

THE MOLAR VOLUMES OF LIQUID METHANE AND DEUTEROMETHANE

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Synopsis

The molar volumes of liquid CH_4 and CD_4 have been measured between 98 and 112°K with a relative accuracy of about $2 \cdot 10^{-4}$. The molar volume of CH_4 is about 1% larger than that of CD_4 over all this temperature range. This difference is tentatively interpreted as resulting from (a) a translational quantum effect and (b) small differences in the intermolecular forces.

1. *Introduction.* The fact that CH_4 has a smaller vapour pressure than CD_4 over the whole liquid range¹⁾ cannot result from the quantization of the translational motion of the molecules which always gives the lowest vapour pressure to the heaviest molecule²⁾. It was therefore suggested by one of us (A.B.) that the difference in the vapour pressure of CH_4 and CD_4 results partly from small differences in the intermolecular forces of these molecules³⁾.

Careful measurements of the second virial coefficient of CH_4 and CD_4 by Thomaes and Van Steenwinkel have confirmed this view⁴⁾ and it seems therefore interesting to extend such investigations to other thermodynamic properties. Here we report some measurements of the molar volumes of CH_4 and CD_4 at saturated pressure in the temperature range 98–112°K. This property was chosen because it can be measured with a relatively high accuracy.

2. *Experimental technique.* We give here a brief description of the cryostat we used and which is designed to cover the range of temperatures from 70°K to 300°K (see fig. 1). Its main features are as follows:

- a vacuum tight copper shield (a) (with a window);
- a copper radiation shield (b) (also with a window) in contact with the liquid air or nitrogen reservoir (c);
- a copper block (d) held at constant temperature by the following device: an adjustable valve (e) maintains a flow of refrigerant to the reservoir (f) and heat exchanger (g), while a platinum thermometer (h) fixes the current

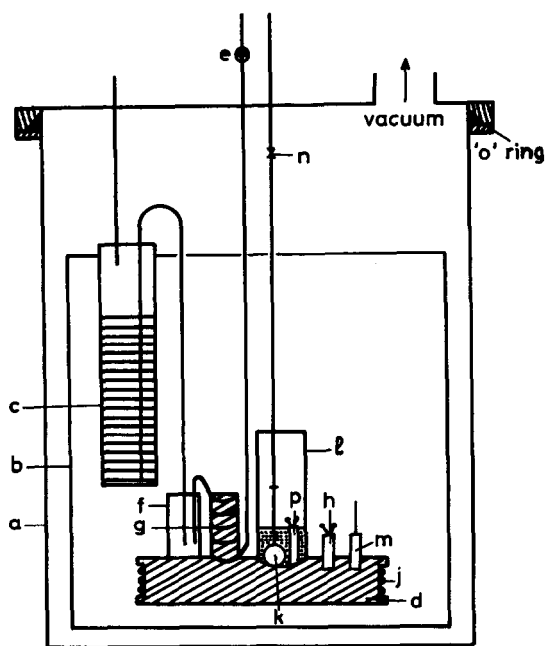


Fig. 1. Scheme of the cryostat

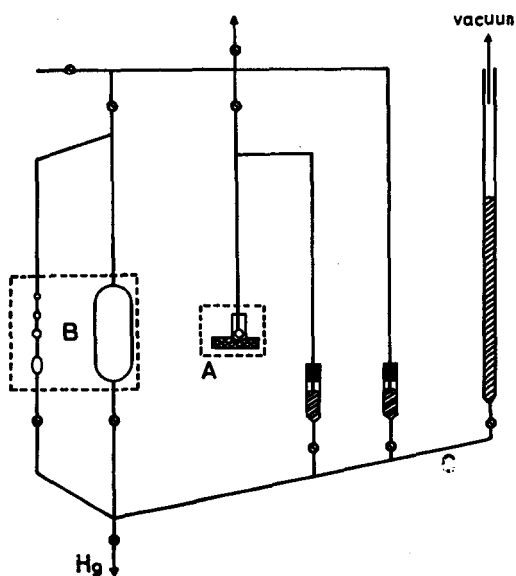


Fig. 2. General scheme of the apparatus; A: cryostat, B: compressor + thermostat, C: manometers.

intensity in the heating resistance (*j*) (proportional regulating system); the constancy of temperature reached is $2-3 \cdot 10^{-3}^\circ\text{K}$;

a known amount of substance (CH_4 or CD_4) is condensed into the calibrated pyrex bulb (*h*) ($v = (0.64824 \pm 0.00004) \text{ cm}^3$ at 20°C) surmounted by a calibrated capillary; this bulb is enclosed in a radiation screen (*l*) with a small window in it in order to be able to measure the height of the liquid into the capillary with a cathetometer; the temperature of the bulb is measured with a platinum thermometer (*p*) (calibrated against CH_4 vapour pressure); a good thermal contact between the copper block (*d*), the bulb (*h*) and the thermometer is established by silicon grease;

a vapour pressure thermometer (*m*) gives a further check on the temperature;

the connexion between the pyrex bulb (*h*) and the upper part of the apparatus consists of a glass to metal seal (*n*).

The amount of substance introduced in the bulb is determined from pressure measurements in a mercury compressor (see fig. 2). Adequate corrections were allowed for dead spaces, gas imperfections and variations of the bulb volume with *T*.

3. *Experimental results.* The methane was obtained from the company "L'Air Liquide", Liège, Belgium, and was further purified by fractional distillation. It was shown to be 99.99% pure by mass spectrometry. The observed triple point temperature and pressure

$$T_t = 90.640 \pm 0.004^\circ\text{K}$$

$$P_t = 87.77 \pm 0.02 \text{ mm Hg,}$$

agreed closely with the recent literature¹): $T_t = 90.66^\circ\text{K}$, $p_t = 87.50 \text{ mm Hg}$.

The deuteromethane was obtained from Merck and Co, Canada. It was shown to contain 2.73% CD_3H , 0.05% N_2 , and 0.003% O_2 by mass spectrometry.

The measured molar volumes of CH_4 at sixteen temperatures and of CD_4 at eleven temperatures are listed in tables I and II. They are accurately represented by the following quadratic equations in *T*, derived by the method of least squares:

$$v_{\text{CH}_4} = 31.9435 - 1.7608 \cdot 10^{-2} T + 6.6493 \cdot 10^{-4} T^2 \text{ cm}^3 \quad (3.1)$$

$$v_{\text{CD}_4} = 30.9108 - 0.7135 \cdot 10^{-2} T + 6.2429 \cdot 10^{-4} T^2 \text{ cm}^3, \quad (3.2)$$

with the respective mean quadratic deviations: 0.006 and 0.005 cm^3 . The relative accuracy is thus roughly $1.5 \cdot 10^{-4}$ in both cases; because of the uncertainty upon the volume of the calibrated cell, the final error on v_{CH_4} and v_{CD_4} is of the order of 0.008 cm^3 .

Actually what we called above v_{CD_4} is the molar volume of a mixture of

TABLE I

Experimental molar volumes of CH ₄			
T°K	Exp. vol. cm ³ mole ⁻¹	calc. eq. (3.1)	difference
98.20	36.631	36.626	+0.005
99.57	36.775	36.782	-0.007
100.88	36.937	36.934	+0.003
102.17	37.087	37.085	+0.002
103.55	37.255	37.250	+0.005
104.88	37.406	37.411	-0.005
106.24	37.584	37.578	+0.006
106.28	37.585	37.583	+0.002
107.57	37.754	37.743	+0.011
107.59	37.743	37.746	-0.003
107.63	37.754	37.750	+0.004
108.96	37.906	37.919	-0.013
108.17	37.917	37.920	-0.003
110.27	38.098	38.087	+0.011
110.29	38.083	38.089	-0.006
111.59	38.263	38.259	+0.004

TABLE II

Experimental molar volumes of CD ₄			
T°K	Exp. vol. cm ³ mole ⁻¹	calc. eq. (3.2)	difference
98.29	36.254	36.247	+0.007
99.58	36.400	36.400	0.000
100.93	36.554	36.557	-0.003
102.22	36.705	36.712	-0.007
103.48	36.858	36.865	-0.007
104.76	37.021	37.022	-0.001
106.32	37.217	37.216	+0.001
107.62	37.390	37.381	+0.009
108.97	37.554	37.555	-0.001
110.29	37.726	37.726	0.000
111.65	37.904	37.905	-0.001

97.3% CD₄ and 2.7% CD₃H. Assuming as usually that the volume of a mixture of hydrogeno- and deuterocompounds varies almost linearly with the *H* and *D* percentages, we extrapolated our results to 100% CD₄; this correction to (3.2) is very small (~ -0.003 cm³) and leads to:

$$v_{\text{CD}_4} = 30.9037 - 0.7063 \cdot 10^{-2}T + 6.2469 \cdot 10^{-4}T^2 \text{ cm}^3. \quad (3.3)$$

The difference between the molar volumes of CH₄ and CD₄ is then given by

$$\begin{aligned} \Delta v &= v_{\text{CH}_4} - v_{\text{CD}_4} \\ &= 1.0398 - 1.0545 \cdot 10^{-2}T + 0.4024 \cdot 10^{-4}T^2 \text{ cm}^3 \end{aligned} \quad (3.4)$$

with a relative accuracy of about $3 \cdot 10^{-2}$; Δv remains roughly equal to 1% of v_{CH_4} in the covered range of temperatures.

The absolute values of v_{CH_4} reported here are about one percent larger than those of Keyes⁵⁾ but it should be noticed that the dispersion in our experimental points is about ten times smaller than for this author. The reproductibility of our measurements which extended over several weeks and included various runs (at both ascending and descending T), was excellent and we believe therefore that our values for v_{CH_4} are worthy of consideration.

To our knowledge no data have been published yet in the literature for v_{CD_4} .

4. *Theoretical interpretation of Δv .* Let us tentatively assume that:

a) the intermolecular pair potentials for CH_4 and CD_4 are *isotropic* and *conformal* i.e.

$$\begin{aligned} u_{\text{CH}_4}(r) &= \varepsilon_H \varphi(r/\sigma_H), \\ u_{\text{CD}_4}(r) &= \varepsilon_D \varphi(r/\sigma_D); \end{aligned} \quad (4.1)$$

ε (= energy) and σ (= length) are characteristic of the molecular species, φ is a *universal* function and r is the intermolecular distance;

b) the translational motion of the molecules is quantized in the liquid region.

Under these assumptions CH_4 and CD_4 follow the generalized *quantum theorem of corresponding states* of De Boer^{6) 7)} and their molar volumes may be written as

$$\begin{aligned} v_{\text{CH}_4}(T) &= \sigma_H^3 [v_0(\tilde{T}_H) + v_1(\tilde{T}_H) \Lambda_H^2 + \dots] \\ v_{\text{CD}_4}(T) &= \sigma_D^3 [v_0(\tilde{T}_D) + v_1(\tilde{T}_D) \Lambda_D^2 + \dots] \end{aligned} \quad (4.2)$$

where $\tilde{T} = kT/\varepsilon$ (reduced temperature) and Λ is the translational quantum parameter

$$\Lambda^2 = h^2/M\varepsilon\sigma^2 \quad (4.3)$$

(M = molecular mass); $v_0(T)$ and $v_1(T)$ are *universal* functions.

In the present case Λ is sufficiently small to neglect higher order terms in (4.2). Also the relative differences in ε_D , ε_H and σ_D , σ_H , i.e.

$$\delta = \varepsilon_D/\varepsilon_H - 1, \quad \rho = \sigma_D/\sigma_H - 1, \quad (4.4)$$

are expected to be very small (less than or equal to $\sim 1\%$). The following expression may then be derived from (4.2) by means of a Taylor expansion:

$$\begin{aligned} \Delta v(T)/v_{\text{CH}_4}(T) &= -3\rho + \left(-\frac{T}{v_{\text{CH}_4}} \frac{dv_{\text{CH}_4}}{dT} \right) \delta \\ &\quad - (\Lambda_D^2 - \Lambda_H^2) \frac{v_1(\tilde{T}_H)}{v_0(\tilde{T}_H) + v_1(\tilde{T}_H) \Lambda_H^2}. \end{aligned} \quad (4.5)$$

The problem now is to see

a) if a relation such as (4.5) is compatible with the experimental results of section 3, and

b) which values of δ and ρ should be adopted.

We first estimate the last term of (4.5). The second virial coefficient data for CH_4 indicate that $\epsilon_H/k = 148^\circ\text{K}$, $\sigma_H = 3.82 \text{ \AA}$ ⁸). This gives:

$$A_H^2 = 0.057 \quad \text{and} \quad A_D^2 - A_H^2 = -0.0114.$$

(We neglect small differences between ϵ_D , σ_D and ϵ_H , σ_H in A_D^2 , which correspond to higher order effects). Our measurements of section 3 extend from 98 to 112°K which corresponds to

$$0.66 < \tilde{T} < 0.76$$

in reduced units. In this region the ratio

$$A(\tilde{T}) = \frac{v_1(\tilde{T})}{v_0(\tilde{T}) + v_1(\tilde{T}) A_H^2}$$

may be estimated from the earlier analysis of the quantum theorem of corresponding states by De Boer and Lunbeck⁷); this gives: $A(\tilde{T}) = 0.33 \pm 0.03$ and consequently

$$A(\tilde{T})(A_D^2 - A_H^2) = -0.0038 \pm 0.0004. \quad (4.7)$$

Substituting (4.7) into (4.5) and defining:

$$Z(T) = \Delta v(T)/v_{\text{CH}_4}(T), \quad X(T) = \frac{T}{v_{\text{CH}_4}} \frac{dv_{\text{CH}_4}}{dT}, \quad (4.8)$$

gives:

$$Z(T) = -3\rho + X(T) \delta + (0.0038 \pm 0.0004). \quad (4.9)$$

The way to obtain δ and ρ is clear:

a) we plot Z versus X for T between 98 and 112°K by using formulae (3.1) and (3.4); if the assumptions made in the beginning of this section are correct, this should give an almost straight line; fig. 3 shows this to be indeed the case;

b) the best estimates of δ and ρ are then obtained by the method of least squares; taking into account the respective errors ± 0.01 and 0.0002 upon X and Z , we found:

$$\begin{aligned} \delta &= -0.015 \pm 0.005, \\ \rho &= -0.0037 \pm 0.0007. \end{aligned} \quad (4.10)$$

These figures are close to the previous estimates of Thomaes and Van Steenwinkel⁴):

$$\delta \simeq -0.01, \quad \rho \simeq -0.002, \quad (4.11)$$

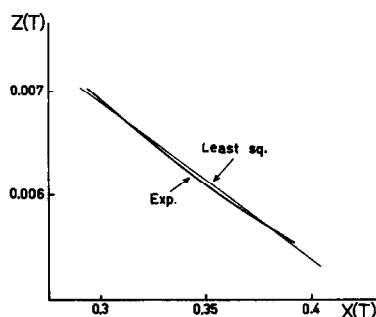


Fig. 3. Plot of $Z(T)$ versus $X(T)$; ($98 < T < 112^\circ\text{K}$)

which gives further support to the view that the intermolecular forces are slightly different in CH_4 and CD_4 .

However, these values of δ and ρ seem quite inconsistent with other properties of CH_4 and CD_4 (vapour pressure and triple point data), which tends to indicate that assumption (a) is an oversimplification: orientational forces and quantum rotational effects should probably be retained. This point is now under investigation.

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