per mole—has been combined (*4*) with this ΔH_f° and that for SO_4^{-2}(aq.) from NBS Circ. 500 (*10*) to yield ΔH_f° = −13.9 kcal. per mole for Co^{+2}(aq.). Subsequent publication of part of the successor to NBS Circ. 500 by Wagman *et al.* (*11*) suggests that these calculations should be revised to conform with new data for sulfuric acid and sulfate ion. These calculations yield $\Delta H_f^\circ = -212.55$ kcal. per mole for $CoSO_4$(c.), which is then combined with the ΔH° of solution of $CoSO_4$(c.) and the new ΔH_f° for SO_4^{-2}(aq.) to yield $\Delta H_f^\circ = -14.0$ kcal. per mole for Co^{+2}(aq.). Combination of this ΔH_f° with the previously reported $\bar{S}_2^\circ$ gives $\Delta G_f^\circ = -13.4$ kcal. per mole for Co^{+2}(aq.).

Combination of our ΔH_f° with the ΔH_f° cited above for Co^{+2}(aq.) and ΔH_f° for H_2O (*11*) gives $\Delta H_f^\circ = -129.4$ kcal. per mole for pink $Co(OH)_2$. Feitknecht and Schindler (*3*) have reviewed solubility data for cobalt hydroxide and recommend $K_{sp} = 2 \times 10^{-16}$ for pink $Co(OH)_2$. This K_{sp} leads to $\Delta G^\circ = 21.4$ kcal. per mole for the standard free energy of solution. By combination with ΔG_f° values for Co^{+2}(aq.) cited above and OH^-(aq.) (*11*) we obtain $\Delta G_f^\circ = -110.0$ kcal. per mole for pink $Co(OH)_2$. Further combination of ΔG_f° with ΔH_f° and entropies (*6*) of Co, H_2, and O_2 leads to $S^\circ_{298} = 22.3$ cal. per degree per mole for pink $Co(OH)_2$.

This S°_{298} for $Co(OH)_2$ is 9.6 cal. per degree per mole greater than the entropy (*6*) of CoO. Reliable third law entropies (*11*) for MgO, $Mg(OH)_2$, CaO, and $Ca(OH)_2$ lead to corresponding differences of 8.5 and 10.4 cal. per degree per mole for these pairs of compounds. Less certain entropies for $Cd(OH)_2$ and $Zn(OH)_2$ calculated by combination of ΔH_f° and K_{sp} data (*8, 10*) and third law entropies (*6*) for CdO and ZnO lead to entropy differences between the hydroxide and oxide of 9.7 (Cd) and 9.4 (Zn) cal. per degree per mole. Therefore, apparently, entropies of $M(OH)_2$ compounds can be estimated reliably by adding ~9.5 cal. per degree per mole to the S°_{298} value of the corresponding oxide.

It has long been believed that the MO and $M(OH)_2$ compounds of transition elements are about equally stable in contact with water, which means that $\Delta G^\circ \cong 0$ for reactions of the type

$$MO + H_2O(liq.) = M(OH)_2$$

Free energies of formation lead to ΔG° values of −1.9, −2.0, and +0.2 kcal. per mole for reactions of this type involving Co, Cd, and Zn, respectively. Similar, but less certain, calculations can also be made for several compounds of transition elements in higher oxidation states. Thus, the free energy of hydration (by liquid water) of many oxides of transition elements apparently have small (usually negative) ΔG° values. However, ΔG° values for hydration of MgO and CaO are −6.5 and −13.2 kcal. per mole.

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Fluorine Bomb Calorimetry

Enthalpies of Formation of the Diborides of Zirconium and Hafnium

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The energies of combustion in fluorine of zirconium diboride ($ZrB_{1.993\pm0.006}$) and hafnium diboride ($HfB_{2.003\pm0.006}$) were measured in a combustion bomb calorimeter. These results, when combined with the enthalpies of formation of ZrF_4, HfF_4, and BF_3 previously obtained by similar techniques, gave $\Delta Hf^\circ_{298.15}$ values of $-77._9 \pm 1._5$ and $-78._6 \pm 2._1$ kcal. (g.f.m.)$^{-1}$ for $ZrB_{1.993\pm0.006}$ and $HfB_{2.003\pm0.006}$, respectively.

RECENT interest in refractory borides for possible high temperature applications has prompted a number of concurrent studies of the thermodynamic properties of zirconium and hafnium diborides. Some of these studies deal with vaporization processes (*2, 19, 21, 23, 44, 51*), oxygen bomb calorimetry (7, 14), low- (*47, 49*) and high- (*45*) temperature heat capacities, and relative stabilities (*4, 33, 38*). In this work accurate values of the enthalpies of formation were sought by the method of fluorine bomb calorimetry.

EXPERIMENTAL

Preliminary Observations. Kuriakose and Margrave (*22*) have observed the fluorination of zirconium and hafnium diborides in low-pressure fluorine at elevated temperatures.

In our trial experiments, conducted in a glass combustion bomb (*30*), the diboride powders reacted spontaneously at room temperature when exposed to fluorine at high pressures, and usually burned vigorously. Rapid and nearly complete combustion (96 to 99.8%) was assured by the addition of a small amount of sulfur. These experiments also indicated that a massive zirconium disk (~85 grams) would serve as a suitable sample support.

Calorimetric System. The calorimeter (*10*, laboratory designation ANL-R2) and the two-chambered reaction vessel (*31*) for spontaneously combustible materials (laboratory designation Ni-2-T-1) were similar to those already described. The system was calibrated with benzoic acid (National Bureau of Standards sample 39i) whose certified energy of combustion was 26.434 ± 0.003 abs. kjoules per gram under prescribed conditions. For the zirconium diboride series, seven calibration experiments, some preceding and some following the fluorine combustions, yielded an average value for $\mathcal{E}$(Calor.), the energy equivalent of the calorimetric system, of $3359.7_2 \pm 0.0_8$ cal. per degree. For the hafnium diboride series, nine calibration experiments gave an average value for $\mathcal{E}$(Calor.) of $3359.7_7 \pm 0.1_5$ cal. per degree. The uncertainties are standard deviations of the mean.

Materials. Specimens of the diborides were supplied by Arthur D. Little, Inc., in the form of zone-refined bars, designation numbers ZrB_2-85 and HfB_2-773. Similar zone-refined bars were also supplied to a number of other investigators (*2, 19, 22, 44, 45, 47, 49*).

The bars were lightly etched in aqueous $HF—HNO_3$ to remove a slight film of oxide, and were then pulverized in an iron, shock-type mortar. The 100- to 325-mesh fractions, from which tramp iron had been magnetically removed, were retained for the combustion experiments. Spectrographic analysis showed no significant increase in the iron content of the specimens.

The results of analysis on representative samples of the specimens are given in Table I. Boron was determined by the differential titration method of Frank (*9*) modified by the use of $BaCO_3$ instead of $CaCO_3$ in the separation procedure. Total zirconium and hafnium contents were determined gravimetrically by the method of Kriege (*20*). The appropriate gravimetric factor was determined experimentally by the use of high-purity (99.95%) zirconium metal as a standard. Carbon, oxygen, hydrogen, and nitrogen were determined by vacuum fusion, and the metal impurities by spectrographic methods. The excellence of the material balances indicates that no significant amounts of impurities were overlooked. Photomicrographs of representative portions of the zirconium diboride bar showed a minor phase. X-ray powder diffraction analysis showed hexagonal zirconium diboride as well as faint lines which could be ascribed to cubic ZrC. Uncombined carbon was sought by the dissolution method of Kriege (*20*), but none was found. These observations, together with the nature of the reported high-temperature phase diagrams (*29*), led us to assume that all the carbon (plus the minor amounts of oxygen and nitrogen) in the specimens was present in the cubic phase as (Zr,Hf)(O,C,N). The amount of the minor phase was consistent with this assumption.

Table I. Specimen Analysis

Element	Zirconium Diboride, P.P.M.	Hafnium Diboride, P.P.M.
C	1363	394
O	231	220
N	36	8
H	8	10
Ti	50	200
Zr	...	500
Hf	400	
V	100	
Cr	50	
Fe	500	
Mo	50	
Mg	50	
	%	%
Total Impurities	0.28 ± 0.07	0.13 ± 0.05
Boron	18.86 ± 0.04	10.75 ± 0.02
Zirconium	80.84 ± 0.16	
Hafnium		89.17 ± 0.18
	99.98 ± 0.18	100.05 ± 0.19

The metallic impurities were assumed to substitute for Zr or Hf in the diboride phases. After subtraction of the amounts of zirconium or hafnium present in the cubic phase, the calculated atom ratios of boron to total metal in the boride phases were 1.993 ± 0.006 for the zirconium diboride specimen and 2.003 ± 0.006 for the hafnium diboride specimen.

The kindler was sulfur from the same lot that was used to determine the enthalpy of formation of SF_6 (*32*).

The fluorine was obtained commercially from the General Chemical Co. and had a purity of 99.8%, as determined by mercury titration.

Blank Experiments. The operation of the two-chambered reaction vessel introduces two thermal effects: The first is endothermic and arises from expansion of fluorine into the bomb; the second is exothermic and arises from reaction of fluorine with the bomb surfaces and adsorbed impurities such as water. Experiments showed that the magnitude of the combined effect could be made smaller and more reproducible by overnight evacuation of the bomb and introduction of gaseous boron trifluoride.

The combined thermal correction was determined by blank experiments in which fluorine was expanded into a bomb in which no sample was present. All other procedures were identical with those in a typical combustion. A series of six blank experiments, interspersed among the calorimetric combustions of both diborides, gave an average exothermic effect of $12.5_8 \pm 1.0_3$ (s.d.) cal. per experiment.

Experimental Procedure. The zirconium disk was tared and then weighed with a thin layer of sulfur (~50 mg.) spread evenly on top. The diboride was then placed in a cone-shaped pile on top of the sulfur and the disk was reweighed and placed under the retaining ring of the bomb head. The fluorine tank was evacuated, filled with fluorine to 12 or 15 atm., and attached to the bomb. The bomb, which was washed after each combustion, was evacuated overnight with an oil diffusion pump and then filled with 200 torr of BF_3. The reaction vessel was placed in the calorimeter and the experiment was started. After the initial rating period, the tank valve was opened to allow fluorine to expand into the bomb and ignite the sample.

Postcombustion Examination. After representative experiments, portions of the combustion bomb gases were examined by infrared analysis in an 8-cm. nickel cell equipped with silver chloride windows. The significant bands observed in the infrared spectra were attributed to SF_6 from the kindler and to BF_3 and CF_4 from the sample. In other experiments the bomb was evacuated, and then opened in an inert atmosphere to obtain portions of the white, partially sublimed, solid products for x-ray diffraction analysis. The diffraction patterns were identical with those obtained from the products produced in the calorimetric combustion of zirconium (*10*) and hafnium (*11*) in fluorine.

The amount of unreacted diboride sample in the solids remaining on the disk was determined by analyzing for boron by the method of Ross, Meyer, and White (*34*).

Dissolution was accomplished by a K_2CO_3 fusion. The method was calibrated (uncertainty ± 3%) with known amounts of the diboride.

After each combustion the zirconium support disk was washed, scrubbed with a rubber policeman, and dried. A small loss in weight was observed and attributed to the fluorination of the disk.

RESULTS

The results of seven zirconium diboride and six hafnium diboride combustion experiments are presented in Tables II and III, respectively. The results are expressed in terms of the defined calorie equal to (exactly) 4.1840 absolute joules. The corrections to standard states were applied in the usual manner (*13*). The entries in the tables are either self-explanatory or have been previously used and explained (*11, 13*). The auxiliary data needed for Tables II and III are given in Table IV.

For calculation of ΔE_{sulfur} and $\Delta E_{\text{support}}$ the energies of combustion of sulfur and zirconium were taken as −9.0624 (*32*) and −4.995 (*10*) cal. per mg., respectively. For calculation of ΔE_{gas}, the coefficients $(\partial E/\partial P)_T$ and μ [in the equation of state $PV = nRT\,(1-\mu P)$] were estimated by the method of Hirschfelder, Curtiss, and Bird (*12*), from the intermolecular force constants for F_2 (*50*), BF_3 (*25*), and SF_6 (*24*). The coefficients as functions of composition at 25° C. are:

$$\mu = 8.03 \times 10^{-4}\,(x_1^2 + 4.61\,x_2^2 + 13.2\,x_3^2 + 4.67\,x_1x_2 + 8.56\,x_1x_3 + 16.1\,x_2x_3)\text{atm.}^{-1} \quad (1)$$

$$(\partial E/\partial P)_T = -1.78\,(x_1^2 + 2.67\,x_2^2 + 7.04\,x_3^2 + 3.30\,x_1x_2 + 5.44\,x_1x_3 + 8.93\,x_2x_3)\text{ cal. atm.}^{-1}\text{mole}^{-1} \quad (2)$$

where x_1, x_2, and x_3 represent the respective mole fractions of F_2, BF_3, and SF_6 in the mixture. Because of the inclusion of the blank correction, the initial state of the fluorine was taken as its hypothetical condition after expansion into the bomb. The internal volumes of the tank and bomb were 0.242 and 0.309 liter, respectively.

The thermal corrections for the combustion of the impurities in the specimens were made on the basis of the phase analysis presented in the section on materials. Carbon, oxygen, and nitrogen were assumed to form CF_4, O_2, and N_2, respectively. Hydrogen was assumed to be present as H_2O, which formed HF and O_2. The trace metals were assumed to substitute for Zr or Hf without any thermal effect and to form their most stable fluorides.

DERIVED DATA

The derived data are presented in Table V and refer to the following combustion and formation reactions.

$$ZrB_{1.993 \pm 0.006}(c) + 4.990\,F_2(g) \rightarrow ZrF_4(c) + 1.993 \pm 0.006\,BF_3(g) \quad (3)$$

$$HfB_{2.003 \pm 0.006}(c) + 5.004\,F_2(g) \rightarrow HfF_4(c) + 2.003 \pm 0.006\,BF_3(g) \quad (4)$$

$$Zr(c) + 1.993 \pm 0.006\,B(c) \rightarrow ZrB_{1.993 \pm 0.006}(c) \quad (5)$$

$$Hf(c) + 2.003 \pm 0.006\,B(c) \rightarrow HfB_{2.003 \pm 0.006}(c) \quad (6)$$

The uncertainties given are uncertainty intervals (*35*) equal to twice the combined standard deviations arising

Table II. Results of Zirconium Diboride Combustions

Combustion No.	1	2	3	4	5	6	7
Sample introduced, g.	0.73624	0.74978	0.75353	0.76568	0.40101	0.40194	0.40000
Unburned sample, g.	0.00914	0.00172	0.00200	0.00174	0.00384	0.00165	0.00446
m', sample burned, g.	0.72710	0.74806	0.75153	0.76394	0.39717	0.40029	0.39554
m'', sulfur, g.	0.04089	0.04304	0.03893	0.04277	0.04268	0.04078	0.03944
Δt_c, deg.	1.86544	1.92353	1.92253	1.95930	1.07607	1.07844	1.06353
$\mathcal{E}(\text{Calor.})(-\Delta t_c)$, cal.	−6267.36	−6462.52	−6459.16	−6582.70	−3615.29	−3623.26	−3573.16
$\Delta E_{\text{contents}}$, cal.	−11.97	−12.18	−12.32	−12.40	−6.85	−6.78	−6.78
ΔE_{sulfur}, cal.	370.56	390.05	352.80	387.60	386.78	369.56	357.42
$\Delta E_{\text{support}}$, cal.	1.35	2.05	0.30	0.10	0.95	1.90	0.65
ΔE_{gas}, cal.	−0.19	−0.20	−0.20	−0.20	−0.09	−0.09	−0.09
ΔE_{blank}, cal.	12.58	12.58	12.58	12.58	12.58	12.58	12.58
$\Delta Ec°/M$(sample), cal. g.$^{-1}$	−8107.59	−8114.62	−8124.76	−8109.30	−8112.19	−8109.35	−8113.92

Mean $\Delta Ec°/M$ (sample) = −8113.1 ± 2.2 (s.d.) cal. g.$^{-1}$
Impurity correction = −32.2 ± 1.7 (s.d.) cal. g.$^{-1}$
$\Delta Ec°/M$ ($ZrB_{1.993}$) = −8145.3 ± 2.8 (s.d.) cal. g.$^{-1}$

Table III. Results of Hafnium Diboride Combustions

Combustion No.	1	2	3	4	5	6
Sample introduced, g.	1.19963	1.19800	0.60266	0.60090	0.60371	0.59879
Unburned sample, g.	0.04656	0.03264	0.00788	0.00742	0.01151	0.00843
m', sample burned, g.	1.15307	1.16536	0.59478	0.59348	0.59120	0.59036
m'', sulfur, g.	0.04697	0.05012	0.04787	0.04661	0.04744	0.04999
Δt_c, deg.	1.71371	1.73649	0.94802	0.94225	0.94093	0.94654
$\mathcal{E}(\text{Calor.})(-\Delta t_c)$, cal.	−5757.67	−5834.21	−3185.13	−3165.74	−3161.31	−3180.16
$\Delta E_{\text{contents}}$, cal.	−11.12	−11.41	−6.12	−6.16	−5.99	−6.03
ΔE_{sulfur}, cal.	425.66	454.21	433.82	422.40	429.92	453.03
$\Delta E_{\text{support}}$, cal.	13.18	2.15	1.55	1.15	0.65	0.35
ΔE_{gas}, cal.	−0.21	−0.21	−0.10	−0.10	−0.07	−0.07
ΔE_{blank}, cal.	12.58	12.58	12.58	12.58	12.58	12.58
$\Delta Ec°/M$(sample), cal. g.$^{-1}$	−4611.67	−4613.93	−4612.46	−4609.88	−4607.95	−4607.87

Mean $\Delta Ec°/M$ (sample) = −4610.6 ± 1.0 (s.d.) cal. g.$^{-1}$
Impurity correction = −11.6 ± 2.0 (s.d.) cal. g.$^{-1}$
$\Delta Ec°/M$ ($HfB_{2.003}$) = −4622.2 ± 2.2 (s.d.) cal. g.$^{-1}$

Table IV. Auxiliary Data at 25° C.

		c_p, Cal. Deg.$^{-1}$, G.$^{-1}$			$S°$, Cal. Deg.$^{-1}$ Mole^{-1}
Zr	*(40)*	0.0659	Zr	*(40)*	9.29
S	*(36)*	0.168	Hf	*(41)*	10.91
ZrB_2	*(49)*	0.102	B	*(16)*	1.403
ZrF_4	*(48)*	0.148	ZrB_2	*(49)*	8.59
HfB_2	*(47)*	0.059	HfB_2	*(47)*	10.24
HfF_4	*(18)*	0.100			
		$\Delta Hf°$, Kcal. Mole^{-1}			C_v, Cal. Deg.$^{-1}$ Mole^{-1}
			BF_3	*(16)*	10.07
ZrC	*(26)*	−47.0	F_2	*(8)*	5.50
ZrO	[a]	−130	SF_6	*(32)*	21.14
ZrN	*(27)*	−87.3			
HfC	*(26)*	−52.3			ρ, G. Cc.$^{-1}$
HfO	[a]	−131			
HfN	*(15)*	−88.2	Zr	*(43)*	6.505
CF_4	*(46)*	−221	S	*(42)*	2.065
HF	*(46)*	−64.8	ZrB_2	*(28)*	6.09
TiF_4	*(11)*	−394.2	HfB_2	*(1)*	11.2
VF_5	*(3)*	−335	ZrF_4	*(6)*	4.61
MoF_6	*(39)*	−372.4	HfF_4	*(11)*	7.13
CrF_3	*(36)*	−265.2			
FeF_3	*(3)*	−235			Atomic Weight
MgF_2	*(37)*	−268.7			
ZrF_4	*(10)*	−456.80 ± 0.25	B	*(5)*	10.811
HfF_4	*(11)*	−461.40 ±0.85	Zr	*(5)*	91.22
BF_3	*(17)*	−271.65 ± 0.22	Hf	*(5)*	178.49

[a] Estimated value.

Table V. Derived Data at 25° C.

	$ZrB_{1.993}$	$HfB_{2.003}$
$\Delta Ec°/M$, cal. g.$^{-1}$	-8145.3 ± 7.2	-4622.2 ± 6.8
$\Delta Ec°$, kcal. (g.f.m.)$^{-1}$	$-918.5_1 \pm 0.9_7$	$-925._1 \pm 1._4$
$\Delta Hc°$, kcal. (g.f.m.)$^{-1}$	$-920.2_8 \pm 0.9_7$	$-926._9 \pm 1._4$
$\Delta Hf°$, kcal. (g.f.m.)$^{-1}$	$-77._9 \pm 1._5$	$-78._6 \pm 2._1$
$\Delta Sf°$, cal. deg.$^{-1}$ (g.f.m.)$^{-1}$	-3.53 ± 0.1	-3.48 ± 0.1
$\Delta Gf°$, kcal. (g.f.m.)$^{-1}$	$-76._8 \pm 1._5$	$-77._6 \pm 2._1$

from the following sources: $\Delta Ec°/M$(sample), ε(Calor.), ΔE_{blank}, $\Delta E_{\text{impurities}}$, the mass of unburned sample, the auxiliary enthalpies of formation of zirconium, hafnium, and boron fluorides, and the boron-to-metal ratios in the specimens. The uncertainty in the boron-to-metal ratio has a particularly strong effect on the uncertainty in the enthalpy of formation of the diborides, contributing about 60% of the total uncertainty for zirconium and about 35% for hafnium.

The enthalpies of formation of nonstoichiometric compounds are conveniently compared on a gram-atomic basis. In this work the enthalpies of formation of the diborides of zirconium and hafnium were $-26.0_3 \pm 0.5_0$ and $-26.1_7 \pm 0.7_0$ kcal. per gram-atom, respectively. From oxygen bomb combustions Huber, Head, and Holley *(14)* found $-25.9_0 \pm 0.5_4$ kcal. per gram-atom for their better characterized sample of zirconium diboride ($ZrB_{1.985 \pm 0.003}$). From a report which was available to us in abstract form only the oxygen bomb calorimetric result of Epel'baum and Starostina *(7)* was calculated to be $-24._6 \pm 1._1$ kcal. per gram-atom for a reported composition of $ZrB_{2.05}$. The agreement between the present result for zirconium diboride and that of Huber, Head, and Holley *(14)* is particularly gratifying in view of the difference in method, fluorine *vs.* oxygen combustion, and the difficulty of characterizing nonstoichiometric borides.

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The System NH_3–$H_5P_3O_{10}$–H_2O at 0° and 25° C.

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Measurements were made of solubility in the system NH_3–$H_5P_3O_{10}$–H_2O at 0° and 25° C. and of the hydrolysis of tripolyphosphate at 25° C. The 0° C. solubility isotherm consists of four branches in the pH range 2.5 to 8.3; the saturating phases are $(NH_4)_3H_2P_3O_{10}\cdot H_2O$, $(NH_4)_4HP_3O_{10}$, $(NH_4)_9H(P_3O_{10})_2\cdot 2H_2O$, and $(NH_4)_5P_3O_{10}\cdot 2H_2O$. At 25° C. rapid hydrolysis at low pH restricted the range in which equilibrium could be established, but in the pH range 5.1 to 8.7 the 25° C. isotherm consists of three branches; the saturating phases are $(NH_4)_9H(P_3O_{10})_2\cdot 2H_2O$, $(NH_4)_5P_3O_{10}\cdot 2H_2O$, and $(NH_4)_5P_3O_{10}\cdot H_2O$. The hydrolysis of tripolyphosphate at 25° C. in the pH range 4 to 9 is expressed by the first-order rate equation $\log[(P_3O_{10})_0/(P_3O_{10})_t] = kt$, in which t is time, days, and $k = 1.4\,(H)^{1/2}$, where H is the activity of the hydrogen ion and is calculated as $H = 10^{-pH}$.

IN THE continuing study of the properties of the ammonium polyphosphates (*1*), phase relationships in the system ammonia–tripolyphosphoric acid–water were determined at 0° C. over the pH range 2.5 to 8.3, and at 25° C. over the pH range 5.1 to 8.7. Hydrolysis of the tripolyphosphate at 25° C. also was evaluated.

The ammonium tripolyphosphates and their solutions were prepared by ammoniation and vacuum evaporation of 0.3*N* tripolyphosphoric acid that was prepared by ion exchange from solutions of recrystallized pentasodium tripolyphosphate. To minimize hydrolysis of the tripolyphosphate, all operations were carried out at temperatures below 10° C.

Techniques similar to those used in preparing the crystalline ammonium pyrophosphates (*1*) were used to prepare five ammonium tripolyphosphates. In these preparations, $(NH_4)_3H_2P_3O_{10}\cdot H_2O$ was obtained as coarse monoclinic prisms, $(NH_4)_4HP_3O_{10}$ as relatively large monoclinic plates, $(NH_4)_9H(P_3O_{10})_2\cdot 2H_2O$ as monoclinic tablets, $(NH_4)_5P_3O_{10}\cdot H_2O$ as triclinic plates, and $(NH_4)_5P_3O_{10}\cdot 2H_2O$ as monoclinic tablets. The morphological and optical properties of these salts have been published (*2*).

In the solubility study, the complexes, in capped plastic bottles, were equilibrated with occasional manual agitation in a cold room at 0° ± 0.5° C. or with mechanical rocking in a water bath at 25° ± 0.02° C. The approach to equilibrium was followed by periodic petrographic and x-ray examination of the solid phases, and by determinations of composition and pH of the liquid phases.

Phosphorus was determined gravimetrically as quinolinium molybdophosphate (*4*), and nitrogen was determined by distillation of ammonia with sodium hydroxide; pH was determined with a glass electrode in a commercial meter. Hydrolysis of the tripolyphosphates during equilibration was checked by one-dimensional paper chromatography (*3*).

Equilibrium at 0° C. was established in 26 to 120 days without significant hydrolysis. The results are summarized in Table I, and plotted in Figure 1. Two of the three invariant solutions were determined: the solution saturated with $(NH_4)_3H_2P_3O_{10}\cdot H_2O$ and $(NH_4)_4HP_3O_{10}$ at pH 3.72, and the solution saturated with $(NH_4)_9H(P_3O_{10})_2\cdot 2H_2O$ and $(NH_4)_5P_3O_{10}\cdot 2H_2O$ at pH 5.35. The solution saturated with $(NH_4)_4HP_3O_{10}$ and $(NH_4)_9H(P_3O_{10})_2\cdot 2H_2O$ was not determined but has a pH between 4.93 and 4.95 and a composition between 9.75 and 9.86% N and 37.69 and 38.09% P_2O_5.

Hydrolysis of the tripolyphosphate was significantly faster at 25° than at 0° C. and restricted the equilibrium study at 25° C. to the region of pH above 5. Equilibrium at 25° C. was established in 5 to 17 days for 10 complexes in which hydrolysis was not serious. The results are summarized in Table I and plotted in Figure 1. The saturating