

study of molecular hydrogen ions produced from the ethylene $C_2H_2D_2$ is also of interest. It is possible to tell whether the molecular hydrogen ions formed come from two atoms belonging to the same radical, or whether all the combinations of hydrogen atoms are possible. In the first case the ratio DD/HD would be 0, and in the second case it would be $\frac{1}{4}$. Using first a hot tungsten filament as electron source, the ratio obtained was $\frac{1}{4}$. But because of a possible thermal decomposition of the ethylene against the filament, the same experiment was repeated with an oxide

coated filament, and gave the result 1/15. The comparison between the two results shows clearly that in the first experiment the most important role was played by the molecular hydrogen ion coming from thermodissociation. With the oxide coated filament, this effect is far less important. In view of this, we can assume the true ratio to be less than 1/15. This is strongly in favor of the first assumption mentioned before.

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An Atomic Distribution Function for Liquid Sodium

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An atomic distribution function for liquid sodium is developed. A simple liquid model of the quasi-solid type is assumed in which each atom is trapped by its immediate neighbors in a small spherical cell within which it is free to move about. The resulting distribution function contains three parameters which are evaluated by fitting the function to the experimental distribution curves for liquid

sodium given by Trimble and Gingrich. An approximate value of the free volume of the liquid as a function of the absolute temperature is obtained. By means of the free energy equation the entropies and latent heats of fusion and vaporization for liquid sodium are calculated and compared with the observed values.

INTRODUCTION

IN a recent article, Trimble and Gingrich¹ have given atomic distribution curves for liquid sodium at temperatures of 100°C and 400°C. These curves, which are derived by an analysis of the x-ray diffraction patterns of the liquid,² give the radial atomic configuration in the liquid. Presumably they should yield important information about the liquid state of sodium.

For a profitable use of atomic or molecular distribution curves, it is of considerable value to represent them by an analytical function. Prins³ has proposed a series of error functions for the general liquid distribution function. This representation is based upon a "smeared out" model of the corresponding crystalline solid. Bernal⁴ has

generalized the treatment to some extent. For the case of monatomic or quasi-monatomic liquids, assumed to possess molecular homogeneity,⁵ he has shown that the distribution function of a liquid can be derived from a knowledge of its intermolecular potential function. Unfortunately this potential function is not known in many cases, or, if known, is expressed in a form so complex as to destroy its utility.

The purpose of this paper is to develop a distribution function for liquid sodium somewhat different in form from that proposed by Prins. A direct consequence of this development is the determination of the so-called free volume of liquid sodium.

FREE ENERGY EQUATION AND FREE VOLUME

The concept of free volume has been very fruitful in the study of liquids and gases. Guggen-

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¹ Trimble and Gingrich, *Phys. Rev.* **53**, 278 (1938); also, Tarasov and Warren, *J. Chem. Phys.* **4**, 236 (1937).

² Zernike and Prins, *Zeits. f. Physik* **41**, 184 (1927).

³ Prins, *Physica* **3**, 147 (1936).

⁴ Bernal, *Trans. Faraday Soc.* **33**, 27 (1937); also, Kirkwood, *J. Chem. Phys.* **3**, 300 (1935).

⁵ All interior molecules of the liquid have statistically equivalent molecular environments.

heim⁶ has shown that its use effects an essential simplification in the expression for the free energy (Helmholtz) of a simple liquid. It is assumed that the potential energy of a simple liquid has a pronounced minimum for a certain set of molecular configurations, and is effectively infinite for all others. This particular set of configurations is characterized by assigning to each molecule in the liquid a small volume v within which it is more or less free to move independently of the other molecules without appreciably altering the condition of minimum potential energy for the entire assembly. This volume may be called the free volume of the molecule. On this assumption the free energy of a simple liquid is given approximately by the equation,⁷

$$F = -NkT[\ln J(T) + \ln v] + \Phi. \quad (1)$$

In Eq. (1) Φ is the minimum potential energy of the molecular assembly and $J(T)$ is the ordinary partition function for the molecules. The other symbols have their usual significance. For a monatomic liquid at moderate temperatures $J(T)$ may be assumed to take its classical value, $(2\pi mkT/h^2)^{3/2}$.

According to Guggenheim Eq. (1) is valid either for a quasi-solid model of a liquid in which the molecules are not allowed to change places, or for an imperfect gas model in which the molecules are allowed to change places. Eyring and his associates,⁸ who have made material contributions to the theory of the liquid state, appear to hold a slightly different point of view on this matter.⁹

Lennard-Jones and Devonshire¹⁰ have been very successful in accounting for the main features of the liquid and gaseous states of those molecular aggregates whose molecular potential may be satisfactorily represented by the well-

⁶ Guggenheim, Proc. Roy. Soc. **A135**, 181 (1932); also, Fowler, *Statistical Mechanics* (second edition), p. 522 *et seq.*

⁷ Not valid for helium and hydrogen.

⁸ Eyring and Hirschfelder, J. Phys. Chem. **41**, 249 (1937); Kincaid and Eyring, J. Chem. Phys. **5**, 587 (1937); Hirschfelder, Stevenson and Eyring, J. Chem. Phys. **5**, 897 (1937).

⁹ According to Eyring *et al.* the communal sharing of free volume by the molecules in a liquid contributes a term, $-NkT$, to its free energy. Cf. Gurney and Mott, J. Chem. Phys. **6**, 222 (1938); Fowler, *Statistical Mechanics* (second edition), pp. 191-192.

¹⁰ Lennard-Jones and Devonshire, Proc. Roy. Soc. **A163**, 53 (1937); **A165**, 1 (1938). Lennard-Jones, *Physica* **4**, 941 (1937). Wheeler, Ind. Acad. Sc. Proc. **4**, 291 (1936).

known function, $\lambda/r^{12} - \mu/r^6$. They consider each molecule in the liquid or dense gas as being temporarily trapped in a cell by its immediate neighbors. The effective volume of the cell constitutes the free volume for the molecule. Thus Φ in Eq. (1) may be determined as a function of the specific volume and v as a function of the specific volume and temperature of the liquid. Hence the free energy is known.

Eventually it may be possible to apply some such method as that of L.-J. and D. to liquid sodium. A fairly good approximation for Φ (in the solid state) appears to be available.¹¹ A corresponding expression for v is needed. It will be shown that an analysis of the atomic distribution curves for liquid sodium apparently yields good values of v at 100°C and 400°C and, in addition, gives the approximate variation of v with the absolute temperature.

DEVELOPMENT OF ATOMIC DISTRIBUTION FUNCTION

In developing the atomic distribution function for liquid sodium a quasi-solid model for the liquid is adopted. This model is essentially equivalent to that proposed by L.-J. and D., i.e., each atom in the liquid is assumed to be trapped

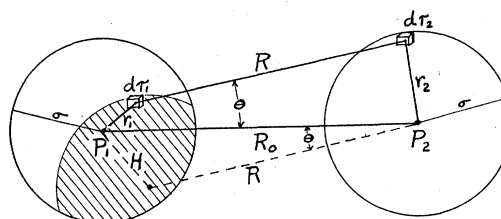


FIG. 1. Atomic cells of two neighboring atoms. The shaded portion of the left sphere represents the volume integral in Eq. (6). It is generated by the motion of $d\tau_1$ when the line R of fixed length and direction is moved parallel to itself through all positions consonant with the condition that $d\tau_1$ and $d\tau_2$ remain in their respective spheres.

(at least temporarily) in a small spherical cell by its immediate neighbors. In order to proceed it is necessary to make some assumption concerning the form of the potential energy function within the cell. The papers of L.-J. and D. suggest two general types of functions. One is the ordinary parabolic type used extensively in the theory of

¹¹ Fröhlich, Proc. Roy. Soc. **A158**, 97 (1937); also, Bardeen, Phys. Rev. **53**, 683 (1938).

solids. The other is the discontinuous box type in which the potential is practically constant throughout the cell except at the cell boundary where it becomes infinite. Since this latter form appears to give a better correspondence with the experimental data, it will be assumed in the following development.¹²

Let the distance between the cell centers P_1 and P_2 of two nearest neighboring atoms in the liquid be R_0 as shown in Fig. 1. About each center let us describe a sphere of radius σ . Let the volume v of each sphere represent the free volume for the atom trapped within it. The probability that atom 1, i.e., its center, lies in the volume element $d\tau_1$ having coordinates x_1, y_1, z_1 with respect to P_1 may be written in the form,

$$p(x_1, y_1, z_1)d\tau_1/v, \quad (2)$$

where $p = \begin{cases} 1 & \text{if } r_1 = (x_1^2 + y_1^2 + z_1^2)^{1/2} < \sigma \\ 0 & \text{if } r_1 > \sigma \end{cases}$.

A corresponding expression may be written for atom 2.

The probability of atom 1 lying in $d\tau_1$ and atom 2 lying in $d\tau_2$ will be¹³

$$p(1)p(2)d\tau_1d\tau_2/v^2. \quad (3)$$

Let us replace the coordinates x_2, y_2, z_2 by a new set X, Y, Z defined by the linear relations,

$$\begin{aligned} x_2 &= x_1 + X - X_0, \\ y_2 &= y_1 + Y - Y_0, \\ z_2 &= z_1 + Z - Z_0, \end{aligned} \quad (4)$$

where X_0, Y_0, Z_0 are the relative coordinates of the cell centers, and X, Y, Z are the relative coordinates of the two atoms at $d\tau_1$ and $d\tau_2$. Making these transformations in expression (3), we get,

$$(1/v^2)p(x_1, \dots)p(x_1 + X - X_0, \dots) \times dx_1 dy_1 dz_1 dX dY dZ. \quad (5)$$

The probability of relative coordinates X, Y, Z occurring between the two atoms may be obtained from (5) by integrating over all x_1, y_1, z_1

¹² The development given is based upon classical principles. It is unlikely that the use of the quantum theory would lead to very different results except for light atoms or low temperatures. *Vide*, e.g., Slater, Phys. Rev. **38**, 237 (1931); also, Uhlenbeck and Beth, Physica **3**, 729 (1936).

¹³ The events are assumed to be independent.

with fixed X, Y, Z , viz.,

$$(1/v^2)dXdYdZ \int \int \int p(x_1, \dots) \times p(x_1 + X - X_0, \dots) dx_1 dy_1 dz_1. \quad (6)$$

If we bear in mind the conditions to which the p function is subjected in (2), it is clear that the volume integral in expression (6) is equal to the volume common to two intersecting spheres, each of radius σ , whose centers are separated by the distance,

$$H = [(X - X_0)^2 + (Y - Y_0)^2 + (Z - Z_0)^2]^{1/2} = [R^2 + R_0^2 - 2RR_0 \cos \theta]^{1/2},$$

where θ is the angle between R and R_0 as shown in Fig. 1. The volume common to the two intersecting spheres is

$$v \left[1 - \frac{3H}{4\sigma} + \frac{H^3}{16\sigma^3} \right].$$

Substituting this quantity in expression (6) and writing dX, dY, dZ in spherical coordinates, we get,

$$1/v \left[1 - \frac{3H}{4\sigma} + \frac{H^3}{16\sigma^3} \right] R^2 \sin \theta dR d\theta d\phi. \quad (7)$$

Expression (7) is the probability that the two atoms will have relative spherical coordinates of R, θ, ϕ , the line joining the cell centers giving the direction of the polar axis. A direct integration of this expression over θ and ϕ gives the probability of finding the two atoms within a distance R to $R+dR$ of each other. The integration limits for ϕ and θ are, respectively, 0 to 2π and

$$0 \text{ to } \theta_0 = \cos^{-1} \left[\frac{R^2 + R_0^2 - 4\sigma^2}{2RR_0} \right].$$

The integration gives¹⁴

$$\frac{2\pi R^2 dR}{v} \left[\frac{4\sigma^2 - (R_0 - R)^2}{2RR_0} + \frac{|R_0 - R|^3 - (2\sigma)^3}{4\sigma RR_0} - \frac{|R_0 - R|^5 - (2\sigma)^5}{80\sigma^3 RR_0} \right]. \quad (8)$$

¹⁴ It is clear from the development that (8) is only valid for the interval, $R_0 - 2\sigma \leq R \leq R_0 + 2\sigma$. Outside this interval the probability in question is zero.

A rearrangement of terms in this expression and the substitution, $v = 4\pi\sigma^3/3$, give

$$\frac{3RdR}{5R_0\sigma} \left[1 - \frac{5(R_0 - R)^2}{4\sigma^2} \right] \times \left\{ 1 - \frac{|R_0 - R|}{2\sigma} + \frac{|R_0 - R|^3}{40\sigma^3} \right\}. \quad (9)$$

Let N_0 be the average number of nearest neighbors surrounding an atom in the liquid, and let $\rho_0(R)$ be the density of these atoms at distance R from the given atom. Then the probability of finding a neighboring atom at distance R from this given atom is $(4\pi R^2 \rho_0(R) dR) / N_0$. This quantity must equal that given in (9), hence,

$$4\pi R \rho_0(R) = \frac{3N_0}{5\sigma R_0} \left\{ 1 - \frac{5(R_0 - R)^2}{4\sigma^2} \right\} \times \left[1 - \frac{|R_0 - R|}{2\sigma} + \frac{|R_0 - R|^3}{40\sigma^3} \right], \quad (10)$$

for $R_0 - 2\sigma \leq R \leq R_0 + 2\sigma$.

$4\pi R \rho_0(R) = 0$, for all other R .

In Eq. (10) $\rho_0(R)$ represents the density of the nearest neighbors of any atom, i.e., the density of those atoms whose cell centers lie on the first coordination sphere of radius R_0 . It is assumed that this density is practically the total density of atoms for the interval, $0 \leq R \leq R_0$. Thus in this interval Eq. (10) gives the atomic distribution function of the liquid.

In order to extend the range of the distribution function it is necessary to consider density contributions from atoms whose cell centers lie on coordination spheres of order higher than the first. If ρ_i is the density contribution of the N_i atoms lying on the $i+1$ coordination sphere of radius R_i , then the total density $\rho(R)$ is given by the equation,

$$4\pi R \rho(R) = 4\pi R \sum_{i=0} \rho_i(R), \quad (11)$$

where $\rho_i(R)$ is given by an equation of the same form as Eq. (10) with N_0 and R_0 replaced by N_i and R_i .

On the assumption of molecular homogeneity in a liquid it seems clear that N_i and R_i should be functions of N_0 and R_0 . Bernal⁴ has pointed

this out and has given rough estimates of N_i and R_i for the second and third coordination spheres in terms of those of the first. So far as the author is aware, the general problem has not been solved. Assuming the existence of such relationships there remain in Eqs. (10) and (11) the three parameters σ , N_0 and R_0 , to be determined. In the next section of this paper it will be shown that approximate values of these parameters for liquid sodium may be obtained by an analysis of its atomic distribution curves.

DETERMINATION OF PARAMETERS

The method of determining the parameters σ , N_0 and R_0 for liquid sodium is simply that of fitting the distribution function given in Eq. (10) to the experimental values given by T. and G. Because of the difficulty of obtaining reliable values of N_i and R_i in terms of N_0 and R_0 , Eq. (10) is used, and hence, only that part of the experimental curve for which $R \leq R_0$.^{15, 16}

Let us rewrite Eq. (10) in the form,

$$\sigma^2 = \frac{y_0}{y_0 - y} \frac{5(R_0 - R)^2}{4} \times \left[1 - \frac{|R_0 - R|}{2\sigma} + \frac{|R_0 - R|^3}{40\sigma^3} \right], \quad (12)$$

where $y = 4\pi R \rho_0(R)$ and $y_0 = (3N_0)/(5\sigma R_0)$. It is clear that y_0 is the maximum value of y . By constructing a table of $y \sim R$ values obtained from the $4\pi R^2 \rho(R)$ curve given by T. and G., it is an easy matter to determine values of y_0 and R_0 . By substitution of these values of y_0 and R_0 in Eq. (12) and use of successive pairs of experimental values of y and R , the equation may be solved for σ by iteration. The constancy of σ for different $y \sim R$ values is an indication that Eq. (10) is approximately correct, at least. The results of the calculation are shown in Table I.

An examination of Table I shows that the variation in the values of σ for each distribution curve is small. There is very little change in

¹⁵ Unfortunately this portion of the curve is influenced considerably by the large angle part of the experimental scattering curve; thus its exact shape is not as reliable as would be desirable.

¹⁶ It is assumed that the overlap from the second coordination sphere of atoms is negligible up to this point.

TABLE I. Calculated values of σ .

	R in A	y(exp.)	σ in A		R in A	y(exp.)	σ in A
A. Temperature 100°C				B. Temperature 400°C			
max.	3.79	2.45		max.	3.80	1.84	
1	3.00	0.39	0.62	1	3.00	0.56	0.76
2	3.20	0.88	0.60	2	3.20	0.99	0.78
3	3.40	1.57	0.60	3	3.40	1.37	0.76
4	3.60	2.17	0.58				
			Ave. 0.60				Ave. 0.77
$R_0=3.79\text{A}$		$y_0=3N_0/5\sigma R_0=2.45$		$R_0=3.80\text{A}$		$y_0=1.84$	
$\sigma=0.60\text{A}$		$\sigma/T^{3/2}=0.0311$		$\sigma=0.77\text{A}$		$\sigma/T^{3/2}=0.0297$	
$N_0=9.28$ atoms				$N_0=8.95$ atoms			

the values of N_0 and R_0 in going from 100°C to 400°C for liquid sodium, but there appears to be a considerable increase in the value of σ , and hence, in the free volume of the liquid. It is found that $\sigma/T^{3/2}$, T being the absolute temperature of the liquid, has practically the same value at 100°C and 400°C. Consequently it seems safe to assume that $\sigma/T^{3/2}$ is constant over the indicated temperature range.

It is of interest to compare the values of $y=4\pi R\rho(R)$ as calculated by Eqs. (10) and (11), from the parameter values given in Table I-A, with those values given by the experimental curve of T. and G. for 100°C. In the interval, $0 \leq R \leq R_0$, Eq. (10) is used. In order to extend the range beyond $R=R_0$, Eq. (11) is used along with the approximate values of N_1 , N_2 , R_1 and R_2 as given by Bernal.⁴ The results are shown in Table II and Fig. 2.

APPLICATIONS

It is now possible to make use of the free energy equation (1) in order to determine some of the properties of liquid sodium. The free volume per atom of liquid sodium may be written in the form, $v=4\pi\sigma^3/3=bT^{3/2}$, since σ is approximately proportional to $T^{3/2}$. The value of b is 126×10^{-30} cm³ degrees^{-3/2} from Table I-A. $J(T)$ is assumed to take its classical value, $[2\pi mkT/h^2]^{3/2}$. Making these substitutions in Eq. (1), we obtain for the free energy of liquid sodium

$$F = -NkT \left[\ln \left(\frac{2\pi mkT}{h^2} \right)^{3/2} + \ln (bT^{3/2}) \right] + \Phi. \quad (13)$$

In Eq. (13) both b and Φ are unknown functions of the specific volume of the liquid. Hence

it is not possible to obtain the equation of state. It is, however, quite feasible to determine the entropy of liquid sodium by means of the relation, $S = -(\partial F/\partial T)_V$. Using this relation, the entropy is given by the equation,¹⁷

$$S = - \left(\frac{\partial F}{\partial T} \right)_V = Nk \left[\ln \left(\frac{2\pi mkT}{h^2} \right)^{3/2} + \ln (bT^{3/2}) + 3 \right]. \quad (14)$$

TABLE II. Comparison of values of $y=4\pi R\rho(R)$ as calculated by Eqs. (10) and (11) from the parameter values given in Table I-A with the values given by the experimental curve of Trimble and Gingrich. Temp. 100°C; $\sigma=0.60\text{A}$; $N_0=9.28$; $R_0=3.79\text{A}$.

R in A	$4\pi R^2\rho(\text{exp.})$	$4\pi R\rho(\text{exp.})$	$4\pi R\rho(\text{calc.})$	
2.6	0	0	0	
2.8	0.40	0.14	0.06	
3.0	1.16	0.39	0.34	
3.2	2.83	0.88	0.87	
3.4	5.32	1.57	1.57	
3.6	7.81	2.17	2.19	
3.8	9.31	2.45	2.45	
$R > R_0$	$N_1=6$	$R_1=5.1$	$N_2=13$	$R_2=6.2$
4.0		8.31	2.08	2.23
4.2		6.32	1.51	1.66
4.4		5.49	1.25	1.13
4.6		5.15	1.12	0.90
4.8		5.15	1.07	0.96
5.0		5.32	1.06	1.15
5.2		5.82	1.12	1.21
5.4		6.57	1.22	1.17
5.6		7.32	1.31	1.27
5.8		8.73	1.51	1.56
6.0		10.15	1.69	1.94
6.2		12.32	1.99	2.14

¹⁷ $\partial\Phi/\partial T$ is assumed to be negligible. Φ is presumably a function of the temperature through the Fermi energy of the electrons, a factor which becomes important at high temperatures. $Nk/J=1.986$ cal. degree⁻¹ mol⁻¹; $mk/h^2=1.215 \times 10^{14}$ c.g.s. units; $b=126 \times 10^{-30}$ c.g.s. units.

The value of the entropy of liquid sodium at its melting point (370.5°K) as calculated by Eq. (14) with conversion from ergs to calories is 15.7 cal./degree/mol. The corresponding entropy of solid sodium at this temperature, as taken from the work of Simon and Zeidler,¹⁸ is 13.9 cal./degree/mol. The difference of these two values, 1.8 calories degree⁻¹ mol⁻¹, is the entropy of fusion of sodium. The latent heat of fusion corresponding to this entropy change is 2.8 kilojoules per mol. This may be compared with the observed value of 2.65 kilojoules per mol as given in the *International Critical Tables*. No doubt the good agreement is fortuitous to some extent since the entropy of fusion of sodium is small compared with the entropies of the solid and the liquid at the melting point. Also there is some variation in the value of S for the solid as given by different authors.

The specific heat at constant volume for liquid sodium may be obtained from Eq. (14) by means of the relation, $C_V = T(\partial S/\partial T)_V$. The calculation yields the classical value $3Nk$ which is approximately correct. The values of C_V for the alkali metals appear to rise somewhat above the classical value.¹⁸

At the boiling point of sodium under atmospheric pressure (1153°K) the entropy of the liquid as determined by Eq. (14) is 22.4 cal. degree⁻¹ mol⁻¹.¹⁹ The approximate entropy of the vapor at this temperature may be calculated by the equation,²⁰

$$S_{\text{vapor}} = Nk[\ln(2\pi mkT/h^2)^{3/2} + \ln(V/N) + 5/2 + \ln 2], \quad (15)$$

where V is the volume of a mol of the vapor at

¹⁸ Simon and Zeidler, *Zeits. f. physik. Chemie* **A123**, 383 (1926); Rodebush and Rodebush, *International Critical Tables*, Vol. 5, p. 88.

¹⁹ The extrapolation to such high temperatures may not be justifiable.

²⁰ The vapor is assumed to be a perfect gas except for the multiplicity of the ground state of the sodium atom which introduces the term $Nk \ln 2$. The appreciable number of Na_2 molecules present at this temperature is neglected. *Vide.*, e.g., Loomis and Nusbaum, *Phys. Rev.* **40**, 380 (1932).

the boiling point. The calculation gives $S_{\text{vapor}} = 43.4$ cal. degree⁻¹ mol⁻¹. The entropy of vaporization is thus 21.0 cal. degree⁻¹ mol⁻¹ at the boiling point and the corresponding latent heat of vaporization 102 kilojoules per mol. The observed value is 105 kilojoules per mol. This excellent agreement is partially explained by the fact that V/N for the vapor is about 10^5 times as large as is v for the liquid at the boiling point.²¹ Hence a relatively large error in v would

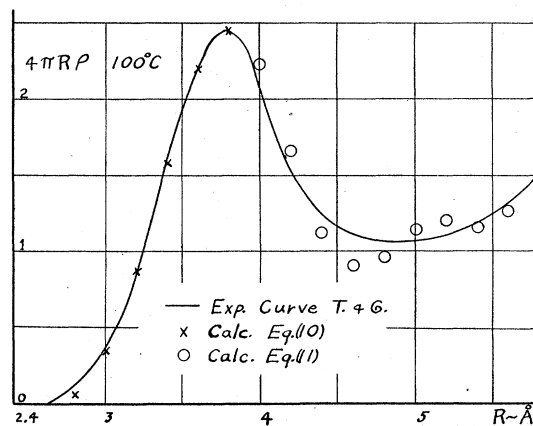


FIG. 2. Values of $4\pi R\rho$ plotted as a function of R .

not greatly affect the value of the entropy of vaporization. This fact coupled with the observation that V/N is practically the same for all vapors under like conditions of temperature and pressure seems to form the basis of Trouton's rule²² as modified by Hildebrand, namely, that the entropies of vaporization of all pure liquids are the same at temperatures where the vapor concentrations are the same.²³

It is a pleasure to acknowledge the writer's indebtedness to Professor J. C. Slater for his stimulating aid in the inception and solution of this problem, and to Professors N. S. Gingrich and B. E. Warren for their very helpful suggestions and information.

²¹ At the b.p. of sodium V/N for the vapor is 1.56×10^{-19} cc per atom while v for the liquid is 4.90×10^{-24} cc per atom.

²² Trouton, *Phil. Mag.* [5] **18**, 54 (1884).

²³ Hildebrand, *J. Am. Chem. Soc.* **37**, 970 (1915); see also reference 10.