in correcting to the standard state from the calorimeter solutions and results in no difference in the heat of formation of oxides of praseodymium and terbium of the same composition.

Acknowledgment.—The authors wish to thank C. L. Sieglaff and E. D. Guth for their help in the preparation of some of the samples.

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[CONTRIBUTION FROM THE ARGONNE NATIONAL LABORATORY]

Heat of Reaction of Irradiated Graphite with Potassium[1]

BY W. PRIMAK AND L. A. QUARTERMAN

RECEIVED JANUARY 28, 1956

The heats of reaction of fast neutron irradiated graphite samples and potassium were determined. The difference between the specific heats of reaction of irradiated and unirradiated graphite (excess heat of reaction) was in all cases much smaller than the difference between the specific heats of combustion of the respective irradiated graphite samples and unirradiated graphite (excess heat of combustion; energy content). The excess heat of reaction as a function of irradiation was found to saturate sooner than the energy content. A single determination indicated that hydrocarbons are produced in small quantity in the hydrolysis of the irradiated graphite–potassium compound but not in the hydrolysis of the unirradiated graphite–potassium compound suggesting the formation of some potassium carbide in the reaction of irradiated graphite and potassium.

Introduction

An account of the discovery of property changes in graphite exposed to energetic neutrons was given by Burton.[2] A review of this work is given by Burton and Neubert.[3] It was Szilard[4] who first suggested that energy should be stored in graphite under irradiation. The presence of stored energy in irradiated graphite was demonstrated by differential thermal analysis independently by Maurer and Ruder,[5] by Leaf and Novick,[6] and by Wheeler and O'Connor.[7] It was suggested by Neubert[8] that it would be desirable to find the change in energy content by means of heat of combustion measurements. It was arranged to have this work performed at the National Bureau of Standards by Rossini and Prosen.[9] Some of these results and many more recent ones obtained under Prosen's direction are given in a review paper by Woods, Bupp and Fletcher.[10] The increase in energy content, amounting to from several cal./g. to several hundred cal./g. is small compared to the heat of combustion of graphite (nearly 8000 cal./g.). The determination of the increase in energy content using the heat of combustion therefore requires very precise calorimetry. It was suggested by Gordon[11] that since the heat of reaction of graphite with potassium was much smaller (about 100 cal./g.) a much easier determination of the increase in energy content of graphite on irradiation could possibly be developed by the use of this reaction.

Experimental

The irradiated graphite samples were cut from pieces of irradiated AGOT-K graphite[10] remaining from other work done by Neubert and his co-workers or from samples obtained from the General Electric Company (Hanford Atomic Products Operation). The heats of combustion of these samples had been determined at the National Bureau of Standards. The heat of reaction with potassium was determined in the manner described by Quarterman and Primak.[12] The rate of reaction of the irradiated graphite with potassium was very rapid, the temperature rises occurring more rapidly than the thermocouple e.m.f. recorder pen could move.

The hydrolysis, for which the results are given below, was performed in the following manner. Small samples of the graphite were introduced into the apparatus filled with purified helium at several mm. pressure. When the desired quantity of the graphite–potassium compound had been prepared, the apparatus was evacuated, and an excess of gas-free water was introduced. A sample of the evolved gases was dried by storing it over sublimed P_2O_5. A sample of the dried gas was then taken for mass-spectrometric analysis.

Results

Heats of reaction for a number of samples are given in Table I. The exposure units are described by Woods, Bupp and Fletcher,[10] and a further interpretation of them may be found in an article by Primak.[13] A comparison of the excess heat of reaction with the energy content[14] is also effected in Table I.

The hydrolytic products which were sought were hydrocarbons. A blank, 7.0 g. of potassium, and another blank, 7.6 g. of potassium and 3.79 g. of unirradiated graphite, both gave approximately 100% hydrogen. A run, 10.6 g. of potassium and 2.66 g. of graphite irradiated 1406 Mwd/aT, gave mass spectrometer peaks corresponding to 99.53% H_2, 0.38% CH_4, 0.09% C_2H_6.

Discussion

From the data given in Table I, it is seen that under the conditions maintaining in the Hanford test-holes, the energy content increases at first at a rate about 1 cal./g. per Mwd/aT and that within

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] M. Burton, *J. Phys. Colloid Chem.*, **51**, 618 (1947).

[3] M. Burton and T. J. Neubert, *J. Appl. Phys.*, **27**, 557 (1956).

[4] L. Szilard, unpublished.

[5] R. J. Maurer and R. C. Ruder, *J. Appl. Phys.*, **27**, 571 (1956).

[6] B. Leaf and A. Novick, unpublished.

[7] J. A. Wheeler and J. J. O'Connor, unpublished.

[8] T. J. Neubert, unpublished.

[9] F. D. Rossini and E. J. Prosen, unpublished.

[10] W. K. Woods, L. P. Bupp and J. F. Fletcher, Paper A/Conf. 8/P/746, "Proceedings of the International Conference on the Peaceful Uses of Atomic Energy," United Nations, New York, N. Y., 1956, Vol. 7, p. 455.

[11] S. Gordon was associated with the present work at its inception.

[12] L. Quarterman and W. Primak, THIS JOURNAL, **74**, 806 (1952).

[13] W. Primak, submitted.

[14] The energy content is defined as the difference in the heats of reaction of an irradiated and an unirradiated sample when the end products are in the same state. It is thus the difference in the heat contents at the temperature at which the calorimetry is performed. The excess heat of reaction is used here to designate the difference between the specific heats of reaction with potassium of an irradiated and an unirradiated sample.

TABLE I

EXCESS HEATS OF REACTION AND ENERGY CONTENTS

Irradiation exposure[c] (Mwd/aT)	Heat of reaction with potassium (cal./g.)				Excess heat of reaction[b] (cal./g.)	Energy content (cal./g.)
	Sample 1	Sample 2	Sample 3	Sample 4		
45	104	100	100	102	21	38
45[a]	87	86	83		4	
188	137	151	147		64	109
407[a]	94	99	98		16	
595	163	162	164	163	82	174
829	199	203			120	230
1195	197	192	194		113	250
1406	217	219			137	297
1960	237	256	243		164	380

[a] The low values of the excess heat of reaction suggest these samples had been annealed subsequent to irradiation. [b] Assuming the heat of reaction of unirradiated graphite is 81 cal./g. [c] Energy developed by fission in adjacent uranium (megawatt days per adjacent ton) during the irradiation.

the first few hundred Mwd/aT the rate declines to about 0.15 cal./g. per Mwd/aT at which level it is maintained for at least nearly 2000 Mwd/aT. The excess heat of reaction is in every case less than the energy content. It seems to increase at first at a rate about $^1/_2$ cal./g. per Mwd/aT and within the first few hundred Mwd/aT has declined to a rate about 0.05 cal./g. per Mwd/aT. The excess heat of reaction therefore does not correspond to the energy content, and it must be concluded that the end products of the reaction of irradiated and unirradiated graphite are not in the same state. The current hypotheses of the nature of the disorder in fast neutron irradiated graphite suggest what these differences are. A review of some of these hypotheses is given by Hennig and Hove[15] to which the reader is referred for details. The nature of the interlamellar compounds are discussed in several papers by Hennig and co-workers.[16]

The disorder in fast neutron irradiated graphite is quite complex. In the early stages of irradiation most of the effects observed seem to be due to interstitially located essentially unbound carbon atoms. At least some of these seem mobile at quite low temperatures and seem to bear a negative charge as indicated by their paramagnetic resonance. It is to the essentially unbound carbon atoms that most of the initial rapid increase in the energy content is attributed and is characterized by its rather low annealing temperature, less than several hundred °C. As the irradiation progresses, there appear increasing amounts of property changes which do not anneal until much higher temperatures, extending even into the graphitization range of temperatures while the amounts of property changes which can anneal at low temperatures even decline somewhat. These property changes which anneal at higher temperatures are assumed to be due to aggregates of carbon atoms, to gross disorder corresponding to degraphitization, and to some of the vacant lattice positions.

It is thus seen that potassium in combining with fast neutron irradiated graphite could both (a) engage in reaction which would decrease the heat of reaction and (b) engage in reaction which would increase the heat of reaction as compared to that of unirradiated graphite. It was previously shown[12] that the heat of reaction of potassium with poorly graphitized carbon is less than the heat of reaction of potassium with well graphitized carbon. The only reasonable explanation for this is that the ratio of potassium to carbon is less for the compound formed with poorly graphitized carbon than for the compound formed with well graphitized carbon. It must be assumed that gross disorder produced by irradiation causes a similar effect.

There are also effects which should increase the heat of reaction. The graphite–potassium compound is a donor compound in the sense used by Hennig and Dzurus[16]; *i.e.*, at least some of the potassium atoms surrender an electron to the conduction band of graphite and enter interlamellarly as positively charged potassium ions. Under these conditions, the formation of a potassium carbide from the reaction of the positively charged potassium ions and the negatively charged carbon atoms which are interstitially located should be facilitated. The heat of reaction to form such a compound should be much greater than the heat of reaction per carbon atom to form the interlamellar compound and could therefore account for a considerable fraction of the excess heat of reaction. Such a compound would be expected to generate hydrocarbons on reaction with water, and hydrocarbons were indeed found. From the data which are given it can be computed that $2.3(10^{-3})$ and $1.1(10^{-3})$ are the fractions of carbon atoms which yielded methane and ethane, respectively, in the irradiated graphite sample which was thus examined. These results are comparable to Hennig and Smaller's[17] results for the saturation value of the paramagnetic species formed in graphite on extended irradiation. Although it is cautioned that there is but a single unconfirmed result and that the possibility of hydrocarbon formation from a surface contamination has not been excluded, it is still tempting to associate the methane with interstitial carbon atoms and the ethane with interstitial carbon atoms aggregated into pairs.

It is therefore seen that it would be difficult at the present time to account quantitatively for the excess heat of reaction of potassium with irradiated graphite. It probably arises partially from some or all of the following: the annealing of interstitial carbon atoms to crystallite boundaries and various imperfections, and the aggregation of trapped interstitial carbon atoms which are freed during formation of the interlamellar compound. There is also the possibility of some of it arising from the reaction of potassium with trapped interstitial carbon atoms. While these effects add to the heat of reaction, it is also quite certain (by analogy with the behavior of other disordered carbons) that less potassium reacts with the irradiated graphite than with the unirradiated graphite, this constituting a subduction from the normal heat of reaction. Thus the gross disorder which adds greatly to the energy content on extended irradiation probably contributes noth-

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(15) G. R. Hennig and J. E. Hove, Paper A/Conf. 8/P/751, "Proceedings of the International Conference on the Peaceful Uses of Atomic Energy," United Nations, New York, N. Y., 1956, Vol. 7, p. 666.

(16) *E.g.*, G. R. Hennig and M. Dzurus, *Phys. Rev.*, **98**, 227 (1955).

(17) G. R. Hennig and B. Smaller, to be published.

ing to the excess heat of reaction with potassium and indeed probably does the reverse.

Acknowledgments.—We are indebted to T. J. Neubert and S. Gordon for suggesting this problem and for guiding the work in its early stages. We are indebted to Dwight Hutchison and Louis Pobo for having performed the mass spectrometry.

LEMONT, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SOUTHERN CALIFORNIA]

The Thermodynamic Properties of Dilute Alkali Metal Amalgams[1]

BY HAROLD L. FRIEDMAN AND KENNETH SCHUG[2]

RECEIVED JANUARY 30, 1956

The thermodynamic properties of ternary amalgams containing Na with K, Rb, Cs or Sr have been investigated by an equilibrium method. The results, together with independent data for Na amalgam, yield properties of the binary amalgams of K, Rb, Cs and Sr. When combined with data from other sources these provide information on the formation of the alkali metal amalgams from the elements and the deviations from Raoult's law of these solutions. For the process M(Hg, Hyp. 1 molal) = M^+(gas) + e^-(gas), ΔH decreases from Li to Cs, but ΔS increases strongly, becoming +30 e.u. for Cs. This and several other amalgam properties are consistent with the hypothesis that the alkali metals are ionized in the amalgams and that only the electron tends to enter the mercury phase from the gas phase. Then the positive ions tend to escape the amalgam, the more so the larger the ion, but this tendency is overcome by the forces leading to electroneutrality of the phase. The detailed form of the activity coefficients in the amalgams is consistent with a Brönsted specific ion interaction between the electrons and the positive ions in the amalgam in a way similar to that first suggested by C. Wagner. The temperature coefficients of the activity coefficients reflect the large entropy effects in solvation.

Introduction

The amalgam partition method[2] for the investigation of the energetics of non-aqueous solutions of electrolytes involves the equilibrium interchange of two metal species, M_1 and M_2, between an amalgam phase (Hg) and an electrolytic solution phase (es)

$$\frac{1}{z_1}\,M_1{}^{z_1+}\,(\text{es}) + \frac{1}{z_2}\,M_2(\text{Hg}) = \frac{1}{z_1}\,M_1(\text{Hg}) + \frac{1}{z_2}\,M_2{}^{z_2+}\,(\text{es}) \qquad (1)$$

in which $z_1{}^+$ and $z_2{}^+$ are the ionic charges in the electrolytic solution. Equilibrium concentration measurements in such a system, when suitably extrapolated to zero solute concentration in each phase, lead to the standard free energy change of reaction (1), $\Delta F_1{}^0$. If the free energies of M_1(Hg) and M_2(Hg) are known, $\Delta F_1{}^0$ leads to the relative $\Delta F_f{}^0$ of $M_1{}^{z_1+}$(es) and $M_2{}^{z_2+}$(es). In the present work, however, we employ electrolytic solutions in water, in which the ionic free energies are known, and the objective is to obtain the thermodynamics of M_2(Hg), with M_2 = K, Rb, Cs and Sr, from measurements on reaction (1) with M_1 = Na. For this purpose the thermodynamics of Na(Hg) obtained by Bent and Swift[3] from measurements on e.m.f. cells will be used as a basis.

It was found early in the present work that the e.m.f. experiments which lead to the currently accepted[4] $\Delta F_f{}^0$ of Cs^+(aq) had given temperature coefficients which were inconsistent with our amalgam partition results, as well as with the accepted entropy of Cs^+(aq).[4] It is planned to discuss this discrepancy in a report on the redetermination of $\Delta H_f{}^0$ of Cs^+(aq) which is now in progress, but for this paper the value, $\Delta F_f{}^0(Cs^+aq) = -70.3$ kcal./mole, based upon the calorimetric investigation of Rengade[5,6] will be used.

Likewise some of our own experimental results are clearly in need of refinement but the discussion of amalgam properties which is presented here is based upon magnitudes and correlations which are firmly established by the data in their present form.

Part of the data for reaction (1) comes from a series of investigations by G. M. Smith and his associates, made many years ago.[7,8] The results of their experiments as well as ours may be expressed as concentration products for reaction (1)

$$R(M_1/M_2) = (m_1/m_{1w})^{1/z_1} \times (m_{2w}/m_2)^{1/z_2} \qquad (2)$$

and with appropriate activity coefficients we obtain

$$-\Delta F_1{}^0/2.303RT = \log R(M_1/M_2) - \log\,[\gamma_1{}^{1/z_1}/\gamma_2{}^{1/z_2}] + \log\,[f_1{}^{1/z_1}/f_2{}^{1/z_2}] \qquad (3)$$

which is used in the reduction of the data. The sum of the first two terms on the right of eq. 3 appears in the presentation of the data and is designated log $R'(M_1/M_2)$. A glossary of the symbols used in eqs. (2) and (3) and in the rest of the paper is given here

m_{iw} = molality (moles/kg. of solvent) of species i in the aqueous phase
m_i = molality of species in the amalgam phase
$\Delta F_i{}^0$ = Gibbs free energy increase for reaction i with each product and reactant in hypothetical one molal standard state
f_i = stoichiometric activity coefficient of species i in the amalgam phase, hyp. 1 *M* std. state
γ_i = ionic activity coefficient of species i in the aqueous phase, hyp. 1 *M* std. state
$\bar{\gamma}_i$ = ionic activity coefficient of species i in the amalgam phase

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[1] (a) This research supported by the U. S. Atomic Energy Commission. (b) From the thesis submitted by Kenneth Schug to the Graduate School of the University of Southern California in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] K. Schug and H. L. Friedman, THIS JOURNAL, **76**, 3609 (1954).

[3] H. E. Bent and E. Swift, *ibid.*, **58**, 2216 (1936).

[4] F. D. Rossini, D. Wagman, W. H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, 1952, Washington, D. C.

[5] E. Rengade, *Ann. chim. phys.*, [8] **14**, 540 (1908).

[6] W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938.

[7] G. M. Smith and T. R. Ball, THIS JOURNAL, **39**, 179 (1917).

[8] (a) G. M. Smith and S. A. Braley, *ibid.*, **39**, 1545 (1917); (b) L. S. Wells and G. M. Smith, *ibid.*, **42**, 185 (1920).