231. Low Temperature Thermodynamics
The Excess *Gibbs* Function and the Volumes of Mixing for the System Methane + Propane at 90.68K

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Dedicated to Professor *C. G. Boissonnas* on his 70th birthday

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Summary. The excess *Gibbs* function G^e and the excess volumes of mixing V^e have been measured at the methane triple point (90.68 K) for the system methane + propane. They were compared with *McGlashan's* recent theory for mixtures of molecules of different sizes.

Introduction. – The system methane + propane has already been investigated between 90K and 110K by *Cutler & Morrison* [1] (excess *Gibbs* function) and by *Shana'a & Canfield* [2] (excess volumes), but the two groups did not work at the same temperature. So it was decided to determine both excess functions at the triple point of methane, which can easily be reproduced. The simultaneous determination of G^e and V^e yields very useful data for a theoretical study of the mixture.

Experimental. – The experimental procedure, already fully described elsewhere [3], will only be briefly outlined here.

Known amounts of propane and methane were condensed into a pyknometer of about 1.8 cm³ capacity, which was itself surrounded by a cryostat containing methane at its triple point. The main experimental difficulty with this system was caused by the relatively high viscosity and low vapour pressure (less than 0.001 Torr) of propane at low temperatures.

The vapour pressures above the mixture were measured in a first set of experiments with the pyknometer filled to about ²/₃ of its capacity. This allowed a larger surface of the liquid to be in contact with the vapour phase. In a second set of experiments, the volumes of the mixtures were measured and the pyknometer was filled up to the stem (1 mm diameter).

The gases were purified by fractional distillation of the liquids. Methane (of industrial origin) had to be distilled several times; its purity was checked by the constancy of its triple point pressure: found 87.67 ± 0.03 Torr against 87.64 ± 0.02 Torr as found earlier in this laboratory [4]. Propane from *Matheson & Co.*, stated to be 99.5 per cent pure, was distilled only once.

Results. – The exact mole fractions of the mixtures were determined by an iterative computer programme which took into account the dead spaces above the liquid and in the manometer (thermostatted near 25 °C), the temperature gradients, and also the imperfections of the vapour phase. The total vapour pressures found are

Table 1. *Vapour pressures of mixtures of methane + propane at 90.68 K* (given in international Torr)

x (propane)	0.2196	0.3026	0.3597	0.4815	0.5479	0.6280	0,7326
p (Torr)	75.86	72.11	69.69	63.07	58.61	51.58	39.81

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given in Table 1. The corrected total vapour pressure p^* corresponding to an ideal vapour phase was also computed.

The excess *Gibbs* function G^e for a binary liquid mixture of mole fraction x (component 2), in equilibrium with the vapour phase of composition y, is given by *Guggenheim* [5]:

$$G^e (T, p, x) = R\,T\,(1 - x) \ln \left[(1 - y)\,p^* \,/\, (1 - x)\,p_1^0\right] + R\,T\,x \ln[y\,p^* \,/\, x\,p_2^0] \qquad (1)$$

or simply

$$G^e (T, p, x) = R\,T\,(1 - x) \ln \gamma_1 + R\,T\,x \ln \gamma_2 . \qquad (2)$$

p_1^0 and p_1^0 are the vapour pressures of the pure components of the mixture, at temperature T, and γ_1 and γ_2 are the activity coefficients in the mixture of composition x.

G^e is usually expressed in the form (3) and the parameters A, B, etc., are adjusted by using relation (1).

$$G^e (T, p, x) = x\,(1 - x)\,[A + B\,(1 - 2\,x) + C\,(1 - 2\,x)^2 + \ldots] \qquad (3)$$

In our system, however, the vapour pressure of pure propane is so small that the vapour phase in equilibrium with the mixture is virtually pure methane ($y = 0$), and so only γ_1 can be determined experimentally. This means that relations (1) and (3) cannot be used directly to obtain the excess *Gibbs* function, but this can be overcome, since [5]

$$R\,T \ln \gamma_1 = \mu_1^e\,(T, p, x) = G^e - x\,(\delta\,G^e \,/\, \delta\,x) \qquad (4)$$

From (3) we get

$$R\,T \ln \gamma_1 = x^2\,[A - B\,(4x - 3) + C\,(12x^2 - 16x + 5) + \ldots] \qquad (5)$$

This relation can be used to determine the parameters A, B and C by a least squares fit, and then G^e itself from (3).

Our results could be expressed by equation (6), (a third parameter, C, did not improve the fit substantially).

$$G^e (T, p, x) = x\,(1 - x)\,[722.9 + 335.6\,(1 - 2x)] \pm 3 \text{ J mol}^{-1} \qquad (6)$$

The curve and the experimental points are shown in Fig. 1. G^e is clearly asymmetric, with a maximum of 188 J mol^{-1} near $x = 0.4$, which is consistent with measurements near 100K [1].

The excess volume of mixing V^e is defined as

$$V^e (T, p, x) = V_m - (1 - x)\,V_1^0 - x\,V_2^0 \qquad (7)$$

where V_1^0 and V_2^0 are the molar volumes of the pure components and V_m is the molar volume of the mixture of composition x. We used the following values for 90.68K:
V_1^0 (methane) $= 35.666$ cm^3 mol^{-1} from earlier determinations [4],
V_2^0 (propane) $= 60.83$ cm^3 mol^{-1}, this work.

The molar volumes of the mixtures and the excess volumes are given in table 2.

Table 2. *Molar volumes and excess volumes of mixtures of methane + propane at 90.68 K*

x (propane)	0.2241	0.2677	0.3696	0.4928	0.7254
V_m (cm³ mol⁻¹)	40.85	41.90	44.43	47.55	53.60
V^e (cm³ mol⁻¹)	− 0.45	− 0.50	− 0.53	− 0.51	− 0.32

Our results for V^e, shown in Fig. 2, are given by

$$V^e (T, p, x) = - x (1 - x) [2.05 + 1.03 (1 - 2 x)] \text{ cm}^3 \text{ mol}^{-1}. \qquad (8)$$

The absolute error is about 5%, depending on the accuracy of V_2^0 itself.

V^e is negative (contraction on mixing) and it is asymmetric, with a maximum near $x = 0.4$, like G^e. This strong asymmetry has also been found by [2], who worked at 108.2K.
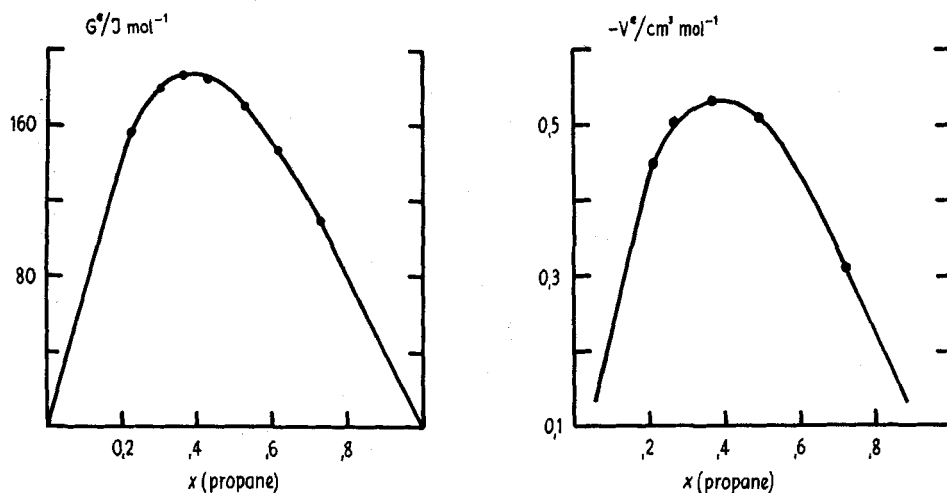
The excess Gibbs *function G^e* (Fig. 1) *and the excess volumes of mixing V^e* (Fig. 2) *for the system* methane + propane at 90.68 K

The temperature coefficient $\partial V^e / \partial T$ appears to be negative, and the values of V^e at 100K, interpolated from the two sets of experiments, agree with the predictions from the theory of corresponding states for this system [1]. For $x = 04$, for example,. the interpolated value is − 0.69 against − 0.70 cm³ mol⁻¹ predicted.

Negative excess volumes on mixing with negative temperature coefficients are also observed for higher hydrocarbon mixtures near room temperature [6].

Discussion. – *Cutler & Morrison* showed that their values for G^e agreed with the predictions from a quasi-lattice theory, and also with the consequences of the theory of corresponding states applied to mixtures of chain molecules. The latter is also confirmed by our study of V^e.

It seemed, however, that our values of G^e and V^e, at the same temperature, could also be used in connection with a more general theory of excess thermodynamic functions, than lattice-type theories. *McGlashan*'s recent theory [7] for mixtures of molecules of different sizes seemed to be most appropriate. It is a one-fluid theory

using either *van der Waals'* or *Guggenheim's* equations of state as a physical basis, and it agrees nearly as well with experiment as more elaborate theories of liquid mixtures [6]. Moreover, it is interesting to test the theory with molecules which differ not only in size, but also in shape, since propane is not spherical.

Table 3 shows the relation between experimental and predicted values of the excess functions. H^e was obtained at 100K by [1] from measurements of the heats of vaporization of methane from mixtures with propane, and it was corrected to 90.68K. This excess function is not very accurate. The quantities in brackets have been used as adjustable parameters to calculate the other quantities. ξ is a correction factor in the geometric combining rule $\varepsilon_{AB} = \xi\,(\varepsilon_{AA} \cdot \varepsilon_{BB})^{1/2}$ which appears in the theory.

Table 3. *Comparison of calculated and experimental values for the excess functions of the system methane + propane at 90.68 K*

		ξ	G^e (J mol^{-1})	H^e (J mol^{-1})	V^e (cm^3 mol^{-1})
$x = 0,5$	experiment	–	180	117	– 0.51
	v.d. Waals	(1)	– 186	– 254	– 1.54
	Guggenheim	(1)	– 190	– 400	– 1.17
	v.d. Waals	0.887	(180)	162	– 1.15
	Guggenheim	0.937	(180)	87	– 0.82
$x = 0.35$	experiment	–	187	125	– 0.53
	Guggenheim	(0.937)	196	113	– 0.77

Guggenheim's equation of state gives the best agreement when G^e is used as an adjustable parameter, and it also gives a good prediction as to the general shape of the G^e and H^e curves. For V^e, it suggests a more symmetrical curve. The agreement is similar to that found for other systems, but the departure from the geometrical combining rule is relatively large. This possibly includes a correction for the difference in the shape of the molecules.

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