HEAT OF FORMATION OF CARBON DIOXIDE AND OF THE TRANSITION OF GRAPHITE INTO DIAMOND

By Edward J. Prosen, Ralph S. Jessup, and Frederick D. Rossini

ABSTRACT

A recalculation of data previously reported on the heats of combustion of graphite and diamond, together with consideration of some new data on graphite, yielded the following selected "best" values for the heats of combustion of graphite and diamond and of the transition of graphite into diamond:

C (c, graphite)$+O_2$ (gas)$=CO_2$ (gas); $\Delta H^{\circ}_{298.16}=-393,447\pm45$ int. j/mole$=$ $-94,051.8\pm10.8$ cal/mole

C (c, diamond)$+O_2$ (gas)$=CO_2$ (gas); $\Delta H^{\circ}_{298.16}=-395,343\pm96$ int. j/mole$=$ $-94,505.1\pm22.9$ cal/mole.

C (c, graphite)$=$C (c, diamond); $\Delta H^{\circ}_{298.16}=1896\pm85$ int. j/mole$=453.2\pm$ 20.3 cal/mole.

CONTENTS

I. INTRODUCTION

As a result of a recalculation of the data previously reported on the heats of combustion of graphite and diamond [1, 2, 3],[1] together with consideration of some new data on graphite [4], revised "best" values have been obtained for the heat of formation of carbon dioxide and for the heat of transition of graphite into diamond.[2]

II. RECALCULATION OF THE DATA OF DEWEY AND HARPER ON GRAPHITE

For the reaction

$$C \text{ (c, graphite)}+O_2 \text{ (gas)}=CO_2 \text{ (gas)} \qquad (1)$$
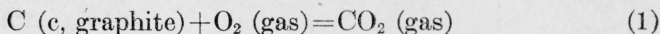
the data of Dewey and Harper [1] previously yielded [3] the value

$$\Delta H^{\circ}_{298.16}=-393,317\pm110 \text{ int. j/mole.} \qquad (2)$$

This value was based on the 1934 NBS value for the heat of combustion of benzoic acid [5], which was used by Dewey and Harper for

[1] Figures in brackets indicate the literature reference at the end of this paper.
[2] Revised values for the corresponding free energies are given in another report [10].

determining the energy equivalent of their calorimeter. The conversion of their data to the new 1942 value for the heat of combustion of benzoic acid [6] requires a correction of $+0.0336$ percent, following the procedure described on page 262 of reference [6]. On the new basis, the data of Dewey and Harper [1] yield for reaction (1)

$$\Delta H^\circ_{298\cdot 16} = -393,449 \pm 100 \text{ int. j/mole.} \tag{3}$$

III. RECALCULATION OF THE DATA OF JESSUP ON GRAPHITE

For reaction (1), the data of Jessup [2] previously yielded

$$\Delta H^\circ_{298\cdot 16} = -393,363 \pm 51 \text{ int. j/mole.} \tag{4}$$

The values originally reported by Jessup [2] from his experiments on the B calorimeter system were based solely on a value of the energy equivalent determined with electrical energy, although a determination of the energy equivalent of this system was also made with benzoic acid. In the present recalculation of Jessup's data, the reported results of the benzoic acid calibration have been converted to the new value for benzoic acid [6], and combined with the results of the electrical calibration by weighting the two mean values of energy equivalent inversely as the squares of their assigned uncertainties.[3] The value obtained in this way for the energy equivalent of Jessup's B calorimeter system is higher by 0.0038 percent than that originally reported. The values originally reported by Jessup [2] from his experiments on the C calorimeter system were based on calibration experiments performed with benzoic acid. Conversion to the new value for benzoic acid according to the prescribed procedure [6] requires a correction of $+0.0107$ percent. The effect of applying the above corrections to the values reported by Jessup for the energy equivalents of his B and C calorimeter system is to raise his value for the heat of reaction (1) by 0.0071 percent, so that his finally recalculated result for this reaction becomes:

$$\Delta H^\circ_{298\cdot 16} = -393,391 \pm 55 \text{ int. j/mole.} \tag{5}$$

IV. SUMMARY OF THE DATA ON GRAPHITE

Including the new data reported by Prosen and Rossini [4], which are based on measurements with electric energy, the values (and assigned uncertainties [7]) for the heat of reaction (1) are as follows:

From	$\Delta H^\circ_{298\cdot 16}$
Dewey and Harper [1]	$-393,449 \pm 100$ int. j/mole.
Jessup [2]	$-393,391 \pm 55$ int. j/mole.
Prosen and Rossini	$-393,502 \pm 55$ int. j/mole.

[3] The term assigned uncertainty as used here denotes $\sqrt{d^2+a^2}$, where d is twice the standard deviation of the mean calculated from the deviations of individual results from the mean value of energy equivalent, and a is an allowance of 0.010 percent for errors in electrical measuring instruments in the case of an electrical calibration, or for error in the value used for the heat of combustion of benzoic acid in the case of a calibration with this substance.

Weighting these values inversely as the squares of their assigned uncertainties,[4] there is obtained for reaction (1)

$$\Delta H^{\circ}_{298 \cdot 16} = -393,447 \pm 45 \text{ int. j/mole.} \tag{6}$$

Using the factor 1/4.1833 [9], this becomes

$$\Delta H^{\circ}_{298 \cdot 16} = -94,051.8 \pm 10.8 \text{ cal/mole.} \tag{7}$$

V. HEAT OF TRANSITION OF GRAPHITE INTO DIAMOND

The present "best" value for the heat of transition of graphite into diamond may be obtained from the experiments performed by Jessup [2], in which the same calorimeter system was used for both graphite and diamond (macrocrystalline). By treating the data essentially as described by Prosen and Rossini in the determination of the heats of isomerization of the hexanes [8], there is obtained from Jessup's data on the *C* calorimeter system the following value for the ratio of the heat evolved, per gram of carbon dioxide formed, in the combustion of diamond to that in the combustion of graphite: 1.004820 ± 0.000216. With the value for the heat of combustion of graphite given by eq 6, there is obtained for

$$C \text{ (c, diamond)} + O_2 \text{ (gas)} = CO_2 \text{ (gas)}; \ \Delta H^{\circ}_{298 \cdot 16} = -395,343 \pm 96 \ int. \ j/mole = -94,505.1 \pm 22.9 \ cal/mole, \tag{8}$$

and for

$$C \text{ (c, graphite)} = C \text{ (c, diamond)}; \ \Delta H^{\circ}_{298 \cdot 16} = 1896 \pm 85 \\ int. \ j/mole = 453.2 \pm 20.3 \ cal/mole. \tag{9}$$

VI. REFERENCES

[1] P. H. Dewey and D. R. Harper, 3d, J. Research NBS **21**, 457 (1938) RP1139.
[2] R. S. Jessup, J. Research NBS **21**, 491 (1938) RP 1140.
[3] F. D. Rossini and R. S. Jessup, J. Research NBS **21**, 491 (1938) RP1141.
[4] E. J. Prosen and F. D. Rossini, J. Research NBS **33**, 439 (1944) RP 1619.
[5] R. S. Jessup and C. B. Green, J. Research NBS **13**, 469 (1934) RP721.
[6] R. S. Jessup, J. Research NBS **29**, 247 (1942) RP1499.
[7] F. D. Rossini and W. E. Deming, J. Wash. Acad. Sci. **29**, 416 (1939).
[8] E. J. Prosen and F. D. Rossini, J. Research NBS **27**, 289 (1941) RP1420.
[9] E. F. Mueller and F. D. Rossini, Am. J. Phys. **12**, 1 (1944).
[10] D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer, and F. D Rossini, National Bureau of Standards. Unpublished.

WASHINGTON, August 16, 1944.

---

[4] The resulting uncertainty of the weighted mean [7] becomes ±36 j/mole, but has been arbitrarily increased to ±45 j/mole.