

agree very well with those of Pitzer and Gwinn⁷ and they conclude that the potential barrier restricting rotation is about but a little less than 800 cal. mole⁻¹. Calculation of the potential barrier from their data leads to a value of about 600 cal. mole⁻¹.

The calculation of the potential barrier from the entropy measurements reported here is given below. "I.C.T." constants are used for the statistical calculation.

TABLE VIII

CALCULATION OF THE ENTROPY OF NITROMETHANE FROM MOLECULAR DATA

Ideal Gas State, $T = 298.1^\circ\text{K.}$, $P = 1 \text{ atm.}$ cal. deg. ⁻¹ mole ⁻¹	
Translation	38.25
External rotation	23.51
Vibration	1.88
Internal rotation (assumed free)	2.15
Entropy corresponding to free internal rotation	65.79
Entropy from calorimetric data	65.73
Reduction in entropy due to restriction of internal rotation	0.06

The entropy tables of Pitzer and Gwinn¹² show that the 0.06 cal. deg.⁻¹ mole⁻¹ corresponds to a six-fold potential barrier of 500 cal. mole⁻¹, in good agreement with the values 800 and 600 cal. mole⁻¹. The limits of accuracy of all the above determinations make values in the range 0–1000 cal. mole⁻¹ possible, but taking all the results together, the magnitude of the potential barrier

(12) Pitzer and Gwinn, *J. Chem. Phys.*, **10**, 428 (1942).

restricting the internal rotation in nitromethane would appear to be rather definitely established in the range of the above determinations.

The possibility that the value might lie in the range 8000–10,000 cal. mole⁻¹ is definitely excluded by the entropy determination.

We thank Dr. Jerome Martin of the Commercial Solvents Corporation for supplying the sample of nitromethane and Drs. J. E. Gordon and L. Guttman for assistance with the calorimetric measurements.

Summary

The heat capacity of solid and liquid nitromethane has been determined from 13 to 300°K.

The melting point is 244.73°K. (0°C. = 273.1°K.). The heat of fusion is 2319 cal. mole⁻¹.

The vapor pressure at 25° was found to be 3.666 cm. and the heat of vaporization at this temperature as measured calorimetrically is 9147 cal. mole⁻¹.

The observations were used to calculate the entropy of nitromethane in the ideal gas state at 298.1°K. and 1 atm. The value found was 65.73 cal. deg.⁻¹ mole⁻¹. As customary, this value does not include the entropy due to nuclear spin.

Combining the above entropy value with calculations based on available molecular data, the six-fold potential barrier restricting internal rotation in the nitromethane molecule is found to be 500 cal. mole⁻¹, in good agreement with values of 800 and 600 cal. mole⁻¹ found by Pitzer and Gwinn, and De Vries and Collins, respectively, from measurements of heat capacity of the gas.

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Crystal Structure of Sodium Borohydride

BY A. M. SOLDATE

The unexpected properties of sodium borohydride, such as its stability in vacuum at temperatures as high as 400°,¹ give interest to an investigation of its structure, hitherto unreported.

Experimental Methods and Results.—A sample of powdered sodium borohydride was kindly supplied by Dr. H. C. Brown of Wayne University, who reported it as being 98–99% pure. Specimens suitable for X-ray photography were obtained by sealing powdered material in thin-walled Pyrex capillaries about 0.5 mm. in diameter. To ensure adequate protection of this hygroscopic substance, the procedure was carried out over sulfuric acid in a sealed enclosure.

Powder photographs were made with copper

(1) Private communication from Dr. H. I. Schlesinger, The University of Chicago.

K α radiation filtered through nickel in a cylindrical camera with a 5-cm. radius. The twenty reflections observed were indexed on the basis of a cubic cell with $a_0 = 6.15 \text{ \AA}$. More precise lattice constant measurements using sodium chloride as an internal standard gave $6.151 \pm 0.009 \text{ kX}$ for the value of a_0 . No reflections with mixed indices were observed, the lattice is, therefore, face-centered.

The unit cell, being face-centered, must contain a multiple of four sodium borohydride molecules. It was assumed that the correct number of molecules in the unit cell is four. The density calculated with this assumption is 1.074 g./cc. No experimental value is known to us, but this value is a reasonable one. There are two ways in which the sodium and boron atoms can be arranged in the unit cell:

- (A) 4Na at 0 0 0, $0\frac{1}{2}\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$
 4B at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}00$, $0\frac{1}{2}0$, $00\frac{1}{2}$
- (B) 4Na at 0 0 0, $0\frac{1}{2}\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$
 4B at $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, $\frac{1}{4}\frac{3}{4}\frac{3}{4}$, $\frac{3}{4}\frac{1}{4}\frac{3}{4}$, $\frac{3}{4}\frac{3}{4}\frac{1}{4}$.

By use of Pauling-Sherman f values² and by neglect of the scattering power of the hydrogen atoms, intensities were calculated for both arrangements of the sodium and boron atoms. Table I shows good agreement between intensities calculated on the basis of arrangement A and observed intensities. The net effect of absorption and temperature corrections, omitted here, was estimated to be small.

TABLE I

A COMPARISON OF OBSERVED INTENSITIES AND INTENSITIES CALCULATED WITH SODIUM AND BORON ATOMS IN ARRANGEMENT A

(hkl)	Calcd. intensity	Obs. intensity ^a
111	231	m+
200	562	vs
220	386	s
311	138	m
222	130	m-
400	72	f
331	51	f
420	145	m-
422	105	f+
333-511	31	f-
440	33	f-
531	24	vf
442-600	65	f
620	45	f-
533	7	vvf
622	38	f-
444	15	vvf+
711-551	14	vvf
640	47	f-
642	108	f

^a s, Strong; m, medium; f, faint.

Intensities calculated for the second arrangement were in marked disagreement with those observed. For example, the calculated intensity of the line {220} is much greater than that of {200} and the calculated intensity of {331} is greater than that of {420}.

With the assumptions that each boron atom is

(2) L. Pauling and J. Sherman, *Z. Krist.*, **81**, 1 (1932).

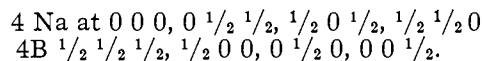
surrounded by a tetrahedral configuration of four hydrogen atoms and that the structure consists of BH_4^- and Na^+ ions, intensities were calculated for two arrangements of BH_4^- tetrahedra: (1) a completely random distribution of tetrahedra in positive and negative configurations (mirror images) with hydrogen atoms on cube diagonals; (2) tetrahedra all positive or all negative throughout the structure with hydrogen atoms on cube diagonals. In both instances the calculated intensities of {111} and {400} were the only values which differed from corresponding values of Table I by more than 20%. Agreement between observed and calculated intensities was not improved over that shown in Table I with either arrangement of tetrahedra. It was decided that it was impossible to reach any conclusion as to the positions of the hydrogen atoms from the intensity data obtained here.

With the assumption of a covalent boron-hydrogen bond distance of 1.16 Å., a van der Waals radius of 1.00 Å. for hydrogen, and a crystal radius of 0.95 Å. for sodium, it can be seen that the boron-sodium distance of 3.07 Å. and the boron-boron distance of 4.35 Å. are large enough to cause very little steric hindrance to rotational displacements of BH_4^- tetrahedra. Thus, rotating or oscillating BH_4^- tetrahedra can be reasonably presumed to exist in the structure and statistical distributions of tetrahedra, such as the one already considered, are of relevance.

I thank Dr. Linus Pauling for the suggestion of the problem and for helpful advice during the preparation of this report.

Summary

Powder photographic X-ray data have been used to show that the structure of sodium borohydride is based on a face-centered cubic lattice. The unit cell contains four sodium and four boron atoms arranged in the following manner:



The value 6.151 ± 0.009 kX was found for a_0 .

It is probable that the structure consists of tetrahedral BH_4^- ions and Na^+ ions. The dimensions of the ions would permit oscillation or rotation of the BH_4^- tetrahedra.

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