

Thermodynamic Functions for Fluorine

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solvent. We assumed that this small difference was responsible for such results.

From Debye's equation it appears that, when the refractive index difference between the solution and the solvent is very small, the turbidity of the solution must be also very small.

We planned an experiment to have another test of the value of Debye's equation for very small refractive index differences. Using tetrachlorethane as a solvent and cellulose acetate as a solute we obtained what was desired, because the values of the refractive indices of both are very close to each other. We made the value of $n-no$ very close to zero by the addition of ethylene chloride to the solution. We prepared a mixture of solvents of the same composition and we presumed that the turbidity due to the solute would be very small because of the negligible value of $n-no$.

The turbidity of the solution was found to be one time and a half that of the solvent mixture. This yields a value of about ten million for the molecular weight compared with a viscosity molecular weight of 60,000 for the same polymer.

TABLE I.

Solvent	Solute	$\left(\frac{n-no}{c}\right)^2$		Molecular weight	
				(Light scattering)	(Viscosity)
Ethylene chloride	GR-S	27.2	$\times 10^{-3}$	140,000	125,000
Carbon tetra-chloride	GR-S	14.4	$\times 10^{-3}$	120,000	125,000
Toluene	GR-S	3.1	$\times 10^{-3}$	1,000,000	125,000
Tetrachloroethane	Cellulose acetate	0.036	$\times 10^{-3}$	10,000,000	60,000

Table I gives the value of light-scattering molecular weight compared with viscosity molecular weight. For each solution we give the value of $[(n-no)/c]^2$.

The results of turbidity measurements are in good agreement with viscosimetric determinations for the first solutions where the value of $[(n-no)/c]^2$ is large enough. When this value decreases, the difference between viscosimetric and light-scattering determinations increases very rapidly.

The results tabulated in Table I indicate that Debye's equation is correct only under certain conditions and one of those conditions is to have a large enough value of $n-no$.

¹ P. J. Debye, *J. Phys. Colloid Chem.* 51, 18 (1947).

The Structure of Nitrosyl Chloride from the Microwave Absorption Spectrum

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September 13, 1950

THE recent note¹ on the microwave absorption of NOCl gave the values for the moments of inertia listed in Table I.

TABLE I.

	Microwave		Electron diffraction NOCl ^{3,5}
	NOCl ^{3,6}	NOCl ^{3,7}	
I_C	152.59 \pm 0.04	153.05 \pm 0.08	156.7
I_B	147.33 \pm 0.03	148.12 \pm 0.08	147.7
I_A	5.27 \pm 0.07	4.93 \pm 0.16	9.05

Those obtained by electron diffraction² are listed for comparison. (All moments of inertia are expressed in units of 10^{-40} c.g.s.)

Calculation of the molecular dimensions from the microwave data leads to a bond distance for NO in NOCl which is less than

1.080 Å. This is so much less than 1.150 Å which is the NO distance³ in the nitric oxide molecule that it would seem to be an unlikely value for the NO distance. The entropy at 298°K calculated⁴ with the electron diffraction value of the least moment of inertia agrees within the experimental error with the observed value, whereas the entropy calculated with the least moment of inertia obtained from microwave absorption gives a value which is 1.0 entropy unit lower than the observed value. This is well beyond the discrepancy permitted by experimental error.

The observed frequencies for the transitions between rotational levels were used for determining I_C and I_B whereas I_A was found from the sum rule ($I_C = I_B + I_A$) since the data are not sufficiently accurate to obtain I_A from the frequency reported for the $1_{-1} \rightarrow 2_{-2}$ transition.

The microwave value for I_A obtained from the sum rule is not compatible with the geometry of the molecule nor the observed value of the entropy, whereas the value of I_A determined by electron diffraction is quite suitable.

Higher accuracy in determining the frequencies in the microwave spectra is needed before a value for I_A can be obtained with an accuracy which is comparable to that obtained by electron diffraction, viz., $9.05 \pm 0.50 \times 10^{-40}$ c.g.s. unit.

¹ Pietenpol, Rogers, and Williams, *Phys. Rev.* 77, 741 (1950).

² J. A. A. Ketelaar and K. J. Palmer, *J. Am. Chem. Soc.* 59, 2629 (1937).

³ G. Herzberg, *Diatomic Molecules* (Prentice-Hall, Inc., New York, 1939), p. 490.

⁴ W. G. Burns and H. J. Bernstein (in press).

Thermodynamic Functions for Fluorine

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September 21, 1950

MOLECULAR data were used by us¹ some years ago to calculate the entropy, free energy, and heat capacity of fluorine gas. Our results, however, were subject to slight uncertainties since the value of the internuclear distance of the molecule came from a preliminary electron diffraction result of Brockway² and the vibrational frequency, in the absence of a direct spectroscopic measurement, had to be estimated by the use of Badger's rule.³

These two sources of uncertainty have now been removed, as Rogers, Schomaker, and Stevenson⁴ have reported a more precise electron diffraction result and, recently, Andrychuk⁵ has observed the Raman spectrum of gaseous fluorine. It has thus seemed useful to recalculate our 1939 results using the new molecular constants. At the same time, we have thought it worth while to use the revised values of the natural constants, Avogadro's number, Planck's constant, etc. For the latter purpose, we have taken the working formulas given by Wagman *et al.*⁶

Our earlier values for the internuclear distance and vibrational frequency, with their estimated probable errors were $r_0 = 1.45 \pm 0.05$ Å; $\omega_0 = 856 \pm 17$ cm⁻¹; the revised values are $r_0 = 1.435 \pm 0.01$ Å; $\omega_0 = 892.1 \pm 2$ cm⁻¹. With the latter data, we have calculated the thermodynamic quantities shown in Table I by the

TABLE I. Thermodynamic functions of fluorine gas, F₂ (in cal./mole).

$T, ^\circ K$	$-(F^\circ - H^\circ)/T$	S°	C_p°
298.16	41.412	48.484	7.466
300	41.455	48.530	7.474
400	43.510	50.734	7.853
500	45.139	52.519	8.135
600	46.498	54.020	8.331
800	48.696	56.453	8.566
1000	50.446	58.379	8.691
1200	51.905	59.970	8.763
1400	53.156	61.325	8.809
1600	54.253	62.503	8.839
1800	55.228	63.546	8.860
2000	56.108	64.480	8.876

well-known methods for the rigid rotator-harmonic oscillator molecular model. In comparing our present results with the earlier ones, it will be observed that the latter are larger in each case. The differences in the free energy function, $-(F^0 - H_0^0)/T$ range from 0.08 to 0.14 cal./mole, the two figures referring to 298.16° and 2000°, respectively. For the entropy, the corresponding differences are 0.09 to 0.16 and for the heat capacity, 0.06 to 0.00. It should be remembered, however, that these variations are from two sources: change in the fundamental natural constants and change in the molecular constants.

Lack of a reliable value for the heat of dissociation of fluorine into atoms or the heat of dissociation for another fluorine containing molecule prevents us from recalculating equilibria involving fluorine or fluorine compounds. This difficulty was discussed in our earlier paper and has been considered more recently by Gaydon,⁷ Potter,⁸ and Nathans.⁹ It appears that this source of uncertainty can only be removed when further experimental data are available.

- ¹ G. M. Murphy and J. E. Vance, *J. Chem. Phys.* **7**, 806 (1939).
² L. O. Brockway, *J. Am. Chem. Soc.* **60**, 1348 (1938).
³ R. M. Badger, *J. Chem. Phys.* **2**, 128 (1934); **3**, 710 (1935).
⁴ Rogers, Schomaker, and Stevenson, *J. Am. Chem. Soc.* **63**, 2610 (1941).
⁵ D. Andrychuk, *J. Chem. Phys.* **18**, 233 (1950).
⁶ Wagman, Kilpatrick, Taylor, Pitzer, and Rossini, *J. Research Nat. Bur. Stand.* **54**, 143 (1945).
⁷ A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules* (Dover Publications, Inc., New York, 1950).
⁸ R. L. Potter, *J. Chem. Phys.* **17**, 957 (1949).
⁹ M. W. Nathans, *J. Chem. Phys.* **18**, 1122 (1950).

The Infra-Red Spectra of Propane and 2,2-Dideuteropropane

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 June 29, 1950

IN an earlier paper¹ the frequency assignments for the vibrational modes of propane were discussed in the light of the infra-red spectra of 1-deuteropropane and 2-deuteropropane. We have since obtained the spectrum of a sample of 2,2-dideuteropropane estimated to be 98 percent pure.² This spectrum, together with that of propane for comparison, is shown in Fig. 1.

The new data show that the three type B_1 bands below 1350 cm^{-1} in the propane spectrum have analogs at markedly lower frequencies in the 2,2-dideuteropropane spectrum.³ The changes on going from propane to 2,2-dideuteropropane are 1336 to 1199, 1053 to 964, 923 to 850 cm^{-1} . These modes, belonging to species B_1 , involve rocking motions of the CH_3 groups and the CH_2 (or CD_2) group about axes normal to the plane of the carbons, and the unsymmetrical C—C—C stretching motion. Since the frequencies of all three modes are sensitive to substitution of CD_2 for CH_2 ,

the CH_2 rocking motion in propane is seen to interact strongly with the CH_3 rocking and unsymmetrical C—C—C stretching motions. It is, therefore, unrealistic to describe the low frequency modes of species B_1 in propane as specific group vibrations.

The present data, together with available Raman data, permit reasonable assignments for the approximate frequencies of all the modes belonging to species A_1 and B_1 in both propane and 2,2-dideuteropropane. These are given in Table I. The ratios for

TABLE I. Frequencies of the A_1 and B_1 modes in propane and 2,2-dideuteropropane.

Symmetry	Propane frequency ^a	2,2-Deutero-propane frequency ^a	Propane modes ^d
A_1	2940 (cm^{-1})	2920 (cm^{-1})	CH_3 u. st.
	2940	2920	CH_3 sy. st.
	2940	2160	CH_2 (CD_2) sy. st.
	1460	1460	CH_2 u. def.
	1460	1062	CH_2 (CD_2) def.
	1380	1380	CH_2 sy. def.
	1155(?)	1140(?)	CH_2 r. plus C—C—C sy. st.
	870	850	C—C—C sy. st. plus CH_2 r.
B_1	372 ^b	370 (est.)	CCC def.
	2940	2920	CH_3 u. st.
	2940	2920	CH_3 sy. st.
	1460	1460	CH_2 u. def.
	1380	1380	CH_2 sy. def.
	1336	1199	CH_2 (CD_2) r. plus
			CH_2 r. and C—C—C u. sy. st.
	1053	964	CH_2 (CD_2) r. plus
			CH_2 r. and C—C—C u. sy. st.
	923	850	C—C—C u. sy. st. plus
			CH_2 r. and CH_2 (CD_2) r.

^a Where bands are nearly superposed the frequency is generally near the center of the absorption. Bands of doubtful origin are indicated by (?), estimated values for unobserved frequencies by (est.).

^b Obtained for gaseous propane by J. R. Nielsen and C. M. Richards (unpublished).

^c The abbreviations u., sy., st., def., r. stand for unsymmetrical, symmetrical, stretching, deformation, and rocking, respectively. When the mode in 2,2-dideuteropropane involves the CD_2 this is placed after CH_2 in parenthesis, i.e., $\text{CH}_2(\text{CD}_2)$.

^d Where possible the modes are characterized by the most important group motions involved in them. They are given in more detail in Table I of reference 1.

TABLE II. Moments of inertia of propane.^a

	I_x	I_y	I_z
$\text{CH}_3\text{CH}_2\text{CH}_3$	67.6	17.3	59.6
$\text{CH}_3\text{CD}_2\text{CH}_3$	70.4	21.9	61.3

^a The z axis is the symmetry axis. The x and y axes are principal axes normal to the z axis, and normal to the plane of the carbons and in this plane, respectively. The units are atomic weight times angstroms squared. The C—C and C—H (or C—D) distances are 1.54 and 1.09 Å, respectively. All angles are tetrahedral except the C—C—C angle which is $111^\circ 30'$ (see K. S. Pitzer, *J. Chem. Phys.* **12**, 310 (1944)).

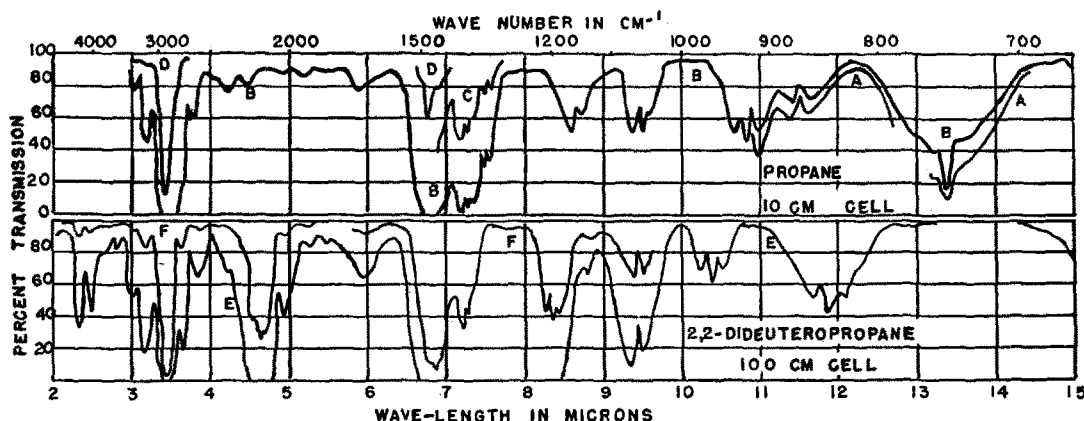


FIG. 1. Infra-red spectra of propane and 2,2-dideuteropropane A, 760 mm; B, 620 mm; C, 100 mm; D, 25 mm; E, 100 mm; F, 20 mm.