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PROJECT 9536

FILE

Route List

1. ~~A. B. Greninger~~ 47
2. ~~W. D. Coolidge~~
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DATE 12-12-46

SUBJECT Pile Chemistry and General Chemistry Weeks Ending December 11, 1946
BI-WEEKLY ABSTRACTS Section C-II

TO File

FROM O. C. Simpson

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ANL-OCS-93
This document consists
of 9 pages, and 3
figures. [redacted]

BI-WEEKLY ABSTRACTS

December 12, 1946

Section C-II

Pile Chemistry and General Chemistry

Weeks Ending December 11, 1946

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HIGH TEMPERATURE PILE PROGRAM

(C. A. Boyd)

Reaction Between Steam and BeO (M. G. Berkman)

A constriction formed in the mullite tube used in the red[redacted] runs. This constriction was caused by a partial collapse of the hottest portion of the reaction tube, thus rendering it no longer suitable for reduced-pressure runs. Several atmospheric-pressure runs were made before the tube was discarded. As in previous runs, the reaction period was 2½ hours.

Run	Temp. of BeO Pellet (°C)	Rate of Steam Condensation (ml/min)	Weight of BeO Lost (%)
60	1400	4.9	1.4
61	1400	3.1	1.2
62	1400	2.3	1.0
63	1400	1.25	0.65

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By Authority of TID-1157
Appd 3/15/57
By D Hoke 1/19/59
R E Savely 12-30-02
PD Amory 1-17-03

The apparatus is being rebuilt so that the reduced-pressure experiments can be continued.

Graphite Impregnation (M. A. Kanter, R. W. Phillips, A. L. King)

Work was continued on the impregnation of fuel rod sections. The tests to be described were made using AGR graphite obtained from the National Carbon Company, having a bulk density of 1.59 g/cc and an ash content of 0.11%.

The variation from sample to sample of the weight percent increase was determined for a number of impregnations in which the solution concentration was maintained at 60 grams UNH per 100 cc aqueous solution.

The procedure used is as follows:

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The fuel tube sections were boiled in water for 30 minutes and fired at 800°C in helium for 30 minutes. They were then boiled in the impregnating solution for 30 minutes, and then refired immediately at 800°C in helium. The runs were made in duplicate. The results are summarized in the following table:

Run	Observed Wt. % Increase Sample 1	Sample 2
1	3.15	3.20
2	3.86	3.91
3	2.58	2.32
4	2.79	-

It will be noticed that although considerable variation in weight % increase occurs between the runs, the duplicate samples for any given run are in reasonably good agreement. This indicates that further study of the effect of the conditions of impregnation should be made.

Further tests were made to determine the cause of the distribution of uranium oxide in the fuel tube. In one case the rod was dropped into liquid nitrogen immediately after removal from the impregnating bath.

The radial sections were then machined off while the material was frozen and the distribution of uranium determined in the regular manner.

Distribution curves characterized by the high surface concentration similar to those shown previously (ANL-OCS-92, November 27, 1946) were obtained. This indicates that the distribution occurs during the actual impregnation and not during the subsequent drying or firing.

<u>Crushing Strength of Neutron Irradiated BeO and BeO-UO$_2$ Samples</u> (S. R. Gaarder, J. R. Gilbreath, J. L. Weeks, D. H. Rich)

Crushing strength determinations have now been completed for all the types of 1/4 inch pellets in all three Hanford bombardments. The results along with the values for the unirradiated standards are shown in Table I and Figures 1 and 2. It may be advisable to run more of the standards and more of the irradiated samples in some cases where the results are somewhat questionable or where large deviations exist.

Inspection of the data for the mixed oxide pellets shows that in every case but one the crushing strength decreased from 20-30% during the 24-day bombardment. In all cases, the crushing strength after the 63-day bombardment was somewhat higher than after the 24-day irradiation (See Figure 2). However, in only one case was this percent increase in crushing strength greater than the average percent deviation. Again during the third irradiation (151 days) no large changes were noted although, in all cases but one, the crushing strength decreased slightly and approached the value obtained after the 24-day irradiation. Without more data it is impossible to determine whether any annealing has occurred, although it does appear that the crushing strengths may be approaching a saturation value. The reason for the large deviations

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TABLE I

Table I

EFFECT OF NEUTRON IRRADIATION ON CRUSHING STRENGTH

Irridiation Time / Crushing Strength Data / Material	None				24 Days				63 Days				131 Days			
	Average Crushing Strength p s i	Avg. % Dev.	No. Samples	Range %	Average Crushing Strength p s i	Avg. % Dev.	No. Samples	Range %	Average Crushing Strength p s i	Avg. % Dev.	No. Samples	Range %	Average Crushing Strength p s i	Avg. % Dev.	No. Samples	Range %
Low Density H-90;2% UO_2 Dens=2.43-2.78	57,100	9.5	9	82 -119	53,900 (94%)*	9.5	6	77 -122	75,600 (132%)*	9.1	6	83 -121	65,000 (114%)*	14.0	5	88 -134
Low Density H-89;10% UO_2	155,100	6.5	6	90 -115	105,200 (68%)	9.7	6	82 -119	109,000 (70%)	16.3	5	80 -124	111,800 (72%)	4.7	6	93 -110
High Density H-90;2% UO_2 Dens=2.76-2.81	131,700	11.7	9	69 -119	106,600 (81%)	12.0	6	80 -125	115,500 (88%)	6.4	5	89 -113	108,100 (82%)	5.9	6	89 -110
High Density H-89;10% UO_2 Dens=2.98-3.08	188,300	13.5	10	78 -124	137,200 (73%)	2.1	5	98 -103	144,100 (77%)	11.9	6	76 -114	135,800 (72%)	1.7	5	96 -103
Low Density H-85-1;Pure BeO Dens=2.80-2.88	-	-		-	-	-		-	84,400	21.8	7	56 -139	100,300	23.9	10	56 -153
Low Density H-85-2;Pure BeO Dens=2.81-2.97	-	-		-	124,900	20.3	10	62 -133	166,700	19.9	10	71 -133	-	-		-
Low Density H-85-3;Pure BeO Dens=2.95-2.98	174,800	13.2	10	64 -122	-	-		-	-	-		-	197,100 (112%)	10.7	10	73 -114
High Density H-78;Pure BeO Dens=2.84-3.00	168,700	4.7	11	85 -109	172,700 (102%)	10.2	13	79 -127	164,700 (98%)	12.8	10	70 -120	183,900 (109%)	11.0	10	83 -118
High Density H-79;Pure BeO Dens=2.88-2.96	171,900	9.0	11	84 -118	183,300 (107%) 203,800 (118%)	9.2 5.8	10 15	75 -113 90 -110	195,600 (114%)	9.1	10	84 -115	198,500 (115%) 201,700 (117%)	10.9 13.3	10 10	80 -125 74 -127

* Figure in parentheses is the percent of the original crushing strength.

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FIGURE 1

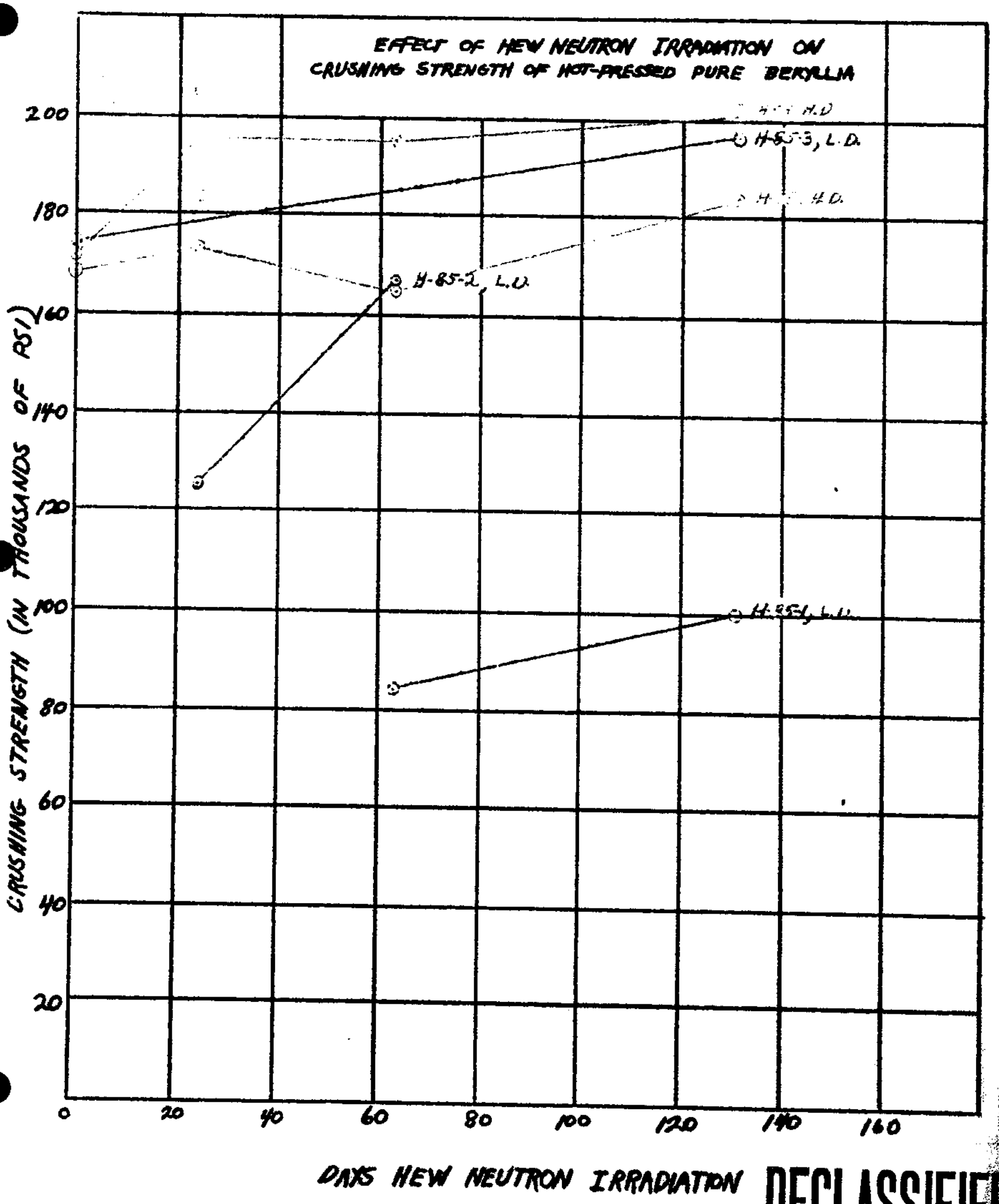

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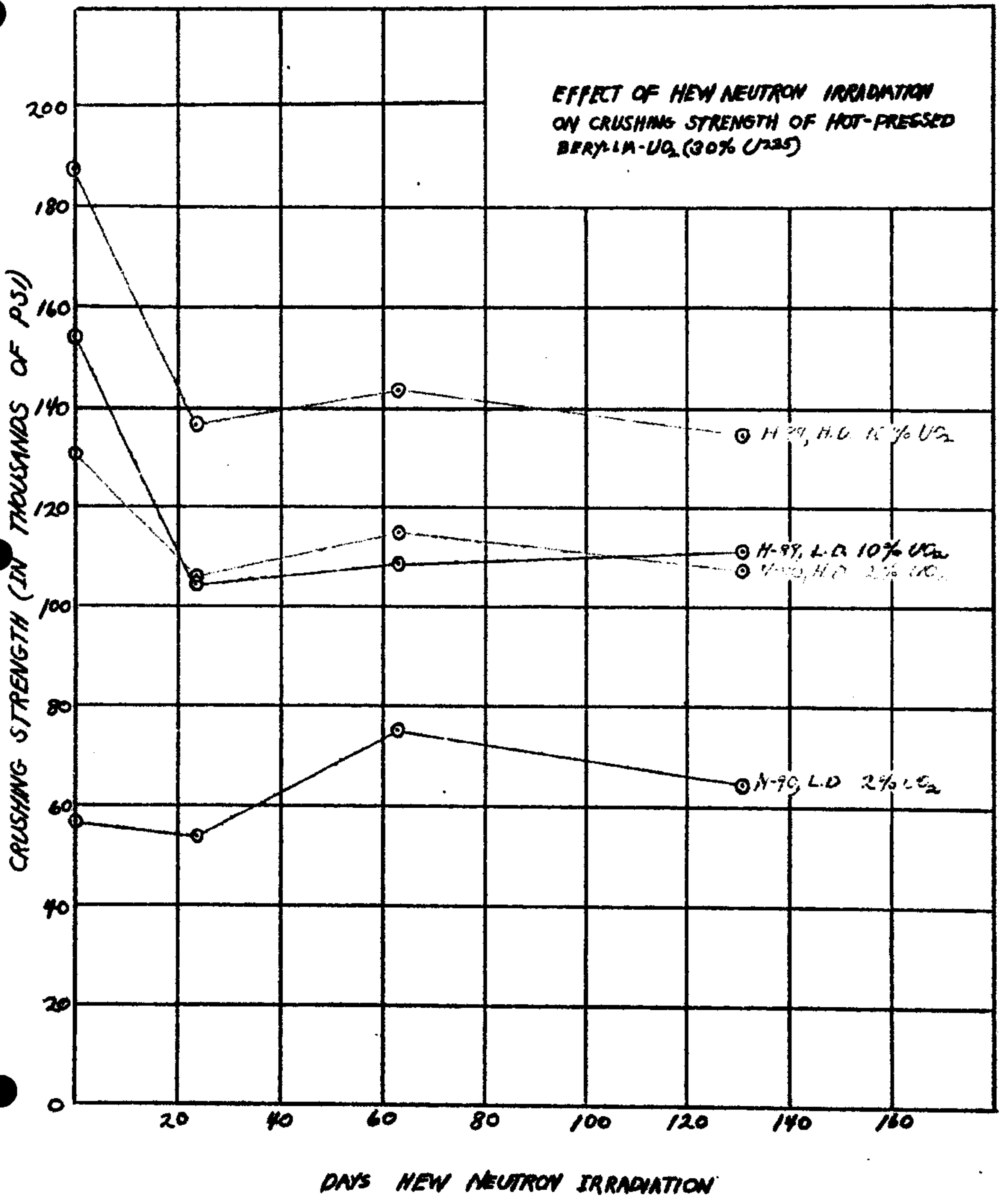
FIGURE 2



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in some cases may possibly be due to varying densities of the individual pellets. (The method used for obtaining crushing strengths should be capable of giving results in which the average deviation is less than 10%. This is an acceptable deviation according to ASTM specifications.)

The results of the tests on the pure BeO pellets are shown in Figure 1. These data indicate quite definitely that neutron irradiation of intensities involved in these experiments does not decrease the crushing strength of pure BeO. Actually, in all cases but one, the crushing strength increased slightly with irradiation time. In almost all cases this increase was less than the average deviation of the results but, nevertheless, there does seem to be an upward trend.

Functional Tests on Beryllia Bricks (C. A. Boyd)

Functional tests on beryllia hexagons have been made to determine the effect of annealing on Boron content. The results indicate that the content is not affected by annealing. Details of these tests are reported in the memorandum ANL-CAB-4, December 16, 1946.

ANALYTICAL CHEMISTRY

(F. S. Tomkins)

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

A. Service Analysis:

1. Fourteen samples of Be metal have been quantitatively analyzed for 15 elements.
2. Twenty-four samples of Be metal have been converted to the oxide and the ultraviolet plates have been completed. The elements in the visible region will be completed some time today.
3. Six samples have been analyzed quantitatively for Be, Al, Mg, Ca for health physics. Three air filter papers were analyzed for Be, also for health physics.
4. Five samples of Sn have been quantitatively analyzed for Be and Sn.
5. Analysis of two samples of graphite have been completed.

B. Research:

1. The Bureau of Standards' Be metal samples were re-analyzed. The metal was again converted to the oxide using quartz beakers, and reagents distilled in quartz.
2. Some time has been spent refocusing and realigning the Hilger spectrograph for the recording spectrophotometer. The quartz optics have been aligned but nothing has been done with the glass optics.
3. The copper spark has been restandardized for 51 elements over a wavelength range of 2300 A° - 7000 A°. Sixty-eight plates have been completed.

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4. The optical shop has promised to have one set of Fabry-Perot plates figured within the next two weeks. When these have been received and coated, work on the Np hyperfine structure will continue.

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

A. Services:

1. Six solutions were analyzed for total hydroxide content.
2. One solution was analyzed for the oxalate content.
3. Two uranium fluorides were analyzed for uranium.
4. One iron sample was analyzed for manganese.
5. Three uranium-zirconium-columbium alloys were analyzed for columbium. The analysis for zirconium will be completed.
6. Controls were run on the analysis of sodium and potassium in equal weight mixtures of the two elements. Sodium was precipitated and weighed as sodium magnesium uranylacetate. Potassium was separated and weighed as potassium perchlorate. Recoveries indicate the two elements can be determined to 0.2% or better of the amount present.
7. Six specimens of beryllium metal have been analyzed for boron. The distribution of values obtained for samples of one specimen can not be explained by variations of the method. It is believed that the specimens are not homogeneous. To prove this a large sample will be dissolved and aliquots taken for analysis. Until this point is cleared up, results must be reported as a range rather than as a definite value.
8. The determination of micro amounts of fluorine in beryllium metal is proving to be a difficult problem. Separation by distillation as hydrofluosilicic acid from perchloric or sulfuric acid is incomplete as ordinarily carried out. Two distillations, the first at 220°C and the second at the standard temperature of 135 ± 2°C, have not given much better results. However, more runs of this type will be made. Distillation at 135° ± 2°C of a larger volume, 600 - 800 ml, will also be tried in an attempt to improve the separation.

   The formation of the strong complex $BeF_4^=$ may be the cause of the inconsistent results.

SPECIAL PROBLEMS

(O. C. Simpson)

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

Since the report issued on November 13, 1946, the method has been analyzed more thoroughly and the literature has been searched for values of the heat of sublimation. The further study of the presently employed method has shown that the slope, a, of the reciprocal apparent temperature vs. time curves is related to the partial pressures of the monatomic form, p_1, and the diatomic

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form, p_2, according to the relation

$$\frac{d \ln a\sqrt{T}}{d(\frac{1}{T})} = \frac{d \ln(p_1 + \sqrt{2}p_2)}{d(\frac{1}{T})} \qquad (1)$$

If one assumes that the degree of dissociation of the diatomic form does not change over the temperature range investigated, then one obtains

$$\frac{d \ln a\sqrt{T}}{d(\frac{1}{T})} = -\frac{2\Delta H_1 + (1 - \alpha)\Delta H_D}{(1 + \alpha)R} = -\frac{\Delta H_3}{R}, \qquad (2)$$

in which α = degree of dissociation of C_2, ΔH_1 = heat of sublimation to the monatomic form, and ΔH_D = heat of dissociation of C_2.

The method which has been employed most frequently during the last ten years is one based on the dissociation energy of carbon monoxide according to the following scheme:

$$CO = C(^3P) + O(^3P) - D(CO) \qquad (3)$$

$$O(^3P) = \tfrac{1}{2}O_2 + \tfrac{1}{2}D(O_2) \qquad (4)$$

$$^*C(^3P) = C(^5S) - E \qquad (5)$$

$$\underline{C_{gr} + \tfrac{1}{2}O_2 = CO - \Delta H_f(CO)} \qquad (6)$$

$$C_{gr} = C(^5S)\ ;\ \Delta H_1 = D(CO) + E - \tfrac{1}{2}D(O_2) + \Delta H_f(CO) \qquad (7)$$

Another cycle which could be employed but which has not received any attention is the following:

$$CN = C(^3P) + N(^4S) - D(CN) \qquad (8)$$

$$N(^5S) = \tfrac{1}{2}N_2 + \tfrac{1}{2}D(N_2) \qquad (9)$$

$$^*C(^3P) = C(^5S) - E \qquad (5)$$

$$C_{gr} + \tfrac{1}{2}N_2 = \tfrac{1}{2}C_2N_2 - \tfrac{1}{2}\Delta H_f(C_2N_2) \qquad (10)$$

$$\underline{\tfrac{1}{2}C_2N_2 = CN - \tfrac{1}{2}\Delta H_D(C_2N_2)} \qquad (11)$$

$$C_{gr} = C(^5S); \Delta H_1 = D(CN) - \tfrac{1}{2}D(N_2) + E - \tfrac{1}{2}\Delta H_f(C_2N_2) + \tfrac{1}{2}\Delta H_D(C_2N_2). \qquad (12)$$

* There is some doubt whether this step should be included since it is not known whether the monatomic form evaporates during sublimation into the ^3P or the ^5S state. One of the reasons for its inclusion was to explain the discrepancy between ΔH_1 obtained from the dissociation energy of carbon monoxide and from an evaporation experiment.

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Unfortunately the values for D(CO), D(CN), $D(N_2)$, $\Delta H_D(C_2N_2)$, $D(O_2)$, and E, all of which have been obtained from spectroscopic or appearance potential data have not been established with certainty. The problem which arises is one of predissociation making it difficult to decide which band system to extrapolate. Besides the uncertainty in these quantities a value for $D(C_2)$ has also not been definitely established. This latter quantity is necessary for the calculation of the equilibrium constant for the dissociation of C_2 and hence α. Without α it is impossible to compare the results obtained in the present study with those previously reported. However, from the extremes of the reported values certain conclusions can be obtained in the light of the present investigation. This is shown below:

The lowest and highest values reported for $D(C_2)$ are 83 kcal [Zeise, Z. Elektrochem 46, 38 (1940)] and 191 kcal [Vaughan and Kistiakowsky, Phys. Rev. 40, 456 (1932)] respectively. If one specifies that

$$D(C_2) \geqq 83 \text{ kcal},$$

then since $\alpha \geqq 0$ and $\Delta H_S = 199$ kcal, one obtains from equation (2) the condition,

$$\Delta H_1 \geqq 142 \text{ kcal}.$$

On the other hand if one specifies that

$$D(C_2) \leqq 191 \text{ kcal},$$

then since $\alpha \leqq 1$, one obtains the condition,

$$\Delta H_1 \leqq 201 \text{ kcal}.$$

Published values of D(CO) which are compatible with these extremes are 255 kcal [White, J. Chem. Phys. 8, 459 (1940)] and 267 kcal [Lozier, Phys. Rev. 45, 752 (1934)] for the evaporation of C in the ^3P state, and 159 kcal [Valatin, J. Chem. Phys. 14, 568 (1946)] for the evaporation of C in the ^5S state. If one takes into consideration the data on the CN cycle, then the most consistent published values are D(CO) = 159 kcal, D(CN) = 906 kcal [Valatin, loc. cit.], $D(C_2) = 173$ kcal [Zeise, loc. cit.], E = 97 kcal [Valatin, loc. cit.], $\Delta H_D = 146$ kcal [White, loc. cit.], $D(O_2) = 118$ kcal [Bichowsky and Rossini, Thermochemistry of Chemical Substances], $D(N_2) = 115.4$ kcal [Valatin, loc. cit.]. All of these values assume that ΔH_1 is for the reaction: $C_3 = C(^5S)$. In view of the large number of uncertainties, however, these values cannot be accepted as being final.

The only value of the equilibrium constant which is in accordance with the values given above is the one given by Zeise (loc. cit.). Using values given in this reference one obtains for the equilibrium constant,

$$\log_{10}K = -\frac{3.776 \times 10^4}{T} + 6.736,$$

for the reaction: $C_2 = 2C(^5S)$. From this equation and the data obtained

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in the present investigation, one obtains the following results:

$$C_2 = 2C;\ \alpha(2384°K) = 0.15.$$

$$2C_S = 2\alpha C + (1 - \alpha)C_2;\ \log_{10}p(\text{mm}) = -\frac{43466}{T} \quad 13.044.$$

$$C_S = C;\ \Delta H_1 = 187.8 \text{ kcal.} \quad (T = 2384°)$$

$$2C_3 = C_2;\ \Delta H_2 = 202.8 \text{ kcal.} \quad (T = 2384°)$$

Remote Control and Hot Laboratory Development (M. Rebenak, F. L. Belletire, R. Miller, R. W. Holmes, H. C. Andrews)

Work is being continued on the B-2 Hot Lab, and it seems possible to have the construction work completed by December 24, 1946. The periscope is about 95% complete. It is being held up by slow delivery of special gears.

The tracks are being fabricated in Hartford's shop. Progress seems to be satisfactory.

The large frame for the crane is designed and materials are being secured for its fabrication. Some parts for the carriage are still being designed and should be completed by December 17, whereupon they will be fabricated in the shop.

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

The installation of an air conditioner in B-4 is nearing its final stages. If all progresses well, we intend to take the generator apart for cleaning and overhauling by the end of next week. After rehabilitation the generator will be used first for gamma bombardments on some G.E. wire insulation.

Determination of Hydrogen in Sodium-Potassium Alloy (E. Rauh, F. Belletire, M. Rebenak, H. C. Andrews)

The procedure consisted in oxidizing about 3 gms of NaK with dried oxygen, reacting the resulting oxides and peroxides with about a threefold excess of heavy water of accurately known D to H ratio, distilling a portion of the water from the resulting hydroxides (light and heavy), and analyzing this distillate for the new D to H ratio.

Any hydrogen in the alloy which is already combined as hydroxide would remain in the solution. Hydrogen dissolved in the alloy as such or combined as hydride, if any, and which could conceivably have escaped into the reaction vessel as gaseous hydrogen was burned in oxygen by a spark and the resulting water vapor condensed into the solution.

The D/H ratios in the original and final water were determined by means of a mass spectrometer at the Argonne by Mr. Omohundro. The results on five samples taken from a steel bottle of NaK obtained from the Argonne showed 0.04 to 0.06 atomic percent of hydrogen.

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GRAPHITE PROGRAM

(T. J. Neubert)

C^{14} Distribution in Graphite (W. Hamill)

Absolute count rates for C^{14} half-life determination involve small corrections (approximately 10%) for end-effects. Using estimated corrections for this effect, based upon G-M tubes of different lengths and diameters, and a tentative value for the C^{14} content, subject to final mass-analysis, a provisional half-life of approximately 7000 years has been obtained.

With the assistance of Mr. Robert Hentz, work has been resumed on burning of Hanford graphite. Studies of the effects of variation of temperature and particle size are now in progress. The effect of leaching with HF and HCl will also be studied. The burning curve (enrichment vs. percent burn) will then be carefully redetermined for two graphites of different irradiation.

Graphite Impregnation (H. A. Kierstead, M. Nagy, L. Fuchs)

AGR graphite samples impregnated with uranium (both natural and 30% enriched) have been prepared, and are now being packaged for irradiation in the CP-3 pile. It is expected that, due to fission recoils, the impregnated samples will suffer many more dislocations than virgin graphite given the same bombardment.

The weights, dimensions, resistances, and elastic moduli have been measured after each step in the impregnation procedure, and will be measured again after bombardment. The weight, resistance, and modulus changes due to impregnation are reported in Table 1. Dimension changes were negligible.

Thermal conductivities have been measured on the impregnated samples only. They will be reported later.

Table 1. Effect of Impregnation on AGR Graphite

Treatment	Percentage Change in		
	Weight	Resistance	Elastic Modulus
Boiled in water, heated to 800°C	-0.09	+0.1	+1.4
Boiled in Acetone-HNO_3 Solution	-0.17	+1.0	+2.1
1 impregnation	+2.65	+0.4	17.
2 impregnations	+4.92	+1.5	23.
3 impregnations	6.61	+2.2	29.

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Density of Irradiated Graphite (G. Hennig, H. A. Kierstead)

An apparatus is being constructed to measure the true density of graphite samples by helium and argon displacement.

[redacted]