C–C determinations cannot be made to within sizable limits of error.

A comparison (Table I) of the observed q values with those calculated for model C (all bond angles tetrahedral, C–C = 1.54 Å., C–H = 1.09 Å.), a consideration of the radial distribution function, and comparisons of visual and calculated intensity curves lead to the following structural parameters and probable limits of error: symmetry $T_d - \bar{4}3m$ (assumed), $\angle HCH = 109°28'$ (assumed), C–H = 1.09 Å. (assumed), C–C = 1.54 ± 0.01 Å., $\angle C_2C_3C_2 = 109.5 \pm 1.5°$.

Acknowledgment.—We thank Professor Verner Schomaker for helpful advice and constructive criticism, Professor V. Prelog (Zürich) for the sample of adamantane used in the investigation, and the International Business Machines Corporation for the loan of the machines used in making calculations. One of us (W. N.) wishes to express his gratitude to Professor Linus Pauling for the many kindnesses extended him; he is also indebted to the American-Swiss Foundation for Scientific Exchange (Montclair, N. J.), to the Stiftung zur Förderung der wissenschaftlichen Forschung an der Bernischen Hochschule, and to the Government of the Canton of Berne for financial support and leave of absence.

Summary

An electron diffraction investigation of the structure of the adamantane molecule in the gas phase has led to values for the structural parameters in agreement with those found in the crystal. On the assumption of symmetry $T_d - \bar{4}3m$, of C–H = 1.09 Å., and of $\angle HCH = 109.5°$, the results are C–C = 1.54 ± 0.01 Å., and $\angle C_2C_3C_2 = 109.5 \pm 1.5°$.

Pasadena 4, California Received November 18, 1947

[Contribution from the Department of Chemistry and Chemical Engineering of the University of Washington]

The System Cesium Fluoride–Hydrogen Fluoride

By R. Virginia Winsor and George H. Cady

Mathers and Stroup[1] have shown that solutions made by melting acid fluorides of cesium may be used at approximately room temperature as electrolytes for the preparation of fluorine. They found that the acid fluorides of cesium have lower melting points than the corresponding salts of potassium, but in their work identified only the previously known compound, CsF·HF. A more thorough study of the system comprises the subject matter of the present article.

Experimental

A 36.0-g. sample of cesium fluoride was prepared from pulverized pollucite following a procedure based upon work of Wells[2] and recommended by Geo. McPhail Smith. The mineral was digested with an equal weight of 6 N hydrochloric acid at about 95° for approximately three days. Solid remaining undissolved was separated by filtration and the filtrate was evaporated to dryness. The product was then dissolved in four times its weight of 4 N hydrochloric acid and, after filtering, one gram atom of iodine was added for each mole of cesium chloride present. The liquid was then heated while an excess of chlorine was passed. As the resulting solution was allowed to cool, the compound $CsICl_2$ crystallized. This salt was purified by three recrystallizations in the presence of a little ICl in solution. Cesium chloride was produced by the thermal decomposition of $CsICl_2$. The chloride was converted to the nitrate which was fused with oxalic acid to form the carbonate. Aqueous hydrofluoric acid was allowed to react with the carbonate and the resulting solution was poured into the silver vessel shown in Fig. 1. Evaporation of the solution left the fluoride. Hydrogen fluoride was then added. The vessel was heated and hydrogen fluoride was removed by vacuum distillation. This process of adding and then removing hydrogen fluoride was repeated a few times with the result that the vessel plus the cesium fluoride came to constant weight.

Hydrogen fluoride was obtained as the vapor by distillation from a cylinder of the commercial anhydrous acid. About half of the material originally present in the cylinder had been removed by evaporation before starting the work on the system.

Cooling or warming curves were determined using the apparatus shown in Fig. 1. This comprised a silver cylinder, A, of 105 ml. capacity equipped with a thermocouple well, B, and a monel metal tube, C, through which materials were added or removed. The composition of the charge was determined by weighing the vessel and its contents. Temperatures were measured with a calibrated copper–constantan thermocouple connected to a potentiometer. Each cooling curve was established by first heating the vessel and then allowing it to cool slowly while being held firmly in a Dewar flask or other well-insulated vessel which was moved rapidly back and forth in a mechanical shaker. Temperatures below that of the room were reached by placing solid carbon dioxide in the Dewar vessel in such a location that the

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[1] F. C. Mathers and P. T. Stroup, *Trans. Am. Electrochem. Soc.*, **66**, 245 (1934).

[2] H. L. Wells, *Am. Chem. J.*, **26**, 265 (1901).

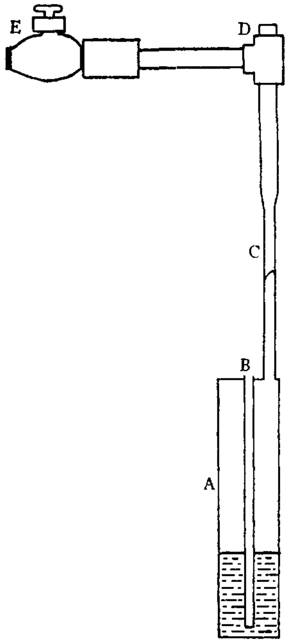

Fig. 1.

refrigerant did not touch the silver cylinder. In a number of cases, both cooling and warming curves were determined.

The temperatures of the observed significant breaks in the curves are shown in Fig. 2. From this diagram the data presented in Table I were selected.

Discussion

The data indicate the existence of four acid fluorides: CsF·HF, CsF·2HF, CsF·3HF and CsF·6HF. The first of these exists in two or perhaps three forms within the temperature range 30° to the melting point 176°. Several attempts were made to determine the number of forms and the transition temperatures, but the experiments gave ambiguous results.

TABLE I

SYSTEM CsF–HF

Mole fraction of HF in solution	Temp., °C.	Type of point	Solid phases present
0.500	176.0	Freezing	CsF·HF
.667	50.2	Freezing	CsF·2HF
.750	32.6	Freezing	CsF·3HF
.857	−42.3	Freezing	CsF·6HF
.453	151.5	Eutectic	CsF·HF and CsF
.639	38.3	Eutectic	CsF·HF and CsF·2HF
.709	16.9	Eutectic	CsF·2HF and Cs·F3HF
.828	−49.5	Eutectic	CsF·3HF and CsF·6HF
< .61	34.4 to 58.8	One or two transition points	Two or perhaps three forms of CsF·HF

In general, an abrupt change in slope in the cooling curve for a sample containing solid CsF·HF occurred at about 56.5°. The corresponding break in the warming curve usually occurred at about 42°. The proximity of the latter temperature to the eutectic point, 38.3°, for CsF·HF and CsF·2HF added to the difficulty of interpreting the experimental observations.

It is almost certain that no additional acid fluorides of cesium will be discovered by extending the study of the system beyond the concentration limits used in this research. In the case of mixtures rich in cesium fluoride, the thermal effect resulting from the freezing of CsF·HF and another solid, probably cesium fluoride, was still readily detected at a mole fraction of hydrogen fluoride of 0.205. It is also the case that the thermal decomposition of molten CsF·HF leaves solid cesium fluoride rather than an acid fluoride. These two facts strongly suggest that no acid fluorides exist which are richer in cesium fluoride than the salt CsF·HF. Since the most dilute solution studied (mole fraction of hydrogen fluoride equal to 0.876) showed no thermal effect due to eutectic freezing down to temperatures as low as −83° and since no other acid fluorides containing over six moles of hydrogen fluoride per mole of metal fluoride are known, it is unlikely that additional compounds exist in this part of the system.

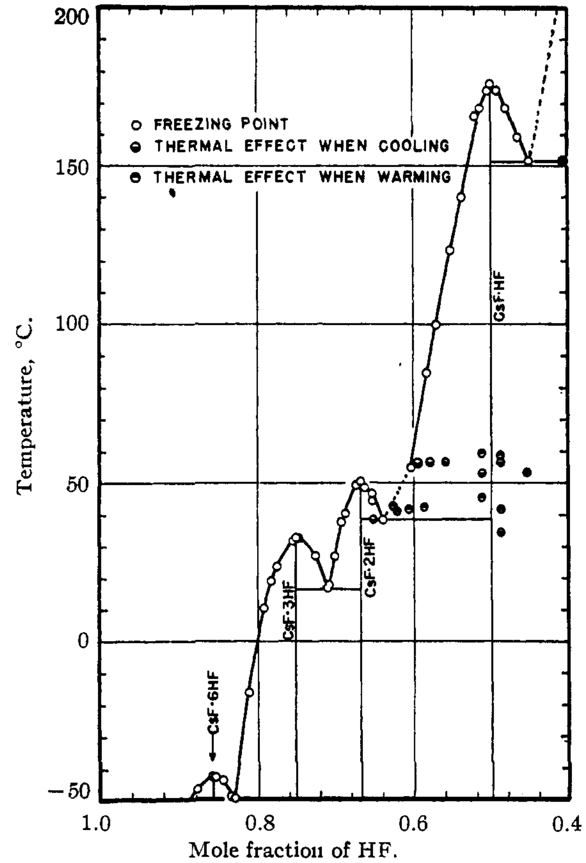

Fig. 2.—The system CsF–HF.

A comparison of the acid fluorides of the alkali metals reveals the following trends with increasing atomic number of the metal: (1) The melting points of corresponding compounds decrease. (2) The corresponding compounds become more stable. (3) The maximum number of moles of hydrogen fluoride capable of combining with one mole of metal fluoride apparently increases. Item (1) is illustrated by the fact that NaF·HF melts at some as yet undetermined temperature above 278°,[3] while the corresponding acid fluorides of potassium,[4] rubidium[5] and cesium melt congruently at 239.0, 205 and 176.0°, respectively. This trend is comparable with that existing for the

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[3] Froning, Richards, Stricklin and Turnbull, *Ind. Eng. Chem.*, **39**, 275 (1947).

[4] G. H. Cady, THIS JOURNAL, **56**, 1431 (1934).

[5] E. B. R. Prideaux and K. R. Webb, *J. Chem. Soc.*, 1 (1937).

normal fluorides whose freezing points are reported to be: lithium fluoride, 870°; sodium fluoride, 980–997°; potassium fluoride, 880°; rubidium fluoride, 760°; cesium fluoride, 684°. Item (2) is illustrated by the heats of formation of the acid fluorides of the type MF·HF from the solid fluorides of the type MF·HF from the solid fluoride of the metal and gaseous hydrogen fluoride. Values given by de Forcrand[6] for the salts progressing from that of sodium to that of cesium are in calories per mole: 17.10, 21.56, 22.58, 23.57. Further evidence for increasing stability is furnished by the temperatures at which the MF·HF compounds decompose to give solid MF and hydrogen fluoride vapor at one atmosphere pressure. The lithium and sodium salts decompose without melting at "below 200°"[7] and at 278°,[3] respectively. Potassium acid fluoride, KF·HF, melts, and the liquid must be heated to about 400°,[4,8] to cause the vapor pressure of hydrogen fluoride to be one atmosphere. The corresponding salts of rubidium and cesium require still higher, but at present unknown, temperatures. Item (3) is illustrated by the formulas for the highest known acid fluorides: LiF·HF, NaF·HF, KF·4HF, RbF·3HF (others may yet be found), CsF·6HF.

Both KF·HF and CsF·HF undergo transitions involving large heat effects. In the case of the former, the heat of transition is larger than the heat of fusion and the modification existing above the transition point is much softer than the low temperature form. The cause of the transition is not known, but it may possibly involve rotation of the HF_2^- ion.

Summary

Cesium fluoride and hydrogen fluoride form the compounds: CsF·HF, CsF·2HF, CsF·3HF and CsF·6HF.

SEATTLE 5, WASHINGTON RECEIVED AUGUST 8, 1947

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[6] M. de Forcrand, *Compt. rend.*, **152**, 1557 (1911).

[7] H. V. Wartenberg and O. Bosse, *Z. Elektrochem.*, **28**, 386 (1922).

[8] Fredenhagen and Cadenback, *Z. anorg. allgem. Chem.*, **178**, 289 (1928).

[CONTRIBUTION NO. 9 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES]

The Heat Capacity, Heat of Fusion and Entropy of Benzene[1]

BY GEORGE D. OLIVER, MARGARET EATON AND HUGH M. HUFFMAN

Because of the importance of benzene in organic chemistry and in industry the Bureau of Mines has considered it desirable to include this material in its research program involving determination of the thermodynamic properties of hydrocarbons and their derivatives.

Low-temperature measurements have been made on benzene by several investigators. Nernst[2] made measurements over the temperature range 20 to 80°K. Huffman, Parks and Daniels[3] made measurements over the temperature range 92 to 300°K. More recently Ahlberg, Blanchard and Lundberg[4] made measurements from 4 to 93°K. These authors used their data, combined with those of Huffman, Parks and Daniels,[3] to calculate the entropy of liquid benzene at 298.1°K. Hence the best experimental value of the entropy of benzene is the resultant of measurements made in different laboratories. It seemed desirable to obtain the value of the entropy from a single set of precise data in order to make a reliable comparison with the entropy calculated from spectroscopic and molecular data.

The Apparatus.—The measurements were made in the apparatus described by Ruehrwein and Huffman.[5] Very briefly, the method is as follows: About 0.6 mole of the material under investigation was contained in a sealed copper calorimeter, which was mounted in the adiabatic calorimetric system. A measured amount of electrical energy was supplied to the calorimeter, and at all times the temperature of the environment was maintained at that of the calorimeter to prevent heat interchange. The initial and final temperatures of the calorimeter were measured by means of a platinum resistance thermometer. The electrical measurements required for determination of the resistance of the thermometer and for electrical energy were made on a "White" double potentiometer in conjunction with a high-sensitivity galvanometer and accurately calibrated resistances. The potential was in terms of a bank of six saturated cadmium cells which had been certified by the National Bureau of Standards. Time measurements were made with an electric stop clock driven by alternating current, the frequency of which was controlled to about 0.001%. The precision of the measurements was in general better than 0.1%, and above 30°K. it is believed that the accuracy uncertainty should not be greater than 0.2%. The energy measurements were made in terms of the NBS international joule and were converted to calories by dividing by 4.1833.

Experimental

The Material.—The benzene used in this investigation was purified at the Laramie station of the Bureau of Mines[6] and supplied to this Laboratory for a check of its purity by a calorimetric melting point determination.

In July, 1944, a melting point study was made on this material but heat capacity measurements were not made at that time, since the laboratory hydrogen liquefier was not yet in operation. The material was left in the sealed calorimeter from July, 1944, until June, 1947, when the measurement of the heat capacity was undertaken. Due to a change in calorimetric technique it was necessary to

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[1] Published by permission of the Director, Bureau of Mines, U. S. Dept. of the Interior. Article not copyrighted.

[2] W. Nernst, *Ann. Physik*, **36**, 395 (1911).

[3] H. M. Huffman, G. S. Parks and A. C. Daniels, THIS JOURNAL, **52**, 1547 (1930).

[4] J. E. Ahlberg, E. R. Blanchard and W. O. Lundberg, *J. Chem. Phys.*, **5**, 539 (1937).

[5] Ruehrwein and Huffman, THIS JOURNAL, **65**, 1620 (1943).

[6] H. M. Thorne, W. Murphy and J. S. Ball, *Anal. Chem.*, **19**, 481 (1945).