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Prediction of thermodynamic properties of ternary liquid solutions including metal alloys

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The free-volume theory of liquid solutions formulated by Flory and also by Patterson for binary systems, has been extended to ternary systems. Numerical calculations have been performed to test the validity of the approach, for a system of organic liquids, for a system of condensed gases, and also for a system of liquid metal alloys. Satisfactory results have been obtained in all cases. Thus, prediction of properties of ternary solutions from a limited number of data concerning pure components and binary mixtures was found possible.

1. Introduction

In his classical work, Tonks [1] has obtained the exact partition function for a one-dimensional liquid of incompressible molecules. An approximate generalization of the formula to the three-dimensional case has been proposed by Flory [2] for single liquids and also for binary mixtures. Patterson and Delmas [3] have demonstrated another way of arriving at the same result; they have taken a corresponding states theory of solutions elaborated by Prigogine and his colleagues [4] and then they have made some specific assumptions concerning molecular interaction potentials. In the following we shall call the approach under consideration the Flory–Patterson theory; we hope to avoid confusion with an earlier theory described by Flory in his monograph [5] and widely used at the present time. Applications of the new theory – as reviewed by Flory [6] and also by Patterson [7] – show in many cases quantitative agreement with the experimental data, for pure components as well as for binary mixtures.

For many practical purposes it is necessary to predict properties of multicomponent liquid solutions from properties of pure components and from data for binary systems. One can, therefore, find in the literature a relatively large number of correlations, describing ternary systems in particular. Most of such correlations, however, have at least two drawbacks. First, they are empirical, unrelated to any description of structure and interactions in solutions on the molecular level. Secondly, they are aimed at a particular group of liquid mixtures; thus a formula is proposed, e.g. for high-pressure systems of liquified gases; it is not expected that the same formula could be used, for example, for liquid metals alloys.

Considerations such as outlined above have determined the object of the present work. We have extended the Flory–Patterson theory to ternary systems. Examples of calculations, performed to test the extension, include a system of organic liquids, a system of liquified gases, and also a metal alloy system.

2. Basic relations

The three-dimensional partition function for the theory under consideration

$$Q = \Omega\ [\xi \mathrm{e}^3 v^* (\tilde{v}^{1/3} - 1)^3]^{Nrc}\, \mathrm{e}^{Nrs\eta/2vkT} \quad (1)$$

is in fact applicable to a mixture of any number of components, provided the parameters are properly defined in terms of concentration. The combinatorial contribution Ω is generally assumed to be given by

$$\Omega = \Sigma_j \phi_j^{-N_j} \qquad (2)$$

where summation extends over all components; N_j denotes number of molecules of jth component, so that the total number of molecules $N = \Sigma_j N_j$.

Let us now explain physical quantities featuring in Equations 1 and 2. It is assumed, that each molecule consists of several segments. We are thus dealing with intersegmental rather than with intermolecular interactions. Consequently, concentrations are expressed in terms of segment fractions:

$$\phi_i = \frac{N_i r_i}{Nr} \equiv \frac{N_i r_i}{\Sigma_j N_j r_j} \qquad (3)$$

where r_i denotes the number of segments in a molecule of component i; calculation of r_i's will be discussed later.

After the combinatorial factor Ω, we have in Equation 1 the term in square brackets, which represents explicitly volumetric effects. The coefficient ξ is a geometric factor; it does not appear in equations actually used in practical calculations. It is assumed that each segment, of volume v, can be compressed down to the hard-core volume v^*. The ratio of these two volumes represents another characteristic parameter called the reduced volume $\tilde{v}$, so that

$$\tilde{v} = \frac{v}{v^*}. \qquad (4)$$

There are at least two methods of calculating concentrations ϕ_i. But, as stressed by Patterson *et al.* [8], the prevailing procedure is to compute them from the incompressible volumes v^*, and this is what we have done in the present work.

The volumetric term in Equation 1 contains also the total number of segments in the mixture Nr. This quantity is defined between denominators of the second and third member of Equation 3; it can easily be seen that r is the average number of segments per molecule. The parameter c appears because of the assumption that the number of translational degrees of freedom of a segment is equal to $3c$. Thus, if a segment would be independent, its c would be equal to unity. For molecules other than monoatomic, when each segment is tied to its neighbours within the same molecule, we have generally $c < 1$. For a molecule of type j, from the values of c of each segment, an average value per molecule c_j may be calculated. One can then calculate c for the whole system by concentration averaging, namely

$$c = \Sigma_j c_j \phi_j \qquad (5)$$

The last, i.e. exponential, term in Equation 1 represents the energetic factor in the partition function. Here s is the mean number of external contact sites per segment. That is, each segment has a certain number of interacting points. From these (similarly as for c's) the average number of interacting sites s_j per segment in a molecule of type j is obtained. Further, again similarly as for the intersegmental degrees of freedom, the averaging for the whole system is performed:

$$s = \Sigma_j s_j \phi_j = \frac{s_i \phi_i}{\theta_i} \qquad (6)$$

The last member of Equation 6 defines the surface fraction θ_i. The interaction energy is represented by the parameter η; writing now specifically for a ternary mixture $i + j + k$, we have

$$\eta = \theta_i^2 \eta_{ii} + \theta_j^2 \eta_{jj} + \theta_k^2 \eta_{kk} + 2\theta_i\theta_j\eta_{ij} + 2\theta_i\theta_k\eta_{ik} + 2\theta_j\theta_k\eta_{jk}. \qquad (7)$$

Thus, η_{ii} represents the energy of interaction of two segments of type i, η_{ij} corresponds to a segment i interacting with a segment of type j, etc. To characterize interaction energies of "mixed" pairs, one can introduce the parameter $\Delta\eta_{ij}$:

$$\eta_{ij} = \tfrac{1}{2}(\eta_{ii} + n_{jj} - \Delta\eta_{ij}). \qquad (8)$$

There are analogous definitions for $\Delta\eta_{ik}$ and $\Delta\eta_{jk}$. One defines, further, hard-core pressures

$$P_i^* = \frac{s_i \eta_{ii}}{2v^{*2}}. \qquad (9)$$

Instead of η_{ij} or $\Delta\eta_{ij}$ one uses rather parameters X_{ij} to represent mixed interactions:

$$X_{ij} = \frac{s_i \Delta\eta_{ij}}{2v^*}. \qquad (10)$$

We retain thus the definition – corresponding to the one introduced by Flory for binary mixtures [2] – which renders $X_{ij} \neq X_{ji}$. Clearly for a ternary system three such parameters are needed. If we decide, however, to use X_{ij}, the natural choice of the remaining parameters – to preserve a certain symmetry – is X_{jk} and X_{ki}. Conversely, the use of X_{ji} suggests taking X_{kj} and X_{ik}. Interaction parameters belonging to the two sets are simply interrelated; let us notice that $\eta_{ij} = \eta_{ji}$ by definition, consequently $\Delta\eta_{ij} = \Delta\eta_{ji}$ and Equation 10 gives $X_{ij} = X_{ji}s_i/s_j$. For the ternary hard-core pressure we can write

$$P^* = P_i^*\phi_i + P_j^*\phi_j + P_k^*\phi_k - \phi_i\theta_j X_{ij} - \phi_j\theta_k X_{jk} - \phi_k\theta_i X_{ki}. \qquad (11)$$

The hard-core temperature is now introduced:

$$T_i = \frac{s_i\eta_{ii}}{2v^* c_i k} \qquad (12)$$

where k is the Boltzmann constant. The last equation in conjunction with Equation 9 gives a relation of the familiar form

$$P_i^* v_i^* = c_i k T_i^*. \qquad (13)$$

In order to have an equation of the form of Equation 13 applicable also to mixtures, and in view of Equation 5, we express the hard-core temperature for the mixture as

$$\frac{1}{T^*} = \frac{1}{P^*}\left(\frac{P_i^*\phi_i}{T_i^*} + \frac{P_j^*\phi_j}{T_j^*} + \frac{P_k^*\phi_k}{T_k^*}\right). \qquad (14)$$

We have been using the parameter v^* independent of concentration, since it is possible to choose numbers of segments in molecules r_i, r_j and r_k so as to have $v_i^* = v_j^* = v_k^* = v^*$. Parameters P_i^*, T_i^* and $r_i v^*$ may be calculated from properties of pure components. The necessary experimental data are molar volume V, isobaric expansivity $\alpha = V^{-1}(\partial V/\partial T)_p$ and isothermal compressibility $\kappa_T = -V^{-1}(\partial V/\partial P)_T$, or else $\gamma = \alpha/\kappa_T$; the calculation procedures are described by Flory [2, 6].

The set of relations given above permits us now to perform the main task, i.e. to write equations for various functions of mixing, or excess functions of mixing. As the configurational or interaction energy U^{c} is

$$U^{\mathrm{c}} = -\frac{Nrs}{2v} \qquad (15)$$

(cf. the last factor in the partition function (1)), we obtain for the molar excess energy of mixing

$$U^{\mathrm{E}} = x_i P_i^* V_i^*\left(\frac{1}{\tilde{v}_i} - \frac{1}{\tilde{v}}\right) + x_j P_j^* V_j^*\left(\frac{1}{\tilde{v}_j} - \frac{1}{\tilde{v}}\right) + x_k P_k^* V_k^*\left(\frac{1}{\tilde{v}_k} - \frac{1}{\tilde{v}}\right) + x_i V_i^*\frac{\theta_j}{\tilde{v}}X_{ij} + x_j V_j^*\frac{\theta_k}{\tilde{v}}X_{jk} + x_k V_k^*\frac{\theta_i}{\tilde{v}}X_{ki} \qquad (16)$$

where $x_i = N_i/N$ and $V_i^* = N_{\mathrm{A}} r_i^* v^*$, with N_{A} the Avogadro number. For the molar excess Gibbs function of mixing we get

$$G^{\mathrm{E}} = U^{\mathrm{E}} + N_{\mathrm{A}}kT\left(x_i \ln\frac{\phi_i}{x_i} + x_j \ln\frac{\phi_j}{x_j} + x_k \ln\frac{\phi_k}{x_k}\right) + 3N_{\mathrm{A}}rkT\left(c_i\phi_i \ln\frac{\tilde{v}_i^{1/3} - 1}{\tilde{v}^{1/3} - 1} + c_j\phi_j \ln\frac{\tilde{v}_j^{1/3} - 1}{\tilde{v}^{1/3} - 1} + c_k\phi_k \ln\frac{\tilde{v}_k^{1/3} - 1}{\tilde{v}^{1/3} - 1}\right). \qquad (17)$$

In Equations 16 and 17 concentrations x_i ought not be confused with pair interaction energy parameters X_{ij}. Other functions are obtainable from Equation 17 by thermodynamics. In particular, for the difference between chemical potential of ith component in solution μ_i and the same component in pure state μ_{ii} one obtains

$$\mu_i - \mu_{ii} = N_{\mathrm{A}}kT\left[\ln\phi_i + \left(1 - \frac{r_i}{r_j}\right)\phi_j + \left(1 - \frac{r_i}{r_k}\right)\phi_k\right] + P^*V_i^*\left(3\tilde{T}_i \ln\frac{\tilde{v}_i^{1/3} - 1}{\tilde{v}^{1/3} - 1} + \frac{1}{\tilde{v}_i} - \frac{1}{\tilde{v}}\right) + \frac{\widetilde{V}_i^*}{\tilde{v}}X_{ij}\theta_j(1 - \theta_i) - \frac{V_j^*}{\tilde{v}}X_{jk}\theta_i\theta_k\frac{x_j}{x_i} + \frac{V_k^*}{\tilde{v}}X_{ki}\theta_i(1 - \theta_i)\frac{x_k}{x_i} \qquad (18)$$

where $T_i = T/T_i^*$. Values of $\tilde{v}$ may be obtained from $\tilde{T}$ as described by Flory [2, 6]; in turn, $\tilde{T}$ is obtainable from Equation 14 in conjunction with Equation 11.

The Flory–Patterson theory was successful in predicting excess functions of mixing on the level of not only first but also second derivatives of Gibbs or Helmholtz functions [9]. While this clearly reinforced the idea of extension to ternary mixtures, one more factor is worth noting. In many approaches to ternary mixtures separate ternary parameters are introduced; finding (or rather adjusting) these involves the necessity of performing first at least some experimental determinations for ternary mixtures. It was interesting to find out, whether ternary parameters could be avoided when using the equations given above. Results of exemplary calculations performed are given in the following sections.

3. Ethanol + benzene + *n*-hexane

The above system has been chosen because its components represent different classes of organic compounds; apart of an aliphatic and an aromatic we have here an associated component. The presence of an alcohol makes the test of the theory more severe. Many theories of solutions fail completely for systems in which association occurs.

Precise experimental measurements of heats of mixing H^E for the system in question have been made by De Q. Jones and Lu [10]; they have studied the ternary system as well as all three respective binaries at 298.15 K. The coverage of the ternary system was fairly extensive, so that De Q. Jones and Lu were able to draw isoenthalpic lines on the concentration triangle.

Our calculations were made using Equation 16; that is, in view of low pressure, the excess energy of mixing U^E has been assumed to be equal to the excess enthalpy of mixing H^E. Parameters for pure components have been calculated in the same way as in [11]. For binary mixtures also a procedure described earlier by one of us [11] has been followed; that is, rewriting Equation 6 as

$$\theta_i = \frac{\phi_i}{\phi_i + \dfrac{s_j}{s_i}\phi_j} \qquad (19)$$

one realizes that a description of a binary mixture involves characteristic (hard-core) parameters for pure components, plus two binary parameters: X_{ij} and s_j/s_i. One can then solve for n experimental points (values of H^E in the present case) a set of n equations in two unknowns. While an *a priori* prediction of the surface ratio s_j/s_i is possible [12], the method does not seem accurate enough [11]. This is why we have obtained for each binary system the respective parameters X_{ij} and s_j/s_i by computer fitting. For ternary mixtures we have used two methods. One was fitting ternary data using known parameters for pure components and finding the binary parameters X_{ij}, X_{jk} and X_{ki} as well as the respective surface ratios. The second method consisted in predicing ternary heats of mixing basing entirely on binary data and on these for pure components.

Experimental data for pure components necessary to calculate the characteristic parameters have been taken for ethanol from [13], for benzene from [14] and for *n*-hexane from [15]. The values obtained are given in Table I.

TABLE I Characteristic parameters for pure components

Component	T (K)	V^* (cm^3 mol^{-1})	T^* (K)	P^* (J cm^{-3})	$\tilde{v}$
ethanol	298.2	46.41	5011	449.0	1.2645
benzene	298.2	69.21	4709	627.6	1.2917
n-hexane	298.2	99.56	4430	431.0	1.3227
N_2	100.0	26.18	1144	243.5	1.5457
Ar	100.0	22.17	1374	280.0	1.3706
O_2	100.0	21.23	1347	373.0	1.3846
Zn	714.0	8.83	24604	5560.0	1.1025
Sn	714.0	16.23	37859	2342.0	1.0626
Cd	714.0	13.03	26640	3798.0	1.0933

Calculations for binary and ternary mixtures have been performed using a non-linear curve-fitting computer program of the type described by Cuthbert and Wood [16]. The program was devised to perform a least-squares estimation of p parameter values $a_1, a_2, \ldots, a_p$ in an equation of the general form

$$y = y(X_1, X_2, \ldots X_m, a_1, a_2, \ldots a_p) \qquad (20)$$

representing a relation between a set of m independent variables $X_1, \ldots, X_m$ and a dependent variable y. The experimental values of X's and y are taken as known from n experiments, with $n > p$. In our case, we have used Equations 16 and 18 as those of the general form Equation 20. For binary systems we had one independent variable x_i and two unknown parameters X_{ij} and s_j/s_i. For ternary systems there were two independent variables x_i and x_j, and five unknown parameters X_{ij}, X_{jk}, X_{ki}, s_j/s_i and s_k/s_i. To apply the non-linear curve-fitting program, we have written a FORTRAN subroutine which calculated the y's of Equation 20 for the experimental concentrations (in the present case as given in [10]) and for a given set of parameter values. The main program then calculated the sum of squares of residuals, i.e. of differences between the y's resulting from the subroutine and the corresponding experimental values. The problem was thus reduced to finding a minimum of the sum of squares of residuals, and the parameter values giving the minimum were accepted as "true" values. For each of such true values, the program supplied the standard error, Student's t function, and 95% confidence limits. In Table II we list for brevity values of the parameters and 95% confidence limits (in parentheses) only. Indices E, B, and H refer to ethanol, benzene and *n*-hexane, respectively.

The first three columns in Table II contain parameters resulting from calculations for binary

TABLE II Characteristic parameters for ethanol + benzene + hexane mixtures for 298.2 K

	Source			
Parameter	E + B	B + H	E + H	E + B + H
X_{EB}	234.7 (205.4 → 264.1)			210.2 (192.6 → 227.8)
X_{BH}		40.52 (39.3 → 41.7)		46.6 (42.9 → 50.4)
X_{HE}			13.27 (11.13 → 15.42)	13.71 (12.79 → 14.64)
s_B/s_E	0.104 (0.086 → 0.121)			0.138 (0.125 → 0.153)
s_H/s_E			0.109 (0.079 → 0.175)	0.135 (0.115 → 0.154)
s_H/s_B		1.055 (0.99 → 1.12)		
δ	26.8	10.9	61.5	22.6 (ternary) 75 (from binary)

systems. Five of these six parameters were used for ternary predictions; in view of redundance of one of the parameters, the s_H/s_E values for ternary calculations were taken as the product of s_H/s_B and s_B/s_E values. The last column contains results from an independent fitting of ternary data. One notices that, for example, the parameter X_{EB} obtained from the binary ethanol + benzene results is fairly close to the respective value obtained from ternary measurements; in fact, there is an intersection region of 95% confidence limits. Similar comparison can be made for other parameters in Table II. At the bottom of the Table residual root mean square values δ characterizing each system are given.

Parameters of Table II may also be considered from the point of view of their physical significance. One would expect, that interaction energy between an alcohol and an aromatic hydrocarbon should be larger than energy of interaction of two hydrocarbons or of an alcohol with a paraffinic hydrocarbon. Inspection of X_{ij} values in the Table shows, that this is indeed the case. One would also expect, that the characteristic surface of an ethanol molecule should be smaller than surface of any of the hydrocarbons containing six carbon atoms. We find that this is confirmed by the surface ratios: s_B/s_E and s_H/s_E which are fractions, while s_H/s_B is of the order of unity.

Values of heats of mixing H^E for the three binary systems obtained using Equation 16 in conjunction with parameters of Table II are listed in Table III. The respective experimental values of De Q. Jones and Lu [10] are given also. As witnessed already by δ values in Table II, the agreement is satisfactory. That is, in spite of association

TABLE III Heats of mixing of binary mixtures ethanol + benzene, benzene + hexane and ethanol + hexane at 298.2 K.

System	x_i	H^E (J mol^{-1})	
		experimental	calculated
E + B	$x_E = 0.0250$	315	247
	0.0586	469	481
	0.1615	795	826
	0.2673	906	913
	0.4668	824	802
	0.5602	705	693
	0.7018	490	493
	0.7074	480	484
	0.9058	158	162
B + H	$x_B = 0.1519$	431	405
	0.2136	543	540
	0.3575	776	778
	0.4678	877	881
	0.5242	893	902
	0.6427	868	873
	0.6497	859	868
	0.6957	820	823
	0.7211	792	791
	0.8075	650	635
	0.9157	346	332
E + H	$x_E = 0.0395$	301	203
	0.0497	328	245
	0.0726	328	328
	0.0730	373	329
	0.1509	488	515
	0.1773	521	554
	0.2707	542	625
	0.3757	584	625
	0.4043	580	615
	0.5680	518	504
	0.6318	488	444
	0.7749	364	285
	0.8399	290	206
	0.9526	159	62
	0.9483	114	68

TABLE IV Heats of mixing of ternary mixtures ethanol + benzene + hexane at 298.2 K

x_E	x_B	H^E (J mol^{-1})		
		experimental	calculated for ternary	predicted
0.4449	0.4449	946	947	838
0.3814	0.3814	1009	999	899
0.2630	0.2630	977	991	924
0.2620	0.2620	977	990	924
0.8850	0.8850	626	613	611
0.0994	0.0994	343	329	338
0.0450	0.0450	872	883	844
0.2557	0.1742	1149	1123	1035
0.1822	0.4123	1162	1135	1045
0.1750	0.4353	1144	1094	1018
0.1073	0.6536	1173	1125	1042
0.1195	0.6143	1113	1066	995
0.0991	0.6802	505	503	496
0.0296	0.9045	676	677	655
0.4614	0.0757	902	903	834
0.3129	0.3770	1047	1053	958
0.3009	0.4009	1065	1072	975
0.2122	0.5774	1139	1135	1038
0.0601	0.8804	642	653	645
0.6709	0.1501	556	542	489
0.5237	0.3383	829	828	731
0.3846	0.5141	1016	1014	903
0.3444	0.5648	1044	1045	936
0.1165	0.8528	768	804	782
0.7172	0.2389	492	535	460
0.6513	0.2170	607	611	539
0.5722	0.1906	702	688	624
0.4203	0.1401	780	781	739
0.4017	0.1338	782	786	747
0.3914	0.1305	781	787	751
0.2586	0.0862	732	746	741
0.1312	0.0437	554	540	565
0.1011	0.4255	1075	1106	1022
0.0964	0.4520	1087	1117	1081
0.0581	0.6699	1002	1038	968
0.0543	0.6916	974	1010	944
0.0154	0.9122	430	429	417

of ethanol, the theory based on the partition function (1) is capable of describing calorimetric behaviour of all three binary systems. To explain this, let us notice that the hard-core parameters for ethanol, as originating from experimental data, comprise necessarily the association behaviour.

The respective calculation results for ternary mixtures are given in Table IV. We have here, apart of experimental values, a series of calculations based on fitting the ternary data and also, as enunciated above, ternary results based only on single and binary data. Understandably, fitted values are somewhat closer to experimental data than the predicted ones (cf. the respective values of δ in Table II).

Calculations similar to those described above have been also made for binary mixtures ethanol + n-heptane and n-heptane + benzene, as well as for ternary mixtures ethanol + benzene + n-heptane. The respective experimental data of heats of mixing at 298.15 obtained by Lu and De Q. Jones [32] have been used. The results obtained are similar to those in the system containing n-hexane, particularly from the point of view of the agreement between calculations and experiment. Given natural limitations as to the quantity of numerical values we could present, we have decided to give full data for one system rather than sketchy data for both. Thus, the data in Tables III and IV enable inspection of behaviour of calculated functions in particular concentration regions (dilute solutions, solutions close to equimolar, and so on), for binary systems as well as for ternary mixtures.

On the basis of the calculations performed, we conclude – again association of alcohol notwithstanding – that single and binary data are sufficient for reasonable prediction of ternary heats of mixing. It is reasonable to infer that such prediction will be numerically better for organic systems which do not contain highly polar or associated components.

4. Nitrogen + argon + oxygen

For the system named above we have used experimental values of activity coefficients f_i of components at 100 K as recommended by Elshayal and Lu [17]; these authors have critically analysed and tested available literature data for all three binary systems as well as for ternary mixtures. As $\mu_i - \mu_{ii} = N_A kT \ln x_i f_i$, with Equation 18 of the general form of Equation 20, our computations were made in the same way as for the preceding system. Table V contains interaction parameters and surface ratios for the binary systems. Indices N, A and O, refer to the respective components with obvious meaning. Characteristic parameters for components are listed above in Table I; they have been obtained by inter- and extrapolation of the values of Abe and Flory [18] and of Höcker and Flory [19].

Table V has the same structure as Table II. Again parameters from binary and ternary calculations may be compared, and overlap regions of 95% confidence limits found. More important, values of residual root mean squares δ for the ternary system show clearly, that prediction from pure components and from binary data is nearly as good as direct fitting.

Results of calculations for binary systems along with the respective experimental data are given in Table VI.

Values of activity coefficients in ternary mixtures, experimental as well as calculated by two methods are given in Table VII. We can only reiterate the conclusion reached for the preceding system about applicability of the theory. In fact, the agreement is excellent.

5. Zinc + tin + cadmium

The idea of extending the Flory–Patterson theory to metallic systems has been tested by one of us [20] for binary alloys. Except for one system exhibiting both positive and negative deviations from the Raoults law, the agreement between theory and experiment was found satisfactory. The main difficulty consisted in finding sufficiently accurate experimental data, for pure components as well as for mixtures. For the present problem, we have found liquid metal activities from EMF measurements in some ternary and even quaternary mixtures given by Ptak and Moser [21]. These authors have analysed the literature data as well as their own and have produced equations for logarithms of activity coefficients of components as functions of temperature and composition. We have chosen $T = 714$ K, as this was the lowest temperature of actual experiments of Ptak and Moser.

TABLE V Characteristic parameters for nitrogen + argon + oxygen mixtures at 100.0 K

Parameter	Source			
	N_2 + Ar	Ar + O_2	O_2 + N_2	N_2 + Ar + O_2
x_{NA}	4.005 (3.991 → 4.018)			4.595 (4.468 → 4.722)
x_{AO}		8.905 (8.902 → 8.909)		9.542 (9.217 → 9.866)
x_{ON}			10.73 (10.69 → 10.76)	8.856 (8.692 → 9.020)
$\frac{s_A}{s_N}$	1.671 (1.661 → 1.682)			1.495 (1.456 → 1.534)
			1.538 (1.528 → 1.548)	1.353 (1.307 → 1.398)
$\frac{s_O}{s_A}$		1.001 (1.000 → 1.001)		
δ	0.0005	0.0001	0.0000	0.0038 (ternary) 0.0088 (from binary)

TABLE VI Activity coefficients of components in binary systems N_2 + Ar, Ar + O_2, O_2 + N_2 at 100.0 K

System	x_i	f_i		f_j	
		experimental	calculated	experimental	calculated
N_2 + Ar	$x_A = 0.0195$	$f_N = 1.000$	1.000	$f_A = 1.163$	1.164
	0.0480	1.001	1.000	1.152	1.152
	0.0813	1.001	1.001	1.139	1.139
	0.1400	1.004	1.004	1.118	1.117
	0.1565	1.004	1.004	1.113	1.112
	0.2222	1.009	1.009	1.093	1.092
	0.3092	1.016	1.016	1.071	1.070
	0.3618	1.022	1.022	1.059	1.058
	0.4142	1.028	1.028	1.049	1.048
	0.4421	1.032	1.032	1.044	1.043
	0.5169	1.043	1.043	1.032	1.031
	0.5703	1.051	1.051	1.025	1.024
	0.6483	1.065	1.065	1.016	1.016
	0.6597	1.067	1.067	1.015	1.015
	0.7485	1.085	1.085	1.008	1.008
	0.7691	1.089	1.089	1.007	1.007
	0.7888	1.094	1.094	1.006	1.005
	0.7982	1.096	1.096	1.005	1.005
	0.8230	1.101	1.101	1.004	1.004
	0.8514	1.108	1.107	1.003	1.003
	0.8685	1.112	1.112	1.002	1.002
	0.8903	1.117	1.118	1.002	1.001
	0.9001	1.120	1.120	1.001	1.001
	0.9444	1.131	1.131	1.001	1.000
	0.9470	1.131	1.132	1.001	1.000
Ar + O_2	$x_A = 0.0323$	$f_A = 1.173$	1.173	$f_O = 1.000$	1.000
	0.0855	1.153	1.153	1.001	1.001
	0.1698	1.123	1.123	1.005	1.005
	0.2519	1.099	1.098	1.001	1.011
	0.3505	1.073	1.073	1.021	1.021
	0.3942	1.063	1.063	1.027	1.027
	0.4506	1.051	1.051	1.035	1.035
	0.5684	1.031	1.031	1.056	1.056
	0.6985	1.015	1.015	1.086	1.086
	0.7736	1.008	1.009	1.106	1.105
	0.8020	1.006	1.006	1.114	1.114
	0.9048	1.002	1.001	1.146	1.146
	0.9429	1.001	1.001	1.159	1.159
	0.9604	1.000	1.000	1.165	1.166
O_2 + N_2	$x_O = 0.0500$	$f_N = 1.001$	1.001	$f_O = 1.211$	1.208
	0.0701	1.001	1.001	1.200	1.196
	0.0995	1.002	1.003	1.184	1.179
	0.1360	1.005	1.005	1.166	1.159
	0.1791	1.008	1.008	1.146	1.138
	0.4248	1.040	1.039	1.064	1.056
	0.4875	1.052	1.050	1.050	1.042
	0.5897	1.075	1.071	1.031	1.025
	0.6376	1.087	1.081	1.024	1.019
	0.8056	1.135	1.121	1.007	1.005
	0.9086	1.168	1.148	1.002	1.001

Characteristic parameters of pure components have been obtained in the following way. Faber [22] gives selected values of molar volumes, isobaric expansivities and isothermal compressibilities of liquid metals close to their respective melting points. For Zn and Cd we have accepted Faber's values of volume and expansivity, assuming that molar volume varies linearly with the temperature. One thus obtains for cadmium V_{Cd} (714 K) = 14.25 $cm^3 mol^{-1}$. Crawley [23] has measured

TABLE VII Activity coefficients of components in ternary mixtures nitrogen + argon + oxygen at 100.0 K

x_N	x_A	f_N			f_A			f_O		
		exp	calc	pred	exp	calc	pred	exp	calc	pred
0.8534	0.1073	1.002	1.003	1.003	1.120	1.128	1.120	1.158	1.164	1.189
0.7405	0.1666	1.008	1.009	1.010	1.099	1.101	1.092	1.134	1.136	1.153
0.6477	0.2627	1.014	1.018	1.019	1.078	1.076	1.068	1.126	1.127	1.140
0.6820	0.2315	1.012	1.014	1.015	1.085	1.085	1.076	1.130	1.131	1.146
0.3270	0.5019	1.058	1.062	1.063	1.032	1.028	1.024	1.097	1.098	1.100
0.2001	0.6869	1.093	1.093	1.089	1.013	1.011	1.009	1.118	1.118	1.118
0.1198	0.6757	1.108	1.105	1.103	1.014	1.012	1.010	1.100	1.100	1.097
0.0663	0.7654	1.130	1.122	1.117	1.007	1.006	1.115	1.115	1.115	1.110
0.4894	0.3020	1.030	1.035	1.038	1.062	1.059	1.051	1.093	1.091	1.097
0.3341	0.4601	1.055	1.059	1.061	1.037	1.033	1.028	1.090	1.089	1.092
0.5687	0.1417	1.023	1.027	1.031	1.098	1.091	1.079	1.084	1.080	1.086
0.5076	0.1598	1.031	1.034	1.040	1.084	1.086	1.074	1.072	1.068	1.073
0.4460	0.1681	1.040	1.044	1.050	1.082	1.084	1.072	1.061	1.056	1.059
0.3527	0.3368	1.051	1.055	1.059	1.053	1.051	1.043	1.069	1.067	1.070
0.2186	0.4806	1.077	1.079	1.082	1.034	1.031	1.027	1.071	1.072	1.072
0.0836	0.5414	1.112	1.107	1.110	1.030	1.028	1.025	1.063	1.064	1.061
0.0882	0.4617	1.111	1.106	1.111	1.042	1.040	1.037	1.048	1.049	1.047
0.1762	0.3672	1.089	1.088	1.095	1.053	1.051	1.046	1.044	1.044	1.043
0.3292	0.1234	1.068	1.070	1.079	1.094	1.100	1.088	1.034	1.030	1.031
0.1812	0.1224	1.111	1.107	1.118	1.109	1.115	1.105	1.015	1.013	1.013
0.1286	0.0955	1.114	1.126	1.138	1.125	1.132	1.122	1.008	1.007	1.007

pyconmetrically densities of liquid Cd. Using his density formula in [23], as well as using his alternative formula from a review on liquid metals [24], one obtains 14.32 cm^{3}mol^{-1}; the agreement is thus within 0.5%. Compressibility of Zn given by Kleppa [25] for 693 K was accepted for 714 K. Compressibility of Cd given also by Kleppa [25] but for 594 K was accepted also. We have made an independent calculation of compressibility of cadmium using the formula of Egelstaff and Widom [26] binding compressibility with surface tension and with temperature; the use of formulas of this type for metals was advocated by Grosse [27, 28]. The result obtained for 714 K was virtually the same as given by Kleppa for 594 K. As for parameters for Sn, we have used the same data as in an earlier paper [20]; density fromula of Schwaneke and Falke [29], a compressibility value of Kleppa [25], the Egelstaff and Widom formula [26], and an equation for surface tension dependence on temperature also from Schwaneke and Falke [29]. The density equation we have used agrees again reasonably well with the one given by Crawley [24], and based on $\rho_{\mathrm{Sn}}(T)$ measurements of

TABLE VIII Characteristic parameters for Zn + Sn + Cd alloys at 714.0 K

Parameter	Source			
	Zn + Sn	Sn + Cd	Cd + Zn	Zn + Sn + Cd
X_{ZnSn}	244.5 (240 → 249)			261.8 (260 → 264)
X_{SnCd}		91.1 (85 → 98)		95.9 (94 → 98)
X_{CdZn}			409.8 (399 → 420)	408.5 (406 → 412)
$\frac{s_{\mathrm{Sn}}}{s_{\mathrm{Zn}}}$	1.259 (1.205 → 1.312)			1.144 (1.121 → 1.168)
$\frac{s_{\mathrm{Cd}}}{s_{\mathrm{Zn}}}$			0.897 (0.858 → 0.936)	0.881 (0.871 → 0.892)
$\frac{s_{\mathrm{Cd}}}{s_{\mathrm{Sn}}}$		0.768 (0.748 → 0.789)		
δ	0.0049	0.0011	0.0027	0.0030 (ternary) 0.0085 (from binary)

TABLE IX Activity coefficients of components in binary alloys Zn + Sn, Sn + Cd and Cd + Zn at 714.0 K

System	x_i	$\log f_i$		$\log f_j$	
		exp	calc	exp	calc
Zn + Sn	x_{Zn} = 0.100	0.179	0.173	0.001	0.001
	0.200	0.157	0.152	0.005	0.005
	0.300	0.135	0.131	0.012	0.012
	0.400	0.114	0.111	0.024	0.022
	0.500	0.094	0.091	0.041	0.039
	0.600	0.073	0.070	0.066	0.065
	0.700	0.053	0.048	0.103	0.106
	0.800	0.034	0.027	0.162	0.171
	0.900	0.016	0.009	0.269	0.276
Sn + Cd	x_{Sn} = 0.100	0.146	0.145	0.004	0.003
	0.200	0.104	0.105	0.011	0.009
	0.300	0.074	0.074	0.021	0.019
	0.400	0.051	0.052	0.033	0.032
	0.500	0.034	0.035	0.047	0.046
	0.600	0.021	0.021	0.063	0.062
	0.700	0.011	0.012	0.081	0.080
	0.800	0.005	0.005	0.100	0.100
	0.900	0.001	0.001	0.121	0.122
Cd + Zn	x_{Cd} = 0.100	0.455	0.451	0.010	0.007
	0.200	0.331	0.336	0.031	0.028
	0.300	0.239	0.242	0.062	0.059
	0.400	0.168	0.168	0.100	0.098
	0.500	0.112	0.111	0.145	0.145
	0.600	0.069	0.067	0.197	0.198
	0.700	0.038	0.036	0.254	0.256
	0.800	0.017	0.015	0.318	0.318
	0.900	0.004	0.004	0.387	0.384

Thresh *et al.* [30]. Characteristic parameters obtained from such a set of data are given in Table I.

Calculations for binary mixtures have been made in the same way as for previous systems. Interaction parameters and surface ratios are given in Table VIII. Calculated and experimental $\log f_i$ values are given in Table IX. We have not converted $\log f_i$ because, as mentioned above, Ptak and Moser gave their equations in terms of logarithms. The computations were then made for ternary mixtures. The results are given in Table X. Structure of the table is the same as of Table VII. Inspection of Table X shows that for ternary alloys the theory is well applicable. Apart of the system Zn + Sn + Cd, we have made similar calculations for the system Zn + Sn + Bi, using activity data from the same source [21]. The results were of the same kind and led to the same conclusions as for alloys containing cadmium; thus, for the same reasons as discussed at the end of Section 3, we omit here the numerical data.

6. Some concluding remarks

We have found that the Flory–Patterson theory extended to ternary mixtures gives satisfactory results, and this for systems considered to be very different and unrelated to one another. In a way, this result could have been anticipated. There is no reason why a theory working for binary systems should cease to be applicable when one adds a third component. As for applicability to systems of different kinds, we believe in the basic unity of the liquid state. We mean by this that, independently of a particular kind of system studied, macroscopic properties are always determined by molecular considerations. From this point of view the evidence found is not surprising either.

Applicability of the theory may have some further consequences. It may be now extended without difficulty to quaternary, quinary and other multicomponent systems; one would expect that when taking these steps one would find similar validity of the approach. Coming back to

TABLE X Activity coefficients of components in ternary mixtures Zn + Sn + Cd at 714.0 K

x_{Zn}	x_{Sn}	$\log f_{Zn}$			$\log f_{Sn}$			$\log f_{Cd}$		
		exp	calc	pred	exp	calc	pred	exp	calc	pred
0.100	0.133	0.330	0.330	0.322	0.094	0.097	0.085	0.016	0.015	0.015
0.100	0.222	0.301	0.299	0.289	0.067	0.070	0.060	0.026	0.026	0.026
0.100	0.311	0.277	0.273	0.262	0.047	0.049	0.042	0.038	0.039	0.038
0.100	0.400	0.257	0.250	0.239	0.032	0.034	0.028	0.052	0.053	0.051
0.100	0.489	0.238	0.232	0.220	0.020	0.022	0.018	0.068	0.068	0.065
0.100	0.578	0.222	0.217	0.204	0.011	0.013	0.011	0.084	0.085	0.079
0.100	0.667	0.208	0.205	0.192	0.006	0.007	0.006	0.103	0.103	0.095
0.100	0.756	0.195	0.196	0.182	0.002	0.004	0.003	0.122	0.122	0.112
0.200	0.131	0.272	0.273	0.268	0.067	0.067	0.054	0.033	0.033	0.032
0.200	0.219	0.248	0.247	0.241	0.047	0.047	0.036	0.046	0.046	0.046
0.200	0.306	0.228	0.226	0.219	0.032	0.032	0.024	0.061	0.061	0.060
0.200	0.394	0.210	0.208	0.200	0.020	0.022	0.016	0.078	0.078	0.074
0.200	0.481	0.195	0.193	0.185	0.012	0.014	0.010	0.095	0.095	0.090
0.200	0.569	0.182	0.181	0.172	0.007	0.017	0.007	0.115	0.112	0.105
0.200	0.656	0.171	0.172	0.162	0.005	0.007	0.005	0.135	0.131	0.122
0.300	0.129	0.218	0.219	0.216	0.051	0.048	0.033	0.059	0.058	0.057
0.300	0.214	0.198	0.199	0.196	0.036	0.034	0.023	0.074	0.074	0.072
0.300	0.300	0.182	0.182	0.178	0.025	0.025	0.016	0.091	0.091	0.088
0.300	0.386	0.169	0.168	0.164	0.017	0.019	0.012	0.110	0.109	0.104
0.300	0.471	0.157	0.157	0.152	0.013	0.015	0.010	0.130	0.127	0.120
0.300	0.557	0.148	0.148	0.142	0.011	0.013	0.010	0.151	0.145	0.136
0.400	0.125	0.168	0.170	0.169	0.046	0.042	0.026	0.093	0.093	0.091
0.400	0.208	0.154	0.154	0.153	0.035	0.033	0.021	0.111	0.110	0.107
0.400	0.292	0.142	0.142	0.141	0.028	0.028	0.018	0.130	0.128	0.124
0.400	0.375	0.132	0.132	0.130	0.024	0.025	0.018	0.150	0.147	0.140
0.400	0.458	0.124	0.124	0.122	0.022	0.025	0.019	0.171	0.165	0.156
0.500	0.120	0.124	0.125	0.125	0.053	0.050	0.034	0.137	0.138	0.135
0.500	0.200	0.114	0.114	0.115	0.046	0.045	0.032	0.156	0.156	0.151
0.500	0.280	0.106	0.106	0.106	0.041	0.043	0.032	0.175	0.174	0.167
0.500	0.360	0.100	0.099	0.099	0.039	0.043	0.034	0.196	0.192	0.183
0.600	0.112	0.087	0.085	0.086	0.076	0.075	0.059	0.192	0.195	0.190
0.600	0.188	0.081	0.079	0.080	0.070	0.072	0.059	0.210	0.212	0.205
0.600	0.262	0.077	0.074	0.076	0.067	0.072	0.060	0.228	0.229	0.219
0.700	0.100	0.056	0.051	0.053	0.117	0.120	0.106	0.258	0.265	0.259
0.700	0.167	0.054	0.049	0.051	0.111	0.117	0.105	0.272	0.279	0.270
0.800	0.075	0.031	0.025	0.027	0.185	0.189	0.179	0.337	0.350	0.343

ternary systems, for instance Hsu and Prausnitz [31] have studied polymer compatibility in such systems using the earlier theory [5]. It has been found by one of us [11] when studying swelling of natural rubber in organic solvents that the Flory–Patterson theory gives distinctly better results than the earlier theory of polymer solutions as described in [5]. Thus, using the new theory instead of the old one should give more information on the subject of solubility of polymers. The same statement is expected to apply even more to Flory–Patterson theory versus empirical approaches, not only to compactibility of polymers but also to other problems involving ternary liquid solutions.

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