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

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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)

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

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 $w_2 \to 0$, *i.e.*, infinite dilution, we obtain

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

where the subscript zero stands for $w_2 \to 0$, *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).

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TABLE I

COMPARATIVE CALCULATION OF ORIENTATION POLARIZATION OF ANILINE AND DERIVATIVES

	System	B	A	C	$P_{2\mu}$ Eqn. (9)[a] $B + A - C$	Eqn. (6)[b]	Eqn. (1)[c]	Original authors[d]
1	Aniline in benzene	0.422	51.372	4.188	47.61	47.36	47.61	47.65
2	Aniline in dioxane	2.961	69.486	8.354	64.09	64.28	64.25	64.19
3	Methylaniline in benzene	0.4980	60.9700	4.2460	57.22	57.02	56.96	56.99
4	Methylaniline in dioxane	3.6130	75.5780	8.9340	70.25	69.99	70.25	70.49
5	Dimethylaniline in benzene	0.5876	55.9100	4.4841	52.01	52.17	52.91	52.89
6	Dimethylaniline in dioxane	4.2534	61.3510	8.6570	56.95	56.65	56.56	56.58
7	Trimethylamine in benzene	0.9753	8.5038	−7.3397	16.82	...	16.93	17.0

[a] Derived quantities are as follows, where α_0, β_0, β_0', γ_0 and γ_0' are the concentration coefficients of α, d, $\vartheta = 1/d$, n and n^2, respectively, which were obtained by statistical least square evaluation of Δ/w_2 for these quantities. Of course, $\beta_0 = -\beta_0'/\vartheta_1^2$ and $2n_1\gamma_0 = \gamma_0'$: (1) $\alpha_0 = 2.933$, $\beta_0' = -0.1720$, $\gamma_0' = 0.2361$; (2) $\alpha_0 = 0.4520$, $\beta_0' = -0.012$, $\gamma_0' = 0.496$; (3) $\alpha_0 = 3.025$, $\beta_0' = -0.1348$, $\gamma_0 = 0.0694$; (4) $\alpha_0 = 4.271$, $\beta_0' = 0.0421$, $\gamma_0 = 0.1623$; (5) $\alpha_0 = 2.4528$, $\beta_0' = -0.09373$, $\gamma_0 = 0.0648$; (6) $\alpha_0 = 3.0568$, $\beta_0' = 0.0843$, $\gamma_0 = 0.13906$; (7) $\alpha_0 = 0.4468$, $\beta_0' = 0.2213$, $\gamma_0 = -0.378$. [b] $[\partial(p - r)/\partial w_2]_0 =$ (1) 0.5086, (2) 0.6580, (3) 0.5269, (4) 0.6209, (5) 0.4253, and (6) 0.4381. [c] The curvilinear regression equations are: $-p = p_1 + bw_2 + cw_2^2 =$ (1) $0.34089 + 0.050005\,w_2 - 0.13787\,w_2^2$; (2) $0.27854 + 0.74349\,w_2 - 0.70365\,w_2^2$; (3) $0.34090 + 0.52860\,w_2 - 0.25007\,w_2^2$; (4) $0.27855 + 0.71518\,w_2 - 0.57908\,w_2{}^2$; (5) $0.34088 + 0.43565\,w_2 - 0.210003\,w_2^2$; (6) $0.34088 + 0.43565\,w_2 - 0.21003\,w_2^2$; (7) $0.34086 + 0.15361\,w_2 - 0.33226\,w_2^2$. [d] Few and Smith assumed $0.05R = P_A$, which has been compensated for in this column, as all our calculations neglect P_A.

It may be mentioned that the possibility of treating refraction by the partial method has already been hinted at by Guggenheim[6] and equation (4) has already been deduced by Everard and Sutton.[7] Now

$$(\,_\infty p_2)\text{ orientation} = p_{2\mu} = \,_\infty p_2 - \,_\infty r_2 \qquad (5)$$

By combining equation (5) with equations (3) and (4), we have

$$p_{2\mu} = (p_1 - r_1) + \left(\frac{\partial(p - r)}{\partial w_2}\right)_0 \qquad (6)$$

$$p_{2\mu} = \left[\frac{3(\epsilon_1 - n_1^2)}{d_1(\epsilon_1 + 2)(n_1^2 + 2)}\left(1 - \frac{\beta_0}{d_1}\right)\right] + \left[\frac{3\alpha_0}{d_1(\epsilon_1 + 2)^2}\right] - \left[\frac{6n_1\gamma_0}{d_1(n_1^2 + 2)^2}\right] \qquad (7)$$

$$p_{2\mu} = b + a - c \qquad (8)$$

$$\therefore P_{2\mu} = B + A - C \qquad (9)$$

where a, b and c are the three specific terms containing α_0, β_0 and γ_0, respectively, and A, B and C are the three corresponding molar terms in equation (7). Equation (7) is an exact equation but it differs from the Guggenheim–Smith equation in that it has an extra term, which we have chosen to call B.

Derivation of Guggenheim Approximate Equation.—Evidently equation (7) transforms into the Guggenheim equation when $B = 0$. Now B reduces to zero under any of the three conditions, *viz.*, (1) $\epsilon_1 = n_1^2$ or (2) $\beta_0 = d_1$ or (3) the atomic polarizability which has been neglected in the above derivation is assumed to be equal to B.

We can write our exact equation (7) also in the following modified form

$$P_{2\mu} = B + \frac{3M_2}{d_1(\epsilon_1 + 2)^2}\left[\frac{\partial(\epsilon - k^2n^2)}{\partial w_2}\right]_0 \qquad (10)$$

where

$$k = (\epsilon_1 + 2)/(n^2 + 2)$$

If $\epsilon_1 = n_1^2$, we have

$$P_{2\mu} = \frac{3M_2}{d_1(\epsilon_1 + 2)^2}\left[\frac{\partial}{\partial w_2}(\epsilon - n^2)\right]_0 \qquad (11)$$

which is exactly the same as the final modified Guggenheim equation of Smith (Smith's equation 9).

Comparative Calculations by the Guggenheim Equation and Our Exact Equation (7).—We have recalculated all data of Few and Smith[8] in the two solvents benzene and dioxane and the results are shown in Table I. Values of α_0, β_0 and γ_0 which have been obtained by statistical least square calculation of Δ/w_2 on the actual data, were not available in Smith[2] and Few and Smith,[8] have also been included.

It would be seen that our calculated values using all the three equations (1), (6) and (9) show excellent agreement with those of the original authors. It is clear therefore that the Guggenheim–Smith procedure which in effect neglects the contribution in our B-term in our exact equation (9) must be in error by at least this amount which is about half to one unit in benzene and a few units in dioxane. An extreme case may be cited to show the danger of an indiscriminate use of Guggenheim procedure. $P_{2\mu}$ for tribromodimethylaniline in dioxane calculated according to our equation (9) is 25.79 cc. ($P_{2\mu} = B + A - C = 6.02 + 38.89 - 19.12 = 25.79$) as against the original authors[9] value 24.89, whereas Guggenheim procedure would lead to an error of about 23% because the B-term alone contributes 6.02 cc. in this case. The error is higher, the more ϵ_1 differs from n_1^2 or the smaller β_0 becomes. Similar conclusions have been arrived at recently by Iyengar[10] from an assumption of linear dependence of specific volume on concentration by purely algebraic method.

In the same table we have included a calculation of trimethylamine with data from Barclay, Le Fèvre and Smythe[11] because Guggenheim[3] using the same data obtained a "surprisingly" low result ($P_{2\mu} = 15.4$). It is evident from our calculations that by neglecting B, $P_{2\mu}$ is bound to be low by about one unit; the remaining part of the dis-

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(6) E. A. Guggenheim, "Thermodynamics," Second Edition, North Holland Publishing Co., Amsterdam, 1950, p. 172.

(7) W. B. Everard, R. A. W. Hill and L. E. Sutton, *Trans. Faraday Soc.*, **46**, 417 (1950).

(8) A. V. Few and J. W. Smith, *J. Chem. Soc.*, 753 (1949).

(9) A. V. Few and J. W. Smith,, *ibid.*, 2663 (1949).

(10) B. R. Y. Iyengar, *Current Science (India)*, **19**, 282 (1950).

(11) G. A. Barclay, R. J. W. Le Fèvre and B. M. Smythe, *Trans. Faraday Soc.*, **46**, 812 (1950).

crepancy is of course due to his using a slightly lower value of α_0.

It may be pointed out that our $P_{2\mu}$ values calculated from the different equations, (1), (7), (9) or (10), the last being not included in the table, show excellent agreement among themselves. Equation (7), (9) or (10) though essentially the same equation, does not, however, give exactly identical values because of statistical treatment of data to obtain the limiting slopes.

Smith has obtained agreement in such cases where $\epsilon_1 \neq n_1^2$ by applying a number of simplified equations. It can be shown easily by an analysis of the above data on A, B and C that the agreement is fortuitous. For example, we cannot neglect B for aniline in dioxane because B is about 4.7% of P_2 and so, if we neglect B and put the atomic polarization, $P_A = 0.05R$ the errors cancel each other.

In another case, he makes the simplification

$$P_{2\mu} = \frac{3M_2\vartheta_1}{(\epsilon_1 + 2)(n_1^2 + 2)}\left[\frac{\partial(\epsilon - n^2)}{\partial w_2}\right]_0 \qquad (12)$$

and obtains fairly good agreement. Comparing this with our complete equation (eqn. 7) it is seen that he is neglecting B and to compensate for that he is increasing the A term by dividing by $(\epsilon_1 + 2)(n_1^2 + 2)$ instead of with $(\epsilon_1 + 2)^2$ and is decreasing the C term by the same procedure which also increases $P_{2\mu}$ to a smaller extent. It just happens that in this case these two increments nearly cancel the error made by neglecting B.

Question of Solution Density Measurements.—The attractive feature of the Guggenheim–Smith equation, however, could be retained without perceptibly sacrificing accuracy. This can be done by neglecting β_0/d_1, in comparison to unity in the B-term in equation (7). In such a case no solution density measurements are required and the equation takes the form

$$P_{2\mu} \backsimeq \frac{3M_2(\epsilon_1 - n_1^2)}{d_1(\epsilon_1 + 2)(n_1^2 + 2)} + \frac{3M_2\alpha_0}{d_1(\epsilon_1 + 2)^2} - \frac{3M_2\gamma_0'}{d_1(n_1^2 + 2)^2} \qquad (13)$$

The error by such approximation would hardly exceed 1% under very unfavorable conditions and would usually be less than 0.2 unit of orientation polarization even in solvents like dioxane. At any event this simplified B-term can be calculated for any solvent and the effect of neglecting β_0 can be easily judged because β_0 generally lies between -0.3 to $+0.3$. In case it seems rather risky to neglect β_0, it is safe to take density measurement correct to only 1% for one solution and calculate $(d - d_1)/w_2$ and use the same value for β_0. The error would be hardly appreciable.

Conclusions.—From the above discussion it is now possible to conclude that for calculations of $_\infty p_2$ it is best to directly employ equation (1) as suggested by Palit and Banerjee,[4] the value of $(\partial p/\partial w_2)_0$ being obtained by least square analysis by expressing p in the form, $p = p_1 + bw_2 + cw_2^2$.

For obtaining $P_{2\mu}$ by simultaneous measurement of dielectric constant, refractive index and density it is advisable to use the complete equation in either of the forms of equation (6) or equation (7) or equation (10), the first one being a little simpler in computation. In case it is intended to avoid solution density measurements, equation (13) should be used, which would usually give results within a few tenths of a unit. However, if great precision is aimed at without series of solution density measurements, it is advisable to take one solution of concentration nearabout the mean of the whole range studied and to measure its density correct to only 1% and therefrom to calculate $(d - d_1)/w_2$ which is used as β_0 in equation (7). The difference in the calculated $P_{2\mu}$ would be hardly perceptible. Another method of making a fairly good estimate of β_0 from refractive measurements alone would be to use equation (4), $_\infty r_2$ being known from bond refraction tables; by the same principle, if β_0 is determined in one solvent it is possible to calculate its value in other solvents by using this equation.

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2-Methyl-2-monoalkylaminopropyl Aromatic Heterocyclic Carboxylates[1]

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Esters of 2-amino-2-monoalkylamino-1-propanols with alkoxybenzoic acids,[2] alkoxycinnamic acids, hydrocinnamic acids, alkoxyhydrocinnamic acids[3] and p-aminobenzoic acids[4] have been prepared for use as local anesthetics. Since several thiophene, furan and pyridine analogs of some benzene-containing local anesthetics have been found to have some activity,[5] it seemed advisable to prepare a few esters of 2-methyl-2-monoalkylamino-1-propanols with furoic acid, nicotinic acid and 2-thiophenecarboxylic acid.

2-Methyl-2-monoalkylaminopropyl furoates were prepared by condensing the alkanolamines with furoyl chloride, with no solvent, and were isolated as the hydrochlorides. The corresponding 2-thiophenecarboxylate hydrochlorides were formed from the alkanolamine hydrochlorides with 2-thiophenecarboxylyl chloride, with no solvent. 2-Methyl-2-n-amylaminopropyl nicotinate was prepared by the reaction, in chloroform solution, of nicotinyl chloride hydrochloride and the alkanolamine hydrochlo-

(1) Acknowledgment is made to Dr. E. Emmet Reid, Research Adviser to the Chemistry Department of the University of Richmond, for his advice in this work.

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