

Specific Heat of Diamond at Low Temperatures

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Measured energy in Japan
David von Seggern
(vorsegg@seismo.unr.edu) University of Nevada
July 2012, page 10
DIGITAL OBJECT IDENTIFIER
<http://dx.doi.org/10.1063/PT.3.1619>
The article by Thorne Lay and Hiroo Kanamori is an interesting one. It discusses the energy released by the 1964 Chilean earthquake. The authors use the relation for seismic energy release rather than total strain energy release. I believe the authors underestimate the total strain energy release by a factor of about 3, or 10 times, depending on the fault plane. Accounting for total strain energy release would increase the earthquake energy number by orders of magnitude. Despite the catastrophic damage potential of nuclear bombs, the forces of nature occasionally unleash much larger energy releases. Although the nuclear bombs are under our control, earthquakes, volcanic eruptions, and extreme weather events are not. However, by judicious preparation and avoidance measures, humans can significantly diminish the damage of natural events.

Comment on this article
By the act of hitting a ball with a bat, one calculates the force energy to deliver the ball to its new location, but one must also take into account that the ball extended its energy release to that which became struck by the ball as its momentum ceased and passed energy to the struck item. Therefore the parameters of the damage extend into the future when the received energy to that pushed upon later becomes released in a new event. Perhaps calculations of one added that in while another's calculations did not. E.M.C.
Written by Edgar McCarvill, 14 July 2012 19:59

Specific Heat of Diamond at Low Temperatures

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(Received November 25, 1952)

Specific heat data on diamond at temperatures between 20° and 300°K are reported. Comparisons of the data have been made with the predictions of the Debye theory. The deviation of the specific heat from the value given by the three-dimensional continuum theory in the low temperature region can be qualitatively described in terms of a superposition of a simple Einstein frequency. It has been found that variations that occur in expressing reduced characteristic temperatures as a function of reduced temperatures for diamond are qualitatively similar to those of the face-centered cubic metals Al, Cu, and Ag.

The values of entropy, enthalpy, and free energy have been determined and tabulated at integral values of temperature from 25° to 300°K. The entropy of diamond at 298.16°K is 0.568 ± 0.005 cal/g-atom/deg.

FOREWORD

AN extension of the measurements on the specific heat of diamond to liquid hydrogen temperature regions is herein reported. Continuous determinations up to room temperature are also included. These measurements were undertaken in pursuance of a general program of determining thermodynamic properties of various modifications of carbon.¹

Prior to this investigation, the specific heat of diamond had not been successfully studied below liquid nitrogen temperatures. The other three diamond-structure elements, germanium, silicon, and (gray) tin have all recently been studied down to liquid helium temperatures.^{2,3} The specific heats of these three elements all show striking variations from the Debye theory.

Pitzer⁴ compared his measurements on diamond with the Debye theory calculations and found small deviations which were outside his experimental errors. These measurements extended down to 70°K. Since the Debye characteristic temperature for diamond is high, there is a possibility that the temperature below which the three-dimensional elastic continuum idea is applicable⁵ might be in the liquid hydrogen region.

EXPERIMENTAL

The sample used in this study consisted of approximately 80 grams of "fragmented board" size -10, +14 mesh obtained from the Carboly Department of the General Electric Company.* Spectroscopic analysis carried out by Mrs. A. P. O'Hara, Schenectady Works Laboratory showed the sample to contain "traces" of Mg, and Al, and "low" concentrations of Si and Fe. Laue x-ray photographs taken by Mrs. B. F. Decker

showed a variation in intensity across some of the spots. This variation indicates that the crystal contained regions of misalignment. No attempt has been made to determine the proportions of the sample that exist as type I and type II diamond. About 20 percent of the crystals selected at random were fluorescent.

The calorimeter used in this investigation is the same as that used previously and is described elsewhere.¹ The accuracy of these measurements compares with the accuracy of the measurements described earlier, except for the temperatures near the liquid nitrogen region and below. The inaccuracy in the results at 70°K may be as large as 5 percent. This inaccuracy increases with decreasing temperature, amounting to about 30 percent at 40°K. Because of the extremely small values of the specific heat in the region of these lower temperatures, the data below approximately 30°K are, of necessity, of heuristic value only. Two independent determinations of the specific heat were undertaken in the region 20°–75°K. The first experiment was carried out in the usual manner with helium exchange gas in the calorimeter can at one atmosphere of pressure. In the second experiment, the calorimeter containing the sample was left open to the high vacuum of the cryostat. Under this latter condition the drift rates were normal up to about 100°K, indicative of the high thermal conductivity of the granular diamond specimen. Prior to these measurements, a complete recalibration of the empty calorimeter had been completed.

RESULTS

The experimental results are presented in Table I. These data along with those obtained by previous investigators are shown in Fig. 1. The specific heat values at the lower temperatures appear on a much enlarged scale.

The values of the thermodynamic functions listed in Table II were obtained from a smooth curve of large graphs of specific heat *versus* T and specific heat *versus* $\log T$ with the aid of Simpson's rule. The Debye characteristic temperatures deduced from the smooth specific heat data are also listed. The difference be-

¹ W. DeSorbo "Heat Capacity of Chromium Carbide (Cr_3C_2) from 13° to 300°K," J. Am. Chem. Soc. (to be published).

² R. W. Hill and D. H. Parkinson, Phil. Mag. **43**, 309 (1952).

³ I. Estermann and S. A. Friedberg, Carnegie Institute of Technology, Technical Report No. 8, U. S. Office of Naval Research Contract N60R1-47, June 30, 1951.

⁴ K. S. Pitzer, J. Chem. Phys. **6**, 68 (1938).

⁵ M. Blackman, Proc. Roy. Soc. (London) **A148**, 365, 384 (1935); **A149**, 117, 126 (1935); **A159**, 416 (1937).

* The author is grateful to Mr. A. J. DeCarlo for the loan of this sample.

tween C_p and C_v , calculated by Magnus' formula,⁶ was smaller than the experimental error throughout the temperature range studied. In Table III the entropy results are summarized.

DISCUSSION OF RESULTS

The specific heat values presented above are somewhat lower than those obtained by Pitzer in the temperature region 190°–260°K. The maximum difference between the two studies amounts to approximately 2 percent at 230°K. Such a difference is larger than the experimental error of both investigations. Outside this temperature region better agreement exists, although the present results are slightly lower throughout.

The variation could be due to differences in (1) impurities, (2) lattice imperfections, or (3) relative amounts of type I or type II diamonds present in the respective samples.

The influence of each of these factors is difficult to assay. It seems probable that the impurity factor is the least important. Pitzer states that the crystals used in his work were reasonably clear. Some of the diamond crystals used in this investigation had some coloration and were presumably less pure. If this is correct, a less pure sample should give higher rather than lower results.

Differences in "degree" of lattice imperfections could help to account for some of the discrepancy. Since diamond has such a high Debye characteristic temperature, any thermal effects caused by lattice irregularities could tend to be more pronounced than in a monatomic lattice having a much lower characteristic temperature.

As for the third factor, Robertson, Fox, and Martin⁷ indicate slight differences between the specific heats of type I and type II diamonds. More recently, Willardson and Danielson⁸ indicate that a single diamond crystal may be partly type I and partly type II. Data are insufficient at this time to evaluate this point.

A comparison of our data with the Debye theory is shown in Fig. 2. Smooth data were used in calculating the Debye characteristic temperatures. The results of previous investigations on diamond are also presented. A peak in the curve is revealed below 160°K. The maximum for this peak occurs at approximately 60°K. Above 160°K the Debye theory can describe the data quite accurately. This agreement obviates the need for "thermal quantum jumps"⁹ used to describe the deviations appearing in the earlier data.

Expressing specific heat data in terms of θ_D vs T curves has often revealed variations from constant values. Estermann³ has pointed out large deviations from the Debye theory found among face-centered and hexagonal close packed crystals. Body-centered cubic

TABLE I. Specific heat of diamond

Mean Temp (°K)	ΔT	C_p cal/g-atom/°K	Mean temp. (°K)	ΔT	C_p cal/g-atom/°K
Corrected for helium exchange gas					
17.40	1.280	(0.0001)	134.78	3.890	0.168
23.12	2.060	(0.0004)	141.28	4.259	0.197
25.26	2.056	(0.0015)	146.55	4.134	0.223
27.22	1.971	(0.0014)	152.64	3.983	0.255
31.00	1.977	0.0021	158.46	3.846	0.288
33.08	2.049	0.0020	164.10	3.725	0.325
62.54	3.538	0.0107	169.53	4.129	0.349
73.20	3.680	0.0178	175.06	4.022	0.377
76.16	3.494	0.0222	179.78	3.904	0.418
79.57	3.337	0.0260	185.29	3.788	0.454
82.36	6.088	0.0307	191.11	3.932	0.497
87.34	4.388	0.0356	196.00	3.832	0.532
93.70	3.776	0.0478	200.29	3.735	0.561
100.33	4.079	0.0576	205.77	3.883	0.606
106.71	3.869	0.0758	210.85	3.784	0.643
112.68	3.701	0.0932	213.09	3.600	0.660
118.02	3.812	0.105	216.67	3.523	0.694
123.42	3.680	0.124	226.77	3.463	0.785
129.11	4.043	0.145	231.79	3.613	0.812

Mean Temp. (°K)	ΔT	C_p cal/g-atom/°K	Mean temp. (°K)	ΔT	C_p cal/g-atom/°K
Corrected for helium exchange gas			No helium exchange gas used		
236.78	3.510	0.864	29.47	2.118	0.0020
241.93	3.816	0.914	36.53	2.679	0.0024
246.39	3.738	0.945	41.63	2.427	0.0032
250.76	3.643	0.989	44.07	2.472	0.0039
257.11	3.318	1.048	52.18	2.806	0.0054
265.99	2.250	1.142	55.20	3.250	0.0068
271.55	3.243	1.200	58.31	2.978	0.0086
277.48	2.707	1.252	66.40	2.774	0.0127
281.26	2.652	1.295	69.30	3.022	0.0156
285.22	2.787	1.341	74.91	2.736	0.0204
290.80	2.788	1.379			
293.51	2.501	1.407			
299.07	2.337	1.469			
300.57	2.330	1.481			

structures have a nearly constant θ_D vs T relationship. While one would expect the variation of θ_D with T to be similar for elements having similar structures, no simple generalization for the temperature dependence of θ_D for crystals of a given structure has been made. Hill and Parkinson² have recently pointed out a similarity, involving this function, in the diamond-structure elements. The peak observed in the θ_D vs T curve for diamond in this study is somewhat similar to those previously observed in the liquid helium temperature region in the studies of the specific heat of the three face-centered metals, Al, Cu, and Ag.¹⁰ This similarity is illustrated in Fig. 3, where the reduced Debye temperature θ_D/θ_∞ is plotted against the reduced temperature T/θ_∞ . The temperature θ_∞ represents the high temperature value of θ_D . The maximum in the peaks fall approximately at the same reduced temperatures. For the three metals the lattice specific heat only is considered.

Peaks as well as dips in the θ_D vs T curves have been observed for other substances in the lower temperature

⁶ A. Magnus, Ann. Physik **70**, 320 (1923).

⁷ Robertson, Fox, and Martin, Proc. Roy. Soc. (London) **A157**, 579 (1936).

⁸ R. K. Willardson and G. C. Danielson, J. Opt. Soc. Am. **42**, 42 (1952).

⁹ F. E. Simon, Sitzber. preuss. Akad. Wiss. **33**, 477 (1926).

¹⁰ Burton, Grayson-Smith, Wilhelm, *Phenomena at the Temperature of Liquid Helium* (Reinhold Publishing Corporation, New York, 1940), p. 136 (contains references).

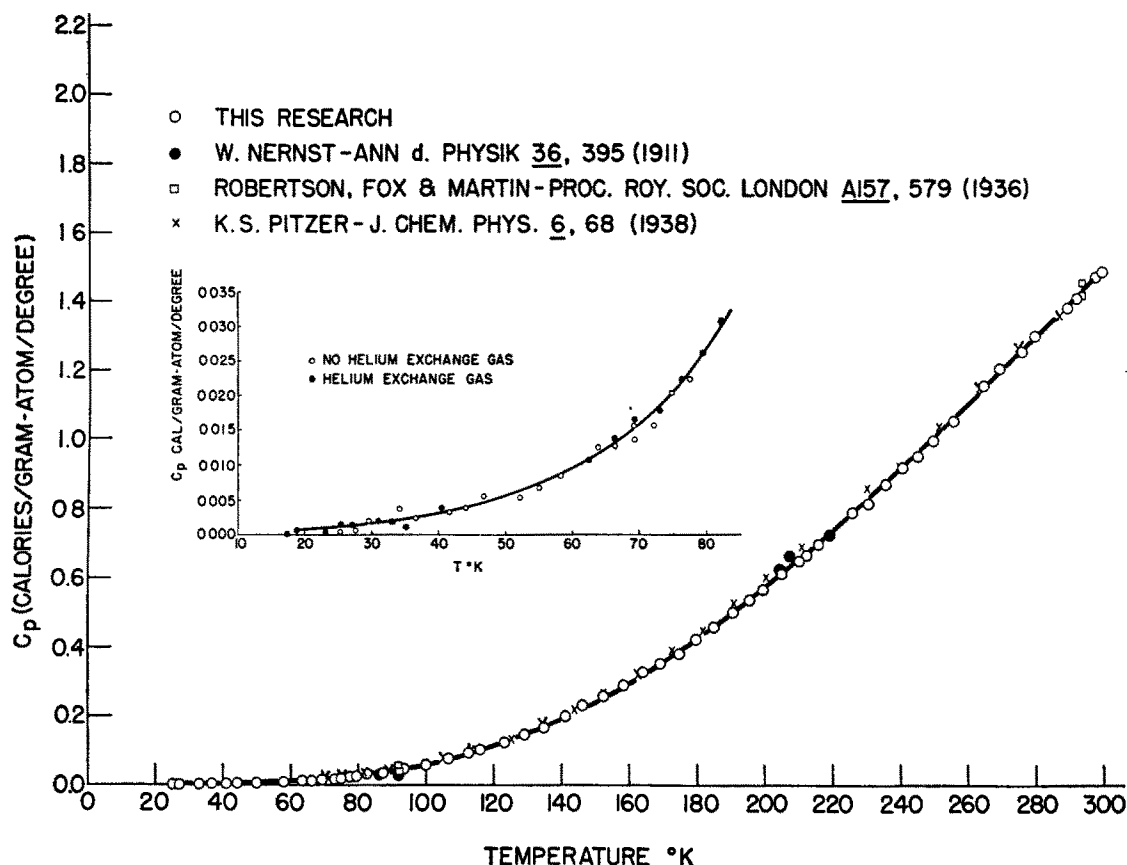


FIG. 1. Low temperature specific heat of diamond; this research and previous investigations.

TABLE II. Thermodynamic functions of diamond based on the smooth curve of specific heats

$T(^{\circ}\text{K})$	C_p cal/g-atom/ $^{\circ}\text{K}$	θ_D	S° cal/g-atom/ $^{\circ}\text{K}$	$H^{\circ} - H_0^{\circ}$ cal/g-atom/ $^{\circ}\text{K}$	$\frac{H^{\circ} - H_0^{\circ}}{T}$ cal/g-atom/ $^{\circ}\text{K}$	$-\frac{(F^{\circ} - H_0^{\circ})}{T}$ cal/g-atom/ $^{\circ}\text{K}$
25	(0.0012)	1822	(0.0007)	(0.0062)	(0.0002)	(0.0005)
30	(0.0018)	1910				
40	0.0034	2060				
50	0.0054	2207	0.0032	0.0832	0.0017	0.0015
60	0.0089	2242				
70	0.0154	2179				
75	0.0203	2129	0.0083	0.3593	0.0048	0.0035
80	0.0262	2086				
90	0.0418	2005				
100	0.0590	1989	0.0192	1.3095	0.0130	0.0062
110	0.0820	1961				
120	0.1120	1928				
125	0.1295	1919	0.0393	3.5749	0.0286	0.0107
130	0.1481	1903				
140	0.1899	1886				
150	0.2391	1869	0.0722	8.0875	0.0538	0.0184
160	0.2941	1858				
170	0.3516	1856				
175	0.3829	1855	0.1202	15.805	0.0902	0.0300
180	0.4156	1854				
190	0.4842	1854				
200	0.5584	1854	0.1828	27.502	0.1374	0.0453
210	0.6382	1853				
220	0.7223	1852				
225	0.7653	1852	0.2601	44.001	0.1955	0.0646
230	0.8078	1854				
240	0.8953	1858				
250	0.9884	1859	0.3524	65.859	0.2635	0.0889
260	1.0859	1857				
270	1.1829	1858				
275	1.2319	1862	0.4596	93.614	0.3403	0.1192
280	1.2810	1859				
290	1.3790	1862				
298.16	1.4615	1861	0.5684	124.785	0.4185	0.1499
300	1.4805	1861	0.5775	127.492	0.4250	0.1526

region. Katz¹¹ has recently attempted to explain some of these variations in terms of single Einstein frequencies which are added to or subtracted from a simple Debye spectrum. He shows that the relative deviation from a constant Debye θ for the low temperature range $0 < T < \theta/10$ may be given by

$$\delta = \frac{\theta - \theta_0}{\theta_0} = -\frac{5}{12\pi^4} \sum_i \frac{\beta_i}{q_i^3} \frac{x_i^5 e^{x_i}}{(e^{x_i} - 1)^2}, \quad (1)$$

where $x_i = q_i \theta_0 / T$. θ_0 is interpreted as the value of θ_D at 0°K . $q_i = \nu_i / \nu_0$, where ν_i is the Einstein frequency and ν_0 is the frequency corresponding to θ_0 . β_i refer to small "weight factors," which may be positive or negative depending on whether the Einstein frequency is added to or subtracted from the Debye spectrum.

If only one Einstein frequency is involved the temperature T_m at which δ has an extreme (maximum or mini-

TABLE III. The molal entropy of diamond

0-25°K (Extrapolated) = 0.0004 cal/g-atom/deg
25-298.16°K (Graphical) = 0.5680
$S_{298.16}^{\circ} = 0.568 \pm 0.005$

¹¹ E. Katz, J. Chem. Phys. 19, 488 (1951).

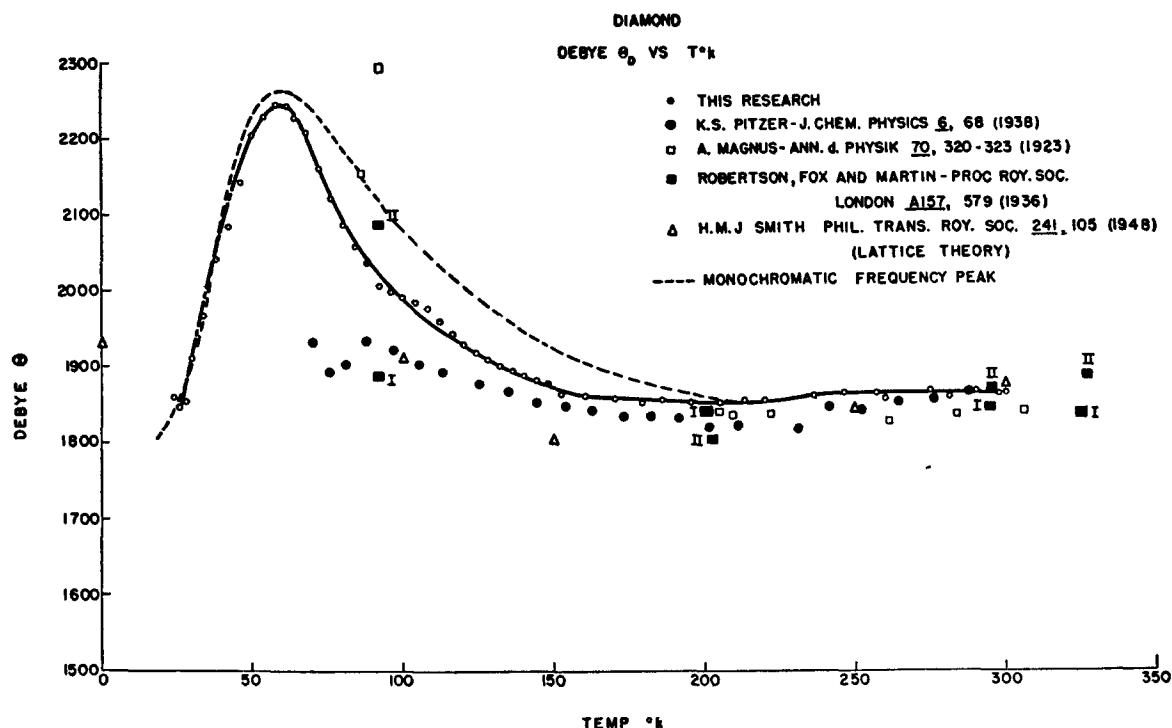


FIG. 2. Characteristic Debye temperatures for diamond calculated from various investigations.

mum) value is given by

$$T_m = \theta_0 q / 4.93. \quad (2)$$

Furthermore, the extreme value of δ is given by

$$\delta_m = -7.3 \cdot 10^{-4} \beta \theta_0^3 / T_m^3. \quad (3)$$

This analysis is applied to the peak observed in the θ_D vs T curve for diamond. The temperature T_m has the observed value of 60°K. If the θ_0 -value for diamond is assumed to be approximately equal to 1800°K, then $\delta_m = 0.247$. The values calculated for q_i and β_i have the values 0.16 and -1.25×10^{-2} , respectively. Thus, by subtracting an Einstein frequency $\nu_i = 0.16\nu_0$ from a Debye spectrum with $\theta = 1800^\circ\text{K}$, one gets a rough fit to the data. This is shown in Fig. 2. Whether or not this treatment has real physical significance is questionable.

From the relationship shown in Eq. (2), the temperature at which the maximum (or minimum) is observed in the θ_D vs T curve is directly proportional to θ_0 , or frequency $(\nu_0)_{\max}$, for an ideal lattice provided the q 's are fixed. If one makes the assumption that θ_0 is equal approximately to the "constant" θ_D value in the higher

temperature region for each of the three metals Ag, Al, and Cu and for diamond, one finds that the temperature T_m for the major peak observed in each of these

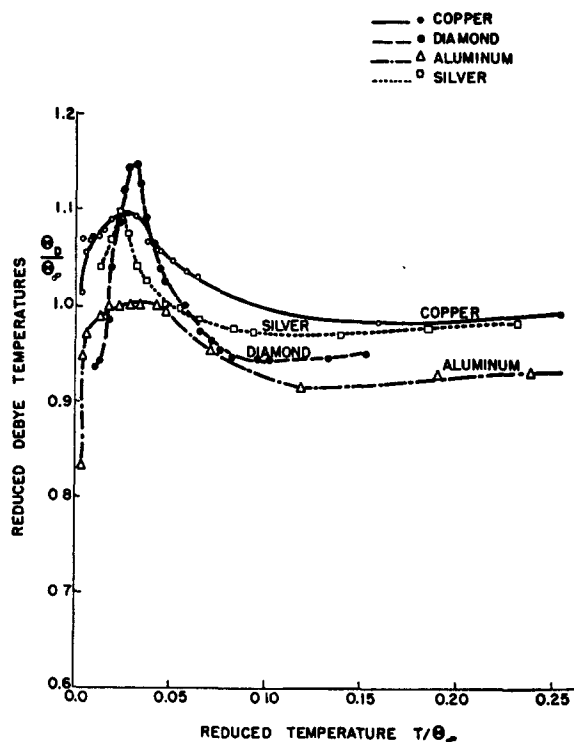


FIG. 3. Reduced Debye characteristic temperatures as a function of reduced temperatures for diamond and three fcc metals Cu, Al, and Ag.

TABLE IV. Peak temperatures in the θ_D vs T curve

Element	$\theta_0 \approx \theta_D$	T_m °K (obs)	T_m (calc)
Ag	216	~6	7
Cu	313	~9	10
Al	419	~14	13.6
Diamond	1800	60	—

monatomic solids forms a linear relationship when plotted as a function of their respective θ_D . This relationship is summarized in Table IV, where $T_m(\text{calc})$ has been obtained by using Eq. (2). The value " q " used in the calculations is that previously obtained for diamond.

The author wishes to thank Mrs. E. L. Fontanella

and Mr. Frank Hudda for their assistance in the experimental work and in the calculations. For the latter, the author is also indebted to Mrs. N. V. Doyle and the calculating group of the Metallurgy Research Department. Criticisms of the manuscript by Dr. R. W. Schmitt are also gratefully acknowledged.

A Calorimetric Calibration of Gamma-Ray Actinometers*†

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(Received November 24, 1952)

The yield for gamma-ray oxidation of ferrous sulfate in air saturated 0.4M sulfuric acid was found to be 15.6 ± 0.3 ferrous ions oxidized per 100 electron volts absorbed. This value was based on calorimetric measurements of cobalt gamma-ray energy absorption in water at intensities of 25 r/sec, 74 r/sec, and 225 r/sec. The yield for reduction of ceric sulfate in air saturated 0.4M sulfuric acid solution, determined by comparison with the ferrous sulfate yield was 2.52 ± 0.05 ceric ions reduced per 100 ev absorbed. The effects of several variables on these yields were investigated.

I. INTRODUCTION

AN accurate determination of the amount of chemical change produced in a suitable actinometer solution as a function of the x-ray energy absorbed affords a simple and rapid method for determining the dose received by other solutions. In the past, calibration of chemical actinometers has been carried out by comparing the ionization current observed in an air-filled ionization chamber and the chemical change produced in a solution contained in a similar chamber placed in the same radiation field. The energy absorbed in the condensed system was calculated from the measured ionization in air.

The oxidation of ferrous sulfate in 0.4 molar sulfuric acid has been chosen for an actinometer by a number of workers. Miller¹ measured the yield for this system using a rigorous application of the Bragg²-Gray³ cavity ion-chamber principle. Using radium gamma-rays and 200-kv x-rays at about 2 r per second he found a yield of 19.7 micromoles/liter/1000 r ($G^4 \sim 20.6$). The same value has also been obtained recently by Hardwick⁵ using x-rays and γ -rays. This value is significantly higher than those reported earlier by Fricke⁶ ($G \sim 18.3$)

and by Shishacow⁷ ($G \sim 16$). Recently Hummell and Spinks⁸ reported yields of 15.8 for 24.5-Mev betatron x-rays and 16.8 for radium gamma-rays.

It seemed to us that this wide discrepancy in values could best be resolved by direct calorimetric measurement of the gamma-ray energy absorbed in the condensed system. Using a 300-curie cobalt-60 source⁹ at intensities of 25 r/sec and 75 r/sec and a 1500-curie source at an intensity of 225 r/sec, we have found it feasible to measure by means of an adiabatic calorimeter the heat liberated in a sample of water during exposure to gamma-radiation. Following this measurement the water in the calorimeter was replaced with an air-saturated 10^{-3} M ferrous sulfate solution in 0.4 molar sulfuric acid and the rate of oxidation of ferrous ions measured. From these measurements the absolute yield was calculated.

Two other methods were used for calibrating the yield for ferrous oxidation. Measurements were made using a cavity ionization chamber. Based on available information on relative electron stopping powers for various materials, the energy necessary to form an ion pair in air and relative gamma-ray absorption coefficients, a yield for ferrous oxidation was calculated. Perhaps more to the point is the calculation of these quantities from the yield for ferrous oxidation measured calorimetrically.

Measurements were also made using 1.33-mv Van de Graaff electrons. The energy absorbed in solution was calculated from voltage and charge input measurements.

The reduction of ceric sulfate solution also provides a

* Paper presented in the meeting on Dosimetry in Intense Radiation Fields at the Conference on Fission Product Utilization, Brookhaven National Laboratory, Upton, Long Island, New York, February 18, 1952.

† This work was performed for the U. S. Atomic Energy Commission.

¹ N. Miller, *J. Chem. Phys.* **18**, 79 (1950).

² W. H. Bragg, *Studies in Radioactivity* (MacMillan and Company, Ltd., London, 1912), p. 94.

³ L. H. Gray, *Proc. Roy. Soc. (London)* **A122**, 647 (1929); **156**, 578 (1936); *Brit. J. Radiology* **27**, 677 (1949).

⁴ The yield (G) refers to ferrous ions oxidized per 100 electron volts energy absorbed by the solution.

⁵ T. J. Hardwick, *Can. J. Chem.* **30**, 17 (1952).

⁶ H. Fricke and S. Morse, *Am. J. Roentgenol. Radium Therapy* **18**, 430 (1927); *Phil. Mag.* **7**, 129 (1929); H. Fricke and E. Hart, *J. Chem. Phys.* **3**, 60 (1935).

⁷ N. A. Shishacow, *Phil. Mag.* **14**, 198 (1932).

⁸ R. W. Hummell and J. W. T. Spinks, *J. Chem. Phys.* **20**, 1056 (1952).

⁹ J. A. Ghormley and C. J. Hochanadel, *Rev. Sci. Instr.* **22**, 473 (1951).