EXTENSION OF THE TUNNEL THEORY
OF LIQUIDS TO MULTICOMPONENT MIXTURES

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An extension of Barker's tunnel theory of the liquid state to binary mixtures of simple liquids is proposed. To test the theory excess functions of 10 equimolar mixtures were calculated. The calculations were carried out for the Lennard-Jones 6—12 potential, and the cross parameters ε_{12}, σ_{12}, were calculated from Lorentz's and Berthelot's combination rules. The agreement between the calculated and experimental values of excess functions is somewhat better than that of Prigogine's average potential model and van der Waals' approximation in the method of pseudopotentials.

The main aim of the statistical thermodynamics of solutions is to determine thermodynamic properties of mixtures from intermolecular forces. A considerable effort has been directed recently to the solution of this problem. A whole series of theories of the liquid mixtures has been developed, which qualitatively predict values of excess functions. Nonetheless, non of the theories has achieved a full quantitative agreement with experiments even for mixtures of simple liquids. The situation on the field of the statistical thermodynamics of pure liquids is even less favourable. In spite of this, the molecular theories of liquids form often a basis of the theories of liquid mixtures. The theories of multicomponent systems are usually more successfull than those of pure liquids on which they rest. This statement is only seemingly illogical, for we are interested in differences between the thermodynamic properties of the mixture and of the pure liquids of which the mixture is composed, and not in the values of thermodynamic functions of the mixture. Some deviations appearing in the theory of pure liquids may be entirely compensated.

In many molecular theories of liquids and liquid mixtures it is assumed that the partition function of a system can be split into two parts. A part due to the internal motions of molecules, independent of the density of the system, and the translation partition function, for the determination of which the classical (non-quantum)

statistical mechanics can be used. Having made these assumptions, the only remaining part of the partition function (for a given temperature T, volume V and a number of particles N), different for liquid and an ideal gas, is the configuration integral Q, defined by the equation

$$Q(N, T, V) = (1/N!) \int_{(V)} \dots \int_{(V)} \exp\left[-\Phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)/kT\right] d\mathbf{r}_1 \, d\mathbf{r}_2 \dots d\mathbf{r}_N , \quad (1)$$

where $\Phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ is the potential energy of the system when molecule 1 is in the position $\mathbf{r}_1$, molecule 2 in the position $\mathbf{r}_2$ *etc.* Generally it is assumed that the function Φ is pairwise additive, *i.e.* we can write

$$\Phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \varphi(|\mathbf{r}_i - \mathbf{r}_j|) \quad (2)$$

and the pair potential φ is most frequently approximated by the Lennard-Jones $6-12$ function

$$\varphi(r) = 4\varepsilon\left[(\sigma/r)^{12} - (\sigma/r)^6\right], \quad (3)$$

where r is the distance between the pair of molecules and ε, σ are intermolecular interaction parameters specific for each substance. In the following the assumptions made above will be regarded as fulfiled.

Direct evaluation of the configuration integral is practically unfeasible. It is possible, however, to replace the multiple (N) integral in equation (1) by a product of simpler integrals, which means to divide the system into a certain number of independent subsystems in a manner enabling to determine the configuration integral of each subsystem. The requirements put on the selection of the subsystems are complementary. Usually, the better the fulfilment of the requirement of independence of the subsystems, the more complex is the evaluation of the configuration integral. Strictly speaking, there are no subsystems perfectly independent of the surroundings, and it cannot be assessed *a priori* to what extent the assumed independence will affect the values of the thermodynamic functions. The principal criterion of success of different theories of liquids is therefore a comparison of calculated and experimental data.

Several years ago Barker proposed the tunnel model of the liquid state[1-3]. Its principal idea consist of the selection of a one-dimensional system as a subsystem in a totally three-dimensional system. The configuration integral of one-dimensional system can be determined accurately in principle. The one-dimensional system containing a large number of molecules will be less dependent on the surroundings than, for example, a one-particle subsystem of the cell theory of liquids. The assumptions regarding the structure of the liquid in the tunnel theory can be summarized into several points: The molecules of the system are divided into capillary tunnels

in which they move predominantly uni-dimensionally. The molecules in the tunnels make small transverse moves independent of the longitudinal moves. The ends of the longitudinal axes of the tunnels form a two-dimensional hexagonal lattice. There is no correlation between the motion of the molecules in individual tunnels.

From the assumption of independence of the transverse and longitudinal motions it follows:

$$Q(N, T, V) = Q_L(l, T)^N \, Q_T(r, T)^N \, , \tag{4}$$

where Q_L and Q_T are the contributions of the longitudinal and transverse motions of the molecule to the configuration integral respectively. The quantities l and r are respectively the length of the tunnel related to a single molecule, and the distance between the axes of the neighbouring tunnels. For the volume of the system we have from the model of the structure:

$$V = (\sqrt{3}/2) \, r^2 l \, . \tag{5}$$

To determine the values of thermodynamic functions at a given temperature and volume, one more relation, apart from Eq. (5), between the quantities r and l is necessary. Following approximation was therefore introduced*

$$r = l \, . \tag{6}$$

To test the theory, the calculated and experimental properties of liquid argon were compared[2]. The predicted values of the volume and the internal energy in the triple point are in excellent agreement with experiment. The calculated entropy deviates by about 30%. The deviation, however, is almost independent of temperature. The critical constants are predicted rather poorly by the tunnel theory.

The purpose of this work is to extend the tunnel theory of the liquid state to multi-component systems. The tunnel theory has many common features with the older cell theory of liquids[4], which has been extended earlier to liquid mixtures[5-7]. It is well-known about the cell theory that it describes the solid phase much better than the liquid phase[3]. It is therefore not surprising that the agreement between the calculated and experimental values of the mixing thermodynamic functions was rather rough. The tunnel theory describes better the liquid state and should be accordingly more successful in determination of the mixing functions. Another advantage of the tunnel theory is that the error of determination of the entropy of pure liquids is almost constant and probably will not effect excessively the values of the mixing functions. In principle, the configuration integral of one-dimensional system can be determined accurately even for multicomponent systems. This advantage is specific for the tunnel theory.

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* A more accurate approach for obtaining a relationship between r and l is by minimizing the free energy with respect to these variables. The approximate relation (6), however, considerably simplifies calculation without causing a substantial deviation in thermodynamic functions[2].

THEORETICAL

EXCESS THERMODYNAMIC FUNCTIONS OF A BINARY MIXTURE

We shall examine a two component system with a total of N particles, of which N_1 is of the kind 1 and N_2 is of the kind 2. We shall assume that the molecules are distributed randomly. With respect to the assumption of independence of the longitudinal and transverse motions of the molecules[2] (see Eq. (4)), following is valid

$$Y = Y_L + Y_T, \tag{7}$$

where $Y = F, G, S, H, U$. Subscript L denotes the contribution of longitudinal and T of transverse motions to the thermodynamic functions.

The configuration integral of a one-dimensional multicomponent mixture, just as that of a pure substance[8-10], can be determined accurately, and for the excess functions one can prove[10-12] that

$$Y_L^E = x_1 x_2 [2Y_L(\varepsilon_{12}, \sigma_{12}) - Y_L(\varepsilon_1, \sigma_1) - Y_L(\varepsilon_2, \sigma_2)], \tag{8}$$

where $x_i = N_i/N$, and $Y(\varepsilon, \sigma)$ is the value of a thermodynamic quantity of a substance with Lennard-Jones parameters ε, σ for a given temperature and pressure. For the length l_M, related to one molecule of the one-dimensional mixture we have

$$l_M = x_1^2 l(\varepsilon_1, \sigma_1) + 2x_1 x_2 l(\varepsilon_{12}, \sigma_{12}) + x_2^2 l(\varepsilon_2, \sigma_2). \tag{9}$$

Parameters $\varepsilon_{12}, \sigma_{12}$ are determined by means of Lorentz's and Berthelot's semi-empirical combination rules

$$\varepsilon_{12} = (\varepsilon_1 \varepsilon_2)^{1/2}, \tag{10}$$

$$\sigma_{12} = (\sigma_1 + \sigma_2)/2. \tag{11}$$

To calculate the contribution of the transverse motions of molecules in the mixture to the excess functions we shall make use of an approximative approach developed in the cell theory of solutions[10]. We shall examine a molecule of the kind i in the field of molecules fixed in the axes of adjacent tunnels. The interaction pair potential between the examined molecule and an "average" neighbouring molecule at the distance ϱ, is approximated by the relation

$$4\bar{\varepsilon}_i[(\bar{\sigma}_i/\varrho)^{12} - (\bar{\sigma}_i/\varrho)^6] = 4\varepsilon_i[(\sigma_i/\varrho)^{12} - (\sigma_i/\varrho)^6] x_i + 4\varepsilon_{ij}[(\sigma_{ij}/\varrho)^{12} - (\sigma_{ij}/\varrho)^6] x_j \tag{12}$$

provided that all molecules in the vicinity of the molecule i are distributed randomly. $i, j = 1, 2, j \neq i$ and $\bar{\varepsilon}_i, \bar{\sigma}_i$ in Eq. (12) are Lennard-Jones parameters describing the interaction of the molecule with a hypothetical average molecule. The pseudointeraction parameters $\bar{\varepsilon}_i, \bar{\sigma}_i$ are obtained from Eq. (12) by comparing coefficients of corresponding powers of ϱ.

$$\bar{\varepsilon}_i = \left(x_i \varepsilon_i \sigma_i^6 + x_j \varepsilon_{ij} \sigma_{ij}^6\right)^2 / \left(x_i \varepsilon_i \sigma_i^{12} + x_j \varepsilon_{ij} \sigma_{ij}^{12}\right), \tag{13}$$

$$\bar{\sigma}_i = \left[\left(x_i \varepsilon_i \sigma_i^{12} + x_j \varepsilon_{ij} \sigma_{ij}^{12}\right) / \left(x_i \varepsilon_i \sigma_i^6 + x_j \varepsilon_{ij} \sigma_{ij}^6\right)\right]^{1/6}. \tag{14}$$

Equations (13) and (14), which were obtained for the first time in the cell theory of solutions, form a basis of a two liquid approximation (or refined version of average potential model) in the method of pseudopotentials[10,14]. In our approach, Eqs (13) and (14) represent only a starting point. To determine the contributions of the transverse motions of molecules to the excess functions, we shall use somewhat different parameters from $\bar{\varepsilon}_i, \bar{\sigma}_i$.

For the free energy of the transverse motions of molecules in the one-component system we can obtain relation[2]

$$F_T/(NkT) = -2 \ln \sigma + 2(4{\cdot}652 \tilde{r}^{-12} - 7{\cdot}925 \tilde{r}^{-6}) \, r/(l \, \tilde{T}) -$$
$$- \ln \left\{ 2\pi \tilde{r}^2 \int_0^{0{\cdot}52} \exp \left[-4(Q(y) \, \tilde{r}^{-12} - P(y) \, \tilde{r}^{-6}) \, r/(l \, \tilde{T})\right] \mathrm{d}y \right\}, \tag{15}$$

where $\tilde{r} = r/\sigma$ and $P(y)$, $Q(y)$ are functions tabulated in Barker's paper[2]. Reduced temperature appears in Eq. (15) always with a factor of l/r which for pure components equals unity with respect to the assumption (6). Eq. (6), however, is a good approximation only if the molecule performs longitudinal and transverse motions at the same reduced temperature. This requirement is not fulfilled in the case of mixture, since we use different parameters ε for description of longitudinal and transverse motions. The reduced temperature of the transverse motion $\tilde{T}'$ we shall approximate by the relation

$$\tilde{T}'_i = \left(kT/\bar{\varepsilon}_i\right) l(\varepsilon_i, \sigma_i)/r(\bar{\varepsilon}_i, \bar{\sigma}_i), \tag{16}$$

when the adjacent molecule in the same tunnel is of the kind i, and by

$$\tilde{T}'_{ij} = \left(kT/\bar{\varepsilon}_i\right) l(\varepsilon_{ij}, \sigma_{ij})/r(\bar{\varepsilon}_i, \bar{\sigma}_i), \tag{17}$$

when the adjoining molecule is of the kind j. Assuming a random distribution of molecules in the mixture, the probability of the neighbouring molecule in the same tunnel being of the kind i is x_i, and of the kind j with the probability x_j. For the

contributions of the transverse motion of molecules to the excess functions of a binary mixture we obtain equation

$$Y_T^E = x_1\{x_1 Y_T[\bar{\varepsilon}_1 r(\bar{\varepsilon}_1, \bar{\sigma}_1)/l(\varepsilon_1, \sigma_1), \bar{\sigma}_1] + x_2 Y_T[\bar{\varepsilon}_1 r(\bar{\varepsilon}_1, \bar{\sigma}_1)/l(\varepsilon_{12}, \sigma_{12}), \bar{\sigma}_1]\} +$$
$$+ x_2\{x_2 Y_T[\bar{\varepsilon}_2 r(\bar{\varepsilon}_2, \bar{\sigma}_2)/l(\varepsilon_2, \sigma_2), \bar{\sigma}_2] + x_1 Y_T[\bar{\varepsilon}_2 r(\bar{\varepsilon}_2, \bar{\sigma}_2)/l(\varepsilon_{12}, \sigma_{12}), \bar{\sigma}_2]\} +$$
$$- x_1 Y_T(\varepsilon_1, \sigma_1) - x_2 Y_T(\varepsilon_2, \sigma_2) . \tag{18}$$

On combining Eqs (7), (8) and (18) we get

$$Y^E = x_1^2\{Y_L(\varepsilon_1, \sigma_1) + Y_T[\bar{\varepsilon}_1 r(\bar{\varepsilon}_1, \bar{\sigma}_1)/l(\varepsilon_1, \sigma_1), \bar{\sigma}_1]\} +$$
$$+ x_1 x_2\{2Y_L(\varepsilon_{12}, \sigma_{12}) + Y_T[\bar{\varepsilon}_1 r(\bar{\varepsilon}_1, \bar{\sigma}_1)/l(\varepsilon_{12}, \sigma_{12}), \bar{\sigma}_1] + Y_T[\bar{\varepsilon}_2 r(\bar{\varepsilon}_2, \bar{\sigma}_2)/l(\varepsilon_{12}, \sigma_{12}), \bar{\sigma}_2]\} +$$
$$+ x_2^2\{Y_L(\varepsilon_2, \sigma_2) + Y_T[\bar{\varepsilon}_2 r(\bar{\varepsilon}_2, \bar{\sigma}_2)/l(\varepsilon_2, \sigma_2), \bar{\sigma}_2]\} - x_1 Y(\varepsilon_1, \sigma_1) - x_2 Y(\varepsilon_2, \sigma_2) . \tag{19}$$

The volume of mixing is still to be determined. Let us place again a molecule of the kind i into some of the tunnels. The cross-section of the tunnel in this location is, with respect to the relation (5), equal to $(\sqrt{}(3)/2) r(\bar{\varepsilon}_i, \bar{\sigma}_i)^2$. The average distance between the examined molecule and the nearest neighbouring molecule in the same tunnel is $l(\varepsilon_i, \sigma_i)$ with the probability x_i, and $l(\varepsilon_{ij}, \sigma_{ij})$ with the probability x_j. This reasoning and Eqs (5) and (9) permit the volume of mixing, V^M, to be determined.

$$V^M = N(\sqrt{}3/2) \{x_1 r(\bar{\varepsilon}_1, \bar{\sigma}_1)^2 [x_1 l(\varepsilon_1, \sigma_1) + x_2 l(\varepsilon_{12}, \sigma_{12})] +$$
$$+ x_2 r(\bar{\varepsilon}_2, \bar{\sigma}_2)^2 [x_2 l(\varepsilon_2, \sigma_2) + x_1 l(\varepsilon_{12}, \sigma_{12})]\} +$$
$$- x_1 V(\varepsilon_1, \sigma_1) - x_2 V(\varepsilon_2, \sigma_2) . \tag{20}$$

METHOD OF CALCULATION

All calculations were carried out for zero pressure of the system and only the knowledge of temperature and Lennard-Jones parameters of pure components was required. To begin with, the parameters $\varepsilon_{ij}, \sigma_{ij}, \bar{\varepsilon}_i, \bar{\sigma}_i$, were determined from Eqs (10), (11), (13), (14). For each individual pair of parameters we solved simultaneously the equation of state[2]:

$$P = [20{\cdot}938 + 9(\partial \ln A_f/\partial C)] \tilde{V}^{-5} - [23{\cdot}880 + 6(\partial \ln A_f/\partial B)] \tilde{V}^{-3} +$$
$$+ (0{\cdot}3497/W) \tilde{T}\tilde{V}^{-2/3} + (2/3) \tilde{T}\tilde{V}^{-1} , \tag{21}$$

where $\tilde{P} = P\sigma^3/\varepsilon$, $\tilde{V} = V/(N\sigma^3)$, $\tilde{T} = kT/\varepsilon$, $B = 4r/(l\tilde{T}) \tilde{r}^{-6}$, $C = B\tilde{r}^{-6}$, $W = kT/(P_L\sigma)$ and P_L is the pressure in one-dimensional system, and the equation of state of the one-dimensional system:

$$\tilde{l} = \int_0^\infty \xi \exp\left[-4(\xi^{-12} - \xi^{-6})/\tilde{T} - \xi/W\right] d\xi \bigg/ \int_0^\infty \exp\left[-4(\xi^{-12} - \xi^{-6})/\tilde{T} - \xi/W\right] d\xi, \tag{22}$$

where $\tilde{l} = l/\sigma$.

The equation of state possesses a solution at zero pressure only for temperature $\tilde{T} \leq 0.948$. This limitation manifested itself only in the calculation for system Ar—Kr and N_2—CO, for which we were not able to determine excess functions for some of the parameters ε used. The intermolecular distances, $l(e, \sigma)$ and $r(\bar{e}, \bar{\sigma})$, were calculated from Eqs (5) and (6). On completion of these calculations, the volume of mixing was determined from Eq. (20). The excess free enthalpy G^E and the enthalpy H^E were determined from Eq. (19). Y_L and Y_T appearing in equation were calculated for prescribed parameters from corresponding relations for pure components[2].

RESULTS AND DISCUSSION

The theory has been worked out for Lorents-Berthelot's liquid mixtures, *i.e.* systems for which the Lennard-Jones $6-12$ potential adequately describes pair intermolecular interactions and combination rules (10) and (11) are valid for interactions between molecules of different kind. Mixtures of inert gases and, to a lesser extent, mixtures containing components with small, nonpolar and effectively spherically symmetrical molecules satisfy these requirements best. To test the theory, binary systems the components of which are Ar, Kr, CH_4, O_2, N_2, CO were selected.

The interaction parameters ε, σ necessary for calculation are available from different experimental sources. Their values obtained by different ways usually differ from each other by several percent. It is a well-known fact that the excess functions are very sensitive to even small inaccuracies in parameters. To examine the effect of this inaccuracies, three different sets of parameters, summarized in Table I, were used in the calculation. Column P1 of the table shows the parameters determined from the measurements of the second virial coefficients of gases[13,14]. Column P2

TABLE I
Values of Lennard-Jones' Parameters ε/k(K) and σ(Å) Used in Calculations

Substance	P1		P2		P3	
	ε/k	σ	ε/k	σ	ε/k	σ
Argon	119·8	3·405	123·2	3·363	119·8	3·405
Krypton	171·0	3·600	171·0	3·600	167·0	3·633
Methane	148·2	3·817	156·0	3·696	152·0	3·740
Nitrogen	95·05	3·698	103·0	3·573	101·3	3·612
Oxygen	117·5	3·580	123·0	3·411	119·8	3·360
Carbon monoxide	102·2	3·763	108·6	3·600	104·2	3·620

Excess Functions of Equimolar Mixtures

System	T, K	G^E, cal/mol				H^E, cal/mol				V^E, cm³/mol			
		experiment	P 1	P 2	P 3	experiment	P 1	P 2	P 3	experiment	P 1	P 2	P 3
Ar–CH₄	91	19·2	30·8	25·7	24·9	24·6	40·0	30·5	29·3	0·18	0·49	0·30	0·30
CH₄–Kr	116	6·7	13·5	3·7	4·2	—	15·3	3·6	4·1	0·00	−0·05	−0·02	−0·03
Ar–Kr	116	20·1	—	29·9	—	—	—	9·9	—	−0·50	—	−0·86	—
CO–CH₄	91	28·0	23·9	20·9	23·0	25·1	−1·2	9·1	7·0	−0·33	−1·04	−0·34	−0·50
N₂–CH₄	91	33·8	—	27·8	—	—	—	8·1	—	−0·21	—	−0·60	—
CO–Ar	84	13·5	22·3	11·4	9·9	14·3	28·6	14·3	11·4	0·10	−0·01	0·01	−0·05
Ar–O₂	84	8·9	4·9	0·4	0·3	12·1	7·2	0·6	0·5	0·14	0·06	0·01	0·01
N₂–Ar	84	8·2	20·0	11·8	10·6	10·2	17·8	11·8	10·5	−0·18	−0·37	−0·12	−0·12
N₂–CO	84	5·5	0·8	0·5	0·1	—	0·1	0·05	−0·05	0·10	−0·02	−0·01	−0·01
N₂–O₂	77	10·0	8·6	8·8	13·9	11·0	0·9	8·4	16·1	−0·21	−0·44	−0·08	−0·03

TABLE III
Comparison of Excess Functions Calculated by Different Methods

System	T, K	G^E, cal/mol				H^E, cal/mol				V^E, cm³/mol			
		experiment	TM	APM	vdW	experiment	TM	APM	vdW	experiment	TM	APM	vdW
Ar–CH₄	91	19·2	29·1	40·6	4·5	24·6	36·5	57·4	−12·4	0·18	0·40	0·72	−0·31
CH₄–Kr	116	6·7	8·8	11·1	—	—	10·7	—	—	0·00	0·00	0·05	—
Ar–Kr	116	20·1	26·2	27·4	9·1	—	−14·9	—	—	−0·50	−0·94	−0·05	−0·78
CO–CH₄	91	28·0	22·9	25·1	17·9	25·1	10·7	19·1	5·5	−0·33	−0·34	−0·50	−0·84
N₂–CH₄	91	33·8	29·2	30·7	—	—	8·6	—	—	−0·21	−0·63	−0·66	—
CO–Ar	84	13·5	15·1	19·0	6·2	14·3	18·2	—	—	0·10	−0·01	0·09	−0·20
Ar–O₂	84	8·9	0·4	0·2	0·2	12·1	0·6	0·5	0·3	0·14	0·01	0·01	0·00
N₂–Ar	84	8·2	17·3	19·1	9·6	10·2	18·1	25·1	10·0	−0·18	−0·13	−0·07	−0·32
N₂–CO	84	5·5	0·4	0·3	0·2	—	−0·1	—	—	0·10	−0·02	−0·03	−0·02
N₂–O₂	77	10·0	13·3	15·5	12·0	11·0	13·4	20·3	12·7	−0·21	−0·10	−0·11	−0·32

shows the parameters determined from the critical constants of substances, assuming that the interaction parameters of krypton are $\varepsilon/k = 171$ K and $\sigma = 3\cdot600$ Å (ref.[14]). In the column P3 of the table, the parameters were selected in such a manner that all involved substances have the same reduced equation of state $\widetilde{V} = \widetilde{V}(\widetilde{T})$ $[P = 0]$. This equation of state was constructed from an empirical dependence of the volume of liquid argon on temperature, provided that the interaction constants of argon are $\varepsilon/k = 119\cdot8$ K and $\sigma = 3\cdot405$ Å (ref.[15]).

Table II compares the values of the excess functions of 10 equimolar mixtures calculated from parameters P1, P2, P3 of Table I with the experimental values. The experimental data shown in the table for systems Ar–CH$_4$, CO–CH$_4$, Ar–N$_2$, N$_2$–O$_2$, Ar–O$_2$ were taken over from the work of Bellemans, Mathot and Simon[14], and for system Ar–Kr, CH$_4$–Kr, N$_2$–CH$_4$, N$_2$–CO, CO–Ar from the work of Bellemans and Vilcu[16]. The calculated values of G^E, H^E and V^E in columns P2 and P3 of Table II differ considerably from the results shown in columns Pl. Because it is apparent that the choice of parameters can considerably misrepresent the results, for quantitative comparison of different theories of the liquid mixtures it is therefore necessary to use (if possible) the same interaction parameters for calculation in all compared theories.

Table III compares the tunnel theory of mixtures (TM) with the refined version of Prigogine's average potential model (APM)[14,16] and with van der Waals' approximation (vdW)[17] in the method of pseudopotentials. In all three theories were used parameters ε, σ, selected by Bellemans, Mathot and Simon[14] as an average of the values calculated from the second virial coefficients, critical constants and viscosities of gases. The combination rules (10), (11) were used in all three theories to determine ε_{12} and σ_{12}. The calculated values of G^E and H^E are for majority of mentioned mixture somewhat higher than the experimental ones in the case of the average potential model and somewhat lower in the case of van der Waals' approximation. The tunnel theory achieves better results, yet the agreement with experiment is not quite satisfactory.

Let us try to discuss possible reasons for deviations of the calculated values of excess functions from the experimental ones. First we shall summarise the assumptions made in calculation which can affect the results: *1*. The tunnel theory in its simple version correctly describes the liquid state. *2*. The distribution of molecules in the mixture is random. *3*. To determine the contribution of the transverse motions of molecule. in the mixture, the two liquid approximation can be applied (Eq. (13), (14)). *4*. The Lennard-Jones $6-12$ potential describes adequately the intermolecular interactions and the accurate values of interaction parameters of pure components ε, σ are known. *5*. For the interactions of molecules of different kind, the combination rules (10), (11) are valid.

In regard to the first point: Some amendments can be made in the tunnel theory, *e.g.*, a correction for the correlation between the longitudinal and transverse motion and between the motion of molecules in adjoining tunnels and abandonment of the

smearing approximation. These improvements which have been discussed in Barker's original paper[2] render the calculation considerably laborious and their effect on the values of the excess functions is hard to assess *a priori*. A combination of the tunnel theory with the theorem of corresponding states seems therefore more expedient.

In regard to the second point: Corrections for deviations from the random mixing approximation have probably no marked effect on the values of the excess functions for mixtures of simple liquids. Introduction of quasi-chemical approximation leads usually to about 5% correction in the excess functions[10,14].

In regard to the third point: As has been already noted, equations (*13*) and (*14*) form a basis of the refined version of the average potential model (or two liquid approximation). It is seen in the Table III that the agreement of the results obtained using this approximation with experiment is somewhat worse than that of the tunnel theory of mixtures. Provided that no compensation of errors occurs, a part of the deviations of the tunnel theory from the experimental values is inflicted by using Eqs (*13*) and (*14*).

In regard to the fourth point: The Lennard-Jones $6-12$ potential has a semiempirical character. A test of the effect of different selected exponents in the Lennard-Jones potential has shown that the differences between the excess functions calculated for $6-12$ and $7-14$ potential can make as much as 50% in the case of the average potential model[14].

As have been mentioned above, even small differences in interaction parameters ε, σ induce considerable uncertainties in the excess functions. Table II shows that the differences between the values of G^E and H^E calculated for different parameters can attain as much as 10 cal/mol, and as much as 0·25 cm³/mol for V^E neglecting one value of V^E for CO—CH₄ system.

In regard to the fifth point: Although the combination rules are not theoretically well founded, their deviations for mixtures of simple liquids are relatively small (about 2%)[18]. Yet, they cause considerable deviations in excess functions. The parameters ε_{12}, σ_{12} can be determined experimentally, *e.g.* from measurements of the second virial coefficients of gas mixtures or critical constants of mixtures. However,

TABLE IV
Values of G^E, H^E, and V^E Calculated from the Tunnel Theory for Given 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	
			experiment	TM	experiment	TM	experiment	TM
Ar–O₂	84	0·982	8·9	13·6	14·3	18·4	0·14	0·07
N₂–CO	84	0·986	5·5	8·3	10·2	13·0	0·10	0·10

there are few of this data. Some authors choose the parameters ε_{12}, σ_{12} so as to achieve the optimum agreement of the excess functions with the experimental values. In this approach, the interaction parameters ε_{12}, σ_{12} become adjustable constants containing, apart from the corrections for the deviations from the combination rules, also the effects of the inaccuracies of parameters ε, σ of pure substances and the flaws specific for individual theories of liquid mixtures.

Let us examine the values of the excess functions of Ar—O_2 and N_2—CO systems in Table III. All three theories fail and predict practically zero values of the excess functions as a consequence of the fact that for both systems $\varepsilon_1 \simeq \varepsilon_2$ and $\sigma_1 \simeq \sigma_2$. The critical temperatures of the mixtures were measured for both systems to determine ε_{12} (ref.[19]). These values differ somewhat from those predicted by Eq. (10). The experimental values of parameters ε_{12} for Ar—O_2, N_2—CO systems are shown in Table IV together with the values of excess functions of equimolar mixtures calculated from the tunnel theory for given experimental values of ε_{12}. In the calculations we used the same values of parameters ε, σ for pure components as in Table III, and σ_{12} was calculated from Eq. (11). The agreement with the experimental values of excess functions is much better than when using the combination rules.

LIST OF SYMBOLS

$B = 4\tilde{r}^{-6} r/(1\tilde{T})$	quantity in the equation of state
$C = B\tilde{r}^{-6}$	quantity in the equation of state
F	free energy
F_T	free energy of transverse motions of molecules
G	free enthalpy
G^E	excess free enthalpy
H	enthalpy
H^E	excess enthalpy
k	Boltzmann constant
l_M	length of the tunnel per one molecule of mixture
$\tilde{l} = l/\sigma$	reduced length of the tunnel per one molecule
N	number of molecules in system
N_i	number of molecules of the kind i in system
P	total pressure
P_L	pressure in one-dimensional system
$\tilde{P} = P\sigma^3/\varepsilon$	reduced pressure
$P(y)$	function of y in the equation of state
Q	configuration integral
Q_L	configuration integral of longitudinal motions of molecule
Q_T	configuration integral of transverse motions of molecule
$Q(y)$	function in the equation of state
r	distance between the axes of adjoining tunnels
$\tilde{r} = r/\sigma$	reduced distance between the axes of adjoining tunnels
r_i	position vector of molecule i
S	entropy

T	absolute temperature
$\tilde{T} = kT/\varepsilon$	reduced temperature
$\tilde{T}_i'$	reduced temperature of transverse motions of molecule of the kind i when the neighbouring molecule in the tunnel is of the same kind
$\tilde{T}_{ij}'$	reduced temperature of transverse motions of molecule of the kind i when the neighbouring molecule in the tunnel is of the kind j
U	internal energy
V	volume
V^E	excess volume
V^M	volume of mixing
$\tilde{V} = V/(N\sigma^3)$	reduced volume
$W = kT/(P_L\sigma)$	quantity in the equation of state
x_i	molar fraction
y	integration variable
Y	thermodynamic function
Y^E	excess thermodynamic function
Y_L	thermodynamic function of longitudinal motions of molecules
Y_T	thermodynamic function of transverse motions of molecules
ε_i	energy parameter in Lennard-Jones potential for interaction of pair of molecules of the kind i
ε_{ij}	energy parameter in Lennard-Jones potential for interaction of pair of molecules of the kind i, j
$\bar{\varepsilon}_i$	energy parameter in Lennard-Jones potential for interaction of molecule of the kind i with "average" neighbouring molecule
ξ	integration variable
ϱ	distance between two molecules
σ_i	geometry parameter in Lennard-Jones potential for interaction of pair of molecules of the kind i
σ_{ij}	geometry parameter in Lennard-Jones potential for interaction of pair of molecules of the kind i, j
$\bar{\sigma}_i$	geometry parameter in Lennard-Jones potential for interaction of molecule of the kind i with "average" neighbouring molecule
Φ	potential energy of the set of molecules
φ	interaction potential of pair of molecules

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