The results for both the hafnium dioxide and the hafnium tetrachloride are regular, no evidence of any anomaly in the heat capacity being found for either substance in the temperature range studied. Measurements for the tetrachloride above 486°K. were precluded because of excessive swelling of the capsule at that temperature, probably due to a very small amount of superficial moisture in the sample. Hafnium tetrachloride has been reported to develop a sublimation pressure of 1 atm. at about 590°K.[5]

Even temperature values of the heat contents above 298.16°K., obtained from smooth curves, are listed in Table II together with matching entropy increments calculated by the method of Kelley.[6]

The heat content data are represented by the following equations derived by the method of Shomate,[7] the temperature range of validity and the mean deviation from the data being given in parentheses

$$\mathrm{HfO_2}:\ H_{\mathrm{T}} - H_{298.16} = 17.39T + 1.04 \times 10^{-3}\ T^2 + 3.48 \times 10^5\ T^{-1} - 6445 \qquad (298 - 1800°K;\ 0.3\%)$$

$$\mathrm{HfCl_4}\quad H_{\mathrm{T}} - H_{298.16} = 31.47T + 2.38 \times 10^5\ T^{-1} - 10{,}181 \qquad (298 - 485°\mathrm{K}.;\ 0.2\%)$$

BERKELEY 4, CALIFORNIA

---

[5] W. Fischer, R. Gewehr and H. Wingchen, *Z. anorg. Chem.*, **242**, 161 (1939).

[6] K. K. Kelley, U. S. Bur. Mines Bull. 476 (1949).

[7] C. H. Shomate, THIS JOURNAL, **66**, 928 (1944).

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Heat Capacity, Heat of Fusion and Heat of Vaporization of Hydrogen Fluoride[1]

BY JIH-HENG HU, DAVID WHITE AND H. L. JOHNSTON

RECEIVED OCTOBER 22, 1952

The heat capacity of 99.8% pure hydrogen fluoride has been measured between 15 and 300°K. No transitions were found, in the solid, as is the case in the other hydrogen halides; this is probably due to the existence of hydrogen bonding in hydrogen fluoride. The heat of fusion at the melting point, 189.79 ± 0.02°K., was found to be 46.93 ± 0.04 cal./g. The heat of vaporization at a pressure of 741.4 mm. and a temperature of 292.61 ± 0.1°K. was found to be 89.45 ± 0.20 cal./g. A comparison of the entropy at 741.4 mm. and 292.61°K., calculated from the heat capacity data and the third law, with that of the spectroscopic value leads to a discrepancy of 17.53 e.u. This has been accounted for by assuming that gas at this temperature and pressure consists of an equilibrium mixture of the monomer, the dimer, the trimer, and so on, these polymers being a consequence of the hydrogen bonding.

Introduction

An examination of the literature on thermal data of hydrogen fluoride leads to the conclusion that a number of discrepancies exist. The heat capacity has been measured by Clusius, Hiller and Vaughan[2a] and by Dahmlos and Jung.[2b] Experiments of the former covered the region 15 to 75°K., while those of the latter covered the range 98 to 273°K. An examination of these experiments indicates that the two sets of data are not in agreement, and, in fact, at the point where the two sets of data should meet, there appears to be evidence of a transition in the solid. Furthermore, the values of the heat of fusion and vaporization determined in these early experiments[2b,3] are quite uncertain.

By analogy with the other halides one would expect, in hydrogen fluoride, the existence of what appears to be second order transitions in the solid, but this possibility is remote. Regardless of whether these transitions are due to rotational oscillation of the molecules below the transition temperature to a phase in which the molecules are freely rotating[4] or to one of order–disorder,[5,6] the existence of the high degree of hydrogen bonding in hydrogen fluoride makes such transitions in the solid improbable.

Finally, the correlation of the spectroscopic data with that of the thermal data has not been settled. This problem is intimately connected with the manner in which these hydrogen bonds manifest themselves in the gas phase, since this ultimately reflects itself in the heat and entropy of dissociation to the ideal monomeric state. Two possibilities have been postulated: one by Hildebrand and Simons,[7a,b] assumed the formation of a six-membered ring, and the other by Briegleb,[8] which postulated the existence of monomer, dimer, trimer, etc., all being in equilibrium.

An attempt has been made in this paper to resolve these difficulties as well as to determine the thermodynamic properties which are important in the reaction: $H_2 + F_2 \rightarrow 2HF$. The work on thermal properties of fluorine, together with the thermodynamics of the reaction, will be reported in a subsequent paper.

Material.—The anhydrous hydrogen fluoride, having a purity of 99.8%, was obtained from the Harshaw Chemical Co. in Cleveland, Ohio. Their analysis indicated the following impurities: SO_2, 0.1%; as H_2SO_4, 0.06%; H_2SiF_6, 0.03%.

An attempt to further purify the material by distillation was made before using it in the calorimeter. Redetermination of the purity by the freezing point method indicated that the purity had not changed significantly. A description of the freezing point experiments are given in a later section of the text.

Apparatus.—The apparatus used in this research is shown schematically in Fig. 1. The calorimeter proper is a cylin-

---

(1) This work was supported in part by the Office of Naval Research under contract with The Ohio State University Research Foundation.

(2) (a) K. Clusius, K. Hiller and J. V. Vaughan, *Z. physik. Chem.*, **B8**, 427 (1930); (b) J. Dahmlos and G. Jung, *ibid.*, **B21**, 317 (1933).

(3) J. H. Simons and J. W. Bouknight, THIS JOURNAL, **54**, 129 (1932).

(4) L. Pauling, *Phys. Rev.*, **36**, 430 (1930).

(5) L. Landau, *Physik. Z. Sowjetunion*, **11**, 26, 545 (1937).

(6) N. L. Alpet, *Phys. Rev.*, **75**, 398 (1949).

(7) (a) J. H. Hildebrand, *J. Chem. Phys.*, **15**, 225 (1947); (b) J. Simons and J. H. Hildebrand, THIS JOURNAL, **46**, 2183 (1924).

(8) G. Briegleb, *Z. physik. Chem.*, **B51**, 9 (1941); **B52**, 368 (1942); **B53**, 225 (1943).

drical container of silver with a volume of 64.6 ml. made by Baker and Co. It is approximately 6 cm. in length and 3.8 cm. in diameter. Twelve radial fins of silver sheet are soldered inside the calorimeter to aid in establishing thermal equilibrium. The calorimeter is wound with about 160 ohms of nylon-covered No. 40 (gold + 0.15% silver) wire which serves as a combination resistance thermometer and heater. The cryostat and the arrangement of the calorimeter in it are similar to another condensed gas calorimeter system used in this Laboratory and which has been described by Johnston and co-workers.[9] The only difference between the present calorimeter and the early condensed gas calorimeter is the use of non-corrosive metals throughout. This, of course, necessitated avoiding any glass or grease lubricants. Thus all the tubes in the system are made of monel and the valves are of needle-type packed with Teflon, thereby being resistant to hydrofluoric acid. All junctions are made by silver solder.

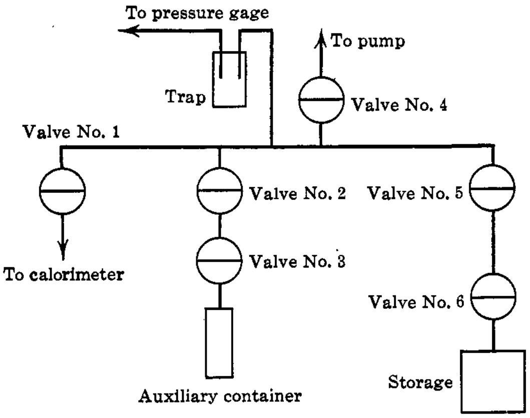

Fig. 1.—Schematic diagram for filling the calorimeter and measuring the heat of vaporization of anhydrous hydrogen fluoride.

Experimental Procedures.—A sample of hydrofluoric acid was first condensed from the storage tank to the auxiliary container and then, after careful weighing, from the auxiliary container to the calorimeter where the measurements were carried out (see Fig. 1). The weight of the sample was 60.643 g.

The experimental procedure for the determination of the heat capacity, heat of vaporization and heat of fusion is identical to that described by Johnston and Kerr[9] in their paper on condensed gas calorimetry.

During measurements of the heat of vaporization, the pressure was controlled by manually adjusting valve No. 1 shown in Fig. 1. The change of pressure was indicated by the mercury level in a glass U-tube, one end of which was connected to the calorimeter and the other open to the atmosphere. The control of pressure was made possible by observing the mercury level through a telescope mounted on a cathetometer. Following this procedure, it was possible to hold the pressure constant to within 1 mm.

Experimental Data

A. The Heat Capacity of Hydrogen Fluoride.—

The experimental data between 15 and 300°K. of both solid and liquid hydrogen fluoride are given in Table I. These data are plotted in Fig. 2 along with those of the previous investigations. The data of Dahlmos and Jung[2b] are only the smoothed values reported in their publication.

TABLE I

HEAT CAPACITY OF ANHYDROUS HYDROGEN FLUORIDE

Mean T, °K.	C_p, cal./°K./mole[a]	Mean T, °K.	C_p, cal./°K./mole[a]
Solid		Solid	
14.79	0.257	127.25	5.584
16.74	.359	134.04	5.796
18.52	.473	140.65	6.013
21.33	.667	147.24	6.248
23.51	.837	153.79	6.512
25.76	1.028	160.67	6.792
28.36	1.252	175.11	7.591
31.37	1.511	181.66	8.543
35.11	1.828	186.11	13.19
39.36	2.135	Melting point 189.79°K.	
44.05	2.414		
48.44	2.668	Liquid	
53.07	2.951	197.89	10.28
57.98	3.209	204.74	10.35
61.09	3.342	211.88	10.40
66.18	3.518	219.25	10.50
71.07	3.715	225.63	10.58
76.56	3.946	233.87	10.72
83.74	4.207	241.00	10.80
87.65	4.342	248.51	10.98
91.60	4.471	256.48	11.19
95.95	4.597	265.06	11.38
101.42	4.776	273.49	11.64
107.98	4.981	281.54	11.88
114.46	5.200	289.09	12.09
120.69	5.411	Boiling point 292.6°K.	

[a] C_p is for the liquid, calculated from experimental C_s data.

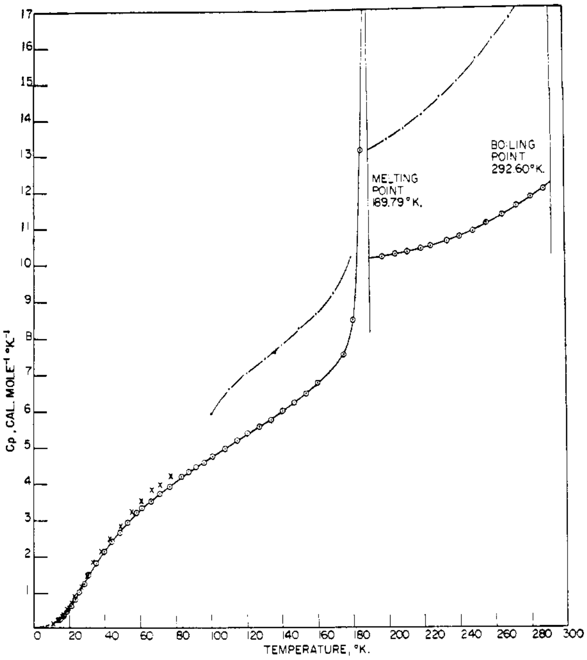

Fig. 2.—Heat capacity of anhydrous hydrogen fluoride: ⊙, this research; ×, Clusius, Hiller and Vaughan; —·—, Dahmlos and Jung (smoothed data).

B. The Determination of the Melting Point and the Sample Purity.—

Determinations of the melting point of the hydrogen fluoride showed that the value varied considerably with the amount melted. From thermodynamic considerations, one would expect the melting point to vary with the amount melted, according to the relationship

$$T = T_m - \frac{RT_m^2}{\Delta H_f}\left(\frac{y}{x + y}\right) \quad (1)$$

where T and T_m are the apparent and true melting

---

[9] H. L. Johnston and E. C. Kerr, THIS JOURNAL, **72**, 4473 (1950).

points of the material, respectively; x, the number of moles of material melted; y, the number of moles of impurity; and ΔH_f, the heat of fusion of the pure material. This relation holds provided: (i) the impurities are completely soluble in the liquid phase; (ii) the solution is sufficiently dilute to justify the assumption of ideality; (iii) the difference between the true and apparent melting points is small compared to the absolute value of the melting point. Since the solution is dilute, this reduces to

$$T = T_m - K(y/x) \qquad (2)$$

where K is a constant equal to $RT^2_m/\Delta H_f$.

In the case of hydrogen fluoride, it was found that a plot of T *vs.* y/x does not lead to a straight line from which T_m can be evaluated, but rises sharply as the material becomes completely melted. A consideration of the possible cause for this effect leads to a possibility arising from the high dielectric constant of hydrogen fluoride.

Since the impurities present are, in general, electrolytes and since the dielectric constant of hydrogen fluoride is of the order of that of water, but of course more acidic than water, all electrolytes in solution are probably weak in nature. Let y be the number of moles of ions in solution and y_0 the moles of ions when ionization of the impurities is complete. For very low concentrations we may assume that the ionization is proportional to the square root of the dilution. Thus

$$y = y_0 - c/(x)^{1/2} - \ldots \qquad (3)$$

where c is a constant. Substituting y into the above equation (2) gives

$$T = T_m - \frac{Ky_0 - c/(x)^{1/2}}{x} = T_m - a/x + c(1/x)^{3/2} \qquad (4)$$

Using the least square method, the constants for the equation are elucidated from the data. The final equation is

$$T = 89.793 - 0.2214\,(1/x) + 0.08616(1/x)^{3/2} \qquad (5)$$

giving as the true melting point T_m of pure HF the value 189.79 ± 0.02°K. The experimental results and a comparison with the temperature calculated from equation (5) are given in Table II.

TABLE II

$1/x$	$T_{\text{obsd.}}$, °K.	$T_{\text{calcd.}}$ °K.	$\Delta T(T_{\text{obsd.}} - T_{\text{calcd.}})$, °K.
3.110	189.576	189.577	−0.001
2.006	189.598	189.594	+ .004
1.623	189.612	189.612	.000
1.363	189.623	189.628	− .005
1.175	189.637	189.643	− .006
1.033	189.662	189.655	+ .007

From the above equation we find: $Ky_0 = 0.2214$ and $K = 76.30$; $y_0 = 0.2214/76.30 = 0.29 \times 10^{-2}$. Assuming that the average ionic weight of the impurity is approximately 35, then the weight of impurity present in the sample (which is 60.64 g.) is approximately 0.10 g.

The purity of the sample is estimated at 99.8% which checks with the original analysis.

C. The Heats of Fusion and Vaporization.—Two direct determinations of the heat of fusion and five of the heat of vaporization were made. The heats of vaporization were determined at a pressure of 741.4 mm. The boiling point at this pressure was found to be 292.61 ± 0.1°K. The experimental results are given in Table III.

TABLE III

Heat of fusion Run	ΔH_f, cal./g.	Heat of vaporization Run	Amount vaporized, g.	ΔH_V, cal./g.
1	46.98	1	20.976	88.51
2	46.88	2	7.154	89.50
Average	46.93 ± 0.04	3	7.192	89.46
		4	7.190	89.27
		5	7.063	90.53
			Average	89.45 ± 0.20

THE CALORIMETRIC VALUE OF THE ENTROPY OF HYDROGEN FLUORIDE

1, solid 0–14°K. (θ = 180)	0.072 e.u.
2, solid 14–189.79°K. (Simpson's rule)	8.069
3, entropy of fusion at 189.79°K.	4.942
4, liquid 189.79–292.61°K. (Simpson's rule)	4.705
5, entropy of vaporization at 292.16°K.	6.117
Total molar entropy of gaseous hydrogen fluoride at 741 mm. and 292.61°K.	23.90 e.u.

Discussion of Results

(a) Comparison with Spectroscopic Data.—An examination of the heat capacity data shown in Fig. 2 indicates that although the data of Clusius, Hiller and Vaughan[2a] are in fair agreement, the data of Dahmlos and Jung[2b] are much too high. Furthermore, as is to be expected, there exists no second order transition in the solid state as is the case in the other hydrogen halides. The values of the melting point and heats of fusion and vaporization are also considerably lower than those of previous determinations, the heat of fusion being 46.93 cal./g. as compared to 54.6 cal./g., and the heat of vaporization being 89.45 cal./g. as compared to 95 cal./g.

A considerable discrepancy exists between molar entropies of gaseous hydrogen fluoride determined calorimetrically and those calculated from spectroscopic data. The spectroscopically calculated values, given by Murphy and Vance[10] and Belzer, Savedoff and Johnston,[11] are 41.49 e.u. and 41.51 e.u., respectively, at 298.16°K. Thus there exists a discrepancy of 17.53 e.u.

It has been well known for a long time from data of state,[7b,12,13] and dielectric constant measurements[14] that gaseous hydrogen fluoride is associated. One can account for this discrepancy from a purely thermodynamic argument, regardless of the manner in which the association due to hydrogen bonding takes place. If one assumes that at infinite attenuation hydrogen fluoride is not associated, the change in entropy on expanding from 741.4 mm. and 292.61°K. to zero pressure at that temperature is

[10] G. M. Murphy and J. E. Vance, *J. Chem. Phys.*, **7**, 806 (1939).

[11] H. L. Johnston, J. Belzer and L. Savedoff, unpublished data.

[12] R. L. Long, J. H. Hildebrand and W. E. Morrell, THIS JOURNAL, **65**, 182 (1943).

[13] K. Friedenhagen, *Z. anorg. allgem. Chem.*, **218**, 161 (1934).

[14] R. A. Oriani and C. P. Smyth, THIS JOURNAL, **70**, 125 (1948).

$$S_{(p=0)} - S_{(p=741.4)} = \frac{H^* - H_{(p=741.4)}}{T_B} - \int_{741.4}^{0} \frac{V\mathrm{d}p}{T} = \frac{\Delta H^* - \Delta H_{(p=741.4)}}{T_B} - \int_{741.4}^{0} \frac{V\mathrm{d}p}{T} \quad (6)$$

where ΔH^* is heat of vaporization to a vacuum and ΔH the heat of vaporization at 741.4 mm. pressure. The difference between the entropy in the ideal state at zero pressure and at 1 atmosphere is given by

$$S^\circ_{(p=760)} - S_{(p=0)} = -\int_{0}^{741} \frac{R}{p}\,\mathrm{d}p - \int_{741}^{760} \frac{R}{p}\,\mathrm{d}p \quad (7)$$

By adding equations (6) and (7) we get

$$S^\circ_{(p=760)} - S_{(p=741)} = \frac{\Delta H^* - \Delta H_{(741)}}{292.61} + \int_{0}^{741} \frac{V\mathrm{d}p}{T} - \int_{0}^{741} \frac{R}{p}\,\mathrm{d}p - \int_{741}^{760} \frac{R}{p}\,\mathrm{d}p \quad (8)$$

Friedenhagen[13] has measured ΔH^* of hydrogen fluoride by pumping on the liquid at 292.70°K. He obtained a value of $\Delta H^* = 7800$ cal. for 20.01 g. Simons and Hildebrand,[7b] Friedenhagen,[13] and Long, Hildebrand and Morrell[12] have made very extensive studies on the vapor density of hydrogen fluoride. From their results, they found that the equation of state can be represented by $pV = (1/z)RT$ where z is interpreted as the association factor. For the purposes of this calculation we may ignore the phenomena of association, and simply regard it as an equation of state. Thus we have at 292.61°K.

$$\begin{aligned} &S^\circ_{(p=760)} - S_{(p=741.4)} \\ &= \frac{7800-1789.89}{292.61} + R\int_{0}^{741.4}\left(\frac{1}{z} - 1\right)\frac{1}{p}\,\mathrm{d}p - R\int_{741.4}^{760}\frac{\mathrm{d}p}{p} \\ &= 20.540 - 1.689 - 0.022 = 18.829 \text{ e.u.} \end{aligned}$$

Adding this to the calorimetrically determined entropy one obtains, 42.73 e.u. at 292.61°K., or $S^0_{(p=760)} = 42.79$ at 298.16°K. This value compares favorably with that calculated from spectroscopic data, considering the uncertainty of ΔH^*.

(b) Calculation of Entropy of Polymerization in the Gas Phase.—From the vapor density of gaseous hydrogen fluoride, Simons and Hildebrand[7b] and later Long, Hildebrand and Morrell[12] considered that the gaseous hydrogen fluoride consists mainly of (HF) and (HF)$_6$, the latter probably of ring structure. Their data were explained by assuming the equilibrium constant between (HF) and (HF)$_6$ to be given by

$$-R\ln K = -\frac{40800}{T} + 199.74 \quad (9)$$

Briegleb,[15] on the other hand, assumed that the gas consists of polymers of an indefinite number of molecules, and on this assumption he calculated, using the vapor density data of Fredenhagen,[13] the equilibrium constants $k_{n,n+1}$'s for the reaction (HF) + (HF)$_n$ = (HF)$_{n+1}$, where $n = 1, 2, \ldots$ at the temperatures 299 and 311°K. An attempt will be made to calculate the entropy of polymerization based upon these two different models in order to see which of the two corresponds to the actual case.

Using equation (9), we calculate $\Delta S = -199.74$ e.u. for the reaction 6(HF) = (HF)$_6$. Assuming we start with one mole of hydrogen fluoride in the form of HF, at equilibrium there will be x moles of (HF)$_6$ formed leaving $(1 - 6x)$ moles of HF. The total number of moles $= 1 - 5x = 1/z$, where z is the association factor. From the data of Simons and Hildebrand,[7b] $z = 3.168$ at $T = 292.6$° K., therefore $x = 0.137$. The entropy of the mixture, starting from one mole of monomer, becomes

$$S = (1 - 6x)S_{\mathrm{HF}} + xS_{(\mathrm{HF})_6} - R\left[(1 - 6x)\ln\frac{1 - 6x}{1 - 5x} + x\ln\frac{x}{1 - 5x}\right] \quad (10)$$

where the latter term corresponds to the entropy of mixing. Inserting numerical values for each of the terms in equation (10), we get for the entropy of polymerization, $\Delta S_{\mathrm{p}} = S_{\mathrm{HF}} - S = 26.93$ e.u. This should account for the discrepancy of 17.5 e.u. between the calorimetric and spectroscopic calculation. Since the calculated value is about 9 e.u. higher than the entropy of polymerization expected from our calorimetric data, it is evident that this model cannot explain the discrepancy.

Using the model proposed by Briegleb,[15] another calculation of the entropy of polymerization was made. Since there are reasons to believe that the data of Long, Hildebrand and Morrell[12] are more accurate than the data used by Briegleb, we have recalculated the $k_{n,n+1}$'s It is found, however, that although the absolute values of $k_{n,n+1}$'s differ 50 to 100% from Briegleb's calculation, the temperature coefficients agree to within the limit of error set by him. It must be remembered that Breigleb used only the data of Fredenhagen at 299 and 311°K. Had he used the experiments at the intermediate temperature, his data would differ considerably from our calculations. Our calculations lead to two equations for the equilibrium constant

$$-R\ln k_{1,2} = -\frac{2400}{T} + 83.20 \quad (11)$$

and

$$-R\ln k_{n.n+1} = \frac{4030}{T} + 12.80,\ n \geqq 2 \quad (12)$$

from which we obtain

$$\Delta S^\circ_{1,2} = S^\circ_{(\mathrm{HF})_2} - 2S^\circ_{\mathrm{HF}} = -83.20 \text{ e.u.}$$

for the reaction 2HF = (HF)$_2$, and

$$\begin{aligned} \Delta S^\circ_{1,n} &= \Delta S^\circ_{1,2} + \Delta S^\circ_{2,3} + \ldots\ldots + \Delta S^\circ_{n-1,n} = -83.20 - (n - 2)(12.80) \\ &= -57.60 - 12.80n, \text{ for } n \geq 2 \end{aligned} \quad (13)$$

for the reaction 2(HF) = (HF)$_2$, 3(HF) = (HF)$_3$, etc.

For the entropy, S, of the whole system, starting from 1 mole of monomer consisting of all these polymers, we get

$$S = \frac{1}{z}\left[S_{\mathrm{HF}}\left(\frac{p_1}{p}\right) + \sum_{j=2}^{\infty} S_{(\mathrm{HF})_j}\frac{k_{1j}p_1{}^j}{p} - \mathrm{R}\left\{\frac{p_1}{p}\ln\frac{p_1}{p} + \sum_{j=2}^{\infty}\frac{k_{1j}p_1{}^j}{p}\ln k_{1j}\frac{p_1{}^j}{p}\right\}\right] \quad (14)$$

where the last term represents the entropy of mixing, p_1 the partial pressure of monomer, p the total

---

[15] G. Briegleb, *Z. physik. Chem.*, **B51**, 9 (1941).

pressure. Thus p_1/p represents the mole fraction of the monomer and $k_{1j}p_1^j/p$ the mole fraction of the polymers. The total pressure, p, is given by

$$p = p_1 + \sum_{j=2}^{\infty} k_{1j}p_1^j \qquad (15)$$

Since z represents the ratio of the number of molecules that exist as a monomer to the number of molecules in the actual gas, we can write

$$z = \frac{p_1}{p} + \sum_{j=2}^{\infty} \frac{jk_{1j}p_1^j}{p} \qquad (16)$$

Substituting equations (13), (15) and (16) into equation (14), we get for the entropy of polymerization, ΔS_p which is equal to $S_{HF} - S$

$$12.80 + \frac{1}{z}(57.60) - \frac{1}{z}(70.40)\frac{p_1}{p} + \frac{R}{z}\frac{p_1}{p}\ln\frac{p_1}{p} + \frac{R}{z}\sum_{j=2}^{\infty}\frac{k_{1j}p_1^j}{p} \times \ln\frac{k_{1j}p_1^j}{p} \qquad (17)$$

Since

$$k_{1i} = \prod_{n=1}^{j} k_{n,n+1} \qquad (18)$$

and $k_{n,n+1}$ for $n > 1$ all have the same value; substituting (11) and (12) into the above equation we obtain

$$k_{1j} = 10^{-0.45673}(10^{0.21197})^j \qquad (19)$$

Substituting equation (19) into (15) and summing

$$p = p_1 + \frac{(0.90)p_1^2}{(1 - 1.659\ p_1)}$$

For a pressure, p, of 741.4 mm., this leads to a value of p_1 = 0.428 atm. Finally, substituting values of p_1, p, k_{1j} and z into equation (17), one obtains $\Delta S_p = 20.2 \pm 2$ e.u. Adding this to the calorimetric data, S^0_{HF} at 741.4 mm. and 292.61°K. becomes 44.10 ± 2 e.u., or S^0_{HF} at 760 mm. and 298.16°K. becomes 44.11 ± 2 e.u. This large uncertainty arises from errors in computing the equilibrium constants. Nevertheless the value leads to a reasonable agreement between the entropy determined calorimetrically and that from spectroscopic calculations, indicating that this model is probably correct. It should be mentioned that using the data of Breigleb, closer agreement can be attained; however, this is still within the estimated uncertainty.

This model is further substantiated by measurement by Oriani and Smyth[14] of the dielectric constant of the gas which shows that its dipole moment increases with pressure, this being impossible if the polymer exists solely in the ring form. The electron diffraction pattern[16] also indicates that the polymer forms a zigzag chain.

(c) **Zero Point Entropy.**—Finally, it is evident that the residual zero point entropy due to the hydrogen bonding cannot be evaluated from the data, due to the large uncertainty of the entropy of polymerization. There is, however, evidence that the fluorine molecule is located centrally between the hydrogen atoms.[17,18] In view of the fact that the values of the entropy from calorimetric data and from the polymerization calculation are higher than the spectroscopic value, even within the uncertainty limits, this is in agreement with our calculations.

Acknowledgments.—We wish to especially thank Mr. Nathan Hallet for the construction and assembly of the apparatus as well as the calibration of the empty calorimeter. We also wish to acknowledge the aid of Mrs. Margaret Thomas in some of the calculations.

---

[16] S. H. Bauer, J. Y. Beach and J. H. Simons, *Z. physik. Chem.*, **61**, 19 (1939).

[17] S. W. Peterson and H. A. Levy, *J. Chem. Phys.*, **20**, 704 (1952).

[18] E. F. Westrum, Jr., and K. S. Pitzer, THIS JOURNAL, **71**, 1940 (1949).

COLUMBUS 10, OHIO

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

New Neptunium Compounds

BY IRVING SHEFT AND SHERMAN FRIED

RECEIVED OCTOBER 10, 1952

This paper reports the preparation and identification of several new compounds of neptunium. In each case the identity of the compound was established from an analysis of the X-ray diffraction pattern by Prof. W. H. Zachariasen of the Physics Department of the University of Chicago.

Neptunium Carbides.—Neptunium dicarbide, NpC_2, was prepared by the action of carbon on neptunium oxide at high temperature.

A few milligrams of neptunium oxide, prepared by precipitation of the hydroxide from solution with subsequent ignition at 500° was placed in the graphite crucible shown in Fig. 1. The apparatus was flushed with hydrogen for half an hour and the crucible heated to 2660–2800° for five minutes using a high frequency generator. The temperature was determined by means of an optical pyrometer. The product formed was a metallic appearing film which was chipped out of the graphite crucible, freed from adhering fragments of graphite and submitted for X-ray analysis. It proved to be neptunium dicarbide, NpC_2, isomorphous with the corresponding uranium compound.

The conditions under which neptunium dioxide can be converted to a recoverable product seem to be fairly critical. At temperatures below 2500° no reaction seems to take place while at temperatures much above 2800° the product seems either to fuse and "soak" into the pores of the crucible or to volatilize away.

Another method of preparing neptunium carbides yielded lower valent compounds. In this case the fluoride of neptunium was treated with lithium vapor at a high temperature in a graphite crucible.