3,3-Dimethylpiperidin (**9c**) *und 2-Imino-5,5-dimethyl-tetrahydropyran* (**11**). 106 g 2-(β-Cyanoäthyl)-isobutyraldehyd [1] werden in 300 ml Methanol in Gegenwart von *Raney*-Nickel bei 120° und einem Druck von 100 atü im Autoklav hydriert. Die fraktionierte Destillation über eine Füllkörperkolonne ergibt 40 g Vorlauf vom Sdp. 70–130°, 33,2 g **9c** vom Sdp. 130–136°, sowie 3,0 g einer Fraktion vom Sdp. 119–144°/10 Torr, die zum Teil fest wird. Durch Umkristallisation aus Petroläther erhält man reines **11** vom Smp. 123–125°.

$C_7H_{13}NO$	Ber.	C 66,10	H 10,30	N 11,01%
(127,19)	Gef.	,, 66,16	,, 10,50	,, 10,97%

MS. (m/e): 127 s.st. (M^+); 112 st. ($M^+ - CH_3$); 99 m. ($M^+ - C_2H_4$); 84 st., 70 st.; 56 s.st. – NMR. ($DCCl_3$): *ca.* 7–8 (br., 1 NH); 3,02 *d* (2 H); 2,36 *t* (2 H); 1,60 *t* (2 H); 1,03 *s* (2 CH_3).

Das Pikrat von **9c** kristallisiert aus Äthanol, Smp. 179–181°.

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245. Physico-Chemical Properties of Deuteriated Compounds

1st Communication

The Molar Volume of *n*-Heptane

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(17.VII.75)

Summary. The molar volumes of mixtures of perdeuteriated and protiated heptane have been measured between –10° and 40° and expressed as a second order polynomial of the weight fraction. The difference in molar volumes of about 0.4 ml/mol decreases with temperature. The possibility of using the density measurement to determine the degree of deuteriation of mixtures of partially deuteriated heptanes was examined. The percent deuteriation calculated by this method deviates systematically from the true values.

1. Introduction. – The measurement of vapour-pressure is the favorite object of study in the field of physico-chemical properties of perdeuteriated compounds [1] [2]. This might stem from the fact that its theory has achieved a high degree of sophistication. Other properties have received much less attention [3]. The probable explanation might be the difficulty in obtaining sufficient amounts of very pure deuteriated compounds at a reasonable price and the lack of theoretical background. Within this series we intend to contribute some results, mainly on deuteriated hydrocarbons, that we collected while producing deuteriated substances for a kinetic research. In the present work we discuss the density of heptane. Our primary goal was to check how well its measurement can be used to determine the degree of deuteriation of partially deuteriated heptane.

2. Experimental Part. – The *n*-heptane used was carefully distilled. No impurities could be detected either in the protiated (*Phillips Research* Grade) or in the deuteriated (99.6% degree of deuteriation) heptane by gas chromatography. The density measurements were done with an oscillator type densimeter (Digital Densimeter DMA 02C, manufactured by *Anton Parr K.G.*). The temperature was measured with a quartz thermometer (*Hewlett Packard* 2801A). For calibration of the densimeter we used *Phillips Research* grade hydrocarbons, air (corrected for ambient humidity) and carefully purified water (distilled and passed through a heated tube). A linear relationship between the density (API-values) and the square of the period of the oscillator was assumed. The average deviation from a straight line amounts to 1–2 · 10^{-4} in density for temperatures between – 10° ÷ 40° and corresponds to the results found by *Benson et al.* [4]. We therefore assume the absolute accuracy of our results to be ±0.02%. It will be shown later that the reproducibility is better by a factor of ten. The concentrations of the mixtures were obtained by weighing the separate compounds and checking by gas chromatography. The degree of deuteriation of a partially deuteriated heptane is also obtained by gas chromatography [5] [6].

3. Mixtures of protiated and deuteriated heptane. – *Sinclair & Vincent* have shown that the concentration dependence of the partial molar volumes in binary systems are better described by weight fractions than by mol fractions [7]. We made the same observation. We tried to express the reciprocal value of the density as a polynomial function of the weight fraction w for measurements at constant temperature:

$$1/d = a_0 + a_1 \cdot w + a_2 \cdot w^2 + \cdots \qquad (1)$$

Polynomials up to eighth order were tried; they did however not improve the results by a significant amount and the coefficients of the higher terms did not converge, so we limited ourselves to polynomials of the second order. All the results were obtained with a series of 17 binary mixtures of completly deuteriated and protiated heptane. A second series was measured at 20° in order to check for systematic errors. The results were identical within the error limits and are given in Table 1. The mean square of the residuals when the results were fitted to equation (1) corresponds to a residual error of a single density measurement of $\pm 5 \cdot 10^{-5}$

Table 1. *Coefficients of 1/d* (ml/g) *vs. w* (eq. (1))

T	a_0	a_1	$a_2 \cdot 10^3$
–10.04°	1.409′642	0.197′555	0.471
0.02°	1.427′116	0.200′045	0.348
10.15°	1.445′014	0.202′395	0.282
15.00°	1.453′542	0.202′844	0.792
19.88°	1.462′381	0.204′056	0.740
24.91°	1.471′508	0.205′135	0.721
30.00°	1.480′955	0.206′658	0.449
40.04°	1.499′606	0.208′540	0.751

The coefficients of eq. (1) can be used to express the molar volume $V_1(w,T)$ of the two compounds as a function of the weight fraction w:

$$\begin{aligned} V_H(w,T) &= V_H^0(T) + b_H(T)\,(1-w)^2 \\ V_D(w,T) &= V_D^0(T) + b_D(T) \cdot w^2 \qquad (2) \end{aligned}$$

where the coefficients $V_i(T)$ and $b_i(T)$ are connected to eq. (1) by the following equations:

$$\begin{aligned} V^0_H(T) &= M_H \cdot a_0 & b_H(T) &= M_H \cdot a_2 \\ V^0_D(T) &= M_D \cdot (a_0 + a_1 + a_2) & b_D(T) &= M_D \cdot a_2 \end{aligned} \qquad (3)$$

V_i and M_i represent the molar volume and the molecular weight (corrected for the degree of deuteriation) respectively.

The temperature dependence of the coefficients of eq. (1), of the molar volumes and of their difference $\Delta V = V^0_H(T) - V^0_D(T)$ is shown in Fig. 1. They can be expressed by the following equations (volumes in ml/mol, T in °).

$$V^0_H(T) \pm 0.020 = 143.003\,(1 + 1.222 \cdot 10^{-3} \cdot T + 1.18 \cdot 10^{-6} \cdot T^2) \qquad (4a)$$

$$V^0_D(T) \pm 0.016 = 143.568\,(1 + 1.238 \cdot 10^{-3} \cdot T + 1.40 \cdot 10^{-6} \cdot T^2) \qquad (4b)$$

$$\Delta V(T) \pm 0.005 = 0.435\,(1 - 4.02 \cdot 10^{-3} \cdot T - 7.2 \cdot 10^{-5} T^2) \qquad (4c)$$

$$b_H(T) \pm 9 \cdot 10^{-3} = 46 \cdot 10^{-3}\,(1 + 0.015 \cdot T) \qquad (4d)$$

$$b_D(T) \pm 9 \cdot 10^{-3} = 53 \cdot 10^{-3}\,(1 + 0.017 \cdot T) \qquad (4f)$$

The errors given on the left sides of equations (4) are the standard deviation of the values for the equation proposed. The molar volumes for the protiated and the fully deuteriated heptane differ by about 0.3%. This value decreases with temperature. This is more clearly seen when one expresses the logarithm of the volume as a function of temperature:

$$\ln(V_H \pm 0.010) = \ln V^0_H + \alpha \cdot T = \ln(143.015 \pm 0.013) + (1234 \pm 4) \cdot 10^{-6} \cdot T \qquad (5a)$$

$$\ln(V_D \pm 0.010) = \ln(142.570 \pm 0.015) + (1256 \pm 5) \cdot 10^{-6} \cdot T \qquad (5b)$$

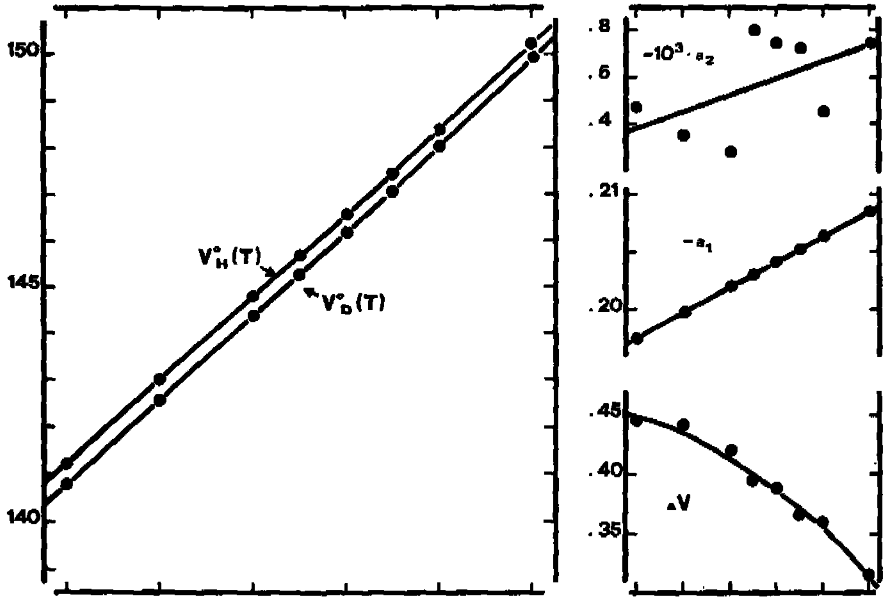

Fig. 1. *The temperature dependence of the molar volumes and their differences* (in ml/mol) *and the coefficients a_1 and a_2 of eq.* (1) (in ml/g)

Eq. (5) fit the temperature dependence slightly better than eq. (4). The thermal expansion coefficient α is significantly larger for the deuteriated compound.

The difference in the molar volumes corresponds to the results for *n*-octane (0.40 ml/mol) and 2,2,4-trimethylpentane (0.40 ml/mol) found by *Dixon & Marr* [8]. We believe that the smaller volume of the deuteriated compound can be explained by the smaller amplitude of the (C–D)-vibration compared of the (C–H)-vibration. With increasing temperature the increased population of the non all-*trans*-conformation tends to smear out this difference. The small but significant quadratic term b(T) is more difficult to understand since the mixture of a deuteriated and a protiated hydrocarbons should form a nearly ideal solution.

4. The degree of deuteriation. – The determination of the degree of deuteriation of a hydrocarbon containing all species between zero and the maximum number of deuterium atoms is a difficult problem. The best solution is probably to burn the hydrocarbon, convert the water into molecular hydrogen and determine its deuterium content by a mass-spectrometer equipped with a double collector. The direct determination from the mass-spectrometric fragmentation is a very unsafe procedure except for very high degrees of deuteriation. We have shown that the degree of deuteriation can be determined by gas chromatography [5]. In order to get the best precision it is necessary to separate all deuteriated species. This can be done routinely and an example is shown in Fig. 2. We have further checked that the response of the FID-detector shows no isotope effect within $<1\%$. We thus assume that the values obtained by gas chromatography are correct within the statistical error. The average standard deviation of a determination is $\pm$ 0.2% in units of the degree of deuteriation. It deteriorates somewhat at very high and very low values. We measured eight mixtures of different degrees of deuteriation. Their distribution is presented in Fig. 3, together with the degree of deuteriation D determined by gas chromatography and with the use of eq. (1). The latter values are the average from determinations at three different temperatures (10°, 20°, 30°) and were calculated by the following equation:

$$D = \frac{1}{16} \sum_{i=1}^{16} i \cdot x_i = w \cdot M_0/(M_{16} - 16 \cdot w) \tag{6}$$

where x_i is the mole fraction of the species $C_7H_{16-i}D_i$ with the molecular weight M_i. From the measurement at three temperatures we can determine the standard error for the determination of D as 0.08%. There is a large and systematic deviation of about 1.5% for D between the values obtained by gas chromatography and by

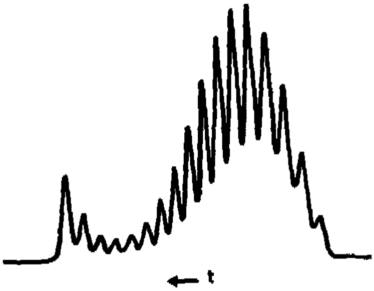

Fig. 2. *The gas chromatogram of a partially deuteriated heptane* (corresponds to Fig. 3e)

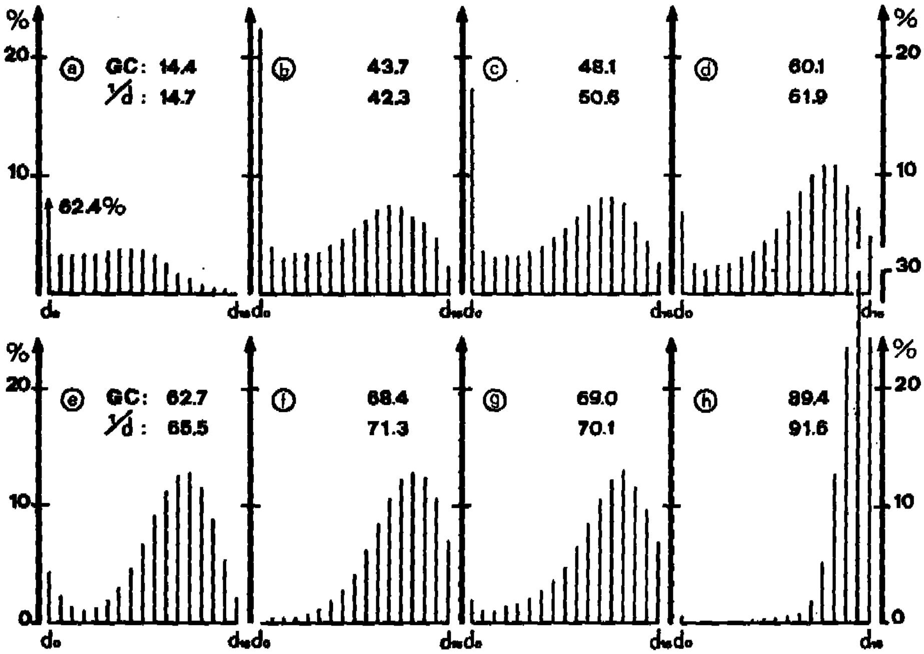

Fig. 3. *The distributions of the mixtures of partially deuteriated heptanes.* The figures given are the degrees of deuteriation determined either by gas chromatography (GC) or by density ($^1/d$)

density measurement. Since we believe that the values obtained by gas chromatography are the correct ones, this means that the determination of degree of deuteriation by density measurement is only correct within 1–2%. In many cases impurities may cause a larger error when determining the density in a routine operation.

The reason for this apparently systematic deviation could be that in a molecule that contains C–H and C–D groups the somewhat different vibration and internal rotation frequencies causes a change in the distribution between the different conformations of the chain and thus in the molar volume, compared with the totally deuteriated or protiated compound. A slight but significant increase of D (in %) with temperature of $(4.1 \pm 0.7) \cdot 10^{-3}/°$ is seen. This would mean that in most cases the difference in D determined by the two methods tends to increase with temperature. Nevertheless we do not know if this very small temperature effect is not due to some systematic error.

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