

MOLAR VOLUMES OF KRYPTON-METHANE MIXTURES AND THE AVERAGE POTENTIAL MODEL

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The molar volumes of liquid mixtures of krypton and methane have been measured at the krypton triple-point T=115.77 K, the lowest temperature at which the whole composition range can be covered. The excess volumes were found to be negative and very small. The experimental values have been compared with those calculated from the Average Potential Model in its refined form. A discussion on the validity of the combination rules, quantum effects and form of the intermolecular potential has been included.

1 - INTRODUCTION

In recent years attention has been drawn to the measurement of molar volumes of binary mixtures of simple liquids, with the aim of testing statistical theories of solutions of non-electrolytes, in particular the so-called Average Potential Model developed by PRIGOGINE and his co--workers (1,2) and also independently by SCOTT (3). For this purpose mixtures of very simple molecules have been selected, involving primarily the rare gases, diatomic molecules like oxygen, nitrogen, and carbon monoxide, and molecules of high symmetry like methane. In most cases the agreement is only moderately good; even when the theory gives a fair account of other thermodynamic properties like the Gibbs energy, it fails with the molar volume, proving to be only of qualitative value at the best(4).

For this reason it is useful to make a careful study of an almost ideal system, since in some respects the theories which we seek to test should then stand the best chance of being successful. Krypton-Methane is such a system, and although it has been dealt with before(5,6) there are reasons for believing that the previous results are not very accurate; moreover the published figures for the excess Gibbs energy(5,6) and the excess molar volume (6,7) are somewhat contradictory. It seemed therefore worthwhile to re-investigate this system in order to check and complete the work already done; the results reported here are part of a detailed investigation on the thermodynamics of liquid mixtures of krypton and methane which will be published elsewhere.

2 - EXPERIMENTAL

Molar volume measurements of methane-krypton mixtures and their pure components were carried out at the triple-point tetmperature of krypton T = 115.77 K, the lowest temperature at which the whole composition range can be studied.

Cylinder gases of the highest purity available were used; they were further purified by fractional

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distillation using a Podbielniak-type column with a Dixon-Lessing gauze rings filling (8). The purity was checked by mass-spectrometric analysis and by measuring the constancy of the triple-point pressure during melting. Values obtained were

KRYPTON
$$P_t = 72.996 \pm 3 \text{ Nm}^{-2}$$

Methane $P_t = 11.691 \pm 2 \text{ Nm}^{-2}$

in excellent agreement with values reported in the literature.

The apparatus used has been described before(8) and consists essentially of a glass pyknometer of $\sim 1.8 \text{ cm}^3$ capacity, surrounded by another glass vessel which contains the cryostat material kept at its triple-point; this double-vessel is in turn surrounded by a jacket to ensure the heat transfer control in the usual way. The refrigerant was liquid oxygen and thermal contact was achieved through an immersed copper rod attached to the base of a cylindrical copper shield enclosing the pyknometer assembly. In this way the temperature could be kept constant within ± 0.001 K for 2-3 hours, long enough to take the readings.

The procedures for making the mixture and for the determination of the molar volume have also been reported before (8,9) and will not be repeated here.

The compositions of the mixtures (liquid and vapour) were computed by an iterative process, using a modified Barker's procedure for the calculation of the activity coefficients(10). Virial coefficients used were those determined by STAVELEY *et al.* at low temperatures (11) and by several authors at room temperature, as quoted by BREWER (12).

Table 1

Molar Volumes (in cm^3 mol⁻¹) of liquid mixtures of krypton and methane at T=115.77 K

$\mathbf{x}_{\mathbf{CH}_i}$	v	Vp = o	$\mathbf{v}^{\mathbf{E}}$	r _v
0	34.312	34.316	0	_
0.33822	35.756	35.762	-0.020	-0.002
0.43100	36.153	36.160	-0.025	-0.002
0.50801	36.489	36.497	-0.022	+0.003
0.60417	36.900	36.909	-0.027	0
0.70169	37.327	37.336	-0.022	+0.004
0.79454	37.723	37.733	-0.028	+0.006
1	38.640	38.652	0	-

The results obtained are presented in table 1, together with the corrected values at zero pressure, as the theoretical expressions for the excess functions refer to a constant total pressure usually taken to be zero. The values of the compressibilities of the pure liquids used in the calculations were determined from recent measurements of the velocity of sound in liquid krypton and methane (13,14), and for the mixtures it was assumed that the compressibility is a linear function of the composition.

The values of V^E , the excess molar volume of mixing, were, of course, given by

$$V^{E} = V - x_{1}V_{o1} - x_{2}V_{o2}$$
 (1)

where V, V_{01} and V_{02} are respectively the molar volumes of the mixture and components 1 and 2,



Fig. 1 — Plot of VE in cm^3 mol⁻¹ against methane mole fraction at T=115.77 K.

and x_1 and x_2 the respective mole fractions. These values of V^E fit the equation

$$V^{E} = x (1-x) [-0.101 - 0.058 (2x-1)]$$
 (2)

where x is the mole fraction of the more volatile component, methane (fig. 1).

The last column of Table 1 gives the excess volume residuals

$$\mathbf{r}^{\mathbf{v}} = \mathbf{V}_{\mathrm{exp}}^{\mathbf{E}} - \mathbf{V}_{\mathrm{calc}}^{\mathbf{E}} \tag{3}$$

where V_{calc}^E is given by equation (2).

The excess molar volumes of krypton-methane mixtures are, therefore, negative, in opposition to the results of FUKS and BELLEMANS (15) who found for the $x_{CH_i} = 0.4318$ solution

$$V^{E} = +0.02 \pm 0.02 \text{ cm}^{3} \text{ mol}^{-1}$$

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MATHOT and LEFEBVRE (7) have also found

$$V^{E} = -0.01 \pm 0.01$$
 cm³ mol⁻¹

over the whole composition range. Our results are, however, more accurate and more reliable than theirs.

For the equimolar solution $x_1 = x_2 = 0.5$ the calculated value of V is small

$$V^{E} = -0.025 \pm 0.002 \text{ cm}^{3} \text{ mol}^{-1}$$

Together with the small value for the excess entropy of mixing $S^E = +0.15 \text{ JK}^{-1} \text{ mol}^{-1}$ (16) this shows that the krypton-methane mixtures are almost regular solutions in the HILDEBRAND sense. (17).

3 — DISCUSSION

Although there are several versions of the Average Potential Model, we will only deal with the refined version as described by BELLEMANS *et al.* (18), which seems to be the most successful of them all.

The Average Potential Model is a combination of the cell model for liquids and the concept of average potential on the one hand, and the theorem of corresponding states, on the other. As usual it is assumed that any pair of molecules A and B interact according to the 12-6 potential function of Lennard-Jones

$$\Phi_{AB}(\mathbf{r}) = \varepsilon_{AB}^{*} \left[\left(\frac{\mathbf{r}_{AB}^{*}}{\mathbf{r}} \right)^{12} - 2 \left(\frac{\mathbf{r}_{AB}^{*}}{\mathbf{r}} \right)^{6} \right] \quad (4)$$

where r is the intermolecular separation and r^*_{AB} , ε^*_{AB} the coordinates of the minimum of the intermolecular potential energy $\Phi_{AB}(\mathbf{r})$.

The parameters ε^* , r^* for the pure components are calculated from some particular properties like viscosity, critical constants and second virial coefficients; values differ according to the property

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chosen, so averages were taken as the best way of minimizing errors (18). For the crossed pair AB it is much more difficult to get reliable direct data and it is common practice to use the combination rules of the arithmetic and geometric means

$$\mathbf{r}_{AB}^{*} = \frac{1}{2} [\mathbf{r}_{AA}^{*} + \mathbf{r}_{BB}^{*}]$$
 (5)

$$\varepsilon_{AB}^* = (\varepsilon_{AA}^* \cdot \varepsilon_{BB}^*)^{1/2} \tag{6}$$

The first one is known to be a very good approximation but the second one less so.

Table 2Molecular parameters for krypton and methane

			Bellemans	BOATO and CASANOVA	LENNARD- JONES 18-6
Kr	ε*/k	(K)	169.3	165.2	222.4
	r*	(A)	3.998	4.111	3.922
CH4	ε*/k	(K)	153.5	152.4	197.8
	r*	(A)	4.198	4.194	4.115

The final expressions for the excess thermodynamic functions depend ultimately on these parameters and are, in fact, very sensitive to them.

The calculated value of V^E , for the equimolar mixture, is $+0.008 \text{ cm}^3 \text{ mol}^{-1}$, very small but positive. Among the possible reasons for this lack of agreement are the importance of multi-body forces, quantum effects, deficiencies of the intermolecular potential function, and failure of the combination rules.

It has been suggested (19) that a correction factor $O < k_{AB} < 1$ should be introduced to account for deviations from the geometric mean

$$\varepsilon^*_{AB} = (1 - k_{AB}) \ (\varepsilon^*_{AA} \cdot \varepsilon^*_{BB})^{1/2} \tag{7}$$

The London theory of dispersion forces indicates in this case $k_{AB} = +0.0025$, which has the effect of bringing the theoretical value of V^E up to + 0.034 cm³ mol⁻¹, a change in the wrong direction. For agreement between the experimental and the calculated values of V^E , a negative k_{AB} is needed, which is contrary to the evidence for most of the binary systems studied hitherto.

Quantum effects can be introduced in the form of DE BOER plots (20) which enabled BOATO and CASANOVA to devise a new method of deriving a self-consistent set of molecular parameters for the rare gases, based on accurate vapour pressure data for different isotopic species (21). We have extended their treatment to methane and the final values are reported in Table 2, along with the previous ones due to BELLEMANS *et al.*

The calculated value is now $V^{E} = -0.030 \text{ cm}^{3}$ mol⁻¹, in excellent agreement with the experiment, but it should be said that the agreement for the excess Gibbs function is a little worse (16).

Table 3

Experimental and calculated values of the excess molar volume for the equimolar mixture of krypton and methane at T=115.77 K

Experimental	-0.025	
 Bellemans	+0.008	
BOATO and CASANOVA	-0.030	
Lennard-Jones 18-6	+0.032	

Finally we consider the possibility of using another form of intermolecular potential; it is known that general experimental evidence requires a pair-potential which is shallower than (1) at large separations, but deeper and steeper near the minimum. A better potential is that due to KIHARA which involves 3 parameters (22), and, for that reason, makes it a less attractive function to deal with. It has been shown, however, that the 18-6 Lennard--Jones function is a good alternative to the Kihara potential, at least as far as virial coefficients, transport and lattice properties are concerned (11,23). Application to the present case gives $V^{E} = +0.032 \text{ cm}^{3} \text{ mol}^{-1}$, in very bad agreement with the experimental value, perhaps because multi--body interactions cannot be ignored in the liquid state. It is interesting that the 12-6 function, although it proves a poor approximation to pure two-body interactions, somehow gives a better

account of the overall effect, behaving like an «effective potential».

In conclusion, this paper illustrates the difficulties involved in quantitatively testing statistical theories of solutions of the type such as the Average Potential Model. The postulates and assumptions made in these theories are such that the quantitative predictions are mostly likely to succeed for mixtures of small, symmetrical and very similar molecules. In this respect, one could scarcely improve on krypton--methane as a test system. But the excess thermodynamic functions are then only slightly different from zero, and while the theories may be said to be successful in correctly forecasting very small excess functions, the actual values which they predict for these functions are still very sensitively dependent on the numerical values which must be introduced into the relevant equations, on the correctness or otherwise of the assumptions used in deriving these equations, and so on.

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RESUMO

Determinaram-se os volumes molares de soluções líquidas binárias de crípton e metano à temperatura do ponto triplo do crípton T=115,77 K. Calcularam-se os volumes de excesso à pressão p=O, que são negativos e muito pequenos. Finalmente compararam-se estes volumes com os previstos pelas teorias estatísticas do estado líquido, em particular o modelo do potencial médio, fazendo-se algumas considerações sobre as hipóteses básicas desta teoria nomeadamente regras de combinação para os parâmetros intermoleculares, efeitos quânticos e forma do potencial de interacção.