ample, iso-C_5H_{12}[7] has a sodium-D index of 1.3580 at 15° and its dispersion ($H_\beta - H_\alpha$) is 0.00619. It is also interesting to note that the index of perfluoro-*n*-pentane is lower than that of the perfluoroisopentane, a situation just opposite to the usual order of molecular properties of the hydrocarbons.[8]

Surface Tension.—The surface tensions for the four compounds examined are listed in Table III together with the value for $\gamma_{20°}$ taken from the smoothed curves. The plot of these values is shown in Fig. 3.

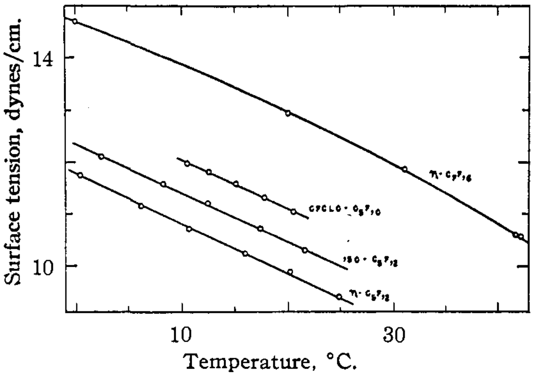

Fig. 3

TABLE III

SURFACE TENSION (DYNES/CM.)

n-C_5F_{12}	Iso-C_5F_{12}	Cyclo-C_5F_{10}	*n*-C_7F_{16}
0.40°—11.73	2.43°—12.11	10.5°—11.99	42.2° —10.57
6.23°—11.16	8.2° —11.59	12.5°—11.82	41.7° —10.60
10.67°—10.72	12.44°—11.21	15.1°—11.59	31.05°—11.86
15.95°—10.25	17.43°—10.72	17.8°—11.32	20.0° —12.96
20.16°— 9.90	21.6° —10.31	20.5°—11.04	0.0° —14.69
24.95°— 9.42			
$\gamma_{20°}$ = 9.87	$\gamma_{20°}$ = 10.48	$\gamma_{20°}$ = 11.09	$\gamma_{20°}$ = 12.96[a]

[a] R. D. Fowler, *et al.*, obtained a value of $\gamma_{20} = 13.6$ for perfluoro-*n*-heptane using a du Noüy interfacial tensiometer; R. D. Fowler, *et al.*, *Ind. Eng. Chem.*, **39**, 375 (1947).

The values for the surface tensions of the fluoropentanes are seen to be lower than any yet reported for compounds normally liquid at room temperature. Again the peculiarity of this molecular property being lower in the normal than in the iso-fluorocarbon is noted.

Acknowledgment.—This work was performed under contract with the Office of Naval Research, U. S. Navy Department.

Summary

The refractive indices over a wide range of wave lengths have been measured at 15° for the compounds: *n*-C_5F_{12}, iso-C_5F_{12}, cyclo-C_5F_{10}, *n*-C_5HF_{11} and cyclo-C_5HF_9. Both magnitude of the indices and dispersion were found to be very low.

The surface tensions of the perfluoropentanes as well as of *n*-C_7F_{16} were measured over a temperature range between 0 and 40°. The value for *n*-C_5F_{12} is lower than any previously reported for a compound normally liquid at that temperature.

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[7] J. Timmermans and F. Martin, *J. Chim. Phys.*, **23**, 747 (1926).

[8] Burger (*cf.* ref. 1) also found that the boiling point, the density and the viscosity of *n*-C_5F_{12} were lower than those of iso-C_5F_{12}.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA]

Thermodynamics of the System KHF_2–KF–HF, Including Heat Capacities and Entropies of KHF_2 and KF. The Nature of the Hydrogen Bond in KHF_2[1]

BY EDGAR F. WESTRUM, JR.,[2] AND KENNETH S. PITZER

This investigation was undertaken to determine whether the proton in the $F-H-F^-$ ion is located in a single potential minimum midway between the fluoride ions or is unsymmetrically placed as in the O–H–O case in ice,[3] etc. The method initially adopted included measurements of the heat capacity from 14° to 500° K. of KF(s) and KHF_2(s). From these data and the statistically calculated entropy of HF(g) the change in entropy can be calculated for the reaction

$$KHF_2(s) = KF(s) + HF(g)$$

This was to be compared with the entropy change from direct heat and equilibrium measurements. If the two results agree, then KHF_2 must have taken on a perfectly ordered structure at low temperatures. However, if the $F-H-F^-$ ion is not symmetrical, one expects either a disordered structure at low temperatures or a transition of some sort where the disorder sets in on heating.

In addition, there are the infrared spectral data of Ketelaar[4] and values of the dielectric constant obtained by us which help in making the conclusions definite.

Experimental

Preparation and Purity of KHF_2.—The crystalline potassium hydrogen fluoride for the calorimetric work was prepared by slowly adding anhydrous potassium carbonate to aqueous hydrofluoric acid; both reagents were "Chemically Pure." The only stated contaminants were maxima of 0.001% H_2SiF_6 in the acid and 0.02% of sodium

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[1] These results are abstracted from the Ph.D. Dissertation of E. F. Westrum, Jr., University of California, 1944, except for the dissociation pressures of KHF_2 measured by E. F. Westrum, Jr., in 1946 and the dielectric constant measured by K. S. Pitzer in 1948.

[2] Present address, Department of Chemistry, University of Michigan, Ann Arbor, Michigan.

[3] L. Pauling, THIS JOURNAL, **57**, 2680 (1935); W. F. Giauque and J. W. Stout, *ibid.*, **58**, 1144 (1936).

[4] J. A. A. Ketelaar, *Rec. trav. chim.*, **60**, 523 (1941).

in the carbonate. The neutralization was carried out entirely in platinum ware, and after addition of a stoichiometric excess of several per cent. acid, the solution was boiled to concentrate it and to drive off any remaining carbon dioxide. Precipitation was effected by controlled cooling, and the mother liquor removed by filtering and washing with distilled water in a large Büchner type funnel constructed entirely from hard, unlaminated bakelite. Several recrystallizations were similarly made from solution containing a very slight excess of acid, with ethyl alcohol used as precipitant and wash solution in the final steps to reduce the high solubility of the salt and improve the yields. The hot, concentrated solution of the salt was in contact only with platinum ware, and the cold solid handled with bakelite paddles and in bakelite filtering apparatus for brief periods. A bakelite pestle was used to reduce the size of any loosely massed crystalline aggregates. The last traces of solvent were removed by prolonged pumping under high vacuum at 40°. Lack of any rise in the heat capacity curves near the ice-point was confirmatory evidence that the samples did not contain appreciable water.

The several batches of thus prepared acid fluoride yielded identical analyses. Microscopically, the crystals appeared to be definitely crystalline, well formed, transparent, and of an average diameter of about 0.1 to 0.3 millimeter. A volumetric, acidimetric determination of hydrogen ion *versus* carbonate-free sodium hydroxide standardized against recrystallized potassium acid phthalate and compared to an acid carefully standardized against reagent mercuric oxide and sodium tetraborate yielded 100.03 ± 0.06% of the theoretical amount. In all the determinations and standardizations weight burets were employed, the fluoride samples weighed in a platinum vessel and the titration performed in a platinum beaker. Identical results were obtained both by direct neutralization and by first precipitating the fluoride ion with calcium chloride. Phenolphthalein and thymolsulfonphthalein were used as indicators. Gravimetric analysis for fluoride by the precipitation of calcium fluoride showed 48.5 ± 0.2% fluoride (theoretical, 48.65%).

Preparation and Purity of Potassium Fluoride.—In order to obtain the potassium fluoride in a form convenient to handle and identical with that in the dissociation equilibrium, a portion of the same batch of the acid fluoride used for the calorimetric measurements was decomposed thermally in a high vacuum. In order to avoid fusion of the acid salt (resulting in a product difficult to handle in platinum under anhydrous conditions), it was necessary to carry out the initial stages of the decomposition at about 200°, safely below the KF–KHF_2 eutective temperature. The salt was heated in a tall platinum beaker within a heavy steel cylinder connected to a copper line and trap so designed as to permit the removal of the trap to allow the HF content to be determined without interruption of the evacuation. At this temperature decomposition was very slow; several days were required to decompose the bulk of the acid fluoride. The last per cent. of HF was removed upon gradually raising the temperature of the system to 295° and maintaining it at this temperature twenty-four hours after no detectable HF was evolved.

The extremely hygroscopic character of the anhydrous KF necessitated handling the salt under practically anhydrous conditions. The "dry-box" (provided with glass sides and top and elbow length rubber gloves fitted through armholes) was of sufficient size to enclose an analytical balance and permit handling the salt in a continuously flowing atmosphere of anhydrous air. To avoid adsorption of even minute amounts of water during storage, the KF desiccator was kept attached to a vacuum system and pumped on constantly through a protecting liquid air trap.

Samples of the anhydrous potassium fluoride dissolved in aqueous solution were neutral to phenolphthalein within 0.01%. The loss in weight on carefully heating small portions of the acid fluoride to constant weight was 25.60 ± 0.04% (theoretical loss $KHF_2 \rightarrow KF = 25.62\%$). This analytical operation is carried out below the eutectic temperature in the absence of moisture because the molten acid fluoride tends to creep over the lip of the platinum crucibles and the anhydrous KF has so great an affinity for water that even in the process of transferring it to a vacuum desiccator, sufficient water is adsorbed so that on reheating the salt is hydrolyzed, giving a basic reaction in aqueous solution.

The Low Temperature Heat Capacities.—The method and the low temperature, vacuum insulated calorimeter and cryostat have been used in previous work in this Laboratory and are described in the literature.[5,6,7] In particular the resistance thermometer used was that employed by Pitzer and Scott for measurements on *m*- and *p*-xylene and its calibration is described by them.[8]

This calibration was used directly on the initial series of heat capacity determinations on KHF_2 (labelled "Series I" in the tabulations of data). Before completing the measurements, certain repairs were made on the electrical wiring of the calorimeter. No changes were made other than the introduction of new 4-strand platinum leads from the same spool of wire (total resistance = 0.231 ohm), the reforming of soldered connections, and the possibility of the introduction of slight strain in the thermometer wire. After securing the remainder of the data on KHF_2, KF, and on the empty calorimeter, the steam point, the ice-point, the oxygen and the hydrogen vapor pressures, and the hydrogen triple-point were redetermined and the resistance of the repaired thermometer was found to be slightly less than that of the original. The deviations showed a definite trend such that when computed for a correction term to the practical resistance–temperature tabulations, the equation for the change in temperature (ΔT) at the tabulated resistance (R) was found to have the form

$$\Delta T° = 0.00224R + 0.0156$$

Suitable correction in the observed temperature and the derivative of temperature could then be made for purposes of computation. The exactness of the correction was confirmed by the excellent agreement obtained on the heat capacity of the empty calorimeter before and after thermometer repairs and the coincidence of the heat capacities of "Series I" and of "Series III" of KHF_2, the latter taken on a new portion of sample after the rewiring.

In both calibrations, the vapor pressure equations for hydrogen and oxygen given by Henning and Otto[9] were employed. The temperature, 273.16°K., was taken as the ice point.

A sample of 68.977 g. of KHF_2 (molecular weight = 78.104) was used for "Series I" determinations and 76.734 g. for "Series II and III." A 62.553-g. sample of KF (molecular weight 58.096) was employed. All weights have been reduced to vacuum. Helium gas at low pressure was used to promote heat conduction within the calorimeter.

Tables I and II and Fig. 1 contain the observed values of the heat capacities. Values of the heat capacity at even temperatures interpolated from smooth curves through the experimental observations are given in Table III. Except at the lowest and highest temperatures the error of these results is believed to be within 0.2%. At the lowest temperatures, the error may be several per cent., and in the region just above room temperature the accuracy of the determination is diminished greatly due to large radiation effects producing uncertainties in the heat capacity—possibly as large as 1%. It is to be noted, however, that the data in this region are not used in the calculation of the entropy at 298°K. Furthermore, the higher temperature heat content data also serve to establish the position and direction of the curve through this region of moderate accuracy of the low temperature cal-

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[5] W. M. Latimer and B. S. Greensfelder, THIS JOURNAL, **50**, 2202 (1928).

[6] O. L. I. Brown, W. V. Smith and W. M. Latimer, *ibid.*, **58**, 1758 (1936).

[7] K. S. Pitzer and L. V. Coulter, *ibid.*, **60**, 1310 (1938).

[8] K. S. Pitzer and D. W. Scott, *ibid.*, **65**, 803 (1943).

[9] F. Henning and J. Otto, *Physik. Z.*, **37**, 633 (1936).

TABLE I

MOLAL HEAT CAPACITY OF POTASSIUM FLUORIDE

T, °K.	C_p, cal./deg.	T, °K.	C_p, cal./deg.
16.05	0.1157	95.06	7.230
17.46	.1647	102.76	7.704
18.55	.2066	111.41	8.206
19.43	.2321	120.39	8.633
19.95	.2609	129.84	9.046
20.70	.3018	140.10	9.439
21.57	.3431	148.20	9.707
22.63	.3995	157.41	9.933
24.91	.5462	167.19	10.17
27.42	.7288	176.98	10.40
30.33	.9457	186.40	10.57
33.97	1.297	196.10	10.74
38.37	1.725	206.05	10.89
43.08	2.219	215.18	11.03
48.28	2.815	223.28	11.10
53.43	3.422	233.33	11.25
58.99	4.066	244.33	11.33
58.50	4.027	255.45	11.43
64.22	4.605	266.69	11.52
67.04	4.893	277.66	11.61
70.51	5.232	288.86	11.66
73.31	5.482	300.35	11.70
80.57	6.143	311.35	11.79
87.81	6.713	322.63	11.82

orimeter. All data are reported in terms of a defined calorie equal to 4.1833 international joules.

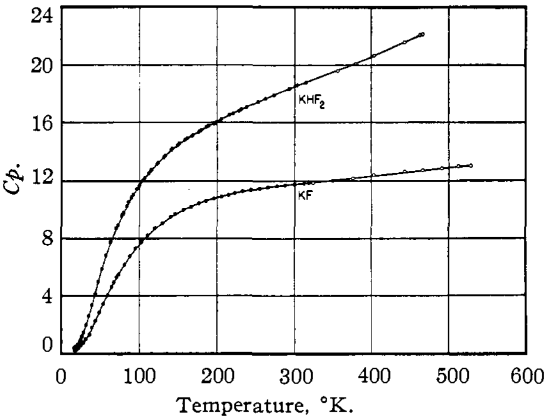

Fig. 1.—The molal heat capacity of KF and KHF_2.

TABLE II

MOLAL HEAT CAPACITY OF POTASSIUM HYDROGEN FLUORIDE

T, °K.	C_p, cal./deg.	Series	T, °K.	C_p, cal./deg.	Series	T, °K.	C_p, cal./deg.	Series
16.02	0.309	III	89.44	10.81	III	186.89	15.64	III
17.34	.345	III	92.38	11.07	1	189.03	15.74	II
18.45	.390	III	96.58	11.41	III	196.34	15.92	III
20.55	.562	III	99.32	11.62	I	198.44	15.97	II
22.64	.769	III	104.10	12.00	III	206.19	16.20	III
23.90	.918	III	106.90	12.19	I	208.52	16.23	II
25.49	1.121	III	111.62	12.50	III	216.25	16.48	III
27.73	1.434	III	113.91	12.63	III	219.17	16.56	II
30.95	1.894	III	115.18	12.73	1	221.57	16.59	III
34.71	2.552	III	122.63	13.14	III	229.65	16.77	II
38.71	3.334	III	124.21	13.24	I	232.30	16.90	III
42.73	4.108	III	131.71	13.62	III	239.39	17.02	II
47.28	4.960	III	133.18	13.71	I	242.91	17.12	III
52.03	5.872	III	140.73	14.07	III	248.89	17.29	II
57.42	6.797	III	142.10	14.12	I	254.28	17.40	III
63.12	7.746	I	149.73	14.42	III	258.25	17.48	II
63.33	7.731	III	151.82	14.49	I	263.38	17.63	III
70.17	8.678	III	158.84	14.76	III	268.56	17.71	II
71.85	8.884	I	161.48	14.84	I	274.89	17.87	III
76.83	9.550	III	168.08	15.07	III	279.83	17.85	II
78.03	9.647	III	170.46	15.14	I	284.18	18.11	III
78.99	9.749	I	177.38	15.35	III	294.33	18.28	III
83.17	10.21	III	179.28	15.44	I	304.09	18.58	III
85.67	10.47	I	180.58	15.39	II	315.79	18.76	III

TABLE III

MOLAL HEAT CAPACITY OF KF AND KHF_2 AT ROUNDED TEMPERATURES

T, °K.	KF, C_p, cal./deg.	KHF_2, C_p, cal./deg.	T, °K.	KF, C_p, cal./deg.	KHF_2, C_p, cal./deg.
20	0.276	0.520	200	10.80	16.01
25	.550	1.054	210	10.95	16.29
30	.922	1.753	220	11.08	16.56
35	1.390	2.607	230	11.20	16.82
40	1.892	3.572	240	11.31	17.06
45	2.444	4.530	250	11.40	17.30
50	3.028	5.490	260	11.48	17.53
60	4.180	7.220	270	11.55	17.75
70	5.176	8.649	280	11.61	17.97
80	6.090	9.865	290	11.68	18.19
90	6.878	10.86	300	11.74	18.40
100	7.554	11.68	320	11.86	18.83
110	8.127	12.39	340	11.99	19.26
120	8.615	12.98	360	12.12	19.70
130	9.049	13.54	380	12.25	20.15
140	9.431	14.03	400	12.38	20.60
150	9.730	14.43	420	12.50	21.06
160	10.00	14.80	440	12.61	21.53
170	10.24	15.12	460	12.72	21.99
180	10.45	15.43	480	12.82	23.96
190	10.64	15.72	500	12.92	23.96

The Heat Content Data at Higher Temperatures.—The heat contents of potassium fluoride and potassium acid fluoride referred to 25° were determined between temperatures of approximately 70° and 270° by the transfer method, in which a capsule containing the sample is heated in a furnace to a determined temperature and at a given moment dropped into a calorimeter of known heat capacity. Inasmuch as the design of the energy and thermometric circuits of the calorimeter[10] and the furnace and calorimeter proper have been described,[11] a brief description and comment on the method will suffice here.

Torpedo-shaped, stream-lined cylindrical capsules 14 mm. in diameter and 9.5 cm. in length containing approximately 0.15 mole of sample were constructed of eight mil sheet silver. The bullet-shaped head was of heavier material to withstand the impact of dropping and the tapered tail terminated in a tube of 3 mm. diameter to facilitate sealing off. Samples from the same portions of pure compounds used for the low temperature measurements were tightly packed into the capsules and weighed following a prolonged evacuation to remove any traces of water adsorbed in the filling process. After filling with helium gas, the tubes were pinched shut and welded electrically to a vacuum-tight seal. The capsule weights remained constant to within several milligrams throughout the determinations. Measurements on an empty capsule (identical to the other two and unfilled save for a silver

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[10] K. S. Pitzer, THIS JOURNAL, 59, 2365 (1937).

[11] M. Mosesman and K. S. Pitzer, *ibid.*, 63, 2348 (1943).

slug to overcome buoyancy) were made at the same temperatures as those of the filled tubes.

TABLE IV

HIGHER TEMPERATURE MOLAL THERMAL DATA FOR POTASSIUM FLUORIDE

Mol. wt., 58.096; sample, 10.071 g. = 0.17335 mole

T, °K.	$H_T - H_{298.16}°$(cal.) Observed	Calculated[a]	C_p (cal./deg.) calcd.[a]
324.6	311	311	11.86
350.2	616	616	12.05
376.2	932	933	12.23
403.7	1271	1271	12.40
443.7	1773	1772	12.63
468.3	2085	2084	12.76
492.2	2390	2391	12.88
512.8	2656	2657	12.98
529.9	2881	2880	13.06

[a] In the range 330–530°K., the data may be represented by: $H_T - H_{298.16}° = 11.266T + 1.929 \times 10^{-3}T^2 + 6.88 \times 10^4T^{-1} - 3761.5$. $C_p = 11.266 + 3.858 \times 10^{-3}T - 6.88 \times 10^4T^{-2}$.

TABLE V

HIGHER TEMPERATURE MOLAL THERMAL DATA FOR POTASSIUM HYDROGEN FLUORIDE

Mol. wt., 78.104; sample, 10.087 g. = 0.12915 mole

KHF_2—Solid Phase-α

T, °K.	$H_T - H_{298.16}°$(cal.) Observed	Calculated[a]	C_p (cal./deg.) calcd.[a]
321.6	434	434	18.79
356.4	1103	1102	19.59
380.8	1587	1587	20.16
404.3	2070	2067	20.70
443.7	2898	2900	21.61
463.7	3335	3337	22.07
465.3	3385	3372	22.11

[a] For the above range the data may be represented by: $H_T - H_{298.16} = 11.353T + 11.56 \times 10^{-3}T^2 - 4413$. $C_p = 11.353 + 23.12 \times 10^{-3}T$.

KHF_2–Solid Phase–β

T, °K.	$H_T - H_{298.16}°$(cal.) Observed	Calculated[b]
468.6	5779	
469.2	6059	
469.2	Transition ($\alpha = \beta$)	
471.3	6166	6168
473.6	6227	6224
473.7	6226	6226
477.3	6318	6319
484.1	6490	6475
493.4	6700	6698
505.9	7139	(Not corrected for premelting)

[b] For the range above, the data may be represented by: $H_T - H_{298.16} = 23.958T - 5123$ (0.07%). $C_p = 23.96$, ΔH transition = 2659 cal./mole.

KHF_2–Liquid

T, °K.	$H_T - H_{296.16}$(cal.) Observed
510.6	7842 (partially melted)
511.9	Melting point
517.4	8854
523.2	8999

These data yield the rough values, $H_T - H_{298.16} = 25T - 4081$, C_p(liq.) = 25, ΔH (fusion) = 1575 cal./mole

A capsule was left in the furnace for at least eight hours, usually longer, and the temperature observed to be constant to about 0.1° for the hour preceding the drop. In accord with the results of other investigators[13] the loss of heat during the drop was practically negligible and no corrections have been applied since the loss of heat from the full capsule was taken to be the same as that from the empty capsule. The apparent heat content of the empty capsule was in good agreement with the heat content of pure silver.[13]

After dropping the capsules into the calorimeter, equilibrium was attained rapidly usually within six to eight minutes. The heat content data on KHF_2 prior to fusion of the sample is in exact agreement with that obtained after the fusion; the attainment of equilibrium was slightly more rapid in the latter case. Correction for dissociation of KHF_2 is negligible even at the highest temperatures employed.

Data on KF and KHF_2 with this apparatus are presented in Tables IV and V and Fig. 2. As evidenced by the agreement of observed and calculated values the method is capable of excellent precision. Assignment of accuracy to the data is a somewhat arbitrary process; but 0.3% would seem to be a conservative estimate of the probable error. The smoothed values of heat capacity presented in Table III above 400°K. come directly from the equations in Tables IV and V. Between 300 and 400°K. the values are obtained by smoothing the low temperature curve into that of the high temperature equation. Since the two curves already agree quite well, there is no appreciable uncertainty in the smoothing process.

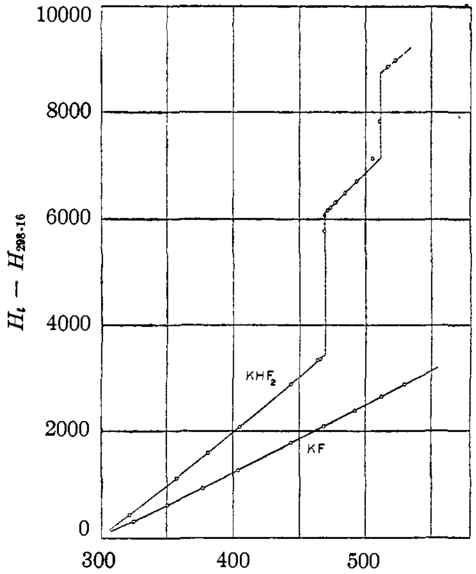

Fig. 2.—The molal heat content of KF and KHF_2.

Below 196°, the stable[14] (alpha) form is a relatively hard solid; at this temperature it undergoes transition to a soft, almost waxy, solid (beta) phase, persisting to the melting point.

The Melting Point and Heat of Fusion of KHF_2.—Although bracketed by the heat content data, the exact temperatures of the KHF_2 transition (solid α = solid β) and of the melting point were determined by thermal analysis.

The following temperatures for the melting point of KHF_2 have been reported: (1) between 215 and 225°[15];

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(12) W. P. White, *Am. J. Sci.*, **4**, 47 (1919).

(13) K. K. Kelley, "Contributions to the Data on Theoretical Metallurgy," II, Bulletin 371, U. S. Bureau of Mines, 1924, p. 45.

(14) G. H. Cady, THIS JOURNAL, **56**, 1431 (1934).

(15) K. Fredenhagen and C. Cadenbach, *Z. anorg. allgem. Chem.*, **178**, 289 (1929).

(2) 227°[16]; (3) 217°[17]; (4) 239°.[14] The necessity for exact stoichiometric composition for the congruent melting point coupled with the dissociation pressure made it desirable to determine the melting point in a closed monel metal can containing about 200 g. of the pure salt. The temperatures were determined in a reëntrant monel metal well by a thermocouple identical to and calibrated simultaneously with the one already described in the furnace for the heat content measurements. The best value obtained of the freezing point from cooling curves in this apparatus was 238.7° (511.9°K.), in good agreement with the value of Cady,[14] which was interpolated from solutions of approximate composition with a thermocouple calibrated "probably not to within 0.1°." As indicated in Table V, the heat of fusion is approximately 1375 cal. per mole.

The Temperature and Heat of Transition of KHF_2.—The pronounced tendency of the β form to supercool several degrees below the transition temperature necessitating an extrapolation for interpretation of the cooling curve made the usual thermal analysis not altogether satisfactory and heating curves were taken through the transition to supplement the data. For this purpose the thermocouple already mentioned in connection with the furnace was used in connection with a Leeds and Northrup Type K-2 potentiometer to measure e. m. f. to 0.1 microvolt. The junction was encased in, and in good thermal contact with, a platinum sheath of about 1.5 mm. diameter and immersed to varying depths up to 3 cm. in deep platinum crucibles containing fused KHF_2. Baffles, alundum and metal foil shielding were used to provide a sufficiently isothermal, non-fluctuating region in the electric tube furnace.

Repeated cooling determinations on several samples in containers of differing geometry and temperature heads extrapolated to transition temperatures of 195.8 to 196.0°. Supercooling was reduced to several tenths of degree in several determinations. The heating curves reproducibly yielded a transition temperature of 196.0° irrespective of thermal head. Our adopted value is then 196.0°C. (469.2°K.). Cady[14] reports a transition temperature of "about 195." The heat of transition is calculated from the difference in the heat contents of the α and β forms at 469.2°K. to be 2659 ± 10 cal. per mole.

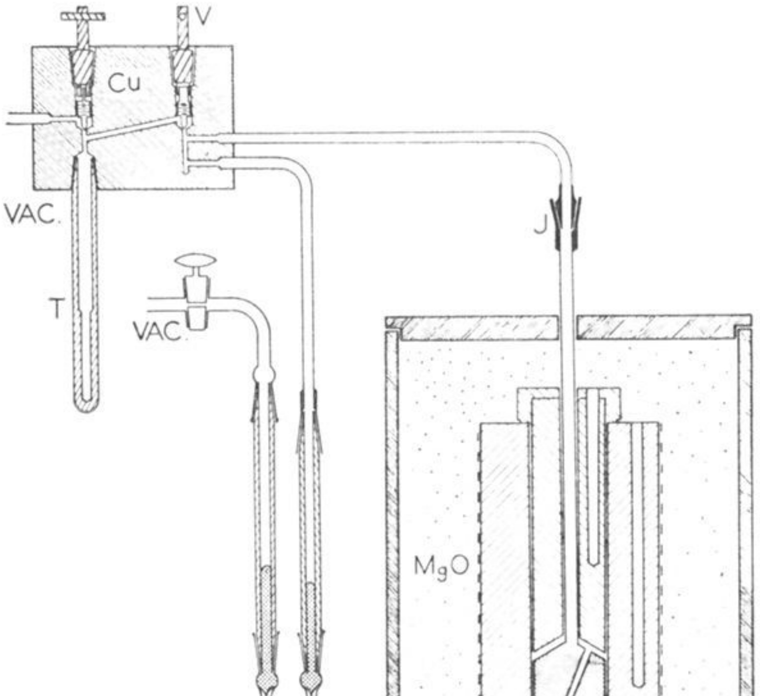

Fig. 3.—The apparatus for measuring the dissociation pressure of KHF_2.

The Heat of Solution of KF and KHF_2.—Determination of the change in heat content of the reaction

$$KF(solid) + HF(gas)(ideal) = KHF_2(solid)$$

was to have been made from measurements of the heat of solution of the three substances in dilute, aqueous, carbonate-free potassium hydroxide solutions. Unfortunately, difficulties with the heat content of polymerizing hydrogen fluoride gas at room temperature prevented completion of this determination. Consequently, only the heats of solution of solid KF and KHF_2 will be reported very briefly. The calorimeter was substantially the same as that used previously in this Laboratory.[10] The results are shown in Tables VI and VII.

TABLE VI

HEAT OF SOLUTION OF POTASSIUM FLUORIDE IN DILUTE POTASSIUM HYDROXIDE SOLUTION

0.06 mole of KF(s) in 1000 g. 0.04 molal KOH at 32.00°

Sample, *in vacuo*	Heat evolved, cal./mole of KF
3.4883 g.	4379
3.4883 g.	4378
3.4883 g.	4378
Av.	4378 ± 10

TABLE VII

HEAT OF SOLUTION OF POTASSIUM HYDROGEN FLUORIDE IN DILUTE POTASSIUM HYDROXIDE SOLUTION

0.03002 mole of KHF_2(s) in 1000 g. 0.0700 molal KOH at 32.00°

Sample *in vacuo*	Heat evolved, cal./mole of KHF_2
2.3447 g.	10,946
2.3447 g.	10,945
2.3447 g.	10,946
Av.	10,946 ± 10

The Dissociation Pressure of β-Potassium Hydrogen Fluoride.—The pure acid salt was contained in a vessel fabricated of platinum sheet, soldered with fine gold, within a massive aluminum aneroid thermostat (see Fig. 3). A platinum tube 7 mm. i. d. extended through the temperature gradient and 3.5 mm. i. d. copper tubing at room temperature connected to the mercury manometer within polymonochlorotrifluoroethylene tubes 5.5 mm. i. d. A copper manifold with vacuum-tight monel needle valves made possible the withdrawal of predetermined amounts of hydrogen fluoride from the system by measuring the volume of liquid hydrogen fluoride at the carbon dioxide point within a transparent trap (T) of the same hydrogen fluoride resistant plastic. The trapped hydrogen fluoride could then be solidified and stored or removed for exact determination, *e. g.*, by titration with standard base. A special Ag–Au solder was used on the copper connections. Flushing with hydrogen prevented oxidation of the interior of the copper line during soldering operations and the system was not exposed to air or moisture after contact with hydrogen fluoride. The thermostat, insulated with magnesia, was provided with an alumel winding and a separately controlled heater around the outlet tube. The temperature of the furnace was controlled to within 0.1° with a Leeds and Northrup Micromax Model S Controller and Recorder.

Identical temperatures were indicated by two iron–

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[16] F. M. Meyer and W. Sandow, *Ber.*, **54**, 759 (1921).

[17] L. M. Dennis, J. M. Veeder and E. G. Rochow, THIS JOURNAL, **53**, 3262 (1931).

constantan couples—one within a reëntrant well and the other silver-soldered to the bottom of the asbestos lagged platinum container. A third couple served to control the thermostat. Furnace and sample temperatures, and cooling curves were continuously recorded and were checked with a Rubicon type B potentiometer at critical times. The couples were calibrated with NBS tin and zinc melting point samples. A cathetometer was used both directly against its scale reading to 0.05 mm. and with an improved optical system and a filar micrometer. Both arrangements were calibrated against a precise steel scale in the plane of the menisci. The identity of meniscus heights was checked occasionally.

Preparation "B" of KHF_2 was made in the general manner already described; another batch, "A," differed only in that ethanol was used to reduce the solubility of the salt. About 0.6 mole of KHF_2 was weighed into the platinum vessel. The system was evacuated and flushed with hydrogen while the lapped copper taper joint (J) was positively sealed with silver solder. After establishing the absence of leaks in the system, the thermostat was gradually raised to 100° while maintaining a vacuum of 10^{-4} mm. Then (V) was closed, the temperature of the furnace raised to the desired value and the pressures observed after establishment of equilibrium.

In general the equilibrium temperature was approached both from higher and lower temperatures. Then at constant temperature, pressure equilibrium was approached from higher and lower values by changing the amount of mercury in the manometer or by opening valve (V) momentarily and admitting or abstracting hydrogen fluoride. Equilibrium was generally obtained within twenty minutes at constant temperature. No change in the equilibrium pressures was observed in several instances when the system was maintained at constant temperature for periods of four to eight days.

The dissociation pressure data are summarized in Table VIII and shown in Fig. 4. The temperatures are accurate within ±0.05° and the pressures in the solid range have average deviations of about 0.02 mm., although difficulty in establishing the identity of meniscus curvature on both mercury columns introduces at least an equivalent uncertainty. The purpose of Series B runs was to establish the absence of partial solubility in the solid and complicating equilibria, involving hypothetical compounds (*e. g.*, 2 KF·HF). No suggestion of either type of behavior was observed.

TABLE VIII

DISSOCIATION PRESSURES OF KHF_2

Mole fraction of HF	Condensed phase	Temperature, °C.	Observed pressure, mm.
	Sample A		
0.4860 (Eutectic)	Liquid	234.6	4.90
		254.7	9.75
		280.6	22.4
		303.8	44.4
	Solid	213.2	2.23
		224.1	3.38
.4427	Liquid (satd.)	230.7	4.25
	Solid	205.4	1.64
		206.3	1.70
		215.3	2.43
		226.4	3.67
.4000	Solid	205.9	1.67
		226.7	3.74
	Sample B		
.4994	Solid	223.1	3.26
.3999		226.4	3.66
.2404		226.4	3.66
.1507		225.8	3.60
.0006		226.7	3.66
		225.8	3.66

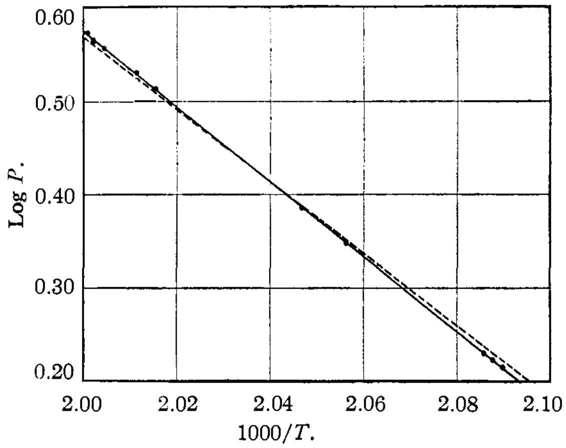

Fig. 4.—The dissociation pressure of KHF_2. Experimental points are shown; the lines are discussed in the text.

Over the short interval of stability of the β-phase the dissociation pressure may be represented by

$$\log P_{\text{mm}} = -(4000/T) + 8.574$$

corresponding to ΔH = 18,300 ± 150 cal./mole, ΔS = 26.05 ± 0.3 cal./mole degree for dissociation, and a pressure of 4.13 mm. at 229.5°, the eutectic temperature for KF–KHF_2. Extrapolation of the liquid data to the eutectic temperature yields 4.07 mm.

Dielectric Constant of KHF_2.—The dielectric constant of solid KHF_2 was measured in a cell constructed of monel metal tubing with small diamond chips as insulating spacers. The material was melted and allowed to solidify in place. Probably some voids were introduced in cooling through the transition, hence the results are presented as only a rough approximation.

The readings were taken on a General Radio impedance bridge balanced by observing the output on an oscilloscope. The conductance was too great at room temperature for satisfactory readings. This may have been caused by impurities; it was not investigated further. At dry ice temperature (∼200°K.) the observed dielectric constant was 4.15 and at liquid nitrogen temperature (∼80°K.) the value was 4.05. No significant frequency dependence was observed over the range 20–20,000 cycles. Both values are probably several per cent. low because of voids as mentioned.

Calculations and Discussion

We shall next complete various indirect thermodynamic calculations and then finally interpret our results in relation to spectroscopic and other data.

Thermodynamic Functions for HF.—Murphy and Vance[18] have calculated various thermodynamic functions for hydrogen fluoride in the ideal gas state from spectroscopic data. Their values will be used here without change.

Entropies of KF and KHF_2.—The heat capacities of KF and KHF_2 have been given above. These values were integrated by graphical or analytical methods to give the results shown in Tables IX and X.

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

TABLE IX

THE ENTROPY OF KF (CAL. PER DEGREE MOLE)

0–16.00°K.	Debye extrapolation	0.04	
16.00–298.16	Graphical integration	15.87	
	Total entropy at 298.16°K.		15.91 ± 0.1
298.16–500	Analytical integration	6.35	
	Total entropy at 500°K.		22.26 ± 0.1

TABLE X

THE ENTROPY OF KHF$_2$ (CAL. PER DEGREE MOLE)

0–16.00°K.	Debye extrapolation	0.10	
16.00–298.16	Graphical integration	24.82	
	Total entropy at 298.16°K.		24.92 ± 0.1
298.16–469.2	Solid α, integration	9.11	
469.2	Transition (2659/469.2)	5.67	
469.2–500.0	Solid β, integration	1.52	
	Total entropy at 500°K.		41.22 ± 0.1

Heat Contents of KF and KHF$_2$.—In addition the heat capacity below 298.16°K. was integrated and the resulting $(H_{298.16} - H_0)$ added to the high temperature heat content equations to give the equations for $(H^0 - H_0^0)$ in Table XI. Also in Table XI are equations for the heat capacity and entropy in the range above room temperature. Equations for $(F^0 - H_0^0)/T$ can be readily derived by subtracting the equation for $(H^0 - H_0^0)$ after division by T from the equation for S^0.

TABLE XI

EQUATIONS FOR THE THERMODYNAMIC FUNCTIONS OF KF AND KHF$_2$

(Units: cal./mole or cal./mole degree)

KF (range 330–530°K.)

$$C_p^0 = 11.266 + 3.858 \times 10^{-3}T - 6.88 \times 10^4T^{-2}$$

$$H^0 - H_0^0 = 11.266T + 1.929 \times 10^{-3}T^2 + 6.88 \times 10^4 T^{-1} - 1371$$

$$S^0 = 25.941 \log T + 3.858 \times 10^{-3}T + 3.44 \times 10^4T^{-2} - 49.82$$

αKHF$_2$ (range 330 to 469.2°K.)

$$C_p^0 = 11.353 + 23.12 \times 10^{-3}T$$

$$H^0 - H^0 = 11.353T + 11.56 \times 10^{-3}T^2 - 758$$

$$S^0 = 26.141 \log T + 23.12 + 10^{-3}T - 46.65$$

βKHF$_2$ (range 469.2 – 500°K.)

$$C_p = 23.96$$

$$H^0 - H_0^0 = 23.96T - 1469$$

$$S^0 = 55.17 \log T - 107.68$$

Free Energy and Entropy of Dissociation of KHF$_2$.—The measurements of the equilibrium constant for the reaction

$$\mathrm{KHF_2(s) = KF(s) + HF(g)}$$

were described above. A best value of log K at 500° K. was selected and the free energy change calculated therefrom. This free energy value combined with the other thermodynamic data, already discussed, yields the remaining quantities summmarized in Table XII. This gives a very complete picture of the thermodynamic properties of this system. It seems impractical to specify the uncertainty in each of the values listed but the general magnitude is 0.1 cal./degree mole or 50 cal./mole. Possible accumulations of error could affect certain values by several times this amount.

TABLE XII

SUMMARY OF THERMODYNAMIC VALUES

(Units: cal./mole or cal./mole degree)

		298.16°K.	500°K.
	C_p^0	6.963	6.969
	S^0	41.527	45.130
HF(g)	$-(F^0 - H_0^0)/T$	34.634	38.207
	$(H^0 - H_0^0)$	2055	3462
	C_p	11.73	12.92
	S	15.91	22.26
KF(s)	$-(F^0 - H_0^0)/T$	7.89	12.50
	$(H^0 - H_0^0)$	2391	4882
	C_p	18.37	23.96
	S	24.92	41.22
KHF$_2$(s)	$-(F^0 - H_0^0)/T$	12.66	20.20
	$(H^0 - H_0^0)$	3655	10511
Reaction	ΔC_p	0.32	−4.07
KHF$_2$=KF + HF	ΔS	32.52	26.17
$\Delta H_0^0 = 20533$	$-\Delta(F^0 - H_0^0)/T$	29.86	30.51
	$\Delta(H^0 - H_0^0)$	791	−2167
	ΔF	11630	5278
	ΔH^0	21324	18366

Possibility of Residual Entropy in KHF$_2$.—We may now inquire whether the correct thermodynamic results have been obtained on the basis of the Third Law and the assumption that KF and KHF$_2$ approach zero entropy at the absolute zero. With its simple sodium chloride type structure there seems no reason to doubt that KF approaches zero entropy. However, we are particularly interested in the possibility that the proton in the FHF$^-$ ion might be unsymmetrically located. If it were and the proton locations in the various FHF$^-$ ions were random, an entropy R ln 2 (1.38 cal./deg. mole) would remain in KHF$_2$ at low temperatures. The agreement of the ΔS of dissociation for KHF$_2$ from third law values, 26.17, with the value from direct measurements, 26.05, indicates that KHF$_2$ does not have residual entropy at low temperatures. The effect of a residual entropy of R ln 2 in KHF$_2$ is also shown in Fig. 4. The solid line is the theoretical line for log P for dissociation of KHF$_2$ based on the ΔS value in Table XII. The dotted line corresponds to a ΔS lower by R ln 2. The experimental data clearly fit the solid curve and not the dotted one. The accuracy of the experimental pressure data appears to be great enough that we may conclude with reasonable assurance that KHF$_2$ did approach zero entropy in our specific heat measurements.

The Nature of the Hydrogen Bond in KHF$_2$.—Before continuing the discussion of KHF$_2$ let us review briefly the nature of hydrogen bonds. Starting with two widely separated fluoride ions, the potential energy of a proton will be given by a curve such as A in Fig. 5 with a minimum near each fluoride ion. As the two fluoride ions move closer together the attraction of the second ion will lower the curve near each minimum and even more in the region between minima. We do not need to consider just how much of this attraction is electrostatic and how much covalent bonding (with resonance because the proton has but a single low-energy orbital). Thus we may expect a potential curve such as B at some intermediate distance. This corresponds to a moderate bond energy (from the lowering of the minimum, if the same absolute energy zero is retained) and a moderate drop in vibration frequency (from the decreased curvature near the minimum). Qualitatively, curve B represents the usual hydrogen bond between two oxygen atoms, as in ice.

The location of additional protons complicates the picture in most cases. Thus in ice the two minima are of different heights because one has the proton between an OH^- ion and an H_2O molecule. However, in KHF_2 these effects should not be large because the FHF^- ions are well separated.

Indeed Ketelaar[19] has shown that for partially deuterated KHF_2 the spectrum is the simple sum of those for the pure KHF_2 and KDF_2, indicating no interaction.

As is shown in Table XIII, the F–F distance in KHF_2 is considerably smaller than the corresponding distance in other hydrogen bonds. Thus it is quite possible that the potential curve for this case is like C in Fig. 5 rather than B. In that case the proton vibration frequency should be very greatly reduced because the potential curve is relatively flat. The frequency values in Table XIII indicate that this is the case.

The energy values in Table XIII come from Pauling[20] for the first three cases and from Ketelaar[4] (his second calculation) for KHF_2. These likewise indicate that the bond in KHF_2 is an extreme case. Davies'[20a] calculations based on an electrostatic model for the FHF^- ion yield a binding energy of 47.3 kcal, in satisfactory accord with Ketelaar's upper limit.

TABLE XIII

CHARACTERISTICS OF HYDROGEN BONDS

Bond	Frequency, cm.$^{-1}$	Distance (O–O or F–F)	Energy, kcal.
O–H free	3650	..	..
O–H ··· O in ice	3250	2.76 Å.	4.5
O–H ··· O in dimeric formic acid	3030	2.67	7.1
F–H free	4140	..	..
F–H ··· F in $(HF)_n$ polymers	3440	2.55	6.7
[a]F–H–F in KHF_2	1450	2.26	27

[a] The proton is centrally located in KHF_2 but unsymmetrically located in the other cases.

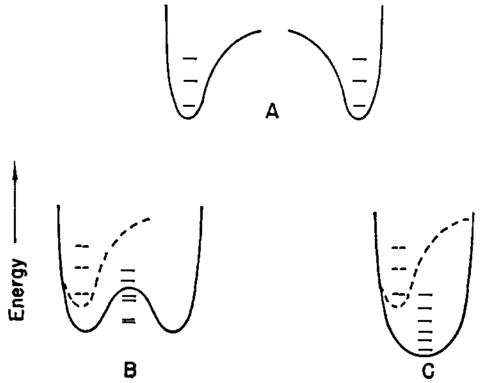

Fig. 5.—Possible potential curves for the proton in a hydrogen bond.

We are now ready to make our final decision between potential curves like B or C for the $F–H–F^-$ ion in KHF_2. If there exists an intermediate potential hill (as in B) it cannot be very high or wide. With its small mass, the proton will have a considerable probability of penetrating this potential barrier, and as a result the two lowest energy states will be split into a doublet as is shown in B. Let the energy separation of this doublet be ϵ. We shall discuss the three possibilities ϵ smaller than, about equal to, or larger than kT at the beginning of our heat capacity measurements (~16° K.).

If ϵ is much less than $16k$, then the crystals of KHF_2 would have an entropy $R \ln 2$ greater than was calculated from our data and extrapolation below 16°. This possibility of a residual entropy has been eliminated.

If ϵ were of the general magnitude $16k$, then the heat capacity curve would be anomalous in this range. No such anomaly is present in Fig. 1. Our previous publication[21] discussed this possibility in more detail and eliminated it.

There remains the possibility that ϵ is much larger than $16k$. In this case the special heat capacity contribution arising from the excitation from the lowest to the next higher quantum state might be lost in the larger and rapidly rising lattice heat capacity. Examination of the actual curves indicates that ϵ/k must be at least 100° K. or ϵ at least 70 cm.$^{-1}$. Rough application of quantum mechanics indicates that the largest permissible central potential hill is 7 kcal. high and 0.3 Å. thick. The thermodynamic data above will not eliminate this possibility. However, it would be difficult to reconcile this potential curve with the infrared spectrum as reported by Ketelaar.[4] This spectrum shows two very intense peaks at 1222 and 1450 cm.$^{-1}$, respectively. There appear to be only two plausible interpretations of these peaks. One is that both peaks arise from the longitudinal

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(19) J. A. A. Ketelaar, *J. Chem. Phys.*, **9**, 775 (1941).

(20) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939.

(20a) M. Davies, *J. Chem. Phys.*, **15**, 739 (1947).

(21) K. S. Pitzer and E. F. Westrum, Jr., *J. Chem. Phys.*, **15**, 526 (1947).

vibration of the proton along the F–F line (ν_3) the doubling arising because of a double minimum curve. This is Ketelaar's interpretation. However most of the 228 cm.$^{-1}$ splitting must come in the upper state. In the analogous motion in ammonia the lower state splitting is 1 cm.$^{-1}$ as compared to 32 cm.$^{-1}$ for the excited pair of states. Thus it seems very unlikely that one third of the total splitting arises from the lower pair of states in KHF_2. Also, as Polder[22] has shown, the corresponding splitting for KDF_2 should be very much less than that for KHF_2 whereas actually it is just the same fraction of the over-all frequency.

By contrast, there is no difficulty with our interpretation[21] of the 1450 cm.$^{-1}$ peak as ν_3 for a single minimum potential curve (type C) and 1222 cm.$^{-1}$ as ν_2, the transverse oscillation of the proton across the F–F axis.[23]

The dielectric constant offers another very good qualitative indication of the nature of a hydrogen bond.[24] If the potential curve has the double minima, then one has effectively an orientable dipole of considerable magnitude. Unless these dipoles are so coupled as to cancel one another, a high temperature dependent dielectric constant should result. This is the case for ice and water, hydrofluoric acid gas polymers and liquid, and liquid formic acid. Probably the dipoles cancel by symmetry in formic acid dimer. However, the dielectric constant of KHF_2 is low, the value 4.1 given above being about that expected for a simple ionic lattice. Also the change with temperature is practically zero. Since cancellation of dipoles could hardly occur in KHF_2, this is strong confirmation of the single minimum potential curve for the $F–H–F^-$ ion.

Forces within the HF_2^- Ion.—In view of the fact that Ketelaar expected the deformation frequency, ν_2, to lie much lower than 600 cm.$^{-1}$, it may be in order to offer some further justification of our assignment of ν_2 to the 1222 cm.$^{-1}$ spectral peak.

Let us calculate the longitudinal and transverse protonic frequencies on a very simple model. We assume that the proton is attracted to each fluoride ion by the same force-distance relation as applies in HF molecule. The Morse function

$$V = 53{,}000\ [1 - e^{-2.2(r-0.92)}]^2\ \text{cm.}^{-1}$$

with r the H–F distance in Å., was obtained from the spectroscopic data for hydrogen fluoride.[25] In terms of this potential curve the force constants for proton motion in HF_2^- are

$$k_{\text{transverse}} = \frac{2}{r}\left(\frac{\partial V}{\partial r}\right)_0$$

$$k_{\text{longitudinal}} = 2\left(\frac{\partial^2 V}{\partial r^2}\right)_0$$

where the derivatives are evaluated at the H–F distance in HF_2^- ion, 1.13 Å. Carrying out the frequency calculations in the usual manner one obtains for the transverse frequency,[26] ν_2, approximately 1800 cm.$^{-1}$ which is rather higher than the observed 1222 cm.$^{-1}$. For the longitudinal frequency, ν_3, one finds approximately 2300 cm.$^{-1}$ as compared to the observed 1450 cm.$^{-1}$. This is as good agreement as one could expect from such a crude model. However, it does prove that the 1222 cm.$^{-1}$ value for ν_2 is reasonable. Also the qualitative model of the force in ν_2, an attraction of the proton toward each fluoride ion, is probably correct. Naturally, there is a repulsive force between the two fluoride ions which balances the net attraction of each fluoride for the proton.

Conclusions.—Considering the entire array of thermodynamic, spectroscopic and dielectric data, it seems certain that the potential curve for the proton in the $F–H–F^-$ ion is of the single minimum type. Also in view of the extreme characteristics of this hydrogen bond as indicated in Table XIII, the HF_2^- ion may be the only example of the single minimum type. Certainly, the high dielectric constant of polymeric gas and liquid HF, and of most substances containing O–H–O bonds indicates that the proton is unsymmetrically located in these cases.

Summary

The heat capacities of KF and KHF_2 have been measured from 15 to 500° K. and the heat contents and entropies calculated therefrom. For KF(s) and KHF_2(s) $S°_{298}$ is 15.91 and 24.92 cal. per deg. mole, respectively. The transition temperature in KHF_2 is 469.2° K. and the heat of transition 2659 cal. per mole. The melting point of KHF_2 is 511.9° K. Heats of solution of KF and KHF_2 in dilute KOH were measured. The dissociation pressure of KHF_2 was measured over the range 478–575° K. The pressure in the solid–solid range (478–500° K.) is given by the equation $\log p_{\text{mm}} = 8.574 - 4000/T$. The dielectric constant of KHF_2 was observed at dry ice and liquid nitrogen temperatures. The value found, 4.1, may be too low by several per cent. because of voids in the sample.

All the above data together with those for HF from the literature were correlated to give values for the thermodynamic properties of the reaction $KHF_2(s) = KF(s) + HF(g)$. These establish that KHF_2 reaches zero entropy when cooled to 0° K. and does not contain residual randomness as does ice and possibly some other hydrogen bonded substances. The nature of hydrogen bonds is discussed and it is shown from a consideration of

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(22) D. Polder, *Nature*, **160**, 870 (1947).

(23) Very crude infrared absorption measurements have been made in which the KHF_2 crystal orientation was varied. The relative absorption intensity of the 1222 and 1450 peaks changed in a manner consistent with the present assignment.

(24) D. Polder (ref. 22) discussed the temperature dependence of dielectric constant for KHF_2, reaching similar conclusions.

(25) C. Herzberg, "Molecular Spectra: Diatomic Molecules," Prentice-Hall, New York, N. Y., 1939.

(26) It may be noted that if the H–F distance in the FHF-ion were still the equilibrium distance of an HF molecule, then the transverse force constant and frequency would be zero. The non-zero value arises from tension in the H–F interactions coupled with repulsion in the F–F interaction.

thermodynamic, spectral and dielectric data that the potential curve for the proton in the F–H–F$^-$ ion has a single minimum at the midpoint.

RECEIVED DECEMBER 8, 1948

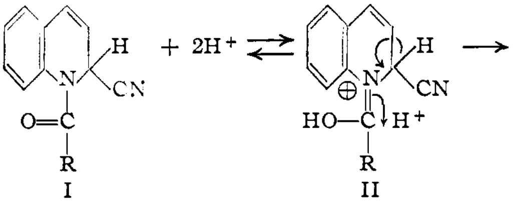
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

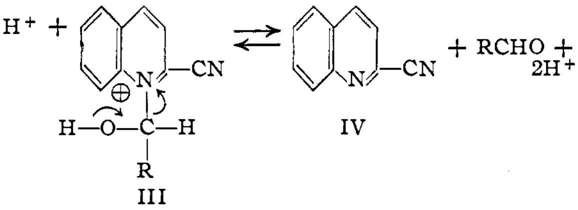
Mechanism of the Acid Catalyzed Formation of Aldehydes from Reissert Compounds

BY WILLIAM E. MCEWEN AND ROBERT N. HAZLETT

A general method for the preparation of an aldehyde from an acid chloride is first to convert the acid chloride to a Reissert compound, a 1-acyl-2-cyano-1,2-dihydroquinoline (I), by reaction with quinoline and aqueous potassium cyanide solution,[1,2,3] by reaction with quinoline and potassium cyanide in liquid sulfur dioxide[4] or by reaction with quinoline and liquid hydrogen cyanide in anhydrous benzene[5,6]; then to convert the Reissert compound to an aldehyde plus quinaldic acid by reaction with concentrated hydrochloric acid. The mechanism of the latter reaction is the subject of this investigation.

We propose that the first step in this reaction is the coördination of a proton with the amide oxygen of the Reissert compound (I) giving the conjugate acid (II).[7] By simultaneous loss of a proton from the 2-position of the quinoline ring and gain of a proton by the original carbonyl carbon atom, the complex (III) is formed, which then dissociates to an aldehyde and quinaldonitrile (IV). Under the conditions of the reaction the quinaldonitrile is hydrolyzed to quinaldic acid.[8] Doubtless an important driving force in the reaction is the gain in resonance energy attendant on conversion of the dihydroquinoline to a completely aromatic system.





Evidence in support of the proposed mechanism has been obtained by a reaction of 1-benzoyl-2-cyano-1,2-dihydroquinoline (V) with hydrochloric acid in the presence of an excess of *p*-chlorobenzaldehyde. In addition to quinaldic acid and benzaldehyde, a significant quantity of *p*′-chlorobenzoin quinaldate (XI) was formed. Also the isomeric ester, *p*-chlorobenzoin quinaldate (XII) was obtained by reaction of 1-(*p*-chlorobenzoyl)-2-cyano-1,2-dihydroquinoline (VI) with hydrochloric acid in the presence of an excess of benzaldehyde.[9] The mechanism proposed earlier accounts for the formation of these esters assuming that the conjugate acids of the *p*-chlorobenzaldehyde (VII) and benzaldehyde (VIII) compete with the proton in the acceptance of an electron pair to form a new bond with the original carbonyl carbon atom of the Reissert compound, thus forming the complex (IX).[10]

Three schemes can be proposed as to how the esters XI and XII are obtained from the complex (IX): (1) The complex (IX) dissociates to quinaldonitrile and the free chlorobenzoin, which then undergo an acid catalyzed condensation to the ester by way of an imino ether. (2) The quinaldonitrile formed by dissociation of IX first undergoes hydrolysis to quinaldic acid, which is then esterified by reaction with the chlorobenzoin. (3) The complex IX gives the ester (XI or XII) via an intramolecular cyclization to the imino ether complex (X).[11] The first two possibilities were disproved when it was found that neither quinaldo-

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(1) Reissert, *Ber.*, **38**, 1603 (1905); **38**, 3415 (1905).

(2) Sugasawa and Tsuda, *J. Pharm. Soc. Japan*, **56**, 557 (1936).

(3) Rupe, Paltzer and Engel, *Helv. Chim. Acta*, **20**, 209 (1937); Rupe and Frey, *ibid.*, **22**, 673 (1939); Gassmann and Rupe, *ibid.*, **22**, 1241 (1939).

(4) Woodward, THIS JOURNAL, **62**, 1626 (1940).

(5) Grosheintz and Fischer, *ibid.*, **63**, 2021 (1941).

(6) Buchanan, Cook and Loudon, *J. Chem. Soc.*, 325 (1944).

(7) Another important contributing resonance structure is one in which the oxygen atom bears the formal positive charge; *cf.*, Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 181.

(8) There is little probability that the cyano group is hydrolyzed to a carboxyl group prior to aldehyde formation. Woodward and Kornfeld [THIS JOURNAL, **70**, 2508 (1948)] have found that 1-benzoyl-2-carbomethoxy-3-acetyl-1,2-dihydroquinoline on treatment with hydrochloric acid at room temperature gives 1-benzoyl-3-acetyl-1,2-dihydroquinoline-2-carboxylic acid, and on treatment with hydrochloric acid at 100° gives benzoic acid and an unidentified oil. No benzaldehyde is formed.

(9) Reissert obtained a trace of benzoin quinaldate on reaction of 1-benzoyl-2-cyano-1,2-dihydroquinoline with hydrochloric acid.[1] The quantity of the ester was significantly increased by adding an excess of benzaldehyde at the start of the reaction.

(10) There is some degree of analogy between this reaction and the benzoin condensation. The intermediate IX is similar to one of the intermediate products of the benzoin condensation, C_6H_5C-(OH)(CN)CH(O$^{\ominus}$)C_6H_5, and the intermediate III might be termed a "vinylog" of an aldehyde cyanohydrin; *cf.* Luder and Zuffanti, "Electronic Theory of Acids and Bases," John Wiley and Sons, Inc., New York, N. Y., 1946, p. 148.

(11) A fourth alternative, that the cyano group of V or VI is hydrolyzed to a carboxyl group prior to formation of a complex similar to IX, is excluded for the reason indicated in reference 8.