A NEW MOLECULAR THEORY
OF LIQUID MIXTURES

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A new theory of solutions is proposed combining some features of the recently developed tunnel theory of liquid mixtures and of the theorem of corresponding states. To test the theory, excess functions of 10 equimolar Lorentz-Berthelot's binary mixtures were calculated. The agreement between the calculated and experimental values of G^E, H^E and V^E is very good. It cannot be, however, regarded as quantitative. The effect of inaccuracies of the Lennard-Jones parameters ε, σ for the pure components and of the cross parameters ε_{12}, σ_{12} (calculated from the combination rules) on G^E and V^E is calculated in this work. A one percent deviation in parameters inflicts inaccuracies in the excess functions comparable with their values.

For a number of years considerable attention has been focused on the problem of the relationship between the thermodynamic functions of liquid mixtures and parameters describing the energy of interaction between molecules of the same and different kind. An important role in solving this problem has been played by the theorem of corresponding states (TCS) (ref.[1]), for its application circumvents the difficult task of determining the configuration integral. TCS described rather well the behaviour of simple liquids and it can be derived by means of statistical mechanics on the basis of several general assumptions.

The first attempt to utilize TCS in statistical thermodynamics of mixtures was the theory of conformal solutions[2]. It expresses the excess thermodynamic functions as powers of the differences of the interaction parameters. Unfortunately, the validity of TCS without supplementary assumptions suffices only for determination of the coefficients of the first powers[3]. Further progress in the theory of liquid mixtures was achieved when Prigogine and coworkers formulated the average potential model (APM) of solutions[4]. Scott[5] arrived independently at essentially the same model. APM combines the theorem of corresponding states with the cell model of solutions, retaining from the cell theory only the manner of determining of average interaction parameters in the mixture. The values of the excess functions of simple liquid mixtures calculated in APM are in qualitative agreement with the experimental data[6]. Quantitatively, the situation is not sufficiently satisfactory and it remains an open issue whether the difference between the experi-

mental and calculated values of excess functions is induced predominantly by the inaccuracies of interaction parameters. It seems, however, that a combination of model theories of liquids with TCS is presently the most effective approach to the theory of solutions.

The tunnel theory of the liquid state[7] has been extended recently to multicomponent systems[8]. The tunnel theory of liquids rests on a model of the liquid structure, which divides the configuration integral, Q, of the system into a part, Q_L, due to the longitudinal (one-dimensional) motions of molecules and a part, Q_T, due to the tranverse motions.

$$Q = Q_L \cdot Q_T \qquad (1)$$

The configuration integral of a one-dimensional system can be evaluated accurately in principle and this advantage of the tunnel model is preserved for multicomponent systems as well. The tunnel theory predicts relatively satisfactorily the values of excess functions of mixtures of simple liquids. The agreement between the calculated and experimental values is in most cases better than that for APM.

In this paper we shall attempt to combine TCS with the tunnel theory of mixtures. The idea of this approach, which avoids the necessity of solving the configuration integral Q_T of the transverse motions of the molecules in Eq. (1), is to decrease the laboriousness of the calculation and to suppress the errors appearing in the tunnel theory as a consequence of an approximative determination of Q_T.

THEORETICAL

THE THEOREM OF CORRESPONDING STATES

For a system of temperature T, volume V and a number of particles N one can derive in statistical thermodynamics the theorem of corresponding states from the following assumptions:

The partition function of the system can be written as a product of the translational partition function and a factor corresponding to the internal motions of molecules and independent of the volume of the system. The Maxwell-Boltzman statistics can be used to determine the translational partition function. The total potential energy of the system, U, can be replaced by a sum of pair contributions $U(r_1, r_2, ..., r_N) = \sum_{i<j} u(r_{ij})$, and the potential energy of interaction of a pair of molecules at a distance r can be expressed as a product of an energy parameter and a universal function of reduced distance $u(r) = \varepsilon f(r/\sigma)$. The parameters ε and σ characterize the kind interreacting molecules.

The requirement of pairwise additivity of interaction energies is not necessary to derive TCS. We shall need it, however, elsewhere in this paper. The function $u(r)$ we shall approximate by the commonly used Lennard-Jones $6-12$ potential.

$$u(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6] . \qquad (2)$$

The parameters of interaction between a molecule of the kind 1 and a molecule of the kind 2 we shall approximate by the Lorentz-Berthelot semiempirical combination rules

$$\varepsilon_{12} = (\varepsilon_1 \varepsilon_2)^{1/2} , \tag{3}$$

$$\sigma_{12} = (\sigma_1 + \sigma_2)/2 . \tag{4}$$

From the assumptions it follows that the only part of the partition function depending on the volume is the configuration integral Q, which can be written as

$$Q(N, V, T) = \sigma^{3N} q(\tilde{V}, \tilde{T})^N , \tag{5}$$

where $\tilde{T} = kT/\varepsilon$ is the reduced temperature, $\tilde{V} = V/N\sigma^3$ is the reduced volume and q is a universal function of reduced variables. From Eq. (5) one can obtain all configuration thermodynamic quantities as functions of reduced variables.

Empirical dependences of the configuration free enthalpy and of the reduced volume on the reduced temperature at zero pressure have been proposed[6].

$$G_{conf}/NkT = - 3 \ln \sigma - 8 \cdot 379308/\tilde{T} - 4 \cdot 597197 \ln \tilde{T} + 3 \cdot 212199 +$$
$$+ 2 \cdot 301041 \tilde{T} - 0 \cdot 806469 \tilde{T}^2 , \tag{6}$$

$$V/N\sigma^3 = 1 \cdot 347174 - 0 \cdot 997309 \tilde{T} + 1 \cdot 180314 \tilde{T}^2 . \tag{7}$$

To determine numerical values of the coefficients appearing in Eqs (6) and (7), experimental data of liquid argon, krypton, methane, nitrogen, oxygen and carbon monoxide were extrapolated to zero pressure. Parameters ε, σ necessary for the evaluation were determined from the critical constants of the substances and these are shown in Table I.

THE TUNNEL MODEL OF A LIQUID

The tunnel theory is based on following assumptions regarding the structure of the liquid: The molecules move predominantly unidirectionally in capillary tunnels, the walls of which are formed by the axes of adjoining tunnels. The ends of the axes form a two-dimensional hexagonal lattice. The molecules in the tunnels perform small transverse motions which are independent of the longitudinal ones. The motions of molecules in different tunnels are mutually independent. From the model of the structure results Eq. (1) for the configuration integral of the system, and for the volume the relationship

$$V/N = \sqrt{3}/2 r^2 l , \tag{8}$$

where r is the distance between the axes of adjacent tunnels and l is the length of the tunnel per one molecule.

The configuration integral, Q_L, of a one-dimensional system can be determined accurately[4] from the equation

$$Q_L(N, l, T) = \left\{ \exp\left(l/W\right) \int_0^\infty \exp\left[-u(x)/kT - x/(\sigma W)\right] \mathrm{d}x \right\}^N , \qquad (9)$$

where $\tilde{l} = l/\sigma$, $W = kT/(P_L\sigma)$ and P_L is a one-dimensional pressure, provided that the interaction takes place only between the closest molecules. The configuration free energy, F_L, and the equation of state of a one-dimensional system can be determined easily from Eq. (3).

$$F_L/NkT = -\ln \sigma - \tilde{l}/W - \ln\left[\int_0^\infty J(\tilde{T}, W, \xi)\,\mathrm{d}\xi\right], \qquad (10)$$

where
$$J(\tilde{T}, W, \xi) = \exp\left[-4(\xi^{12} - \xi^6)/\tilde{T} - \xi/W\right],$$

$$\xi = x/\sigma , \quad \tilde{l} = \int_0^\infty \xi J(\tilde{T}, W, \xi)\,\mathrm{d}\xi \Big/ \int_0^\infty J(\tilde{T}, W, \xi)\,\mathrm{d}\xi . \qquad (11)$$

In Eqs (10) and (11) the function $u(x)$ was replaced by the Lennard–Jones potential. Following simplifying approximation was introduced in the tunnel theory of pure liquids

$$r = l ,$$

which, together with Eqs (7) and (8), enables the determination of the reduced length l for a given reduced temperature. The quantity W is then given by Eq. (11).

We shall not deal with the contribution of the transverse motions of molecules to the thermodynamic functions. For their determination we shall make use of the theorem of corresponding states. Let us determine the excess functions of a binary mixture containing N_1 molecules of the kind 1 and N_2 molecules of the kind 2 at the temperature T and zero pressure. An extension of the following procedure to systems of more components poses no problem.

For the excess thermodynamic functions of a one-dimensional mixture, assuming a random distribution of molecules, one can derive[4]

$$Y_L^E = x_1 x_2 \left[2 Y_L(\varepsilon_{12}, \sigma_{12}) - Y_L(\varepsilon_1, \sigma_1) - Y_L(\varepsilon_2, \sigma_2)\right], \qquad (12)$$

where $Y(\varepsilon, \sigma)$ is an arbitrary molar thermodynamic quantity of a substance with the Lennard-Jones parameters ε, σ . x_1, x_2 are molar fractions.

In the tunnel theory of mixtures[8] the pseudointeraction parameters $\bar{\bar{\varepsilon}}_i$ and $\bar{\bar{\varepsilon}}_{ij}$, defined by equations

$$\bar{\bar{\varepsilon}}_i = \bar{\varepsilon}_i r(\bar{\varepsilon}_i, \bar{\sigma}_i)/l(\varepsilon_i, \sigma_i) ,$$

$$\bar{\bar{\varepsilon}}_{ij} = \bar{\varepsilon}_i r(\bar{\varepsilon}_i, \bar{\sigma}_i)/l(\varepsilon_{ij}, \sigma_{ij}) , \quad i, j = 1, 2 \quad i \neq j , \tag{13}$$

were introduced for the determination of contributions of the transverse motions to the excess functions. $\bar{\varepsilon}_i$, $\bar{\sigma}_i$ are pseudointeraction parameters used in APM:

$$\bar{\varepsilon}_i = (x_i \varepsilon_i \sigma_i^6 + x_j \varepsilon_{ij} \sigma_{ij}^6)^2/(x_i \varepsilon_i \sigma_i^{12} + x_j \varepsilon_{ij} \sigma_{ij}^{12}) ,$$

$$\bar{\sigma}_i^6 = (x_i \varepsilon_i \sigma_i^{12} + x_j \varepsilon_{ij} \sigma_{ij}^{12})/(x_i \varepsilon_i \sigma_i^6 + x_j \varepsilon_{ij} \sigma_{ij}^6) . \tag{14}$$

Following equation was proposed in the tunnel theory mixtures for the excess functions Y_T^E

$$Y_T^E = x_1^2 Y_T(\bar{\bar{\varepsilon}}_1, \bar{\sigma}_1) + x_1 x_2 [Y_T(\bar{\bar{\varepsilon}}_{12}, \bar{\sigma}_1) + Y_T(\bar{\bar{\varepsilon}}_{21}, \bar{\sigma}_2)] +$$
$$+ x_2^2 Y_T(\bar{\bar{\varepsilon}}_2, \bar{\sigma}_2) - x_1 Y_T(\varepsilon_1, \sigma_1) - x_2 Y_T(\varepsilon_2, \sigma_2) . \tag{15}$$

In this paper we use the same procedure except that we do not calculate quantities Y_T from the configuration integral of the transverse motions in the tunnels, but, with respect to Eq. (1), as a difference $Y - Y_L$.

The excess functions of the whole system, excepting the excess volume, we obtain by combining Eqs (12) and (15)

$$Y^E = x_1^2 [Y_L(\varepsilon_1, \sigma_1) + Y(\bar{\bar{\varepsilon}}_1, \bar{\sigma}_1) - Y_L(\bar{\bar{\varepsilon}}_1, \bar{\sigma}_1)] +$$
$$+ x_2^2 [Y_L(\varepsilon_2, \sigma_2) + Y(\bar{\bar{\varepsilon}}_2, \bar{\sigma}_2) - Y_L(\bar{\bar{\varepsilon}}_2, \bar{\sigma}_2)] +$$
$$+ x_1 x_2 [2Y_L(\varepsilon_{12}, \sigma_{12}) + Y(\bar{\bar{\varepsilon}}_{12}, \bar{\sigma}_1) + Y(\bar{\bar{\varepsilon}}_{21}, \bar{\sigma}_2) - Y_L(\bar{\bar{\varepsilon}}_{12}, \bar{\sigma}_1) - Y_L(\bar{\bar{\varepsilon}}_{21}, \bar{\sigma}_2)] -$$
$$- x_1 Y(\varepsilon_1, \sigma_1) - x_2 Y(\varepsilon_2, \sigma_2) . \tag{16}$$

The relationship for the mixing volume we get on the basis of the following reasoning. Let us fix a molecule of the kind i in the axis of some of the tunnels and let us assume that the closest neighbouring molecule of the same tunnel is also in its axis. Now, two cases can occur: If both molecules are of the same kind, their average distance is $l(\varepsilon_i, \sigma_i)$ and the cross-section of the tunnel in the point of the fixed molecule is $(\sqrt{3}/2)$

$r(\bar{\bar{\varepsilon}}_i, \bar{\sigma}_i)^2$. If the neighbouring molecule is of the kind j, the distance between both molecules is $l(\varepsilon_{ij}, \sigma_{ij})$ and the cross-section of the tunnel in the point of the fixed molecule is $(\sqrt{3}/2) \, r(\bar{\bar{\varepsilon}}_{ij}, \bar{\sigma}_i)^2$. Thus for the excess volume we have, taking Eq. (8) into consideration

$$V^E/N = (\sqrt{3}/2) \{x_1^2 r(\bar{\bar{\varepsilon}}_1, \bar{\sigma}_1)^2 \, l(\varepsilon_1, \sigma_1) + x_2^2 r(\bar{\bar{\varepsilon}}_2, \bar{\sigma}_2)^2 \, l(\varepsilon_2, \sigma_2) + $$
$$ + x_1 x_2 [r(\bar{\bar{\varepsilon}}_{12}, \bar{\sigma}_1)^2 + r(\bar{\bar{\varepsilon}}_{21}, \bar{\sigma}_2)^2] \, l(\varepsilon_{12}, \sigma_{12})\} - x_1 V(\varepsilon_1, \sigma_1) - x_2 V(\varepsilon_2, \sigma_2) \,. \tag{17}$$

RESULTS AND DISCUSSION

To test the theory, G^E, H^E and V^E of ten binary systems composed of A, Kr, CH_4, N_2, O_2 and CO were calculated. For these components the theorem of corresponding states holds best.

The Lennard-Jones parameters of the pure components are summarized in Table I. These parameters are taken from the paper of Bellemans, Mathot and Simon[6] and were calculated from the critical constants of the substances assuming that the interaction constants of krypton are $\varepsilon/k = 171$ K and $\sigma = 3.600$ Å. The cross parameters were calculated from Eqs (3) and (4). Table II compares the calculated and measured values of the excess functions. The experimental data of the systems A–CH_4, A–N_2, N_2–O_2, A–O_2 were taken from the work of Bellemans, Mathot and Simon[6], and of the systems A–Kr, CH_4–Kr, N_2–CH_4 from the work of Bellemans and Vilcu[9].

The agreement between the calculated and experimental values of G^E and H^E is very good for most of the systems. Greater deviations from the experimental values of V^E are found for the systems N_2–CH_4 and A–Kr. As will be shown, the possible causes of these deviations are small deviations from the rule of arithmetic mean (see Eq. (4)). In contrast to the experimental values, the calculated values of the excess functions for systems A–O_2 and N_2–CO equal almost zero as a consequence of the fact that for both systems $\varepsilon_1 \simeq \varepsilon_2$ and $\sigma_1 \simeq \sigma_2$. The critical temperatures were measured for both systems and ε_{12} determined from them[10]. These values are somewhat different than the values obtained from Eq. (3). Table III shows the excess functions of A–O_2 and N_2–CO systems calculated from the experimental values of ε_{12}. To determine σ_{12}, Eq. (4) was used. The agreement between the calculated and experimental values is much better than when using the geometric mean rule for ε_{12}.

It is a well-known fact that even small inaccuracies in interaction parameters inflict considerable errors in excess functions. We shall try to assess quantitatively the effect of parameters on the calculated values of G^E and V^E. Let us assume that the errors in ε and σ of the pure components are so small that

$$\delta_\varepsilon = \left| \frac{\varepsilon - \varepsilon^\circ}{\varepsilon^\circ} \right| \ll 1 \text{ and } \delta_\sigma = \left| \frac{\sigma - \sigma^\circ}{\sigma^\circ} \right| \ll 1 \,.$$

TABLE I

The Lennard–Jones Coefficients of Pure Components

Substance	ε/k, K	σ, A°	Substance	ε/k, K	σ, A°
Ar	123·2	3·363	N_2	103·0	3·573
Kr	171·0	3·600	O_2	123·0	3·411
CH_4	156·0	3·696	CO	108·6	3·600

TABLE II

Excess Functions of Equimolar Mixtures

System	T, K	G^E, cal/mol		H^E, cal/mol		V^E, cm³/mol	
		found	calc.	found	calc.	found	calc.
A–CH_4	91	19·2	23·9	24·6	30·6	0·18	0·24
CH_4–Kr	116	6·7	3·6	—	4·1	0·00	−0·04
A–Kr	116	20·1	26·2	—	25·3	−0·50	−0·09
CO–CH_4	91	28·0	21·8	25·1	19·3	−0·33	−0·41
N_2–CH_4	91	33·8	28·4	—	24·8	−0·21	−0·55
CO–A	84	13·5	10·1	—	13·5	0·10	−0·01
A–O_2	84	8·9	0·3	14·3	0·5	0·14	0·00
N_2–A	84	8·2	10·9	12·1	13·0	−0·18	−0·14
N_2–CO	84	5·5	0·4	10·2	0·3	0·10	−0·01
N_2–O_2	77	10·0	8·5	11·0	9·6	−0·21	−0·12

TABLE III

Excess Functions Calculated form Experimental Values of ε_{12}

System	T, K	$\varepsilon_{12}/\sqrt{(\varepsilon_1\varepsilon_2)}$	G^E, cal/mol		H^E, cal/mol		V^E, cm³/mol	
			found	calc.	found	calc.	found	calc.
A–O_2	84	0·982	8·9	13·1	14·3	18·9	0·14	0·10
N_2–CO	84	0·986	5·5	8·3	10·2	13·0	0·10	0·13

TABLE IV

Effect of Deviation in Parameters ε and σ on Values of G^E and V^E

System	Y^E	$A_{\varepsilon_1}.10^{-2}$	$A_{\varepsilon_2}.10^{-2}$	$A_{\sigma_1}.10^{-2}$	$A_{\sigma_2}.10^{-2}$	$A_{\varepsilon_{12}}.10^{-2}$	$A_{\sigma_{12}}.10^{-2}$	$\sum|A|.10^{-2}$	$Y^E_{exp} - Y^E_{calc}$
A–CH₄	G^E	−0·49	0·64	−4·83	4·61	−7·98	−0·47	19·0	−4·7
	V^E	0·006	−0·009	−0·076	0·069	−0·050	0·476	0·69	−0·06
CH₄–Kr	G^E	−0·32	0·35	1·94	−1·96	−9·23	0·08	13·9	3·1
	V^E	0·011	−0·010	0·010	−0·008	−0·071	0·544	0·65	0·04
A–Kr	G^E	−1·01	1·11	−3·31	3·21	−7·56	−0·78	17·0	−6·1
	V^E	0·025	−0·022	−0·097	0·083	−0·092	0·502	0·82	−0·41
CO–CH₄	G^E	−0·94	0·96	1·00	0·99	−7·34	0·24	11·5	6·2
	V^E	0·032	−0·022	−0·067	0·050	−0·068	0·541	0·78	0·08
N₂CH₄	G^E	−1·08	1·10	−1·28	1·26	−7·02	−0·35	12·1	5·4
	V^E	0·040	−0·026	−0·084	0·061	−0·075	0·543	0·83	0·34
CO–A	G^E	−0·29	0·43	3·27	−3·37	−6·41	0·29	14·1	3·4
	V^E	0·017	−0·016	0·040	−0·028	−0·068	0·479	0·65	0·11
A–O₂	G^E	0·11	0·08	−0·72	0·71	−7·44	0·05	9·1	−4·2
	V^E	−0·003	0·000	−0·007	0·008	−0·051	0·425	0·49	0·04
N₂–A	G^E	−0·42	0·54	2·90	−2·99	−6·16	0·36	13·4	−2·7
	V^E	0·023	−0·019	0·022	−0·020	−0·073	0·477	0·63	−0·04
N₂–CO	G^E	−0·06	0·19	−0·27	0·27	−5·53	0·01	6·3	−2·8
	V^E	0·002	−0·007	−0·012	0·015	−0·100	0·542	0·68	−0·03
N₂–O₂	G^E	−0·40	0·47	2·32	−2·37	−6·44	0·22	12·2	1·5
	V^E	0·018	−0·015	0·013	−0·011	−0·055	0·470	0·58	−0·09

ε and σ are the accurate values of the parameters, and ε^0, σ^0 are the values used in the calculation. Further we shall assume that the deviations from the combination rules (3), (4) are very small, *i.e.* the following is valid accurately

$$\varepsilon_{12} = k_\varepsilon (\varepsilon_1 \varepsilon_2)^{1/2}, \quad \sigma_{12} = k_\sigma (\sigma_1 + \sigma_2)/2, \tag{18}$$

where $|k_\varepsilon - 1| \ll 1$ and $|k_\sigma - 1| \ll 1$.

For an arbitrary excess quantity $Y^E = Y^E(\varepsilon_1, \varepsilon_2, \varepsilon_{12}, \sigma_1, \sigma_2, \sigma_{12})$ at a given temperature and pressure we have:

$$Y^E = Y_0^E + \sum_{i=1}^{2} \left[\varepsilon_i^0 (\partial Y^E / \partial \varepsilon_i)_{\varepsilon^0, \sigma^0} \, \delta_{\varepsilon_i} + \sigma_i^0 (\partial Y^E / \partial \sigma_i)_{\varepsilon^0, \sigma^0} \, \delta_{\sigma_i} \right] +$$

$$+ \, \varepsilon_{12}^0 (\partial Y^E / \partial \varepsilon_{12})_{\varepsilon^0, \sigma^0} \big[(\partial \varepsilon_{12} / \partial \varepsilon_i)_{\varepsilon^0_1} (\varepsilon_1 - \varepsilon_1^0) / \varepsilon_{12}^0 \, + $$

$$+ \, (\partial \varepsilon_{12} / \partial \varepsilon_2)_{\varepsilon^0} (\varepsilon_2 - \varepsilon_2^0) / \varepsilon_{12}^0 + k_\varepsilon - 1 \big] + \sigma_{12}^0 (\partial Y^E / \partial \sigma_{12})_{\varepsilon^0 \sigma^0}$$

$$\big[(\partial \sigma_{12} / \partial \sigma_i)_{\sigma^0} (\sigma_1 - \sigma_1^0) / \sigma_{12}^0 + (\partial \sigma_{12} / \partial \sigma_2)_{\sigma^0} (\sigma_2 - \sigma_2^0) / \sigma_{12} + k_\sigma - 1 \big] =$$

$$= Y_0^E + A_{\varepsilon_1} \delta_{\varepsilon_1} + A_{\varepsilon_2} \delta_{\varepsilon_2} + A_{\varepsilon_{12}} (k_\varepsilon - 1) + A_{\sigma_1} \delta_{\sigma_1} + A_{\sigma_2} \delta_{\sigma_2} + A_{\sigma_{12}} (k_\sigma - 1),$$

$$Y_0^E = Y^E(\varepsilon_1^0, \varepsilon_2^0, \varepsilon_{12}^0, \sigma_1^0, \sigma_2^0, \sigma_{12}^0). \tag{19}$$

The effect of deviations of parameters, ε_1^0, ε_2^0, ε_{12}^0, σ_1^0, σ_2^0, σ_{12}^0, on the values of $G^E(\text{cal/mol})$ and $V^E(\text{cm}^3/\text{mol})$ was calculated. In the calculations we used the values from Table I for ε^0, σ^0 of the pure components. The cross parameters ε_{12}^0 and σ_{12}^0 were calculated from Eqs (3) and (4) for all systems, except A–O$_2$ and N$_2$–CO, for which we used ε_{12}^0 from Table III. The results for $|\delta_{\varepsilon_1}| = |\delta_{\varepsilon_2}| = |\delta_{\sigma_1}| = |\delta_{\sigma_2}| = |1 - k_\varepsilon| = |1 - k_\sigma| = 0.01$ are shown in Table IV. In the last but one column of the table, denoted as $\sum|A|$, are the maximum differences in G^E and V^E brought about by 1% variation of the interaction parameters. The last column of Table IV gives differences between the experimental and calculated values of G^E and V^E, obtained from the results shown in Tables II and III. From the results shown in the last but one column of Table IV it is obvious that 1% inaccuracies in the interaction parameters can render the calculation of the excess functions entirely valueless. From this point of view, we can regard the agreement between the experimental and calculated values as rather fortunate and to attribute the major portion of the differences between the calculated values to small inaccuracies in the interaction parameter used. Furthermore, it can be seen from Table IV that the largest share of the errors in V^E is induced by the deviations of σ_{12} from the values obtained from Eq. (4). It seems that for a majority of mixtures of simple liquids the deviations of σ_{12} from the arithmetic mean rule are much smaller than one percent. The prevaling portion

of errors of G^E is due to the deviations of ε_{12} from the geometric mean rule. The effect of parameters of the pure components on the values of the excess functions is much smaller than the effect of the cross parameters. It is not negligible, however, if the quantitative agreement with the experiment is to be achieved.

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