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ANL-5249

RADIATION EFFECTS ON REACTOR MATERIALS

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DIFFERENTIAL THERMAL ANALYSIS OF IRRADIATED DIAMOND
AND SILICON CARBIDE

by

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Photostat Price \$ 4.80

Microfilm Price \$ 2.70

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Washington 25, D. C.

CHEMISTRY DIVISION

December 1, 1954

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ABSTRACT

It was demonstrated by differential thermal analysis (DTA) that: 1. Catastrophic* amounts of energy can be stored in diamond. 2. Even at low irradiations, the release takes place over several hundred degrees, indicating a spectrum of activation energies. 3. At higher irradiations, the stored energy release is considerably less than the increased energy content and seems not to have been completely released even at the highest temperatures reached. 4. There is some indication of an increased heat capacity below the temperature of stored energy release.

It was shown by DTA that large amounts of energy can be stored in silicon carbide on irradiation. The release was found to be spread out over a greater range of temperatures than in diamond and indicated a larger and higher group of activation energies. Catastrophic release was not achieved. The amount of stored energy released over the range of temperatures used was 140 cal/g in a sample irradiated in a water-cooled testhole at HEW for an exposure of 265 Mwd/aT.

INTRODUCTION

The presence of stored energy in naturally-occurring solids which had been disordered by the passage of energetic atomic particles through them, the metamict minerals, was demonstrated over a century ago, and more recently has been measured both by differential thermal analysis (DTA) and by calorimetric methods.^{1,2} An account of the demonstration of stored energy in reactor-irradiated graphite was given by Lees and Neubert.³ It was demonstrated by Fuchs and Primak, working in

*The temperature rate of stored energy release is greater than the heat capacity of the substance.

¹A. Pabst, Am. Mineralogist 37, 137 (1952).

²A. Faessler, Z. Krist. 104, 81 (1942).

³R. B. Lees and T. J. Neubert, ANL-4307 (1949).

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collaboration with E. J. Prosen and his co-workers, that energy is stored by diamond in a similar way.⁴ Since other measurements indicated that silicon carbide was affected by reactor exposure in a manner similar to diamond,⁵ it seemed desirable to examine irradiated silicon carbide for stored energy. A number of irradiated diamond samples whose energy content had been determined by the heat of combustion method were examined simultaneously to check the DTA method.

EXPERIMENTAL

Three small cylindrical cups, 8-mm diameter, 2-cm high, fabricated from 5-mil platinum sheet (weight 0.728 g each), were mounted with 8-mil nichrome wire stirrups on a silica support frame at the upper end of a long 15-mm silica tube which passed through a large water-cooled ground joint. To the outside of each of the cups under a small sheet of platinum was welded a thermojunction of 2-mil Pt-10% Rh wires. These were connected in a manner which permitted reading the temperature of one of the cups (cup 3) and the differences in temperature of the other two (cups 1 and 2). About 5 cm from the cups, junctions were made to heavier wires of the same composition which led out of the apparatus into an ice bath where junctions were made (a) to a cold junction for the cup-3 thermojunction and thence to copper wire, and (b) to copper wire for the differential thermocouple. The thermocouple emf was recorded on a 10-mv recording potentiometer and the differential thermocouple on a multiple range recording potentiometer usually used on its 0.2-mv range, occasionally on its 0.4-mv range.

A large silica tube closed at the upper end fitted over the cup assembly, above and below which were placed platinum disks to minimize convection. Nitrogen which had been passed over reduced copper oxide maintained at 300-400°C and dried by passage through a tower filled with Drierite was passed into the apparatus through the support tube and escaped past the ground joint. It was permitted to flow through the apparatus at a rate of about 200 ml/min for about 15 minutes before a run and at about 20 ml/min during the run to provide a nonoxidizing atmosphere. The apparatus was heated by a bifilar wound tube furnace of low heat capacity connected to a motor driven variac which was set at 60 volts at the beginning of the run and which shut itself off at 120 volts. At this point about 13.5 amp were passing through the furnace and the temperature of the cups was between 950 and 1000°C. The heating rate was not constant but showed a broad maximum in the central region of temperatures.

⁴L. H. Fuchs and W. Primak, ANL-4466 (1950).

⁵W. Primak, ANL-4952 (1953).

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The apparatus was used in the following manner: Weighed, approximately equal, charges of corundum (40-80 mesh crushed synthetic sapphire, colorless) were introduced into cups 2 and 3. A weighed amount of the substance to be subjected to DTA was introduced into cup 1. The apparatus was now assembled and run. It was then permitted to cool and without disturbing the charges was run again. A third run was often made. The charge in cup 1 was removed to a clean flask by means of suction without disturbing the charges in the other cups. Cup 1 could then be reloaded and the apparatus run again. For all of the runs described here, except 13 and 14, the charges in cups 2 and 3 were 372 and 386 mg, respectively. In runs 13 and 14, the respective charges were 422 and 444 mg.

The following nomenclature is used:

H = heat transferred to or from the cup

t = time

E = thermocouple emf

T = temperature corresponding to E

Q = heat of reaction, latent heat, and permanent changes in $\int C dT$

C = heat capacity of the charge

C' = fictitious heat capacity of everything but the charge

T_0 = fictitious temperature of the cup surroundings

$\Delta E = E_1 - E_2$ as read by the differential couple

ΔT = temperature corresponding to ΔE

k = average heat transfer coefficient for the range of $(T_1 - T_0)$ and $(T_2 - T_0)$

$\xi = \Delta T / (dT_3/dt)$ as a function of T_3

Subscript numbers refer to the cups.

Subscript letters refer to the runs.

For the first run (a):

$$\frac{dH_1}{dt} = k(T_0 - T_1) = -\frac{dQ}{dt} + (C'_1 + C_1) \frac{dT_1}{dt} = -\frac{dQ}{dt} + (C'_1 + C_1) \left(\frac{dT_3}{dt} + \frac{d\Delta T}{dt} \right)$$

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$$\frac{dH_2}{dt} = k(T_0 - T_2) = (C_2' + C_2) \frac{dT_3}{dt}$$

$$k\Delta T = (C_2' + C_2) \frac{dT_3}{dt} + \frac{dQ}{dt} - (C_1' + C_1) \left(\frac{dT_3}{dt} + \frac{d\Delta T}{dt} \right)$$

$$k\xi_a = (C_2' - C_1') + (C_2 - C_1) + \frac{dQ}{dT_3} - (C_1' + C_1) \frac{d\Delta T_a}{dT_3}$$

For the second run (b).

$$k\xi_b = (C_2' - C_1') + (C_2 - C_1) - (C_1' + C_1) \frac{d\Delta T_b}{dT_3}$$

The last term involving $d\Delta T_b/dT_3$ was relatively small and could frequently be neglected. Combining the equations from run (a) and run (b):

$$\frac{dQ}{dT_3} = k(\xi_a - \xi_b) + (C_1' + C_1) \left(\frac{d\Delta T_a}{dT_3} - \frac{d\Delta T_b}{dT_3} \right)$$

In practice the second term $(C_1' + C_1) [(d\Delta T_a/dT_3) - (d\Delta T_b/dT_3)]$ was found to be significant on both shoulders of the peaks and, in some cases, in other portions of the DTA curves.

Since the weights of the charges were known, it seemed feasible to determine the heat transfer coefficients as a function of temperature from the data of the second run (b). When this was attempted, it was found that the heat transfer coefficients obtained from the different runs were inconsistent and possessed peculiar irregularities. Since the DTA curves obtained by repeating the runs were quite regular and reproducible, it was obvious that a systematic effect was involved. An apparatus factor $C'(T)$ was therefore introduced in the following way:

$$k\xi_b = (C_2' - C_1') + (C_2 - C_1) - (C_1' + C_1) \frac{d\Delta T_b}{dT_3} \cdot C'$$

and it was found to rectify the data in a satisfactory manner. In most of the runs $(d\Delta T_b/dT_3)$ was sufficiently small so that its term could be neglected. Because of the low heat capacities of the cups, C_2' could not differ appreciably from C_1' and, further, if this term were neglected any small difference would appear in C' . The values of C' at various temperatures were easily obtained from the data because of the fortuitous circumstances that the heat capacity of diamond increases so greatly with temperature and that with the charges used in the various runs there were available over the whole temperature range particular points at which $\xi = 0$ (i.e., $\Delta T = 0$ since $dT_3/dT \neq \infty$). At these points, accordingly,

$$C' = C_2 - C_1$$

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Once C' had been determined, k could be evaluated from the weights of the samples and the values of ξ . The values of k could be checked from differences as

$$k(\xi_d - \xi_b) = (C_{1d} - C_{1b})$$

The heat capacities used for diamond and corundum were taken from a compendium by Kelley⁶ and the heat capacities of platinum from the International Critical Tables.⁷ They are given in Table I. The data for the evaluation of C' is given in Table II and the results are plotted in Figure 1.

Table I

HEAT CAPACITY OF DIAMOND AND CORUNDUM

Temperature (°C)	Heat Capacity Diamond (cal/g deg)	Heat Capacity Corundum (cal/g deg)	Heat Capacity Platinum (cal/g deg)
100	0.19	0.22	0.032
150	0.224	0.236	
200	0.250	0.248	0.033
250	0.280	0.256	
300	0.300	0.262	0.034
350	0.318	0.268	
400	0.335	0.272	0.034
500	0.368	0.278	0.035
600	0.395	0.284	0.036
700	0.422	0.288	0.036
800	0.445	0.292	0.037
900	0.480	0.297	
950	0.495	0.299	
1000			0.038

⁶K. K. Kelley, Contribution to the Data on Theoretical Metallurgy, U. S. Dept. of Interior, Bureau of Mines, Bulletin 476 (U. S. Government Printing Office, 1949).

⁷International Critical Tables, Vol. 5, (McGraw-Hill Book Co., New York, 1929) p. 93. *ob*

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FIGURE 1.
 C' AS A FUNCTION OF TEMPERATURE.

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Table II
EVALUATION OF C'

Run #	$\xi = 0$ at °C	Wt. of Diamond (mg)	Heat Capacity Diamond (cal/deg)	Heat Capacity Corundum (cal/0.376 g deg)	C'
44	135	346	0.074	0.087	0.013
32	310	236	0.073	0.098	0.025
33	270	236	0.067	0.090	0.023
29	300	264	0.079	0.098	0.019
30	300	264	0.079	0.098	0.019
35	490	232	0.085	0.104	0.019
36	460	232	0.083	0.103	0.020
26	730	160	0.066	0.107	0.041
27	730	160	0.069	0.109	0.040
38, 39	>950	104	0.054	0.113	0.059

The calculation of k now required the evaluation of ξ from the experimental data, the chart records. These were read in the following manner. The cup-3 temperature record was in millivolts. A strip of chart was marked off in degrees according to a standard table of Pt-10% Rh thermocouple emf's. The E_3 vs t record was marked at values of E_3 corresponding to convenient temperatures (50 or 100 degree intervals) and the corresponding values of T_3 and t were read. The slope of the curve was determined at each of these t with the aid of a device similar to that described by Daniels⁸ as a tangentimeter except that a half-silvered mirror was used. The value of ξE was obtained by reading the chart of the other recorder at each time, t , and $d\Delta E/dt$ by reading the slopes at these temperatures. The value of ξ was obtained by dividing ΔE by the slope of the E_3 vs t curve, and $d\Delta T/dT_3$ by dividing the slope of the ΔE vs t curve by the slope of the E_3 vs t curve. A typical set of data is shown by run 38 in Table III. Results of the calculation of k by the two methods above are shown in Figure 2.

⁸F. Daniels, Mathematical Preparation for Physical Chemistry, (McGraw-Hill Book Co., New York, 1928), p. 240.

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Table III

ANALYSIS OF CHARTS FOR DIAMOND-3 (0.104 g SAMPLE)

T_3 (deg)	t (min)	dE_3/dt ($\mu v/min$)	ΔE (20 μv)	ξ (min)	$d\Delta E/dt$ (20 $\mu v/min$)	$d\Delta T/dT_3$ (deg/deg)	T_3 (deg)	t (min)	dE_3/dt ($\mu v/min$)	ΔE (20 μv)	ξ (min)	$d\Delta E/dt$ (20 $\mu v/min$)	$d\Delta T/dT_3$ (deg/deg)
Run 37 (first run)							Run 38 (second run)						
100	8.0	13.5	4.3	0.64	0.68	0.10	100	4.2	12.5	2.1	0.33	0.98	1.6
150	9.8	26	5.8	0.45	0.98	0.075	150	6.5	22	3.2	0.29	0.06	0.05
200	11.2	30	6.7	0.45	0.17	0.113	200	8.2	26	3.2	0.25	-0.17	-0.13
250	12.6	34	6.9	0.41	0.17	0.100	250	9.8	30	2.8	0.19	-0.19	-0.13
300	13.9	37	7.2	0.39	0.17	0.092	300	11.2	33	2.6	0.16	-0.20	-0.12
350	15.1	39	7.5	0.38	--	--	350	13.8	37	2.1	0.12	-0.20	-0.11
400	16.3	40	6.0	0.30	-3.2	-1.50	400	16.4	38	1.6	0.082	-0.20	-0.105
450	17.5	41	4.1	0.20	-1.04	-0.51	450	19.2	36	1.1	0.063	-0.20	-0.11
500	18.8	41	3.2	0.156	-0.60	-0.29	500	22.3	31	0.6	0.037	-0.20	-0.13
600	21.3	37	2.3	0.124	-0.27	-0.15	600	26.0	27	0.2	0.015	-0.20	-0.15
700	24.3	33	1.1	0.067	-0.39	-0.24	700	30.5	21	0.1	0.0095	-0.13	-0.12
800	28.0	26	0.5	0.039	-0.21	-0.16	800	33.2	19	0.1	0.0105	-0.05	-0.05

 δ (37-38)

I	II	III	IV	V	VI	VII	VIII	IX	X
T_3	C_1	$C_1 + C'_1 - C_1$	$\delta d\Delta T/dT_3$	III $\times$ IV	$\delta \xi$	k	$k\delta \xi$	V + VIII dQ/dT_3	IX 0.104 (cal/g deg)
100	0.020	0.033	-1.5	-0.51	0.31	0.15	0.042	-0.47	-4.5
150	0.023	0.034	+0.07	+0.002	0.16	0.16	0.026	+0.028	+0.27
200	0.024	0.033	0.24	0.008	0.20	0.17	0.034	0.042	0.40
250	0.029	0.036	0.23	0.0083	0.22	0.18	0.040	0.048	0.46
300	0.031	0.035	0.21	0.0075	0.23	0.19	0.044	0.051	0.49
350	0.033	0.035	0.11	0.0039	0.24	0.23	0.055	0.059	0.57
400	0.035	0.035	-1.49	-0.052	0.18	0.24	0.043	-0.009	-0.087
450	0.037	0.034	-0.40	-0.014	0.10	0.27	0.027	+0.013	+0.115
500	0.038	0.034	-0.16	-0.0054	0.074	0.30	0.022	0.017	0.16
600	0.041	0.033	--	--	0.061	0.42	0.026	0.026	0.25
700	0.044	0.032	-0.12	-0.0038	0.034	0.57	0.019	0.015	0.14
800	0.046	0.030	-0.11	-0.0033	0.034	0.72	0.024	0.021	0.20

FIGURE 2.

TEMPERATURE DEPENDENCE OF THE
HEAT TRANSFER COEFFICIENT.

X	Run 24	*	Run 30
O	Run 44-38	□	Run 38
+	Run 44		

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The nature of C' requires some discussion. It obviously includes thermocouple deviations, errors in heat capacity data, and asymmetries of k and of heat capacities of the apparatus. However, because of its magnitude and temperature dependence, it is believed to arise mainly from the changing relative temperature distributions in the calorimeter cups and their charges. A peculiar effect was observed in some of the runs in which stored energy release ceased abruptly. When the stored energies in these regions were computed according to the above equations, large negative values were obtained. The consistent occurrence of this result and the previous observation of the stable behavior of the apparatus suggested that some systematic behavior was being observed. Further study of the data revealed that during stored energy release, the temperature of cup 1 had risen above the ambient temperature; when release of stored energy had ceased, the temperature of cup 1 had fallen very rapidly; and it was the large negative slope of the ΔE chart record that was responsible for the calculation giving the large negative value for the stored energy. Two sources for the effect seemed possible: (a) the temperature of the thermocouple changed more quickly than the sample because of a change in the temperature distribution on the cup surface; and (b) the potentiometer-recorder possessed some frictional and inertial peculiarity. The term C' appeared in the calculation of the heat transfer coefficients when the temperature of the cup was rising. It was therefore assumed that a term of the same magnitude but of opposite sign was involved when the temperature of the cup was falling, that is:

$$\frac{dQ}{dT_3} = k(\xi_a - \xi_b) + (C'_1 + C_1 - C') \left(\frac{d\Delta T_a}{dT_3} - \frac{d\Delta T_b}{dT_3} \right)$$

This proved to nearly correct the results leaving only a small negative stored energy, and no attempt was made to further rectify the data. It can be seen from the typical data shown in Table III that $(d\Delta T_a/dT_3 - d\Delta T_b/dT_3)$ made a significant contribution only in the region in which stored energy release ceased.

Irradiation and other data for the samples which were subjected to DTA are given in Table IV. The results of the DTA are given in Figures 3 to 10. The integral,

$$\int_{100}^{800} \frac{dQ}{dT_3} dT_3$$

for the diamond samples, the same integral extended to 900 for the silicon carbide samples, and the energy contents from heat of combustion data obtained by E. J. Prosen⁹ and his co-workers are given in Table V.

⁹E. J. Prosen, private communications: NBS-EJP-2 (Aug. 17, 1950); NBS-5.9-EJP-17, (May 29, 1952); NBS-5.9-26, (Dec. 11, 1952). W. A. Fraser and E. J. Prosen, NBS-D-111, (Feb. 8, 1952); NBS-D-120 (Dec. 10, 1952).

Table IV
DESCRIPTION OF DTA RUNS

Sample	Irradiation Data		DTA Runs	Wt. of Sample Used for DTA (mg)
Diamond 72	153	WB ^a	28, 29, 30	264
Diamond 1	43	WB	31, 33	236
Diamond 2	94	WB	34, 35, 36	232
Diamond 3	183	WB	37, 38, 39	104
Diamond 4	287	WB	25, 26, 27	160
Diamond	408	IU ^b	43, 44	346
Silicon carbide 147	265	WB	13, 14	499 ^c
Silicon carbide	408	IU	45, 46	316

^aIrradiated for an exposure of 153 Mwd/aT in a water-cooled testhole (type B facility) in a Hanford reactor.

^bIrradiated in the CP-3' converter for 408 Initial Change units (electrical conductivity of spectroscopic graphite rods) as described in ANL-5003. This irradiation would have produced a damage in graphite equivalent to about 10 WB.

^c422 mg corundum in cup 2.

Table V
INTEGRALS OF THE DTA CURVES

Sample	Released Stored Energy (cal/g)	Energy Content (cal/g)
Diamond 72	160	154
Diamond 1	45	31
Diamond 2	100	90
Diamond 3	170	198
Diamond 4	190	279
Diamond 408	29	unknown
Silicon carbide 142	140	unknown
Silicon carbide 408	8	unknown

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DIFFERENTIAL THERMAL ANALYSIS CURVES.

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FIGURE 7.
DIAMOND 4

FIGURE 8.
DIAMOND 408 IU
○ Stnd. Scale
○ 10x Scale

FIGURE 9.
SiC 142

FIGURE 10.
SiC 408 IU

DIFFERENTIAL THERMAL ANALYSIS CURVES.

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DISCUSSION

I. General Character of the Results; Their Precision:

From an examination of Table V, it would seem that the accuracy of the method is about 20 to 30% in the range around 50 170 cal/g. The difference between the released stored energy and the energy content of Diamond-4 is too great to be attributed to experimental error, and it is therefore assumed that not all of the stored energy was released. Since there is evidence of graphitization in the upper range of annealing temperatures employed, it may not be possible to release all of the stored energy by annealing. The results for Diamond-408 seem somewhat high. However, the behavior of diamond in the initial stages of irradiation seems to show some peculiarities, and more work will have to be done to understand it. It seems evident that not all of the stored energy of the silicon carbide sample was released at the highest temperatures employed. Within the precision of the method, the stored energy per atom of SiC-142 and Diamond-4 are quite comparable. The released stored energy per unit dosage in SiC-408 seems to be about 1-1/2 times as great as in SiC 142. However, this is not unreasonable in view of the low precision in the SiC-408 determination and in view of the shapes of the DTA curves, which indicate most of the stored energy in the former sample was released but not in the latter. There appear to be two peaks in the DTA curves of irradiated SiC, one in the low temperature region about 200°C, where the major peak in graphite and diamond occurs, and a larger one above 500°C in the case of SiC-408 and near 1000°C in the case of SiC-142. The double peaks in the DTA curves of diamond have quite a different origin.

II. Catastrophic Stored Energy Release:

Catastrophic stored energy release is here defined as a temperature rate of release greater than the heat capacity of the system.

Case 1. Instantaneous Stored Energy Release (dQ/dT a function of T only)

Should a substance find itself at a temperature T_i at which for a virtual rise in temperature the stored energy release per degree exceeds the heat capacity, then under adiabatic conditions the temperature will instantaneously reach the temperature T_f determined by

$$\int_{T_i}^{T_f} \frac{dQ}{dT} dT = \int_{T_i}^{T_f} C dT$$

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Under practical conditions the temperature will not rise instantaneously because of thermal lags, and T_f will be determined by

$$\int_{T_i}^{T_f} \left(\frac{dQ}{dT} - \frac{dH}{dT} \right) dT = \int_{T_i}^{T_f} (C' + C) dT$$

where H is the heat flowing out of the system past the thermal barrier (the ambient temperature is considered constant here) and C' is the heat capacity of substances other than the one containing stored energy that are within the thermal barrier. The substances within this thermal barrier will be referred to as the system. In general $(C' + C)$ is an increasing function of temperature, and eventually dQ/dT becomes a decreasing function so that the temperature reaches a maximum even if dH/dT is small. However, dH/dT will increase with T . The temperature may then stop rising even though dQ/dT has not begun to decrease relative to $(C + C')$ because dH/dT has become large. Whatever the cause, as soon as the temperature begins to drop it does so very rapidly (exponential decay if Newton's Law applies) because stored energy release has ceased.

If the ambient temperature is rising, $(T - T_0)$ is negative at temperatures below that at which catastrophe occurs, and heat flows into the system in accordance with

$$\frac{dQ}{dT} - \frac{dH}{dT} = \frac{dQ}{dT} - \frac{k(T - T_0)}{dT/dt} = C + C'$$

assuming the approximation of Newton's Law. It is seen that catastrophic stored energy release occurs when the temperature of the system reaches the ambient temperature T_0 . The temperature of the system then rises rapidly until for a virtual rise in T ,

$$\delta(dQ/dT) < \delta(dH/dT) + \delta(C + C')$$

Then simultaneously the temperature begins to fall and stored energy release ceases. This continues until $T = T_0$ when the temperature of the system once more begins to rise, lagging somewhat behind the rising ambient temperature T_0 ; and when it reaches the maximum temperature previously achieved in stored energy release, stored energy release resumes in accordance with the preceding considerations. Since dH/dT is the temperature rate of heat flow along the temperature gradient, it remains constant at $-(C + C')$ during the excursion of the system to lower temperatures. While dQ/dT is a smooth function of T , dQ/dT_0 will show what may be termed "false peaks." After these peaks dQ/dT_0 can become null but not negative. The preceding considerations are illustrated in Figure 11.

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FIGURE II.

CALORIMETRIC BEHAVIOR UNDER CONDITIONS OF CATASTROPHIC INSTANTANEOUS (dQ/dT a function of temperature only) STORED ENERGY RELEASE.

- (a) Behavior of T_0 and T in time.
- (b) Behavior of dH/dT in temperature.
- (c) Behavior of dH/dT_0 in temperature.
- (d) Behavior of dH/dt times the absolute value of $(dT/dt)^{-1}$ (given to separate the overlapping parts of Fig. IIb).

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The behavior of dQ/dT_3 determined experimentally should be similar to dQ/dT_0 considered here. The sharp drop in dQ/dT_3 near $T_3 = 400^\circ\text{C}$ (see Figures 3, 4, 5, 6, and 7) looks much like the quenching of catastrophic stored energy release. From the values of k and $d\Delta T_a/dT_3$, an approximate value of ΔT_a can be calculated. In one case it was found that ΔT_a was 20-40 degrees above ambient just as quenching took place and 40-80 degrees above T_3 . At this point dQ/dT_3 dropped precipitously to slightly negative values and did not assume positive values until T_3 had advanced nearly 100 degrees. The reappearance of stored energy when T_3 had advanced more than by the value of $(T_1 - T_3)$ just before quenching is in accord with the simple theory since the heat capacity of the contents of cup 1 increase greatly with temperature while that of cup 3 does not.

The appearance of negative stored energy at quenching is not in accord with the simple theory unless it is supposed that the heat capacity of the sample on the second run is that much less than the heat capacity on the first run. The quantity of negative stored energy seems too great to be explained in this manner. Examination of the experimental data showed that dQ/dT_3 assumed negative values mainly because of the large negative value of $d\Delta T_a/dT_3$, and is to be attributed to peculiarities of the apparatus as pointed out in the experimental section. Part of the cause was attributed to changes in temperature gradients in the apparatus. However, the behavior of the ΔT -recorder is also blamed for its pen seemed to possess some lag and was underdamped. This would cause extreme values for $d\Delta T_a/dT_3$ in the neighborhood of stored energy quenching. Accordingly, the negative stored energy which is shown in the figures is considered to be a spurious effect. The peculiar behavior of k at certain temperatures in some runs, as shown in Figure 2, may be a related effect.

It may be assumed that the small peaks seen near $T_3 = 200^\circ\text{C}$ result from the quenching of catastrophic stored energy release after a small temperature rise. Since the temperature rise has been small (and also because dT_0/dt has been increasing) stored energy release begins again shortly. However, stored energy release has not been quenched completely (i.e., dQ/dT_3 has not dropped to zero) as the simple theory predicts. An even more severe violation of the simple theory is provided by the long sustained high value of dQ/dT_3 prior to the quenching which appears near $T_3 = 400^\circ\text{C}$, for according to the simple theory, catastrophic release should be evidenced by a sharp rise in dQ/dT_3 followed by a sudden drop. Thermal lags would lessen the steepness of these effects somewhat. Perhaps dQ/dT_3 may be sustained by the catastrophic release and quenching occurring as pulses in the individual grains of diamond. However, if this were the case, it would be expected the phenomenon would sweep the sample in a short time rather than sustain the rise over many hundred degrees.* The probable explanation for the effects is to be found in the consideration that dQ/dT is not a function of T only, but does also depend on time.

* Some additional evidence for the short pulse hypothesis is presented by Primak in another paper (to be published).

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Case 2. Activated Stored Energy Release (dQ/dT is a function of the heating rate).

The broad region of stored energy release both in the diamond and the silicon carbide suggests that a broad distribution of activation energies are involved. Proceeding therefore in a manner similar to Vand's¹⁰ for each activation energy.

$$-\frac{dq}{dt} = -\frac{dq}{s d\tau} = A e^{-\epsilon/\tau} q$$

where, since the quantity of heat associated with each process cannot be distinguished, the processes are counted by the heat involved, q ; and where $1/s$ is the heating rate and τ the temperature in electron volts. The solution is

$$q = q_0 e^{-\beta A E_2(y)}$$

where $\beta = s \tau$, $y = \epsilon/\tau$, q_0 is the stored energy associated with a particular value of ϵ at $\tau = 0$, and E_2 is one of the exponential integrals tabulated by Placzek,¹¹

$$E_2(y) = y \int_y^\infty e^{-x} dx/x^2.$$

The total stored energy in the sample is

$$Q = \int_0^\infty dq \epsilon = \int_0^\infty q_0 \tau e^{-\beta A E_2(y)} dy.$$

In a DTA there is observed the decline of Q with temperature:

$$-\frac{dQ}{d\tau} = \int_0^\infty q_0 \beta A e^{-[y + \beta A E_2(y)]} dy$$

which will be designated $g(\tau)$. It can be shown¹² that $q_0(\epsilon)$ is approximately proportional to $g(\tau)$, and thus in regions of nearly constant stored energy release $q_0(\epsilon)$ is nearly constant. It is therefore pertinent to investigate the case of constant $q_0(\epsilon)$ which is more amenable of mathematical treatment

¹⁰V. Vand, Proc. Phys. Soc. (London), 55, 222 (1943).

¹¹G. Placzek, The Functions $E_n(x)$, National Research Council of Canada, MT-1.

¹²W. Primak, Some Aspects of Stored Energy in Irradiated Graphite.

I. Kinetics of the Release, Nuclear Science and Technology (in press).

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than if it were arbitrary. It seems likely that $\underline{A}$ is in the range of values customarily found for simple first-order chemical reactions.¹² Then one may write using as an approximation the first term of Blanch's asymptotic expansion¹¹

$$E_2(y) \cong e^{-y}/(y+2)$$

Let $v = \exp [-A\beta e^{-y}/(y+2)]$, then $y + \ln(y+2) = \ln A\beta - \ln_2(1/v)$ where $\ln_2 x = \ln(\ln x)$. Since $\underline{y}$ is effective only over a small range, one may write

$$y + \ln(y+2) \cong a + by$$

where $\underline{a}$ and $\underline{b}$ are constants to be determined by the slope and value of $y + \ln(y+2)$ at some point in the middle of the effective region of $\underline{y}$; i.e., where

$$A\beta e^{-y}/(y+2) \sim 1.$$

Then

$$\begin{aligned} g(\tau) &= q_0 \beta A \int_0^1 e^{-y} v \, dv / b v \ln(1/v) \\ &= q_0 \beta A \int_0^1 \exp [-\ln A\beta + \ln_2(1/v) + \ln(y+2)] \, dv / b \ln(1/v) \\ &= (q_0/b) \int_0^1 (y+2) \, dv \\ &= (q_0/b^2) \int_0^1 [\ln A\beta - \ln_2(1/v) + 2b - a] \, dv \\ &= (q_0/b^2)(\ln A\beta + \gamma + 2b - a) \end{aligned}$$

where γ is 0.577.... The region of operation of such a law might be $\tau = 0.05$ to 0.1 ev with the release of Q_T cal/g. Then

$$\begin{aligned} Q_T &= \int_{0.05}^1 (q_0/b^2)(\ln A\beta + \gamma + 2b - a) d\tau \\ &= (q_0/b^2) \left[\tau \ln \tau + \ln A\beta + \gamma + 2b - a - 1 \right]_{0.05}^{0.1} \\ &= (q_0/b^2) [-0.08 + 0.05(\ln A\beta + \gamma + 2b - a - 1)] \end{aligned}$$

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If $\underline{A}$ were about 10^{12} , $\underline{a}$ would be about 2.6, $\underline{b}$ would be about 1.03, hence since $\underline{s}$ is $1.9(10^4)$,

$$q_0/b^2 = 0.57 Q_T$$

$$g(\tau) \cong 0.57 Q_T(\ln A s \tau - 0.04)$$

which is a nearly constant rate of heat evolution rising slightly with temperature and gives approximately the correct average stored energy release. It possesses the property that the greater the heating rate, the smaller is $g(\tau)$, for $\underline{s}$ is the inverse heating rate. (The sample is at a given temperature for a shorter time and its temperature rate of annealing is therefore less.) If catastrophic stored energy release were to start, the heating rate would no longer remain constant and no longer would $t = sT$. The qualitative behavior of $g(\tau)$ under these conditions may be investigated by considering the tempering law $t = sT^p$ where $\underline{p}$ is some power less than unity. The solution now proves to be

$$g(\tau) = (q_0/n^2) [\ln \zeta A + \gamma - m + (p+1)n]$$

where $\zeta = ps\tau^p$ and $\gamma + \ln(\gamma + p + 1) \cong m + ny$. The constants $\underline{m}$ and $\underline{n}$ are smaller for smaller $\underline{p}$, and $\underline{s}$ is decreasing because it is the inverse heating rate. This slower release law begins to operate on a $q(\epsilon)$ which is smaller than it would be had the law operated from the beginning, and hence there is an exaggerated decrease in the stored energy release (dQ/dT as a function of $\underline{T}$). This effect would appear qualitatively for any $q_0(\epsilon)$ except a very sharp peak. It is therefore seen that the increased heating rate resulting from stored energy release is a controlling rather than a catastrophic factor. It is this effect which prevents the instantaneous rise which would occur if dQ/dT were a function of $\underline{T}$ only. The inverse effect would take place were quenching to start, and hence stored energy release can be sustained under catastrophic conditions. Thus, just as the conditions for a steep rise in dQ/dT_3 become more severe, so too do the conditions for quenching; and it therefore seems likely that the severe quenching observed near 400°C occurs as $q_0(\epsilon)$ begins to decrease while only a very mild quenching occurs at 250°C where $q_0(\epsilon)$ is evidently increasing. The resumed release of stored energy (dQ/dT_0) shown by Figure 11 is steep. This was not found for dQ/dT_3 nor would it be expected for the case of activated stored energy release considered here.

Since there is no particular amount of stored energy associated with a given temperature, dQ/dT has no meaning apart from the heating rates of the sample. Even if the data obtained by the method of DTA used here were sufficiently precise to compute dQ/dT and dT/dt , they would be very difficult to interpret because of the complicated form of dT/dt . More precise work with simpler sample heating rates will have to be done to obtain the detailed kinetics of stored energy release. For the present all that can be said is

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that there are broad regions of stored energy release indicative of a broad spectrum of activation energies with some sort of maximum at the activation energies that anneal at about 350°C for diamond and a much more uniform distribution for silicon carbide, and that the peaks and negative stored energies observed in the present DTA are spurious.

III. Physical Considerations of the Nature of Stored Energy Release:

It has been suggested by several (among whom are O. C. Simpson, T. J. Neubert, and G. R. Hennig)¹³ that the higher activation energies may be produced by the processes manifested by the lower activation energies. If the conditions of Vand's original treatment applied, this would not affect the results since his tempering function $Q_{\alpha}(\alpha)$ was so sharp that effectively only one activation energy was annealed at each temperature. Actually a small band of activation energies are being annealed simultaneously. Then, unless the further activation energies produced in the band were all above it, the effect would be some lowering of the apparent order of the reaction. It does not seem possible to refute a contribution from such an effect, for indeed it seems likely that some of the lowest activation energies would anneal to form higher activation energies. In the case of some properties the result would be ambiguous. In the case of the stored energy it would have to involve a heat release. It has been estimated by Hennig and Neubert¹⁴ that such processes in graphite must involve a release of over half the stored energy associated with them and one might reach similar conclusions from the shape of the stored energy as a function of irradiation curve for diamond.⁹ It would thus be difficult to have a long extended region of fairly constant stored energy in tempering if all the higher activation energies were derived from annealing of the lower ones. Further, it is reasonable to believe that the individual processes at the higher activation energies involve the release of a smaller amount of stored energy than the processes possessing the lowest activation energies. It must then be concluded that there were present conditions which give rise to a great many processes involving higher activation energies ab initio.

¹³See e.g., ANL-4196, p. 22.

¹⁴Private communication.

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