V_{jj} \alpha_{jj}) \quad (37)$$

where V^I is the ideal volume of mixing. The results are compared with the experimental values of Diaz Peña and Benitez de Soto⁽¹⁷⁾ in Table 5.

Comments on the extent of agreement seem superfluous.

TABLE 5 Excess Isobaric Expansivities for Hexane (1) + Hexadecane (2) Mixtures at 293.15 K

x_1	$\frac{10^8 \alpha^E}{\text{K}^{-1}}$	
	Experimental ^a	$l = 0$
0.1	-0.029	-0.031
0.2	-0.042	-0.044
0.3	-0.046	-0.047
0.4	-0.044	-0.044
0.5	-0.039	-0.039
0.6	-0.032	-0.032
0.7	-0.023	-0.024
0.8	-0.014	-0.016
0.9	-0.006	-0.008

(a) Ref. 17.

COMPRESSIBILITIES

Calculations for κV have been made analogously as for αV . The parameters again for $l = 0$ and 293.15 K are $(\kappa V)_{mm} = 0.01751 \text{ J}^{-1} \text{ cm}^6 \text{ mol}^{-1}$, $(\kappa V)_{ee} = 0.35388 \text{ J}^{-1} \text{ cm}^6 \text{ mol}^{-1}$, $(\kappa V)_{em} = 0.05134 \text{ J}^{-1} \text{ cm}^6 \text{ mol}^{-1}$. The results for pure components are given in Table 6, excess values

$$\kappa^E = -\frac{1}{\bar{V}} \left(\frac{\partial V^E}{\partial P} \right)_{T,N} + \frac{V^E}{\bar{V}^I} (V_{ii} \kappa_{ii} + V_{jj} \kappa_{jj}) \quad (38)$$

for 6 + 16 mixtures in Table 7. Conclusions reached above are clearly reiterated for isothermal compressibility.

TABLE 6 Isothermal Compressibilities of *n*-alkanes at 923.15 K

<i>r</i>	$\frac{10^3 \kappa}{\text{J cm}^{-3}}$	
	Experimental	<i>l</i> = 0
5	1.89 ^a	1.900
6	1.54 ^a	1.605
	1.605 ^c	
	1.625 ^b	
7	1.34 ^a	1.403
8	1.21 ^a	1.260
	1.258 ^b	
9	—	1.153
10	1.04 ^a	1.072
11	—	1.008
12	—	0.956
13	—	0.914
14	—	0.879
15	—	0.850
16	0.826 ^c	0.824
	0.838 ^b	
	0.84 ^a	

(a) As footnote (a), Table 4; (b) from $\gamma(T)$ relation given by R. A. Orwoll and P. J. Flory, *J. Am. Chem. Soc.*, **89**, 6814 (1967); (c) Ref. 17.

TABLE 7 Excess Isothermal Compressibilities for Hexane (1) + Hexadecane (2) Mixtures at 293.15 K

x_1	$\frac{10^3 \kappa^E}{\text{J cm}^{-3}}$	
	Experimental ^a	<i>l</i> = 0
0.1	-0.046	-0.046
0.2	-0.066	-0.065
0.3	-0.068	-0.069
0.4	-0.067	-0.066
0.5	-0.060	-0.058
0.6	-0.050	-0.047
0.7	-0.038	-0.036
0.8	-0.025	-0.024
0.9	-0.013	-0.012

(a) Ref. 17.

HEATS OF MIXING

In view of Eqs. (11) and (17), at constant pressure Eq. (4) applies also to the sum $UC + PV = H^C$, what should enable immediate calculations of excess heats of mixing. Having already dealt with V , α and κ , according to Eq. (24) the problem comes to that of obtaining n_{ii} for 3 n -alkanes. As H^E is a small difference of quantities several orders of magnitude larger, highly accurate values of n are needed. Apart of parameters we already have at disposal, Eq. (26) demands the knowledge of heats of vaporization and also of second virial coefficients as functions of temperature. While reasonably accurate H^{vap} values can be obtained from Antoine equation for vapor pressures, we encounter practical difficulties concerning $B(T)$. Experimental measurements of second virial coefficients of alkanes of McGlashan and Potter⁽¹⁸⁾ have been made at higher temperatures. Their corresponding states correlation, highly accurate at temperatures of actual experiments, unfortunately does not extend down to the room temperature, particularly for higher values of r . While problems with accessibility of some experimental data do not undermine the validity of Eqs. (24) and (26) based on thermodynamics, we have turned to a roundabout procedure.

Basing on a set of H^E values of some equimolar alkane mixtures compiled by Stoeckli *et al.*,⁽¹⁹⁾ we have generated approximate H^C values of pure substances by a computer procedure. Such set of values is shown in Table 8. It is at least possible to prove that the H^C set is reasonable. We have in fact performed calculations using Eqs. (26) and (24) for n -pentane and n -hexane, where errors of $B(T)$ extrapolation below the experimental range are the smallest, while using Antoine equation constants from Ref. 20. The results are $H^C = -24568 \text{ J mol}^{-1}$ for pentane, and -28283 for hexane, certainly in as good agreement as could be expected with the values in Table 8.

Values of H^C in Table 8 have been obtained using Eq. (36a) and parameters $H_{mm}^C = -7929 \text{ J mol}^{-1}$, $H_{ee} = -14185 \text{ J mol}^{-1}$ and $H_{em}^C = -9745 \text{ J mol}^{-1}$. Using the same parameters and Eq. (30) we have calculated excess heats of mixing. The results along with the experimental values as listed in Ref. 19 are shown in Table 9. By further manipulation we could improve H_{vv}^C parameters and so

the extent of agreement concerning H^E ; for the present essentially illustrative purposes it did not seem worthwhile. We have, however, performed some preliminary calculations of H^E for higher temperatures, in connection with the change of sign of heat of mixing found by McGlashan and his colleagues.⁽²¹⁾ For negative and S-shaped curves of heat of mixing versus composition the same approach was found applicable.

TABLE 8 Configurational Enthalpies
 H^C of n -alkanes at 293.15 K

r	$\frac{-H^C}{\text{J mol}^{-1}}$
5	24504
6	28293
7	32133
8	36003
9	39895
10	43801
11	47717
12	51642
13	55573
14	59508
15	63448
16	67390

TABLE 9 Heats of Mixing of Equimolar Mixtures of
 n -alkanes at 293.15 K

r_i	r_j	$\frac{H^E}{\text{J mol}^{-1}}$	
		Experimental ^a	$l = 0$
5	16	151.3	188.9
6	16	129.0	124.2
		127.5	
7	16	112.0	82.5
8	16	86.5	54.7
10	16	49.2	22.7
6	12	45.5	72.8
5	10	25.5	87.4
6	10	17.4	43.7

(a) Ref. 19.

As calculations described in this paragraph are exemplary, we have confined the results to a single temperature. For the same reason we have not included results of calculations of adiabatic compressibilities, where the pattern is quite similar to that for the respective isothermal quantity. Clearly, a more detailed pursuit of thermodynamic behavior of *n*-alkanes and their mixtures—in particular as a function of temperature—would be worthwhile. In view of recent accumulation of experimental values⁽²²⁾ concerning volumes, expansivities and isothermal compressibilities at a number of temperatures, this, however, would mean embarking on a fairly large—and therefore necessarily separate—project.

Acknowledgements

The author is indebted to all these with whom he has discussed his problems. Comments of Prof. Donald Patterson of McGill University, Montreal, in final stages of this work are acknowledged in particular.

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