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This document consists
of 9 pages, and 2
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January 8, 1947

SEMI-MONTHLY ABSTRACTS

Section C-IA

Pile Chemistry and General Chemistry

Period from December 16 to 31, 1946

INV. 9-47

HIGH TEMPERATURE PILE PROGRAM

(G. E. Boyd)

Graphite Impregnation (M. J. Kanter, W. W. Phillips)

Additional impregnations of high purity AGR graphite were made with scattering of results up to ± 30% from the mean value. In an effort to correlate this scattering with the properties of the individual pieces of graphite, a measure of the internal void volume was taken before each impregnation.

Each sample was boiled in water for 30 minutes. The water was displaced by fresh cold water to reduce the temperature rapidly. Then the samples were weighed while immersed and then impregnated in the same manner as all the previous runs. From this weight in water, the weight in air, and the dimensions of the sample, the % H_2O absorbed (measure of void volume) was calculated.

A fairly linear relationship between % water absorbed and % gain in weight on impregnation was obtained with the data from 13 samples run in one batch. When this was repeated with 15 more samples, the relationship obtained was parallel to but not the same as that obtained with the first group.

Oxidation of Graphite by UNH (D. Schultz)

Since the percent U_3O_8 in the impregnated samples is calculated from the observed weight increase, oxidation of graphite by the UNH during the firing step would introduce an error in the reported U_3O_8 content. The following tests were run to determine the extent of the oxidation.

The exit gas from the furnace in which impregnated samples were fired was passed over hot CuO, thus oxidizing any CO coming from the sample to CO_2. The CO_2 was absorbed in $Ba(OH)_2$ and the unneutralized hydroxide titrated with HCl. The following table gives the apparent % U_3O_8 determined from the weight increase and the true % U_3O_8 corrected for the carbon oxidized:

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Sample #	Apparent % U_3O_8	True % U_3O_8
351	1.19	1.12
352	1.14	1.16
349	1.25	1.27
350	1.55	1.58
141	1.63	1.67
140	2.25	2.29
143	2.35	2.41
356	3.38	3.44
355	3.45	3.50
354	4.39	4.77
353	4.78	4.92
358	7.10	7.35

The above results indicate that the apparent % U_3O_8 calculated from absorbed weight increases may be in error by approximately 2%.

Graphite Impregnation (Recovery Tests) (B. Schultz)

Recovery tests were run on impregnated low density graphite samples that had been heated to 1400°C in a vacuum. Controls were also run using similar graphite samples which had been impregnated and then fired to 800°C and also using untreated graphite.

The recovery process consisted of refluxing the sample in dilute nitric acid ([illegible]) for a 24 hour period. After leaching the graphite samples were ignited and the residue weighed. The results of these tests are summarized in the following table.

Sample #	Treatment	% wt. loss due to leaching	% Residue after ignition
1	impregnated heated to 1400°C	5.43	0.47
2	impregnated heated to 1400°C	5.64	0.43
3	impregnated heated to 800°C	4.26	0.09
4	impregnated heated to 800°C	4.24	0.09
5	blank	0.62	0.11

Samples were also taken from the same rod and ignited without the leaching treatment with the following results.

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Sample #	Treatment	% Residue after ignition	% U_3O_8 after ignition
6	Impregnated heated to 1400°C	4.27	[illegible]
7	Impregnated heated to 1400°C	[illegible]	[illegible]
8	Impregnated heated to 800°C	4.20	[illegible]
9	Impregnated heated to 800°C	[illegible]	[illegible]
10	Blank	0.40	-

The last column of the above table gives results obtained by the analytical group for the percent of U_3O_8 in the residue on the basis of the original weight of the sample. It will be noticed that the difference between the % total residue and % U_3O_8 is approximately the same as the % residue present in the blank with perhaps some indication that impurities distill out on heating.

The results of these tests indicate that the impregnated uranium compound is not leached as easily from the graphite heated to 1400°C as from graphite heated to 800°C.

Reaction Between Steam and BeO ([illegible] Berkman)

The following experiments were carried out at 1400°C at reduced water vapor pressure. The time for each run was 2½ hours.

Run	Temp. of BeO Pellet (°C)	Rate of Steam Condensation (ml/min)	Water Vapor Pressure (mm Hg)	Weight of BeO Lost (%)
64	1400	0*	15	0.29
65	1400	0*	15	0.26
66	1400	0.08	15	0.27
67	1400	0.20	90	0.32
68	1400	0.83	90	0.51
69	1400	0.10	90	0.32

* In runs 64 and 65 no water was collected in the receiver. Due to probable distillation of water both forward and backward through the system, the flow rates for these runs are not known.

[redacted]

<u>Volatilization Tests on Impregnated Graphite</u> (J. Malm, G. Mason, E. Dinkelocker)

A general description of the procedure and significant results to date follows:

Impregnated graphite samples, 2" long and 3/4" diameter, are heated by a high frequency induction heater in a quartz apparatus. The sample rests on a graphite support which in turn sets in a quartz stand. Temperature readings are taken with an optical pyrometer through a window in the top of the apparatus. A Pirani gauge continuously records pressure readings, while intermittent pressure readings are observed with a McLeod gage.

With the sample in place the system is evacuated to a pressure of 1 x 10^{-5} mm of Hg or better and heating begun. The sample reaches temperatures of 1400°C in about one minute; pumping continues throughout the heating. On cooling, the apparatus is washed out several times with hot concentrated HNO_3, the solution taken to a small volume and ether extracted to separate the uranium from volatilized impurities, mainly iron, which interfere in the colorimetric uranium determination. The colorimetric procedure used is described in MonC-28. Ferretti (Health Section) has been attempting to check these analyses by a fluorescent method.

Table I gives the results of several heatings of a sample of impregnated graphite. For comparison Table II is included to show weight changes observed in heating similar graphite pieces containing no U_3O_8.

The weight loss observed in the initial heating of impregnated samples is great enough to conclude that the U_3O_8 initially present is reduced to the carbide. W. H. Zachariason has identified the compound present as UC_2 by X ray analysis. Weight increases observed on allowing the samples to stand in air, along with high pressure readings in subsequent heatings, would seem to indicate that the uranium carbide present after heating at 1400°C partially reacts with the oxygen or moisture in the atmosphere upon removal from the apparatus to reconvert to the oxide. Attempts are being made to avoid exposure of the sample to the atmosphere in runs now in progress by inserting quartz cylinders around the heated samples to collect the volatilized uranium. The collectors are then removed while a stream of purified N_2 is passed over the graphite sample.

The reason for the differences in the analyses of amounts of volatilized uranium by the colorimetric method and by the fluorescent method is not quite clear although any impurities present would tend to make the colorimetric results high.

The uranium loss as determined by the colorimetric method in run 3, Table I will be used to calculate an approximate vapor pressure of the volatile uranium compound. Substituting this value in the equation,

$$p \text{ mm Hg} = \left(7.5 \times 10^{-4}\right) \frac{g}{a} \left(\frac{2\pi R T}{M}\right)^{\frac{1}{2}}$$

where g = weight of material vaporized per second
a = area of surface from which vaporization takes place assumed here to be 13.5% of the total surface area assuming ~ 20% voids in the graphite.

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TABLE I

Impregnated Graphite Sample #2; den = 1.592; % U_3O_8 = ~2.68

Run No.	Time of Heating Hrs.	Temperature °C	Pressure (Pirani) Microns	Wt. before Heating g	Wt. after Heating g	Change in Wt. g	U loss by Colorimetric Analysis µg	U loss by Fluorescent Analysis µg
1	3.00	1405	250 - 0.0	22.4827	22.3296	0.1437	35.5	36
2	4.50	1395	50 - 0.0	22.3333	22.3204	0.0129	22.0	3.7
3	3.00	1385	300 - 0.0	22.3308	22.3218	0.0090	28.3	[illegible]
4	6.00	1385	380 - 0.8	22.3262	22.3011	0.0251	31	31.2

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Table 22

Graphite Blank #2a; den = 1.592

Run No.	Time of Heating Hrs.	Temperature °C	Pressure (Pirani) Microns	Wt. before Heating g	Wt. after Heating g	Change in Weight g	Apparent U Loss (Colorimetric Method) μg
1	3.00	1410	25.0 - 0.0	22.9515	22.9282	0.0233	0
2	2.00	1365	3.5 - 0.0	22.9278	22.9265	0.0013	0
3	3.08	1395	6.0 - 0.0	22.9269	22.9260	0.0009	0
Graphite Blank #2b; den = 1.592							
1	2.08	1415	16.0 - 0.0	22.3752	22.3492	0.0260	12

Table 22

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R = gas constant
T = absolute temperature
M = molecular weight, i.e., 262

a vapor pressure of 1.6 x 10^{-8} mm Hg is obtained for the uranium (dicarbide) at 1385°C. If the uranium compound evaporates from a larger effective surface than assumed here, the vapor pressure would be correspondingly smaller down to a minimum value of approximately 2 x 10^{-9} mm Hg.

ANALYTICAL CHEMISTRY

(F. S. Tomkins)

Spectrographic Laboratory (F. Tomkins, J. K. Brody, I. S. Dubos, J. Faris, M. Walsh)

A. Service Analysis:

1. Twenty-six Be metal samples quantitatively for all impurities.
2. Nine samples of U metal quantitatively for all impurities.
3. One sample of U_3O_8 quantitatively for impurities.
4. Two samples of BeO quantitatively for impurities.
5. Two samples of $BeSO_4$ quantitatively for impurities.
6. Three steel samples qualitatively for impurities.
7. Two residue samples qualitatively for Al, B, Th.

B. Research:

1. A densitometric spectrochemical method for the determination of small amounts of Be in solutions is being developed. The method is a modification of the copper-spark method used extensively in this laboratory and described in detail in previous reports. Limitations on the sample as to solids and acid content are similar to those for the general copper spark procedure. Mo is used as an internal standard. Preliminary runs indicate that a precision of 10% or better can be obtained in the range 0.002 to 0.5 micrograms Be.

2. The restandardization of the copper spark method is practically complete, with the completion of standard plates for 54 elements in the wavelength range 2300 to 7000 A.

3. An all quartz fractionating column is being built in the glass shop for use in the preparation of pure BeO on a larger scale than has been attempted previously. Five pounds of crude Be basic acetate has been received from the Beryllium Corporation and will be used as a starting material in this work.

Wet Chemical Analysis (R. W. Bane, B. Holt, R. Hospelhorn, K. Jensen, R. Telford)

A. Services

1. Three uranium-columbium-zirconium alloys were analyzed for zirconium.

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2. Five solutions were analyzed for their uranium content.
3. Six beryllium metal samples were analyzed for boron. The wide variation of boron values have been due to heterogeneous distribution of boron in the metal. Consistent results have been obtained by dissolving a large sample and taking aliquots. The values obtained in this way check quite well with the average of the large number of values obtained on individual samples of one specimen.
4. Two calcium hydroxide suspensions were analyzed for boron.
5. The work on the separation of micro amounts of fluorine from beryllium is continuing. A double distillation, the first at 220°C and the second at 135°C, was tried on five sets of known samples. The results were erratic and in no case was a good recovery of the spike obtained. The distillation of a larger volume will be tried next in an attempt to improve the separation.
6. The micro chloride distillation apparatus has been assembled. The chloride content of the standard beryllium metal samples will be determined.
7. A number of determinations of beryllium oxide in beryllium metal have been made using the beryllium chloride volatilization apparatus. All results were very high. This is believed to be due to the reaction of some organic material with the beryllium, since after all the beryllium chloride has been volatilized a dark residue which reacts like elemental carbon remains. In order to completely prevent the possibility of any organic matter coming in contact with the beryllium, an all glass apparatus is being built, and hydrogen chloride will be generated from sulfuric acid and hydrochloric acid. In the past, tank hydrogen chloride was used and the apparatus contained several plastic connections.
8. Two samples of NaK are being analyzed for the sodium to potassium ratio. The NaK from the container was run into n-butyl alcohol. After the reaction had ceased, the solution was acidified with hydrochloric acid, water was added, and the mixture shaken well. Three water extractions were made. The aqueous solution was evaporated to dryness, and the salts were ground and mixed well. This salt mixture will be analyzed for the sodium to potassium ratio.
9. Two solutions containing a large concentration of phosphoric acid along with some bismuth are being analyzed for uranium.

SPECIAL PROBLEMS

(O. C. Simpson)

Ionization Potential of Plutonium (E. Rauh)

The proposed method for the determination of the ionization potential of plutonium is based on the two electrode method of Franck[1] with modifications dictated by the properties of the metal. Two identical diodes, one of which is a container for Pu vapor, form two arms of a bridge circuit by means of which the ion current can be measured and the normal space currents can be opposed.

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[1] Compton and Mohler, National Res. Council Bulletin, 9, #48 (1924)

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A series of tests and calculations have been made and from these an apparatus has been designed. The primary features were determined by the vapor pressure of Pu which requires a system 1) that can be used in the range 1200 - 1500°C, 2) that is closed or nearly so to prevent excessive loss of vapor, 3) that is constructed of chemically inert materials of low vapor pressure. A fairly heavy mass, inductively heated, will satisfy 1). An oven arrangement with an opening of such a size as to permit evacuation and yet allow ten hours' heating at 1500°C will satisfy 2). Tantalum, molybdenum, and beryllia have been selected because of their low vapor pressures, high melting points, chemical inertness, and, in the case of the metals, reasonably good machinability. The present apparatus consists of twin tantalum ovens fitted with indirectly heated cathodes in which BeO insulators are used.

The emitting surfaces are tantalum (lowest work function) indirectly heated by tungsten coils. By this arrangement a temperature high enough for sufficient emission and a unipotential source are attained. The tantalum has been raised to 1858°C with none of the energy reradiated, hence in a "field" of 1200°C, it should be possible to reach 2100°C where a 100 ma current can be expected.

The vacuum system, ion guage, optical pyrometer, and induction heater are ready for use. If calculations indicate that the life of the tungsten filaments will not be prohibitively short, the first apparatus will be made and used with copper which has approximately the same ionization potential and vapor pressure as Pu.

Heat of Sublimation and Vapor Pressure of Graphite (R. J. Thorn)

One of the possible errors inherent in the presently employed method is the assumption that the vapor is saturated. If the degree of saturation does not change over the temperature range of the experiment, then this assumption has no effect on the experimental heat of sublimation but it still has an effect on the calculated heat of sublimation for the monatomic form. During the past two weeks some consideration has been given to means of obtaining an estimate of the degree of saturation of the vapor. The line of attack which has been followed is one utilizing a graphite cylinder the upper surface of which is perforated by a number of circular holes of about ¼" depth. There are two conflicting factors which determine the optimum diameter of the holes. (1) The degree of saturation of the vapor issuing from the holes decreases with the hole diameter. (2) The fraction of the upper surface covered with holes increases with the diameter (hexagonal packing of holes) for a fixed distance between hole edges. A compromise between these two factors has to be made. Accordingly, a graphite cylinder with a perforated upper surface has been cut out having 43 per cent of the upper surface covered with holes. The theoretical degree of saturation of the pressure above these holes (dia. = 0.07 in., depth = 0.25") is equal to or greater than 0.94 to the first degree of approximation. Since the limit of accuracy of the weight of the graphite deposit is about 10 μg., one should be able to establish whether the degree of saturation is greater than or less than 0.83 in the case of the flat surface used in the first run.

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Within the next two weeks the perforated cylinder will be baked out and a new series will be started provided the glass shop has completed the repair of the quartz condenser.

Remote Control and Hot Lab Development (M. Rebenak, F. L. Belletire, R. Midder, R. W. Holmes, R. Bloomgren)

Work is being continued on the 3-2 hot lab. The lead wall and lead doors have been completed. Tracks, mirrors and some lighting fixtures have yet to be mounted. Development is being continued on other phases of remote control.

Van de Graaff Generator (H. Andrews, F. Belletire, M. Rebenak)

Despite the fact that the humidifier is still not operating, the generator has been disassembled. It was found very dirty. We feel that within a week or two, baring unforeseen accidents and troubles, bombardment of G. E. material will proceed as previously scheduled.

GRAPHITE PROGRAM

(T. J. Neubert)

Natural Graphite (W. Primak)

During the past month additional specimens of natural graphite have been acquired. Gifts of Madagascar, Ceylon and Mexican graphite have been received from George F. Pettinos (Philadelphia). A gift of graphite from an unnamed source has been received from the Asbury Graphite Mills (Asbury, New Jersey). A gift of Ticonderoga (New York) graphite has been received from Professor Palache (Harvard). A number of samples have been purchased from the Superior Flake Graphite Company (Chicago). Further inquiries are being made in the hopes of acquiring single crystals large enough to manipulate easily.

Apparatus is being ordered and designed which is hoped to permit determination of the properties of a small graphite crystal from several millimeters to a fraction of a millimeter in its external dimensions.

Heat of Dispersion of Graphite in Potassium Metal (L. Quarterman, W. Primak)

Further experiments were performed to determine the heat of reaction of potassium and graphite. The apparatus used was a simple vacuum calorimeter immersed in a constant temperature oil bath maintained at about 80°C. The reaction was found to take place so rapidly that the reaction was effectively complete at about the time the first reading of the temperature could be taken: some 30 - 40 seconds after introducing the sample. The heat of reaction could thus be calculated merely by taking the temperature rise and multiplying it by the heat capacity of the calorimeter parts. For unirradiated graphite a value of 91 cal/gm was obtained while for irradiated

GE-H-10, 355

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graphite (a piece of the "B" end of the "T" bar) 237 cal/gm was obtained. This gives a value of 146 cal/gm stored energy. The value for unirradiated graphite is somewhat lower than that reported in the literature, 120 cal/gm, while the value obtained for the irradiated graphite is somewhat higher than that obtained from other experiments. The large slope obtained in the cooling curve of the reaction makes it difficult to extrapolate the temperatures back to the end of the reaction. This is probably caused in part by the high vapor pressure of potassium at the temperatures used.

The difficulties of introducing unoxidized potassium into the present apparatus and of introducing samples easily made it advisable to redesign the calorimeter before proceeding with a program of determining the heat of reaction for a large number of samples. The results here reported certainly indicate that the energy of irradiation is released in the reaction and that it should be possible to develop on its basis a simple precise method for determining this energy.

<u></u>C^{14} Distribution in Graphite (V. Hamill with [illegible] Libby)

Experiments on C^{14} half life and distribution in irradiated graphite have been concluded. A final report is in preparation and will be issued presently.