melting points of copolymers are ill-defined.[3] It is difficult to understand, however, why the lowering of T_m with reduction in degree of polymerization[2] does not appear to be subject to a corresponding error.

According to the results shown in Fig. 2, dimethylformamide is a far more potent solvent for the polyester than is diphenyl ether. Values of B' estimated from the slopes of the lines are $+8.0$ cal./cc. and -1.8 cal./cc., respectively.

TABLE I

MELTING TEMPERATURE OF POLYMER–DILUENT MIXTURES

Dimethylformamide		Diphenyl ether	
v_1	T_m, °C.	v_1	T_m, °C.
0.078	72.5 ± 0.5	0.123	74.5 ± 0.5
.202	66.5 ± .5	.180	71.5 ± .5
.422	61.5 ± .5	.410	59.5 ± .5
.603	57.5 ± .5	.594	50.5 ± .5

Experimental.—Decamethylene glycol and adipic acid, both carefully purified, were polymerized by heating without added catalysts at 160 to 217° under a reduced pressure of pure nitrogen for a total of 33 hours. A 2% excess of glycol over the amount required stoichiometrically was used in order to compensate loss of glycol by volatilization. The final viscosity at 109° was 1800 poises, corresponding to a number average molecular weight of 11,500.[8]

The solvents, dimethylformamide and diphenyl ether, were of reagent grade. The former was redistilled. Polymer–diluent mixtures were prepared by heating the ingredients with stirring as previously described.[3] The dilatometric procedures have been described elsewhere also.[3,4]

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[8] P. J. Flory, THIS JOURNAL, **62**, 1057 (1940).

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Steroids Derived from Bile Acids. XVII. Dehydrobromination of 3-Keto-4-bromosteroids with 2,4-Dinitrophenylhydrazine[1]

BY WARREN F. MCGUCKIN[2] AND EDWARD C. KENDALL

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When 3-keto-4-bromosteroids are treated with 2,4-dinitrophenylhydrazine in acetic acid hydrogen bromide is eliminated and a Δ^4-steroidal hydrazone is formed.[3a,b] The probable mechanism of this reaction has been discussed. Djerassi[4] believed that hydrogen bromide was eliminated before formation of the hydrazone. Mattox and Kendall[5] suggested that the hydrazone was formed with the atom of bromine at C-4 still intact and that subsequently hydrogen bromide was lost.

Isolation and identification of the 3-hydrazone of the 4-bromosteroid as an intermediate compound did not appear feasible since at room temperature the organically bound bromine rapidly appeared in solution as bromide ion.

It seemed probable that the bromohydrazone would be stable in relatively non-polar solvents, such as chloroform or benzene, but attempts to prepare this intermediate product in such solvents were unsuccessful. For this reason the postulated compound was prepared indirectly by bromination at C-4 of methyl 3,11-diketo-12α-bromocholanate 3-(2,4-dinitrophenylhydrazone) in chloroform. The 3-hydrazone of the 4-bromosteroid was isolated[5] in crystalline form and its physical characteristics were determined. When this compound was dissolved in acetic acid hydrogen bromide was spontaneously eliminated and the Δ^4-steroidal hydrazone was separated in excellent yield.

It has now been shown that when the 3-keto-4-bromosteroid was added to 2,4-dinitrophenylhydrazine in a 1:1 mixture of acetic acid and chloroform at 0° the 3-hydrazone of the 4-bromosteroid was formed and that at this temperature hydrogen bromide was very slowly eliminated. After the acetic acid had been removed by washing at 0° with water, the compound was obtained in a yield of 80% and was found to be identical with the material previously prepared by bromination of the saturated steroidal hydrazone. The separation of this unstable intermediate product furnishes additional support for the mechanism of the reaction suggested by Mattox and Kendall.

Methyl 3,11-Diketo-4,12α-dibromocholanate 3-(2,4-Dinitrophenylhydrazone).—To a solution of 500 mg. of 2,4-dinitrophenylhydrazine in 150 ml. of chloroform and 150 ml. of acetic acid which was freed of air with a stream of carbon dioxide and cooled to 0°, 559 mg. of methyl 3,11-diketo-4,12α-dibromocholanate was added and the mixture was agitated at intervals to effect complete solution. After 1.5 hours at 0°, 300 ml. of water was added, the chloroform solution was separated, washed quickly with dilute acetic acid, 0.10 *N* sulfuric acid, dilute sodium bicarbonate solution and water, and was filtered through a pad of sodium sulfate. The solution was concentrated immediately under reduced pressure to about 5 ml., diluted with 25 ml. of absolute ether and cooled in a Dry Ice–acetone-bath. The yellow crystals (591 mg.) which separated melted at 135–137°; $\lambda_{\max}^{\text{chloroform}}$ 361 mμ, ε 26,400; $[\alpha]_D$ $-162 \pm 2°$ (chloroform).

The melting point, optical activity and absorption spectra of the compound, in both the ultraviolet and infrared regions, were identical with those of an authentic sample which had been prepared by Dr. V. R. Mattox in this Laboratory by bromination of the saturated hydrazone.

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[1] Abridgment of portion of thesis submitted by Mr. McGuckin to the Faculty of the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Fellow in Biochemistry.

[3] (a) V. R. Mattox and E. C. Kendall, THIS JOURNAL, **70**, 882 (1948); (b) V. R. Mattox and E. C. Kendall, *J. Biol. Chem.*, **185**, 601 (1950).

[4] Carl Djerassi, THIS JOURNAL, **71**, 1003 (1949).

[5] V. R. Mattox and E. C. Kendall, *ibid.*, **72**, 2290 (1950).

High Vapor Pressure of *n*-Hexadecafluoroheptane[1]

BY H. T. MILTON AND GEORGE D. OLIVER

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Recently the vapor pressure of this compound below two atmospheres was published with other thermodynamic properties.[2] In the course of testing a method to determine critical temperature and pressure, by means of vapor pressure measurements in the region of the critical point, vapor pressure data were measured on *n*-hexadecafluoroheptane from two atmospheres to the critical point.

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[1] This document is based on work performed for the Atomic Energy Commission by Carbide and Carbon Chemicals Division Union Carbide and Carbon Corporation, Oak Ridge, Tennessee.

[2] G. D. Oliver and J. W. Grisard, THIS JOURNAL, **73**, 1688 (1951).

The sample was taken from a batch of *n*-hexadecafluoroheptane purified in this Laboratory and had a purity of 99.97 mole % as determined from a time–temperature freezing curve. Briefly, the apparatus consisted of two metal boiling point tubes connected to a common pressure system containing helium. The helium pressure in the system was maintained constant while the boiling temperature in each tube was measured with a platinum resistance thermometer.[2] The boiling temperature of the sample in one tube was compared directly with that of water in the other. Thus, the precise vapor pressure of the sample was interpolated from the steam tables[3] by using the boiling temperature of the water.

The present measurements which slightly overlap the former data[2] are listed in Table I. Accuracy of the pressure values is dependent on the accuracy of the steam tables, while the temperature was measured to about ±0.01°. Extrapolated data, based on the low pressure equation, deviate from the experimental data less than 0.1% of the pressure at observed temperatures as high as 136°.

TABLE I

VAPOR PRESSURE OF *n*-HEXADECAFLUOROHEPTANE

$t_{\text{obsd.}}$, °C.	$P_{\text{obsd.}}$, p.s.i.a.[a]	$t_{\text{obsd.}}$, °C.	$P_{\text{obsd.}}$, p.s.i.a.[a]	$t_{\text{obsd.}}$, °C.	$P_{\text{obsd.}}$, p.s.i.a.[a]
94.89	21.53	129.98	54.66	180.01	157.2
100.92	25.62	136.04	62.94	187.98	182.4
104.84	28.61	144.05	75.45	196.05	211.4
110.04	32.96	156.03	97.63	198.24	220.0
117.87	40.47	164.08	115.1	200.79	230.7
125.96	49.53	171.87	134.7	201.5 (t_c)	234 (p_c)

[a] 1 p.s.i.a. = 51.715 mm.

A pressure–temperature plot of the experimental data in the region of the critical point resulted in a line whose slope approached infinity at a temperature of 201.5 ± 0.1° and pressure of 234 ± 2 p.s.i.a. These critical values check previously reported data on *n*-hexadecafluoroheptane determined by another method.[2]

(3) N. A. Osborne and C. H. Meyers, *J. Research Natl. Bur. Standards*, **13**, 1 (1934).

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The Neglected Term in the Guggenheim Equation for Calculation of Dipole Moment from Solution Data

BY SANTI R. PALIT

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For determination of dipole moment in solution it has been the general practice to experimentally obtain dielectric constant, ϵ, refractive index, n and density, d in dilute solutions. Guggenheim[1] has however shown recently from some simplifying assumptions that density data of a very high order of accuracy are not necessary for such calculations, and density values of say 1% accuracy are quite satisfactory for dipole moment calculations. Smith[2] following Guggenheim has gone a step further and has shown that solution density measurements are not at all necessary for such calculations and Guggenheim[3] has very recently reiterated the stand of Smith and has introduced further simplifications.

The above authors have obtained their results under a few assumptions which are not wholly justifiable. Palit and Banerjee[4] have lately proposed that a rational approach to the problem of computation of polarization without involving any assumption should be through the concept of partial specific polarization and the technique already developed and used in the computation of other partial quantities should be applied to such calculations. The purpose of the present note is (1) to demonstrate that the Guggenheim–Smith equation is directly derivable from the method of Palit and Banerjee under some simplified conditions, (2) to deduce the complete equation for such computation, (3) to make an exact analysis of the error introduced by using the Guggenheim–Smith approximate equation, and (4) to obtain a satisfactory and exact answer to the moot question of how far solution density measurements are necessary for the computation of dipole moment.

Derivation of the Complete Equation.—Our starting point is the well known equation of partial quantity, which applied to polarization as suggested by Palit and Banerjee[4] can be expressed as equation (1)

$$ {}_\infty p_2 = (\bar{p}_2)_{w_2 \rightarrow 0} = p_1 + (\partial p/\partial w_2)_{w_2 \rightarrow 0} \qquad (1) $$

where p is polarization and is equal to $\frac{\epsilon - 1}{\epsilon + 2} \times \frac{1}{d}$ according to the well known Debye equation, w is weight fraction, and the subscript 1 and 2 refer to solvent and solute, respectively. Putting the above value of p in equation (1) and carrying out the differentiation, and proceeding to the limit $w_2 \rightarrow 0$, *i.e.*, infinite dilution, we obtain

$$ {}_\infty p_2 = p_1 (1 - (\partial d/\partial w_2)_0/d_1) + \frac{3\,(\partial \epsilon/\partial w_2)_0}{d_1(\epsilon_1 + 2)^2} \qquad (2) $$

where the subscript zero stands for $w_2 \rightarrow 0$, *i.e.*, infinite dilution of the solute. Let us designate the concentration coefficients at infinite dilution of dielectric constant and density by α_0 and β_0, respectively, when we get

$$ {}_\infty p_2 = p_1 \left(1 - \frac{\beta_0}{d_1}\right) + \frac{3\alpha_0}{d_1(\epsilon_1 + 2)^2} \qquad (3) $$

which is the same as the equation of Le Fèvre and co-workers[5] obtained by a different route.

Since refraction, $r = \frac{n^2 - 1}{n^2 + 2} \times \frac{1}{d}$, we can write an exactly analogous equation, *viz.*

$$ {}_\infty r_2 = r_1 \left(1 - \frac{\beta_0}{d_1}\right) + \frac{3\gamma_0'}{d_1(n_1^2 + 2)^2} \qquad (4) $$

where

$$ \gamma_0' = \left(\frac{\partial n^2}{\partial w_2}\right)_0 = 2n_1 \left(\frac{\partial n}{\partial w_2}\right)_0 = 2n_1\gamma_0 $$

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(1) E. A. Guggenheim, *Trans. Faraday Soc.*, **45**, 714 (1949).

(2) J. W. Smith, *ibid.*, **46**, 394 (1950).

(3) E. A. Guggenheim, *ibid.*, **47**, 573 (1951).

(4) S. R. Palit and B. C. Banerjee, *ibid.*, **47**, 1299 (1951).

(5) R. J. W. Le Fèvre and H. V. Vine, *J. Chem. Soc.*, 1805 (1937).