Summary

1. The solubility of hydrogen selenide in water has been determined for the temperature range 15° to 35°.
2. The solubility of hydrogen selenide in aqueous hydriodic acid (concn. 0.2, 0.4 and 2.73 M) at 25° has been measured.
3. The molal heat of solution of hydrogen selenide in water has been calculated from the solubility data and found to be 2431 cal. at 25°.
4. The free-energy decrease for the reaction H_2Se (1 M) = H_2Se (760 mm.) has been calculated for several concentrations of hydrogen selenide.

AUSTIN, TEXAS

[CONTRIBUTION FROM THE BUREAU OF STANDARDS, UNITED STATES DEPARTMENT OF COMMERCE]

THE DETERMINATION OF URANIUM[1]

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Chief among the methods for the determination of uranium are the gravimetric method in which the element is precipitated as diammonium uranate, $(NH_4)_2U_2O_7$, and weighed as uranous uranate, U_3O_8, and the volumetric method in which uranium is reduced by zinc and then titrated with permanganate. The accuracy of the gravimetric method has often been questioned on the score that it is quite difficult to attain the theoretical composition $UO_2.2UO_3$, and various corrective measures such as ignition in oxygen or reduction to uranium dioxide in hydrogen have been proposed. The volumetric method is also usually described as uncertain because the reduction of uranium seldom goes to the same point, and attempts to bring its valence to a definite stage before titration have usually been unsuccessful.

It seems worth while, therefore, to record our experience as to the performance of these methods, especially as both are excellent when simple precautions are observed. In our hands the volumetric method has proved to be as accurate as any that are based on reduction in the Jones reductor, provided the reduction is made in a cool solution and the reduced solution is given sufficient exposure to the air before titration. The gravimetric method also is most excellent when macerated paper is used, and there is no need whatever for special ignition in oxygen or hydrogen.

Experimental Part

The analyses were made with a sulfuric acid solution of uranyl sulfate prepared from a sample of uranous uranate U_3O_8, that had been obtained

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[1] Published by permission of the Director, Bureau of Standards, U. S. Department of Commerce.

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by precipitation with Cupferron according to Holladay and Cunningham.[4] This is an interesting procedure based on the fact that Cupferron precipitates quadrivalent but not sexivalent uranium in hydrochloric or sulfuric acid solution. Elements such as iron, vanadium and titanium can therefore be precipitated by Cupferron and separated from sexivalent uranium and then, after removal of the Cupferron and reduction of the uranium, this element can in turn be precipitated by the same reagent and separated from other elements such as chromium, aluminum and phosphorus.

Volumetric Method

A. Preliminary Tests.—The first tests of the volumetric method dealt with the question as to whether any reduced compound of uranium is reproducible and stable, for it is apparent that an accurate method is impossible if such a compound does not exist. In these tests reductions were made at room temperature in a Jones reductor, a procedure that we have found to be more satisfactory than reduction in hot solution.[5] The reduced solutions were then exposed to the air for various periods of time.

TABLE I

STABILITY OF SULFURIC ACID SOLUTIONS OF URANOUS SULFATE AT 20° TO 25°

Series	Period of exposure to air, min.	0.1 N $KMnO_4$ required, cc.	Remarks
A	1	8.56	Stirred for 1 minute
	5	8.57	Stirred for 1 minute; allowed to stand
	10	8.57	
	20	8.57	
B	1.5	9.24	Stirred for 1.5 minutes
	20	9.25	Stirred for 1.5 minutes; allowed to stand
C	5	24.90	Stirred for 5 minutes
	120	24.89	Stirred for 5 minutes; occasionally thereafter
	240	24.88	
	5	24.90	Rapid stream of purified air bubbled through each reduced solution during period of exposure
	25	24.88	

The results, given in Table I, show conclusively that a given state of reduction can be reproduced and that the reduced compound is stable upon exposure to air for as much as four hours at 20–25°. Subsequent tests showed that this is in the quadrivalent salt. It seemed strange that such marked stability of a sulfuric acid solution of uranous sulfate is seldom, if ever, mentioned in texts. For this reason the experiments were repeated, but with the difference that reductions were made at 60–80°, as is the usual custom. These tests, given in Table II, show that uranous sulfate is not stable in hot solution and explain why no general claims as to stability have been made and why directions usually specify correction for

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[4] Holladay and Cunningham, *Trans. Am. Electrochem. Soc.*, **43,** 329 (1923).

[5] Lundell and Knowles, *Ind. Eng. Chem.*, **16,** 723 (1924).

over-reduction by such expedients as "pouring the solution into a casserole," or "stirring the solution for a few moments," such procedures having given some analysts fairly good results.[6]

TABLE II

INSTABILITY OF URANOUS SULFATE SOLUTIONS AT 60° TO 80°

Time of exposure to air, min.	0.1 N $KMnO_4$ required after exposure at: 60–80°, cc.	20–25°, cc.	Remarks
1.5	9.19	9.25	Stirred for 1.5 minutes
20	17.50	17.75	Stirred for 1.5 minutes; allowed to cool slowly
5	24.75	24.90	Stirred for 5 minutes
120	24.41	24.89	Stirred for 5 minutes; occasionally thereafter as solution stood at edge of steam-bath
240	24.22	24.88	

The reproducibility and stability of a reduced compound of uranium having been established, the next tests dealt with the treatment that was necessary to insure oxidation of the over-reduced compound which is

TABLE III

OXIDIZABILITY OF OVER-REDUCED URANIUM SOLUTIONS AT 20° TO 25°

1 cc. of 0.1 N $KMnO_4$ = 0.01191 g. of uranium

Expt.	Period of exposure to air Min.	0.1 N $KMnO_4$		Remarks
		Actually required Cc.	Required on basis of complete oxidation Cc.	
1	1	8.56	8.57	Reduced solution stirred continuously.
2	1.5	9.24	9.25	Same as Expt. 1.
3	1.5	18.10	17.75	Same as Expt. 1.
4	20	17.76	17.75	Stirred for 1.5 minutes; allowed to stand.
5	1	26.60	25.65	Reduced solution stirred continuously.
6	1	25.00	24.89	Air bubbled through reduced solution continuously.
7	5	24.90	24.89	Same as Expt. 6.
8	5	24.90	24.89	Reduced solution stirred for 5 minutes.
9	20	26.00	25.65	Reduced solution stirred for 1 minute; allowed to stand.
10	20	25.65	25.65	Reduced solution stirred for 1 minute; then occasionally.
11	1.5	9.32[a]	9.25	Reduced solution poured into dish, HF added, stirred.
12	20	9.45[a]	9.25	Reduced solution poured into HF, stirred.
13	15	9.26[a]	9.25	Reduced solution stirred for 5 minutes; poured into HF.
14	As brief as possible	16.66[b]	16.54	
15	10	16.66[b]	16.54	Air bubbled through reduced solution slowly.
16	45	16.60[b]	16.54	Same as Expt. 15.

[a] Hydrofluoric-boric acid added to solution after reduction.

[b] Hydrofluoric-boric acid added to solution before reduction.

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[6] When the tests were completed it was found that Ledoux and Company are quoted in the *Bureau of Mines Bull.*, No. 70 (1913) (A Preliminary Report on Uranium, Radium, and Vanadium, by R. B. Moore and K. L. Kithil), p. 85, to the effect that "Solutions of uranous sulfate are stable in the presence of air and may be exposed to it with impunity. In fact, they may be agitated with air for several minutes without altering the state of oxidation in a measurable degree." These statements have reference to a solution of uranous sulfate obtained in a cool reduction procedure.

always formed in a good reduction. These are listed in Table III and demonstrate that the oxidation is easily accomplished by stirring the reduced solution or by bubbling air through it. Treatment for five minutes suffices in determinations involving as much as 0.25 g. of uranium; from one to two minutes are enough for amounts less than 100 mg. It should be noted, however, that the oxidation is slow if the solution is not agitated as, for example, in Expt. 9. Interesting experiments are Nos. 11 to 16, which involve the presence of hydrofluoric and boric acids in addition to sulfuric acid. The first of these tests was made in order to find out whether hydrofluoric acid accelerates the oxidation of reduced uranium by air as is the case with ferrous sulfate.[7] This was all-important in a method that we planned to use for the determination of uranium dioxide in U_3O_8 residues. Instead of accelerating the oxidation, hydrofluoric acid seemed to retard it and this was confirmed by Expt. 12. It appeared likely that the fluoride of the over-reduced compound is but slightly ionized, so in Expt. 13 the over-reduced compound was oxidized before hydrofluoric acid was added. Perfect results were obtained. Expts. 14 to 16, which were also made in anticipation of other work, showed that while over-reduction of uranium is not as marked in sulfuric-hydrofluoric-boric acid solutions as it is in sulfuric acid solution alone, the over-reduction that does take place is not easily corrected by exposure to the air.

B. Recommended Procedure.—Prepare a solution containing 1% or less of uranium, 5% by volume of sulfuric acid, and no compounds other than uranium that are reduced in the Jones reductor. Add enough permanganate to produce a permanent pink tint, cool the solution to 20–25°, and pass it through a reductor at a rate of 50–100 cc. per minute. Blow clean air through the reduced solution for five minutes or pour the solution into a casserole and stir it for an equal period of time. Titrate with a solution of potassium permanganate that has been standardized against pure sodium oxalate and correct the titration reading for the volume of permanganate required in a blank run, as well as the volume required to obtain an end-point color in the yellow solution. One cc. of 0.1 N potassium permanganate solution corresponds to 0.01191 g. of uranium.

A reductor having a bore of approximately 19 mm. and a 40–45cm. column of 20-30-mesh zinc that has been amalgamated with 1–2% of mercury is very satisfactory. The usual practice in a determination is first to wash the reductor and receiver with dil. sulfuric acid and water if the apparatus has been standing idle, and then to proceed with the reduction proper by drawing through a little dil. sulfuric acid (1:20), next the solution to be reduced, then a little more of the dilute acid and finally enough water to wash out the acid and all of the reduced solution.

In some applications of the reductor the presence of two or more reducible compounds is not objectionable if their effect can be calculated. Thus iron and titanium can be reduced and titrated, the amount of permanganate consumed by the titanium calculated after this element has been determined colorimetrically, and iron then obtained by difference. With the possible exception of iron, this cannot be done in reductions involving uranium, for data are lacking concerning the behavior of the reduction

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[7] Hillebrand, "The Analysis of Silicate and Carbonate Rocks," *U. S. Geol. Surv. Bull.*, **700**, 199 (1919).

compounds upon prolonged exposure to the air. Reductions of uranium should, therefore, be carried out in solutions that are free from iron, titanium, chromium, vanadium and molybdenum, as well as other reducible compounds such as nitric acid and organic matter. Hydrochloric acid is also undesirable for it interferes in the permanganate titration and necessitates the use of a correction mixture.

In all titrations with permanganate it was found desirable to determine the correction for the reagents and reductor and, in addition, the correction for the volume of permanganate required to produce a pink tint in the yellow solution of uranyl sulfate. The first correction was determined by passing a solution of the reagents through the reductor, titrating with the permanganate solution, and then subtracting the small volume of permanganate required to produce the end-point color in the same volume of solution. The second correction was determined by treating the titrated solution of uranium with a few drops of a 0.1 *N* solution of ferrous sulfate, adding from 0.5 to 1 g. of ammonium persulfate, stirring for one minute and then titrating with the permanganate solution until the original end-point was reproduced. The correction for reagents and reductor should not average much more than 0.02 cc. of 0.1 *N* permanganate solution; that for the end-point color varies with the amount of uranium involved and the end-point chosen by the analyst; in the tests described, it amounted to as much as 0.07 cc. in a titration requiring a total of 25 cc.

Gravimetric Method

Practically the only modification of the gravimetric method used in this work consists in adding macerated paper before the solution is filtered. As for other details of the method, it is well known that carbonates and organic matter must be absent from the precipitation and that many elements other than uranium are precipitated by ammonium hydroxide. Expts. 1–4 and 7–9 listed in Table IV show that reproducible results are easily obtained by precipitation with ammonium hydroxide and that it makes no difference whether the precipitate is ignited in air or in oxygen. Further, it is shown that solution of the U_3O_8 residue in nitric acid followed

TABLE IV

IGNITION OF DIAMMONIUM URANATE

(Final ignition at approximately 1100° in all cases)

	Weight after				
Expt.	Ignition in air G. of U_3O_8	Ignition in oxygen G. of U_3O_8	Solution of U_3O_8 in HNO_3, and re-ignition in air G. of U_3O_8	Ignition and cooling in hydrogen G. of "UO_2"	Weight calcd. from volumetric analysis, g.
1	0.1138	0.1135	...	...	0.1137 U_3O_8
2	.1138	.1134	...	...	.1137 U_3O_8
3	...	.1136[a]	0.1137	...	.1137 U_3O_8
4	...	.1136[a]	.1136	...	.1137 U_3O_8
5	...	...	...	0.1118[a]	.1093 UO_2
6	...	...	...	.1115[a]	.1093 UO_2
7	.3517	...	...	...	.3517 U_3O_8
8	.3516	...	...	...	.3517 U_3O_8
9	.3517	...	...	...	.3517 U_3O_8

[a] Preliminary ignitions were made in air and at the lowest possible temperature until carbon was removed. In Expts. 5-6 the residues were then ignited and cooled in hydrogen until the weight was constant.

by evaporation to dryness and re-ignition causes no change in weight. Expts. 5 and 6 in Table IV together with Series D in Table V indicate that the often specified ignition in hydrogen is a dubious procedure at best and cannot in any way be regarded as an improvement over ignition in air.

Recommended Procedure.—Prepare a dil. sulfuric acid solution containing 1% or less of uranyl sulfate and no carbon dioxide, organic compounds, or elements other than uranium that are precipitated by ammonia or that unite with uranium in the presence of this reagent. Add a few drops of methyl red indicator, heat to boiling and then add dil. ammonium hydroxide that is free from carbonate until the indicator just changes to a distinct yellow. Stir in macerated paper in amount equal to one-half of a 9cm. sheet, filter and wash the precipitate with a hot 2% ammonium nitrate solution. Dry the wet paper and precipitate in a platinum crucible, ignite over a Tirrill burner or in an electric muffle under good oxidizing conditions at as low a temperature as possible until carbon is destroyed, and then with the crucible in a slanting position over the full flame of a Tirrill burner or its equivalent. Finally cover and continue the heating for a minute. Cool in a desiccator and weigh as U_3O_8.

Determination of Uranium Dioxide in U_3O_8 and "Uranium Dioxide" Residues

Theoretically, the weighed U_3O_8 residue should have the composition $UO_2.2UO_3$. It is apparent that determinations of its uranium dioxide and total uranium contents are desirable checks on a determination, especially if the uranium was originally associated with elements that might escape complete separation and finally contaminate the U_3O_8. A determination of the uranium dioxide content of a U_3O_8 residue by Hillebrand's method[8] is somewhat tedious as the residue, together with sulfuric acid, must be sealed in a hard-glass tube filled with carbon dioxide and heated at 150–175° for some time before the tube can be broken and the solution titrated. It seemed quite likely that uranium dioxide or U_3O_8 could be easily decomposed by treatment with hydrofluoric and sulfuric acids and that the solution could be titrated with permanganate after the addition of boric acid. Preliminary experiments showed that such a method was satisfactory in every way, as the decomposition of the oxide is rapid, no oxidation of the uranous compound takes place and the presence of boric acid permits direct titration with permanganate. The data given in Table V show that analyses of residues that have received the same treatment can be expected to agree very closely, for like titrations differ by no more than one drop of the permanganate solution (0.04 cc. = 0.0004 g. of uranium dioxide). It is interesting to note in Series A that the U_3O_8 contained more than the calculated amount of uranium dioxide in spite of final ignition in oxygen, while in Series B there was too little uranium dioxide after the nitric acid treatment. In

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[8] Hillebrand, *U. S. Geol. Surv. Bull.*, No. 78. Treadwell-Hall, "Analytical Chemistry," J. Wiley and Sons, New York, 1924, vol. 2, p. 528.

no case, however, was the variation in uranium dioxide sufficient to affect an ordinary weighing of U_3O_8, for the calculated effects were less than 0.1 mg. The tests in Series D showed that complete reduction of U_3O_8 had not been attained in spite of the thorough ignition in hydrogen.

TABLE V

ANALYSIS OF WEIGHED U_3O_8 AND "URANIUM DIOXIDE" RESIDUES

Series	Weight of U_3O_8,[a] g.	UO_2 content, g. Calcd.	UO_2 content, g. Found	Effect of variation in the UO_2 content on the weight of U_3O_8, g.
A	0.1135[b]	0.0363	0.0374	−0.00007
	.1134[b]	.0363	.0370	− .00004
B	.1137[c]	.0365	.0356	+ .00005
	.1136[c]	.0364	.0354	+ .00006
C	.3516[d]	.1128	.1128	.00000
	.3517[d]	.1128	.1129	+ .00001
	Weight of "UO_2"			
D	.1118[e]	.1093	.0724	
	.1115[e]	.1093	.0720	

[a] All U_3O_8 residues had been ignited at approximately 1100°.

[b] Thoroughly ignited in air, then in oxygen.

[c] Ignited gently in air then in oxygen, dissolved in nitric acid, and again ignited in air.

[d] Ignited in air.

[e] U_3O_8 ignited gently in air, then ignited and cooled in hydrogen. Complete reduction to uranium dioxide should have given 0.1093 g. in each case.

Recommended Procedure.—Treat the weighed residue of uranium dioxide or U_3O_8 with 10 cc. of hydrofluoric acid, crush any small lumps with a platinum or Bakelite rod and stir for three to five minutes. The material will not dissolve completely because of the insolubility of uranous fluoride. Treat the solution with 10–20 cc. of dil. sulfuric acid (1:1), stir for a few moments and transfer to a beaker containing 100 cc. of a cool, saturated solution of boric acid. Stir until the salts are in solution, titrate with standard permanganate solution and correct for the end-point color as previously described.

After the determination of the uranium dioxide content, the total uranium content of pure U_3O_8 can be accurately determined by evaporating the titrated solution to fumes to sulfuric acid, diluting and then proceeding with reduction as in the volumetric method. When hydrofluoric acid is not removed before the reduction, the results will be a little high. It goes without saying that ferrous sulfate cannot be used as an aid in correcting for the end-point color in the first titration if the total uranium is to be sought.

It seems likely that the value for uranium dioxide that is found will represent the true uranium dioxide content of the weighed residue. The value for total uranium will also be correct if the U_3O_8 is pure or the contaminants are not reduced in the reductor. Examples of such contaminants are aluminum and zirconium. If, however, any contaminating substance is reduced, the result for total uranium will be too high and will exceed the calculated content if the reducible compound is the only contaminant. Such are vanadium and titanium. In any event, it is quite certain that contaminants will have a distinct effect on the U^{IV}-to-U^{VI} ratio.

Comparison of the Gravimetric and Volumetric Methods

The data given in Table VI verify what was expected as a result of the work that had gone before, namely, that results obtained by the recommended gravimetric and volumetric methods should agree within experimental error. In fact, the results are in better agreement than could be expected, for one drop of the 0.1 N solution of permanganate that was used in the volumetric method represented 0.3 mg. of uranium.

TABLE VI

COMPARISON OF RESULTS OBTAINED BY WEIGHING AS U_3O_8 AND BY REDUCTION AND TITRATION

Expt.	1	2	3	4	5
U obtd. by weighing as U_3O_8, g.	0.0965	0.0963	0.2983	0.2982	0.2983
By reduction and titration, g.	.0963	.0964	.2985	.2983	.2982

Summary

When simple precautions are observed, uranium can be determined accurately by weighing as U_3O_8 after precipitation as diammonium uranate, $(NH_4)_2U_2O_7$, or by titration with permanganate solution after passage through a Jones reductor.

In the gravimetric method it is recommended that macerated paper be used and that the precipitate be ignited in air. A simple method is given by which the uranium dioxide content of the U_3O_8 can be quickly checked by titration with permanganate after solution in hydrofluoric and sulfuric acids and addition of boric acid.

In the volumetric method it is recommended that the reduction be made in dil. sulfuric acid solution (1:20) at 20° to 25° and that the reduced solution be vigorously agitated by stirring or by a stream of pure air for five minutes before titration. It is shown that such exposure to the air insures complete oxidation of the over-reduced compound to the quadrivalent state and results in no further oxidation whatever.

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A STUDY OF THE PHYSICAL PROPERTIES OF NITROMETHANE

BY JOHN WARREN WILLIAMS

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For many years the study of molecular rearrangements has received considerable attention from organic chemists. Various physical and chemical properties of certain substances made it evident that there were exceptions to the general rule of structural organic chemistry which states that every pure organic compound possesses a definite and fixed configuration which may be expressed by a single structural formula. For example, in the case of the so-called nitro compounds, Holleman,[1] Hantzsch and

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[1] Holleman, *Ber.*, **33**, 2913 (1900).