TABLE IV

THERMODYNAMIC PROPERTIES OF *l*-ALANINE, CAL. DEG.$^{-1}$ MOLE^{-1}

T, °K.	$Cp°$	$S°$	$\frac{H° - H°_0}{T}$	$\frac{-(F° - H°_0)}{T}$
10	0.118	0.040	0.030	0.010
15	.400	.133	.100	.033
20	.920	.314	.236	.079
25	1.607	.591	.439	.152
30	2.412	.954	.699	.255
35	3.286	1.391	1.006	.385
40	4.151	1.887	1.346	.541
45	4.997	2.425	1.704	.720
50	5.832	2.995	2.076	.919
55	6.640	3.589	2.454	1.135
60	7.414	4.200	2.836	1.364
70	8.850	5.452	3.594	1.859
80	10.19	6.722	4.335	2.387
90	11.44	7.996	5.056	2.940
100	12.56	9.260	5.752	3.509
110	13.61	10.51	6.419	4.088
120	14.60	11.73	7.059	4.674
130	15.56	12.94	7.677	5.264
140	16.49	14.13	8.274	5.855
150	17.38	15.30	8.851	6.445
160	18.24	16.45	9.411	7.035
170	19.08	17.58	9.956	7.622
180	19.89	18.69	10.49	8.206
190	20.68	19.79	11.00	8.786
200	21.46	20.87	11.50	9.364
210	22.23	21.93	12.00	9.937
220	23.00	22.98	12.48	10.51
230	23.80	24.02	12.95	11.07
240	24.60	25.05	13.42	11.63
250	25.41	26.07	13.89	12.19
260	26.22	27.09	14.34	12.74
270	27.02	28.09	14.80	13.29
280	27.82	29.09	15.25	13.84
290	28.60	30.08	15.70	14.38
300	29.36	31.06	16.14	14.92
310	30.11	32.04	16.58	15.46
273.15	27.27	28.41	14.94	13.46
298.15	29.22	30.88	16.06	14.82
310.15	30.12	32.05	16.58	15.47

our value of 7.996 for *l*-alanine. In the case of glycine the difference is even greater. Parks, *et al.*,[5] give $S°_{90} = 7.55$ cal. deg.$^{-1}$ mole^{-1} which differs by 1.35 cal. deg.$^{-1}$ mole^{-1} from our value of 6.197 cal. deg.$^{-1}$ mole^{-1}. In both cases it will be seen that the extrapolation procedure led to too high a value for $S°_{90}$. As will be seen from Tables III and IV $S°_{10}$ amounts to only 0.02 cal. deg.$^{-1}$ mole^{-1} for glycine and 0.04 cal. deg.$^{-1}$ mole^{-1} for *l*-alanine, in each case $<0.2\%$ of $S°_{298}$.

We have rejected the temptation to recalculate the free energy changes associated with formation of peptide bonds involving glycine and *l*-alanine. More reliable data on the entropies of peptides as well as more precise heats of combustion on all compounds involved will be required before existing uncertainties[8] can be resolved. Nevertheless it is clear that, for example, in the formation of glycylglycine the $T\Delta S$ term in the equation for the free energy would be affected to the extent of *ca.* 800 cal. by our values for $S°_{298.15}$ for glycine. This is considerable in a reaction which on the basis of older figures involves only some 3500 cal. at 298°K.

[8] H. Borsook, *Recent Advances in Protein Chemistry*, **8**, 127 (1953).

[CONTRIBUTION NO. 2561 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIFORNIA]

The Preparation of $(Nb_6Cl_{12})Cl_2 \cdot 7H_2O$[1]

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RECEIVED MARCH 17, 1960

$Nb_6Cl_{14} \cdot 7H_2O$ was first prepared in 1913 by reduction of $NbCl_5$ with sodium amalgam, but the yield was not high and some recent attempts to use the method for large-scale preparations have been disappointing. An investigation has been made of the use of other metals as reducing agents, of which cadmium was found to be the most satisfactory. Essential details of a new procedure for preparing $Nb_6Cl_{14} \cdot 7H_2O$ from metallic niobium are given.

The complex chloride of niobium $Nb_6Cl_{14} \cdot 7H_2O$ was first prepared in 1913[3]; its properties were shown to correspond to the formula (Nb_6Cl_{12})-$Cl_2 \cdot 7H_2O$. X-Ray diffraction studies of concentrated solutions[4] showed the configuration of the $Nb_6Cl_{12}{}^{++}$ ion to be an octahedral grouping of niobium atoms with chlorine atoms on the radial perpendicular bisectors of the edges of the octahedron. New interest in the complex ions $Nb_6Cl_{12}{}^{++}$ and $Ta_6Cl_{12}{}^{++}$ has been aroused by their proposed use for the growth of isomorphous protein crystals suitable for X-ray analysis.[5] Attempts were made in this Institute to prepare the compounds (Ta_6Cl_{12})-$Cl_2 \cdot 7H_2O$ and $(Nb_6Cl_{12})Cl_2 \cdot 7H_2O$ for incorporation into protein crystals. The former compound was prepared without difficulty by the method described by Lindner and Feit.[6] Several attempts in these Laboratories by other investigators to repeat the preparation of the corresponding niobium compound were unsuccessful. An investigation of the preparation of this compound therefore was undertaken by us.

First, the preparation of $Nb_6Cl_{14} \cdot 7H_2O$ by the procedure originally used by Harned[3] was repeated. It was successful except for the low yield (about 1%) relative to the amount of $NbCl_5$ used. In an

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[1] This investigation was supported in part by Research Grant H-2143 from the National Heart Institute, Public Health Service.

[2] Sterling Chemistry Laboratory, Yale University, New Haven, Conn.

[3] H. S. Harned, THIS JOURNAL, **35**, 1078 (1913).

[4] P. A. Vaughan, J. H. Sturdivant and L. Pauling, *ibid.*, **72**, 5477 (1950).

[5] L. Pauling, personal communication to R. B. C.

[6] K. Lindner and H. Feit, *Z. anorg. allgem. Chem.*, **137**, 66 (1924).

attempt to improve the yield, a study was made of the reduction of $NbCl_5$ with the metals lead, zinc, magnesium and cadmium. The most satisfactory results were obtained with cadmium (yield about 30%). Because of the difficulties experienced by other investigators in their attempts to prepare $Nb_6Cl_{14}\cdot 7H_2O$, the procedure used is described in some detail.

Procedure.—Niobium pentachloride was prepared by heating metallic niobium in a stream of chlorine gas. About 10 g. of niobium metal (80 mesh, Fansteel Metallurgical Corporation) in a porcelain boat was placed in a horizontal Pyrex glass combustion tube (2.5 cm. × 70 cm.) fitted with spherical joints carrying inlet and outlet tubes. Air was expelled from the apparatus by means of a stream of dry chlorine gas. The tube surrounding the porcelain boat then was heated gently with a Fisher burner to a temperature just sufficient to cause reaction of the chlorine with the niobium and the gradual condensation of the $NbCl_5$ on the walls of the tube immediately adjacent to the heated portion. The $NbCl_5$ deposited in the form of very fine crystals which, depending on their size, appeared to range in color from white to yellow. As the crystals formed, they were melted by gently heating the top portion of the tube with a Bunsen burner, the melted $NbCl_5$ collecting in the lower part of the tube. About 2 hr. was generally required for the complete conversion of 10 g. of metallic niobium to $NbCl_5$. Near the conclusion of the run, the Pyrex tube was inclined slightly downward at the exit end and the $NbCl_5$ was melted and collected in a pool at that end of the tube. When the tube and its contents had cooled to room temperature, the passage of the chlorine gas was stopped and was replaced by a flow of dry nitrogen. When the chlorine had been expelled, the cake of $NbCl_5$ was loosened from the Pyrex tube and transferred as quickly as possible to a large weighing bottle from which air previously had been displaced by a jet of dry nitrogen. Throughout these operations, special precautions were taken to avoid contact of the $NbCl_5$ with air or moisture. The yield of $NbCl_5$ was usually more than 95% of the theoretical.

The entire batch (about 28 g.) of $NbCl_5$ prepared from the chlorination of 10 g. of niobium metal was transferred quickly from the sealed weighing bottle to a porcelain mortar, where it was pulverized under a stream of dry nitrogen and then mixed quickly with cadmium filings (16 g.). The mixture was transferred to a quartz tube (2.5 cm. × 50 cm.) which was closed at one end, the other end being fitted with a rubber stopper carrying a 7-mm. glass tube connected to the vacuum of a water aspirator. The vacuum was applied immediately and the quartz tube was clamped in a horizontal position. Its exit end was wrapped with a wet cloth which served to keep it cool during subsequent heating and to provide a convenient handle by which to manipulate the tube during the run. The mixture of niobium chloride and metallic cadmium, which was near the closed end, was heated gently with a Bunsen burner, starting at a point nearest the open end. The heating was just sufficient to cause a reaction to take place, as evidenced by a blackening of the material. The Bunsen burner was manipulated by hand so as to cause the reaction to proceed slowly toward the closed end of the tube and eventually throughout the entire charge. When the reaction appeared to be complete, the material near the end of the tube was heated to a bright red heat by the use of Meeker burners. This higher temperature, which is essential for the formation of the complex chloride, was maintained for about 1 hour.[7] The yellow deposit which had condensed in the space between the charge and the open end of the quartz tube was shaken down, so as to mix with the main charge, and was also heated. When the heating had been completed, the tube was allowed to cool to room temperature and the aspirator then was turned off.

The complex chloride Nb_6Cl_{14} was isolated from the other products of the reaction by repeated extractions with hot, acidified distilled water, in the following way. The contents of the tube were transferred cautiously to a beaker containing 500 ml. of hot water previously acidified with a few drops of concentrated hydrochloric acid. Caution in making this transfer was necessary because of the presence of some unreduced $NbCl_5$, which reacts violently with hot water. The contents of the beaker were brought to a vigorous boil and allowed to stand overnight. The dark olive-green supernatant liquid was filtered off, and the residue was extracted a second time with about 200 ml. of acidified hot water. This extraction was repeated until no more green color appeared in the extracting liquid; generally the residue from the third extraction could be discarded. The first olive-green extract was heated to boiling and saturated with hydrogen sulfide, the precipitate of cadmium sulfide was filtered off, and the filtrate was tested for complete precipitation. When all of the cadmium had been removed, the hydrogen sulfide was expelled from the solution by boiling and the solution was concentrated by evaporation to about one-third of its volume. The second and third extracts contained negligible quantities of cadmium and were added to the concentrate of the first extract. The combined extracts were transferred to an evaporating dish and evaporated on a water-bath until a heavy brown precipitate settled out of the solution. This precipitate was filtered off on a Büchner funnel and redissolved in one-half liter of water, and the solution was boiled down to about one-third of its volume. In this solution 3 to 4 g. of solid NaCl was dissolved and the mixture was set aside for crystallization of $Nb_6Cl_{14}\cdot 7H_2O$.

The $Nb_6Cl_{14}\cdot 7H_2O$ separated out in the form of microscopic hexagonal plates. After the solution had stood for several hours, the first batch of crystals was filtered off on a sintered glass filter and dried at 70°. The supernatant liquid was concentrated to about half its volume and a second crop of crystals was allowed to form and was removed. This process was repeated until crystallization was complete. The complex is relatively insoluble in a

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(7) A small amount of the corresponding sub-bromide was prepared in a similar manner. It was found that this compound did not form to an appreciable extent at the high temperature required for the preparation of the chloride. A fair yield of the bromide was obtained at a lower temperature.

solution containing an excess of chloride ion, so that when crystallization is complete the supernatant liquid should have only a faint green coloration. The yield of $Nb_6Cl_{14}\cdot 7H_2O$ from 28 g. of $NbCl_5$ was usually about 6.5 g. (32%).

The procedure described above was used for the preparation of 45 g. of $Nb_6Cl_{14}\cdot 7H_2O$. This quantity was obtained as the combined products of eight successive runs in which the yields, calculated on the basis of the amount of $NbCl_5$ used, ranged from 29 to 44%.

Acknowledgment.—We wish to express our indebtedness to Professor Linus Pauling for his stimulating interest in this investigation.

[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY, LOS ALAMOS, NEW MEXICO]

The Solubility of Uranium (IV) Fluoride in Aqueous Fluoride Solutions[1,2]

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RECEIVED FEBRUARY 19, 1960

The solubility of $2UF_4\cdot 5H_2O$ was measured at 25.0° as a function of fluoride ion concentration in mixtures of hydrofluoric and perchloric acids at a constant ionic strength of 0.12 *m*. Uranium was determined by radioassay using U^{233} as a tracer. Equilibrium was established by approaching from both sides. The behavior of the equilibrium solubility, which varied from 1.35×10^{-3} *m* at $[F^-] = 1.9 \times 10^{-5}$ *m*, through a minimum of 0.12×10^{-3} *m* at $[F^-] = 9.6 \times 10^{-4}$ *m*, to 0.37×10^{-3} *m* at $[F^-] = 1.5 \times 10^{-2}$ *m*, is best explained by the existence in solution of the species UF_2^{++}, UF_3^+, UF_4^0 UF_5^-, and UF_6^-.

Introduction

There does not appear to have been any extensive investigation, prior to the present study, of the solubility of UF_4 as a function of fluoride ion concentration. According to Katz and Rabinowitch[3] the most reliable value for the solubility of UF_4 in water at 25° is 10^{-4} mole per liter as determined by R. Kunin. This value is in good agreement with that previously found by investigators[4] who reported the molality of a saturated solution of uranium tetrafluoride in oxygen-free water at 25.0° to be $(1.03 \pm 0.03) \times 10^{-4}$, and at 40.2° to be $(1.94 \pm 0.03) \times 10^{-4}$. They reported equilibration for at least 300 hr. in glass apparatus under a nitrogen atmosphere.

The present investigation was carried out in acid solution to avoid hydrolysis complications[5] and the use of glass apparatus was avoided. A comprehensive effort was made to insure equilibrium conditions by approaching from both sides by an imposed temperature variation.

Experimental

Apparatus and Materials.—All solutions were equilibrated in a platinum cup $2^3/_8''$ in diameter and 4″ high. This cup fitted loosely in a Pyrex jacket equipped with a standard taper 71/60 male joint. The Pyrex cover contained three tubes. The two outer ones were vents for flushing with hydrogen and were equipped with stopcocks. The central tube extended down to a level $1^1/_2''$ above the top of the platinum cup and ended in a standard taper female joint. Into this was fitted a tapered platinum male joint connected to a $^1/_8''$ i.d. platinum tube which extended down to within $^3/_4''$ of the bottom of the cup, flaring out at the end into a sintered platinum frit one inch in diameter. Through this tube samples could be filtered at the temperature of the solution and withdrawn for analysis. All joints and stopcocks were greased with Apiezon "N" lubricant. Fig. 1 shows this assembly.

The cup and container rested on a water-tight Lucite box which was built to house a "Mag-mix" motor, and the whole assembly was immersed in a 27″ × 27″ × 24″ water bath. The bath temperature was measured with a platinum resistance thermometer and was controlled to better than ± 0.01°. The solutions were stirred magnetically by means of a platinum-covered iron magnetic rod $1^1/_2''$ long and $^1/_2''$ in diameter. Because of wear from the platinum–platinum contact with the cup, stirring was done only intermittently.

Samples were withdrawn into commercial weight burets fitted with side arms and stopcocks so that a vacuum could be applied. For runs involving higher concentrations of HF, burets constructed of Lucite were substituted, and the glass parts of the solubility apparatus were coated with melted paraffin.

The solvents were prepared from reagent grade 60% perchloric acid, 48% hydrofluoric acid and redistilled water. The perchloric acid solutions were titrated with sodium carbonate as a primary standard, using a methyl orange xylene cyanole indicator. The hydrofluoric acid was poured into a Lucite weight buret and diluted with water if necessary; weighed portions were titrated with standard NaOH solutions according to the method given.[6] At no time was any fluoride solution allowed to come into contact with any silica. The two acids were mixed in the desired proportions by weight in a polythene bottle.

The solid phase was determined to be $2UF_4\cdot 5H_2O$ by analysis and confirmed by microscopic examination of its optical properties. Two separate portions were prepared, by two different methods, and both products exhibited essentially the same solubility. In the first case uranium peroxide was precipitated from a uranyl nitrate solution containing about 1.4% of the uranium as U^{233}. The peroxide was ignited in air at 850° for 14 hr., converting it to U_3O_8. Since the saturated UF_4 solutions were to be analyzed for total uranium by counting the radioactivity, a portion of this tagged U_3O_8 was reserved for use as a primary standard in determining the specific count rate. The balance was converted to anhydrous UF_4, first by reduction with hydrogen gas to UO_2 at 700°, and then by hydrofluorination with anhydrous HF and H_2 gases at 550° for 5 hr. and then 4 hr. of sintering at 825° in a platinum boat. Approximately 10 g. of tagged UF_4 was so produced, and most of this material was consumed in the preliminary experiments involved in establishing the experimental procedures which finally were adopted.

In the second case uranium peroxide was precipitated from a uranyl solution containing 2.24 g. of U^{233} and 45 g. of U^{238}. About 3 g. of the peroxide was ignited to constant weight at 850°. The remainder of the peroxide was dissolved in dilute aqueous HF in a polythene beaker. The solution was electrolyzed using platinum electrodes

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(1) Work done under the auspices of the Atomic Energy Commission.

(2) A preliminary account was presented before the 135th National Meeting of the American Chemical Society, Boston, April 6, 1959.

(3) J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium," National Nuclear Energy Series, Div. VIII, Vol. V, McGraw-Hill Book Co., New York, N. Y., 1951, p. 372.

(4) H. A. Bernhardt, J. H. Junkins and S. S. Kirslis, *AECD-3412*, June 15, 1949 (declassified).

(5) *Cf.* K. A. Kraus and F. Nelson, THIS JOURNAL, **72**, 3901 (1950).

(6) "Reagent Chemicals, A.C.S. Specifications," 1950, p. 172.