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Revised Long Abstract

# THERMODYNAMIC AND PHYSICAL PROPERTIES OF LIQUID FLUORINE AS CALCULATED BY SIGNIFICANT LIQUID STRUCTURE THEORY



by

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The Significant-Structures Theory of Liquids is one that views a liquid as a solid-like structure with holes of molecular size randomly distributed throughout the solid. Molecules adjacent to such holes can assume gas-like degrees of freedom in moving into such vacancies, the holes presumably moving in the opposite direction to the previous location of the gas-like molecule. The entire structure is, of course, a statistical one. The holes move with the same frequency as the molecules, so that no appreciable long-range structure is discernable by X-ray diffraction.

This model has proven more and more acceptable with increasing reports of its applicability to the calculation of physical and thermodynamic properties of liquids with close agreement with observed values. Such calculations are possible because the partition function for a liquid, according to this theory, becomes a function of the well-known partition functions of the gaseous and solid states. Thus,

$$f_L = (f_s)^{NV_s/V} (f_g)^{N(V-V_s)/V} \qquad (1)$$

where $V_s$ is the molar volume of the solid at the melting point, V is the molar volume of the liquid, and N is Avogadro's number.

This report is one of a series of studies applying this theory to various common and uncommon liquids, ranging from liquified gases to fused salts and molten metals (1), and is the second of a particular sequence on the halogens. Gratifying results were obtained with Chlorine (2), and work is in progress on Bromine. It is hoped that some valuable correlations will result from the study of a family of elements as these.

## DISCLAIMER

The Partition Function for Fluorine.---Fluorine apparently differs considerably from chlorine, which showed an abnormally large increase of nearly 20% in volume upon melting, an abnormally high entropy of fusion of 8.895 e. u., and no solid state transitions. In contrast, fluorine has an entropy of fusion of only 2.28 e. u. Its solid density at the melting point has not been measured, so no comparison on its expansion on melting can be made, but a very definite first order transition, presumably marking the onset of rotation in the solid state, has been noted about eight degrees below its melting point by Hu, White, and Johnston (3).

Consequently, the usual rotation term is included in both gas and solid terms, as well as the internal vibration term. For simplicity, the solid was treated as a three-degree Einstein oscillator. The resulting partition function, then, assumed the following form:

see figure 1

The parameter $n_h$ represents the number of holes accessible to a molecule in addition to its most stable position, and $a'$ represents the energy introduced into the system by expansion, and is related to the heat of sublimation $E_s$ at the melting point. A term $x$ is used to express the ratio $V/V_s$.

Considerations of nearest neighbors in closepacking in relation to the degeneracy term yields the following modified equation, with $n$ and $a$ as new parameters replacing $n_h$ and $a'$, as discussed in earlier articles (4):

See figure 2

The Helmholtz free energy $A$ is found to be the most useful function related to the partition function, since it can be easily converted into other functions. Since $A = -RT \ln f$, and $(\partial A/\partial T)_v = -S$, the paramters can be found by using only melting point data, namely, the melting temperature, the density of the liquid at the melting point, and the entropies of the liquid and solid

FIG. 1

$$f_L = (f_s)^{N\left(\frac{V_s}{V}\right)} (f_g)^{N\left(\frac{V-V_s}{V}\right)}$$

$$f_L = \left\{ \frac{e^{E_s/2T}}{(1-e^{-\theta/T})^3} \frac{8\pi^2 I kT}{2h^2} \frac{1}{(1-e^{-h\nu/kT})} \left[ 1 + n_s e^{-a' E_s/2T} \right] \right\}^{N\left(\frac{V_s}{V}\right)}$$

$$\left\{ \frac{(2\pi m kT)^{3/2}}{h^3} \frac{8\pi^2 I kT}{2h^2} \frac{1}{(1-e^{-h\nu/kT})} \frac{eV}{N} \right\}^{N\left(\frac{V-V_s}{V}\right)}$$

FIG. 2.

$$n_h = \Sigma\left(\frac{V-V_s}{V}\right) = \left(\frac{\Sigma V_s}{V}\right)\left(\frac{V-V_s}{V_s}\right) = n(x-1) \quad \text{WHERE} \quad x = \left(\frac{V}{V_s}\right)$$

$$f = \left\{\frac{e^{E_s/RT}}{(1-e^{-\theta/T})^3}\cdot\frac{8\pi^2 IkT}{2h^2}\cdot\frac{1}{(1-e^{-h\nu/kT})}\left[1+n(x-1)e^{-a\varepsilon_x/RT(x-1)}\right]\right\}^{N\left(\frac{1}{x}\right)}$$

$$\left\{\frac{(2\pi mkT)^{3/2}}{h^3}\cdot\frac{8\pi^2 IkT}{2h^2}\cdot\frac{1}{(1-e^{-h\nu/kT})}\frac{eV_s}{N}\times\right\}^{N\left(n-\frac{n}{x}\right)}$$

at the melting point. Two additional semi-parameters, $\theta$ the Einstein characteristic temperature and $E_s$ the heat of sublimation at the melting point, are calculated to fit the system at the melting point, rather than use experimental values, because of certain assumptions used in the model. For example, a hypothetical solid volume at the melting point was used (representing a solid without holes), as calculated from the reduced volume found from the melting point fit of the function and the known density of the liquid at the melting point. The parameters used in these calculations were as follows:

See Fig. 3

In general, the function will yield a curve of the shape shown in Fig. 4.

See Fig. 4

Since $(\partial A/\partial V)_T = -P$, the slope of the various isotherms gives the pressure, and the vapor pressure of the system at a given temperature will be given by the common tangent at the minima representing solid, liquid and vapor. Also, since $F = A + PV$, an extrapolation of this slope to zero volume yields the Gibbs Free Energy.

Results.—(a) Properties at the boiling and the critical points: The equation was first tested at the boiling point (about $31^\circ$ above the melting point) with the following results:

See Table 1

The Critical Point was found by setting the first and second derivative of pressure with respect to volume at constant temperature equal to zero, and finding by trial-and-error and graphical solution the temperature that satisfies this condition. The critical pressure and volume are then found in the usual manner. Since, this in effect represents the second and third derivatives of the partition function, the critical point constitutes a fairly severe test of the theory.

FIG. 3

$$A = -RT \ln f \qquad \left(\frac{\partial A}{\partial T}\right)_V = -S \qquad \left(\frac{\partial A}{\partial V}\right)_T = -P$$

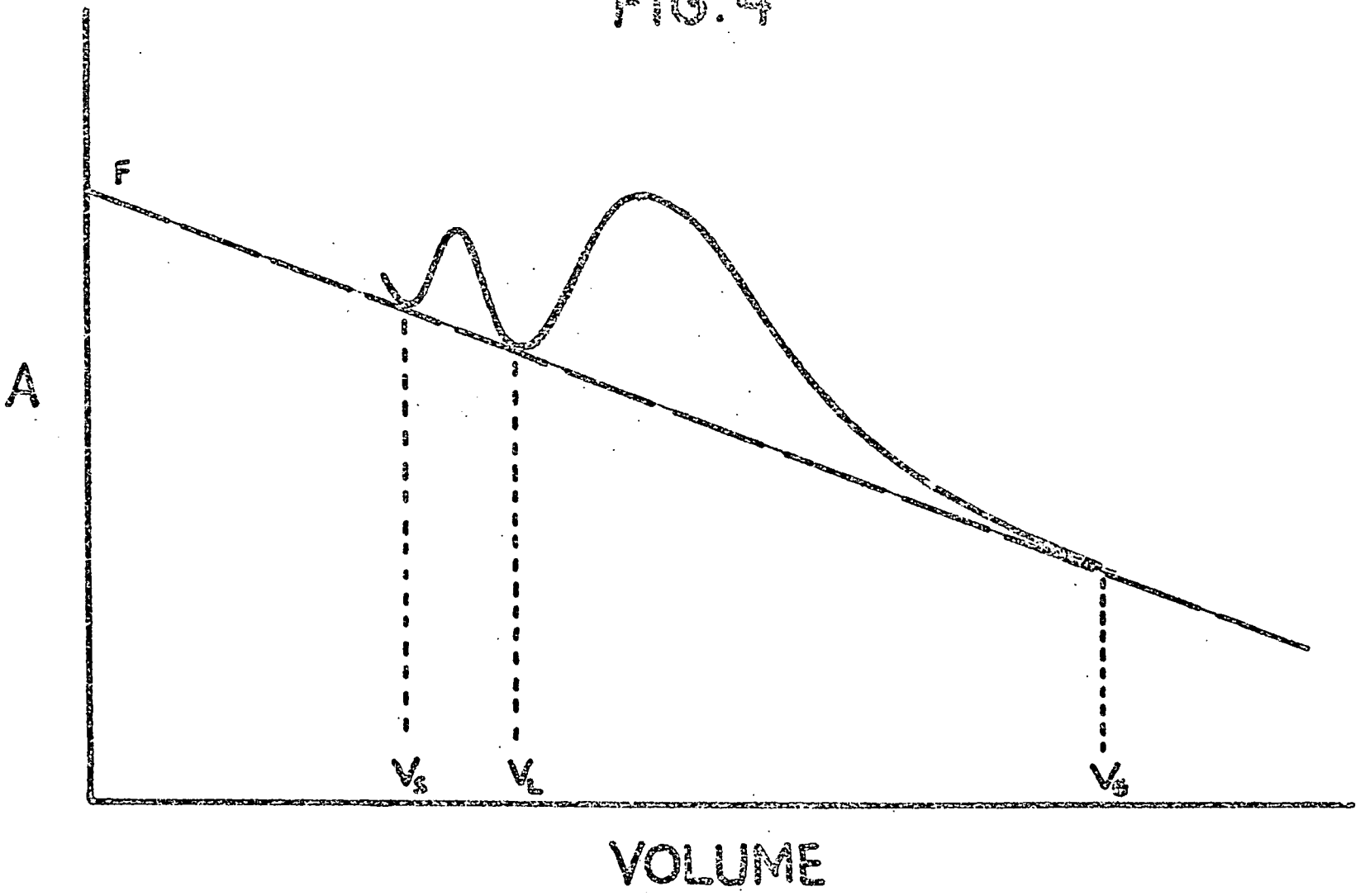
PARAMETERS

$$\begin{cases} a = 0.000592095 \\ n = 14.3 \\ E_s = -1777.4 \\ \theta = 61.70^\circ \end{cases}$$

$V_0 = 21.6015$ BASED ON $(V_L)_{mp} = 22.2927$

AND $(X_L)_{mp} = 1.032$

FIG. 4



# TABLE I

## BOILING POINT DATA FOR FLUORINE
## ($T = 85.02°K$)

| | Calc'd. | Obs'd. | Error, % |
|---|---|---|---|
| LIQUID VOLUME, cc./mole | 24.96 | 25.29 | -1.30 |
| VAPOR PRESSURE, atmos. | 1.0015 | 1.0000 | +0.15 |
| ENTROPY OF VAP'N, e.u. | 18.427 | 18.378 | +0.27 |

The results are given in Table 2.

See Table 2

(b) Vapor pressures and Densities.—Vapor pressures were calculated for every five degrees between the melting point and the boilingpoint. Molar volumes, hence densities, are obtainable from the same calculations. Good agreement was obtained in both cases as shown in the accompanying graphs in figures 5 and 6:

See Figs. 5 and 6

(c) Heat Capacity, Compressibility, and Coefficient of Thermal Expansion.—Differentiation of the expression for entropy with respect to temperature at constant volume, multiplied by T, yields $C_v$. This, in turn, can be converted to $C_p$ by use of a corrective term involving the compressibility $\beta$ and the coefficient of expansion $\alpha$. Figure 7 shows the relationship between these terms and the Helmholtz Free Energy, hence the partition function.

Here, again, as with the critical point, second derivatives of the partition function are involved, with respect to both V and T. Table 3 shows the results obtained. Reasonable values for $\alpha$ and $\beta$ are obtained, as well as for $C_v$, but the values for $C_p$ are from 2 to 9% off from observed values.

See Table 3

(d) Surface Tension.—Since surface tension represents the excess in Gibbs free energy of the surface of the liquid over the bulk of the liquid, and since the Gibbs free energy can be obtained from the relation $F = A + PV$, it is possible to also calculate surface tension. The method employed by Chang, Rao, Eyring, and Matsner (6) was used. Figure 8 shows the equations used to calculate the contribution of the various surface layers to this surface tension. Figure 9 compares the calculated results with observed. The calculated values are a few percent higher than the experimental, but fall along a straight line that extrapolates to about six degrees below the calculated critical temperature,

# TABLE 2

## CRITICAL POINT PROPERTIES OF FLUORINE

| | Calc'd. | Obs'd. | Error, % |
|---|---|---|---|
| CRIT. TEMPERATURE, °K | 151.9 | 144 | +5.49 |
| CRIT. VOLUME, cc./mole | 72.37 | 66.45* | +8.91 |
| CRIT. PRESSURE, atmos. | 62.36 | 55 | +13.4 |

* est'd. from Cailletet-Mathias plot

FIG. 5

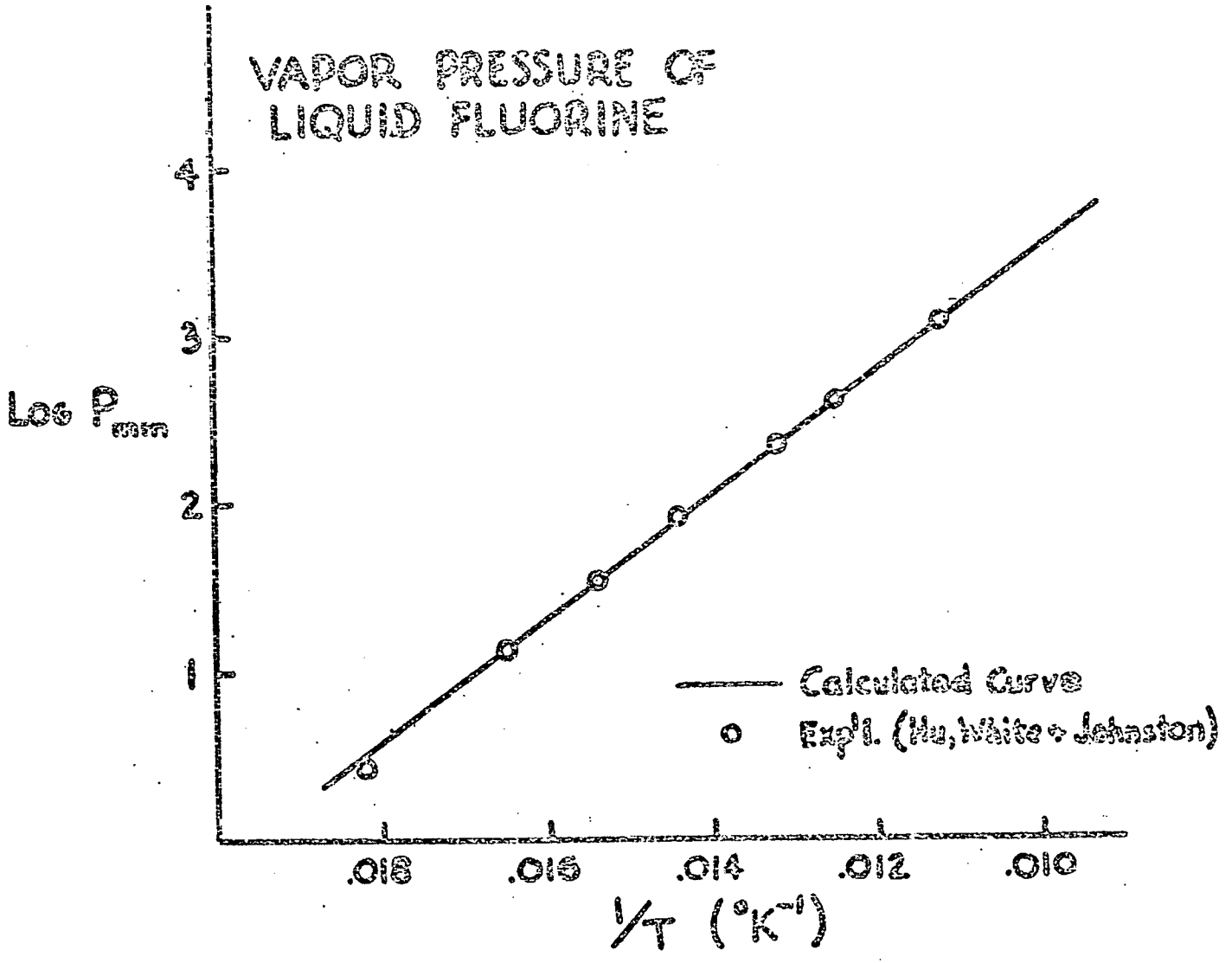
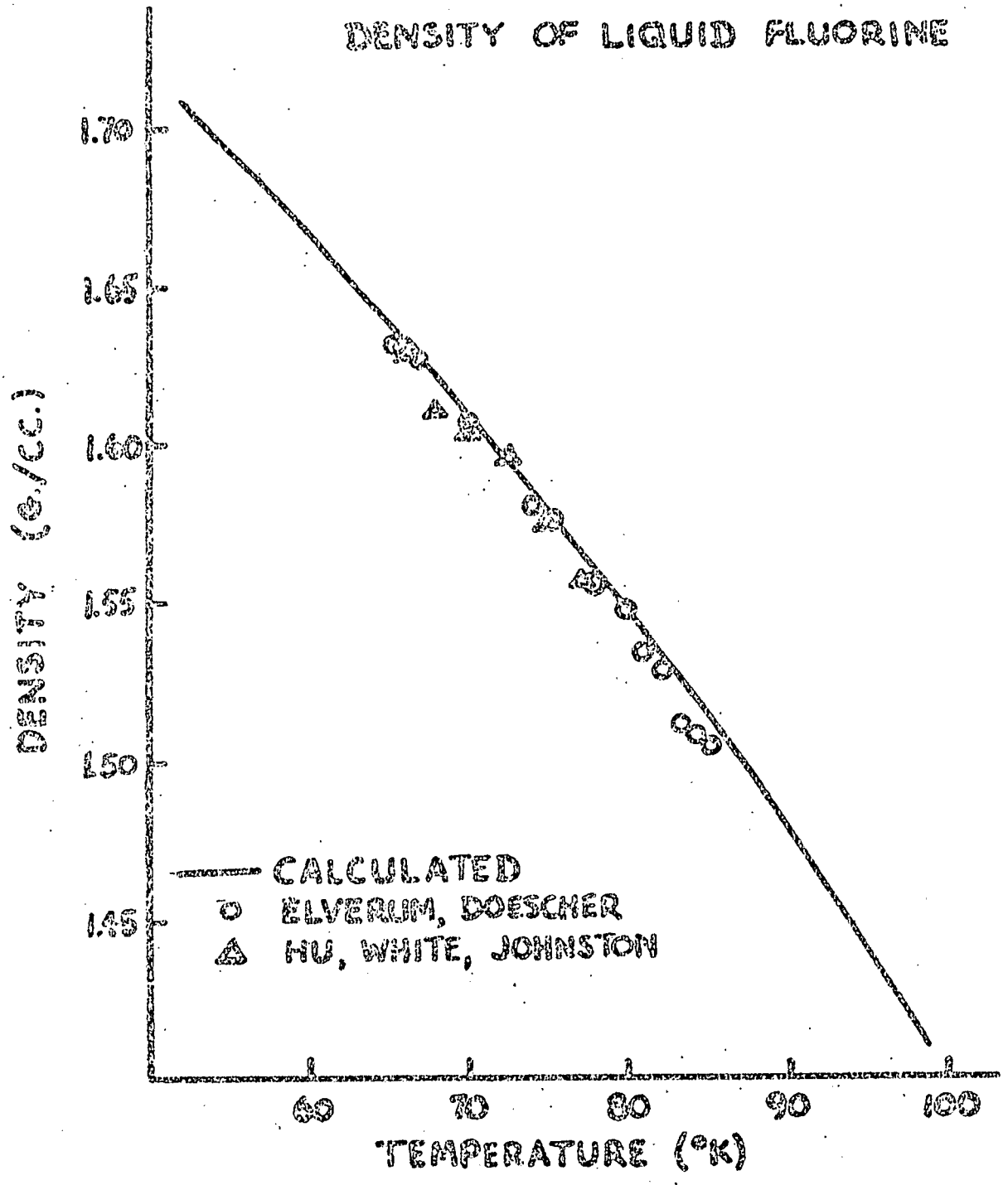

VAPOR PRESSURE OF
LIQUID FLUORINE
Log $P_{mm}$
4
3
2
1
.018
.016
.014
.012
.010
1/T (°K⁻¹)
Calculated Curve
Expl. (Hu, White & Johnston)

FIG. 6


DENSITY OF LIQUID FLUORINE
DENSITY (g./c.c.)
1.70
1.65
1.60
1.55
1.50
1.45
CALCULATED
ELVERUM, DOESCHER
HU, WHITE, JOHNSTON
60
70
80
90
100
TEMPERATURE (°K)

9

FIG. 1

$$\left(\frac{\partial H}{\partial T}\right)_p = -S \qquad T\left(\frac{\partial S}{\partial T}\right)_v = T\left(\frac{\partial^2 A}{\partial T^2}\right)_v = C_v$$

$$C_p = C_v + T\frac{\alpha^2}{\rho\beta}$$

$$\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p = -\frac{1}{v}\left(\frac{\partial p}{\partial T}\right)_v \Big/ \left(\frac{\partial p}{\partial v}\right)_T =$$

$$= -\frac{1}{v}\left(\frac{\partial^2 A}{\partial v \partial T}\right)_{T,v} \Big/ \left(\frac{\partial^2 A}{\partial v^2}\right)_T$$

$$\beta_S = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_S = \frac{-1}{v\left(\frac{\partial p}{\partial v}\right)_S} = -\frac{1}{v\left(\frac{\partial^2 A}{\partial v^2}\right)_T}$$

# TABLE 3

## CALC'D VALUES FOR $\alpha$, $\beta$, $C_v$, and $C_p$ FOR LIQUID FLUORINE

| TEMP.°K | $\alpha \times 10^3$ | $\beta \times 10^5$ | $C_v$ | $C_p$ | $C_p$(obs) | ERROR% |
|---|---|---|---|---|---|---|
| 55 | 3.284 | 5.902 | 7.37 | 12.82 | 13.70 | -6.42 |
| 60 | 3.118 | 6.420 | 7.44 | 12.44 | 13.68 | -9.06 |
| 65 | 3.259 | 7.583 | 7.49 | 12.58 | 13.61 | -7.57 |
| 70 | 3.540 | 9.329 | 7.53 | 12.89 | 13.56 | -4.94 |
| 75 | 3.784 | 11.104 | 7.56 | 13.17 | 13.64 | -3.45 |
| 80 | 4.098 | 13.515 | 7.58 | 13.46 | 13.79 | -2.39 |

11

FIG. 8

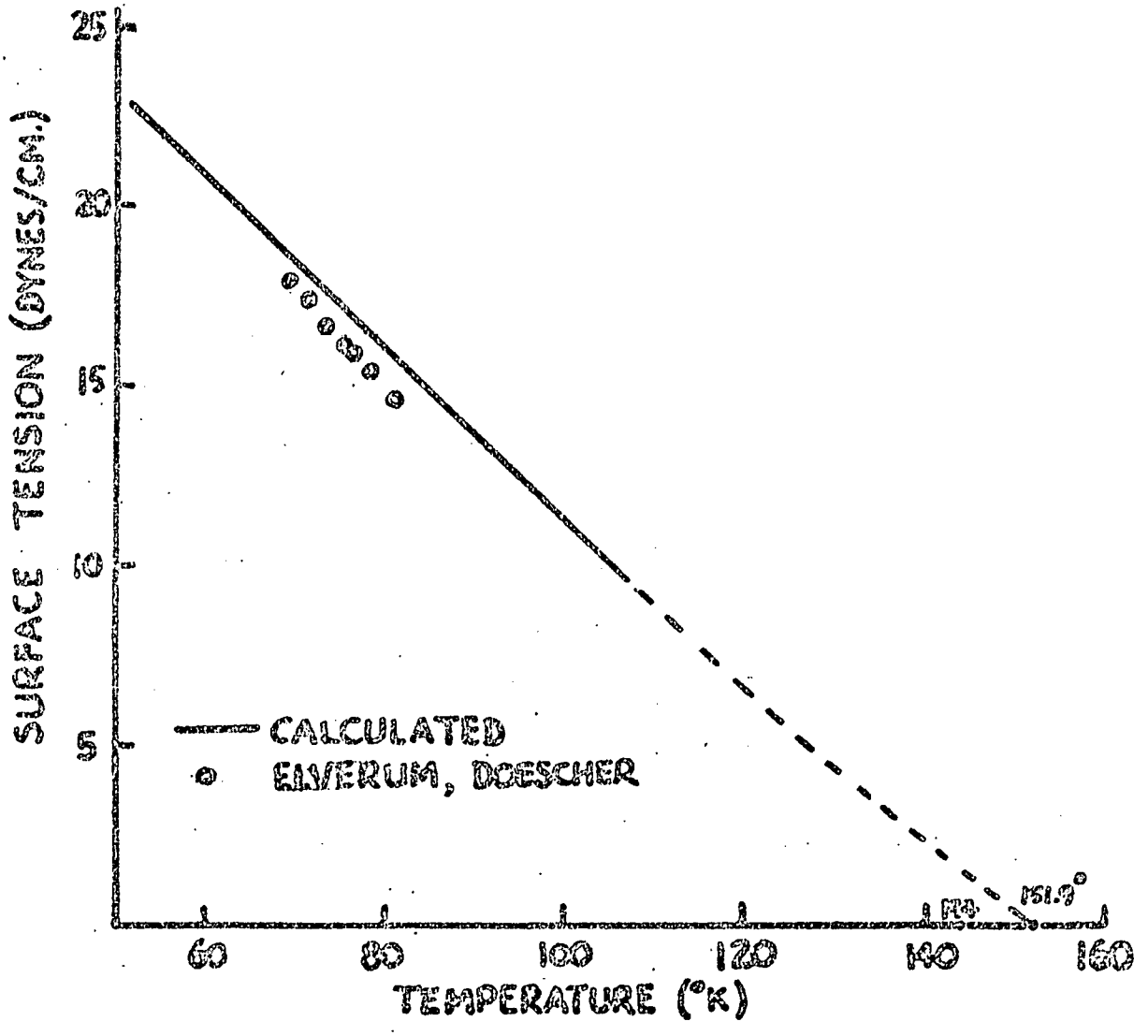
# SURFACE TENSION

$$\gamma = \sum_i \left(E_{s_i} - E_{s_0}\right) \frac{0.9165}{V_{s_i}} \left(\frac{V_{s_i}}{N}\right)^{\frac{1}{3}}$$

$$E_{s_i} = E_{s_0}\left(\frac{6\rho_i}{12\rho_i} + \frac{3\rho_{i+1}}{12\rho_i} + \frac{3\rho_{i-1}}{12\rho_i}\right)$$

FIG. 9

SURFACE TENSION OF FLUORINE



as predicted by the Ramsey-Shield relationship. The experimental values from the literature, it will be noted, extrapolate in a straight line to a temperature about six degrees below the observed critical temperature. At the melting point, the calculated and observed values more nearly approach one another. The fit, then, on surface tension will depend upon how well the critical point was obtained, and if the critical temperature as calculated is high, so will the surface tension, although, since the function was fit at the melting point, the error will be small at the melting point.

(c) Viscosity.---The significant structure theory is also applicable to transport properties of liquids such as viscosity, diffusion, and possibly others such as conduction of heat, sound, etc. when combined with Eyring's Absolute Reaction Rate Theory. Figure 10 gives the equations used, following the methods of Ree, Ree, and Eyring (4). In these, the viscosity of the liquid becomes a volume-dependent function of the viscosity of the solid-like and gas-like components of the liquid. While the gas-like part of the viscosity is the classical one given by kinetic theory, the solid-like part is related to the partition function in that it employs the same parameters. Again, good agreement was obtained with the observed values, as shown in figure 11.

See Fig. 11

Discussion.---It was assumed that the fluorine molecule rotated in the solid state at the melting point, and likewise in the liquid. While density data on solid fluorine is lacking, it is available for the liquid, along with measurements of its molecular dimensions. Pauling lists its van der Waal radius as 1.35 Å, and the electron diffraction data of Rogers and co-workers (5) gives its inter-nuclear distance as 1.435 Å.

A minimum molar volume corresponding to free rotation for all the molecules can be calculated, assuming liquid fluorine to consist of face-centered, cubically close-packed spheres of 2.078 Å radius (1.35 + 1.435/2).

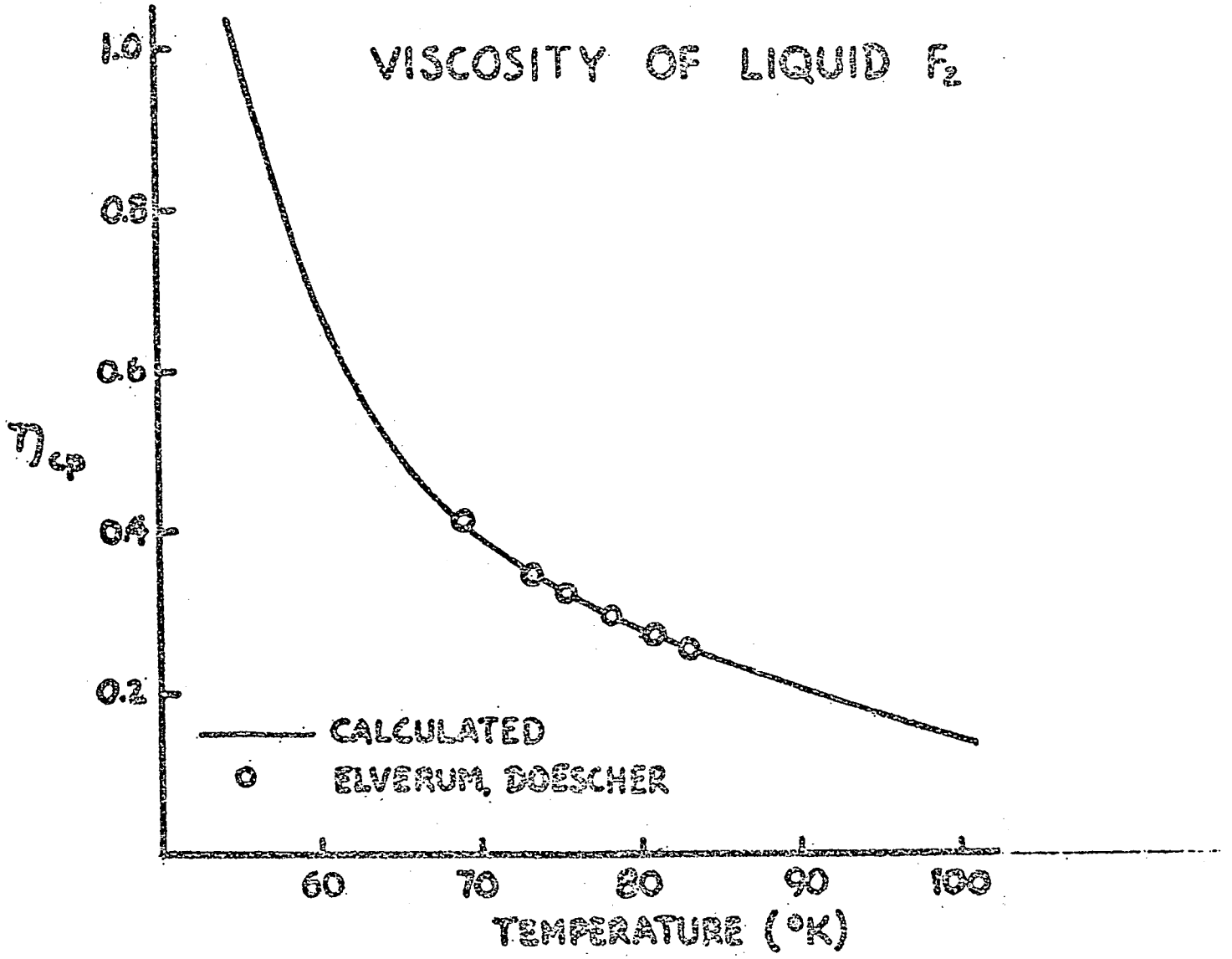
FIG. 10

# VISCOSITY

$$\eta_L = \frac{V_s}{V}\eta_s + \frac{V-V_s}{V}\eta_G$$

$$\eta = \frac{Nh}{X}\cdot\frac{1}{(1-e^{-\theta/T})}\cdot\frac{6}{\pi n}\cdot\frac{e^{\alpha E_s/RT(\chi-1)}}{(V-V_s)} + \left(1-\frac{1}{\chi}\right)\frac{2(mkT)^{1/2}}{3\pi^{3/2}d^2}$$

FIG. 11


VISCOSITY OF LIQUID $F_2$
1.0
0.8
0.6
0.4
0.2
$\eta_{cp}$
CALCULATED
ELVERUM, DOBSCHER
60
70
80
90
100
TEMPERATURE (°K)

Applying the formula $V_m = 4\sqrt{2}\ r^3N$ yields a value of 37.586 cubic centimeters per mole. The observed value for the molar volume of the liquid at the melting point is 22.2927 cc., indicating that either all the molecules are not rotating at the melting point or that their rotation is seriously restricted.

If we consider two-dimensional rotation, where the molecules would occupy oblate ellipsoids rather than spheres, and if we inscribe each ellipsoid in a hexagonal tile-shaped volume that packs without voids, we obtain a value of 24.33 cc, using the formula $2\sqrt{3}\ r^2d(N)$, where d is 2 x 1.35 Å. This value checks closely with the observed volume of 22.29 cc for liquid fluorine at its melting point. Comparison with chlorine reveals that the molar volume observed for liquid chlorine at the melting point was considerably less than that required for even two-dimensional rotation.

The molar volume for liquid fluorine obtained at its boiling point is 24.96 cc., which compares even better with the value required for two-dimensional rotation, but still falls considerably short of that for three-dimensional rotation. A similar agreement between the molar volume observed at the boiling point with that calculated for two-dimensional rotation was observed with liquid chlorine. In both chlorine and fluorine, the molar volumes at the critical point nearly doubled the calculated volume required for three-dimensional rotation.

From the preceding, it is concluded that solid-state transitions probably mark the onset of two-dimensional rotation and that three-dimensional rotation is not generally developed until temperatures are reached in the vicinity of the boiling point.

Summary.—The theory of significant structures for liquid has been applied to liquid fluorine over the entire liquid range from its melting point of 53.54°K to its critical temperature at 144°K, using only melting point data and such physical constants as atomic weight, moment of inertia, and fundamental frequency of the molecule to find the essential parameters for the partition function.

The following properties were calculated with reasonably good agreement with experimentally observed values: vapor pressure, density, entropy of vaporization, critical temperature-pressure-volume, heat capacity at constant volume and constant pressure, thermal coefficient of expansion, compressibility, surface tension, and viscosity.

## REFERENCES

(1) Eyring, Henry; Ree, Taikyue; and co-workers in series of articles in the Proceedings of the National Academy of Science, 44: 683 (1958) to present.

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(3) Hu, J; White, D.; and Johnston, H. L. Jour. Amer. Chem. Soc. 75: 5642 (1953)

(4) Ree, Teresa S.; Ree, Taikyue; and Eyring, Henry. Proc. Nat. Acad. Sci. 48: 501 (1962)

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(6) Chang, Sofhun; Ree, Taikyue; Eyring, Henry; and Matzner, Ingrid. 1962 Second Symposium on Thermophysical Properties, Princeton Univ. Progress in International Research on Thermodynamic and Transport Properties, by ASME.