than otherwise are obtainable but it also reveals fine distinctions which, in the commonly adopted practices of evaluation, are entirely lost.

SHAWINIGAN FALLS, QUE. RECEIVED APRIL 9, 1942

[CONTRIBUTION FROM THE WESTERN REGION, BUREAU OF MINES, U. S. DEPARTMENT OF THE INTERIOR]

Heat Content of Manganese Dioxide and Carbonate at High Temperatures[1]

BY G. E. MOORE[2]

In the course of a program of investigation of the thermodynamic properties of manganese compounds being conducted at the Pacific Experiment Station of the Bureau of Mines, some measurements of the heat content of manganese dioxide and manganese carbonate (rhodochrosite) above 25° have been made. These data are required for accurate thermodynamic calculations on the dissociation equilibria of these substances and on certain proposed hydrometallurgical processes involving them. The entropies from low-temperature specific heat data have been reported.[3,4]

Method and Materials

The procedure employed is the so-called "drop" method; the apparatus has been described.[5] The samples were contained in a platinum-rhodium alloy capsule having a snugly fitting but not gas-tight cap.

The manganese dioxide was part of the sample used by Kelley and Moore, prepared by decomposing aqueous manganous nitrate, followed by careful and complete dehydration. Analysis gave substantially 100.0% MnO_2. The density was carefully measured with a pycnometer under carbon tetrachloride and found to be[6] d^{25}_4 5.11_8; this is somewhat higher than the value reported by Krüll[7] (d^{25}_4 4.943) for a similarly prepared material.

The manganese carbonate sample was a portion of the rhodochrosite used by Anderson,[4] who reported the impurities as 2.0% calcium carbonate, 0.1% silicon dioxide and 0.1% ferrous carbonate. The results given below were corrected for 2.0% calcium carbonate using data compiled by Kelley[8]; the correction amounted to about 0.3%.

In each case, the highest temperature of the measurements was that at which dissociation began to occur, as evidenced by a slight loss in weight.

Results

The experimentally determined heat contents above 298.16°K. are given in Table I, in the order in which they were obtained. The results are expressed in defined calories (1 calorie = 4.1833 int. joules) per gram formula weight, computed in accordance with the 1941 International Atomic Weights. It is estimated that the error in these data probably is about 0.5% at the higher temperatures, increasing to about 1.5% below 400°K. Table II is a summary of values at 100° intervals read from smooth curves through the data, together with the calculated entropy increments above 298.16°K. in cal./g. f. w.-deg.

TABLE I

HEAT CONTENTS ABOVE 298.16 °K.

$MnCO_3$ (g. f. w. = 114.94)		MnO_2 (g. f. w. = 86.93)	
T, °K.	$H^0_T - H^0_{298.16}$, cal./g. f. w.	T, °K.	$H^0_T - H^0_{298.16}$, cal./g. f. w.
419.3	2592	406.7	1546
476.1	3961	405.6	1530
476.2	3954	501.2	3035
467.4	3715	509.9	3184
471.7	3853	572.8	4236
542.1	5609	573.0	4233
608.8	7330	358.3	847
660.3	8716	341.2	587
594.0	6973	662.0	5757
		663.0	5767
		733.7	6992
		777.9	7762

TABLE II

HEAT CONTENTS AND ENTROPIES ABOVE 298.16 °K. AT 100 ° INTERVALS

	$MnCO_3$		MnO_2	
T, °K.	$H^0_T - H^0_{298.16}$, cal./g. f. w.	$S^0_T - S^0_{298.16}$, cal./g. f. w. deg.	$H^0_T - H^0_{298.16}$, cal./g. f. w.	$S^0_T - S^0_{298.16}$, cal./g. f. w. deg.
400	2160	6.22	1445	4.18
500	4550	11.55	3021	7.69
600	7095	16.19	4687	10.72
700	9800	20.36	6413	13.38
800	..	...	8186	15.75

The data show no irregularities in the range investigated; they may be represented to within about 0.3% by the following equations, derived from the data in Table II. The equations for C_p were obtained by differentiating the corresponding heat-content equations.

---

[1] Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior. Not copyrighted.

[2] Chemist, Western Region, Bureau of Mines.

[3] K. K. Kelley and G. E. Moore, THIS JOURNAL, **65**, 782 (1943).

[4] C. T. Anderson, *ibid.*, **56**, 849 (1934).

[5] J. C. Southard, *ibid.*, **63**, 3142 (1941).

[6] The density measurements were made by Dr. E. H. Huffman of this Station.

[7] F. Krüll, *Z. anorg. allgem. Chem.*, **208**, 135 (1932).

[8] K. K. Kelley, U. S. Bur. Mines, Bull. 371.

MnO_2 (298–780°K.):

(1) $H_T - H_{298.16} = 16.60\,T + 1.22 \times 10^{-3}\,T^2 + (3.88 \times 10^5/T) - 6359$

(2) $C_p = 16.60 + 2.44 \times 10^{-3}\,T - (3.88 \times 10^5/T^2)$

(3) $S_T - S_{298.16} = 38.223 \log T + 2.44 \times 10^{-3}\,T + (1.94 \times 10^5/T^2) - 97.491$

$MnCO_3$ (298–660°K.):

(4) $H_T - H_{298.16} = 23.36\,T + 3.76 \times 10^{-3}\,T^2 + (5.69 \times 10^5/T) - 9208$

(5) $C_p = 23.36 + 7.52 \times 10^{-3}\,T - (5.69 \times 10^5/T^2)$

(6) $S_T - S_{298.16} = 53.789 \log T + 7.52 \times 10^{-3}\,T + (2.845 \times 10^5/T^2) - 138.540$

Equation (2) gives $C_p = 12.96$ at 298.16°K., in excellent agreement with the value obtained by Kelley and Moore, 12.92.[3] Equation (5) gives $C_p = 19.2$ at 298.16°K., whereas Anderson[4] obtained 19.5 at this temperature; this is satisfactory agreement, in view of the fact that the uncertainty in both methods of measurement is the greatest in this temperature region.

There appear to be no previous pertinent measurements on either of these substances in the temperature range investigated.

Summary

The heat contents of manganese dioxide and manganese carbonate above room temperature have been determined up to 505 and 320°, respectively.

The data have been summarized by means of tables and algebraic equations.

BERKELEY, CALIFORNIA RECEIVED APRIL 2, 1943

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

A Versatile Apparatus for Photolysis Studies in the Gas Phase. I. Acetone and Iodine Mixtures

BY SIDNEY W. BENSON AND GEORGE S. FORBES

The work of Gorin[1,2] and more recently Blacet and co-workers[3,4] on the photolysis of aldehydes and ketones in the presence of iodine vapor have yielded what is perhaps the most direct evidence available on the nature of the primary process in these reactions. Since the activation energy for the reaction of free radicals with iodine molecules is usually zero or close to zero, by working with a sufficient concentration of iodine vapor, all free radicals can be converted to iodides and secondary reactions reduced to a negligible factor. Identification of the iodides will then reveal the identity of the free radicals formed in the primary process.

In this manner Gorin[2] has established that at 3130 Å. the primary process in the photolysis of acetone is the formation of methyl and acetyl radicals. By a further comparison of the products with those formed in the absence of iodine he was able to arrive at a value for the quantum yield of this reaction of about 0.95.

It has been the aim of the present investigation to repeat Gorin's work at other wave lengths and under more favorable experimental conditions, and then extend it to further reactions. Unfortunately the present emergency has necessitated a halt in the work so that results of a preliminary nature only have been obtained for the photolysis of acetone at a wave length of 2537 Å.

To reduce secondary reactions as much as possible, it was decided to perform the photolysis in a flow system. This is especially desirable since both methyl iodide and acetyl iodide absorb slightly in the region around 2537 Å. Under the conditions of flow used the concentration of products in the light path never exceeded 1% of the reactants. In static systems this may frequently run as high as 20%. Because of the novelty of the flow system the experimental procedures are given in detail.

Experimental Procedures

Light Source.—Approximately monochromatic light (2537 Å.) was obtained from a specially constructed mercury resonance lamp (Fig. 1). Melville[5] has shown that it is possible to get an efficiency of 10% from a resonance lamp filled with neon or argon. About 90% of this output will be in the 2537 Å. resonance line,[6] obviating the necessity of filters or monochromators. The circular portion of the lamp (Fig. 1) was used as the emittor and was constructed by Macalaster-Bicknell Co., from fused quartz. The electrodes were mounted by the Hanovia Chem. Co., who also filled the lamp with mercury and argon at a pressure of 6 mm. The auxiliary lamp (Fig. 1) was designed after Thomas's[7] resonance lamp. This

---

[1] Gorin, *Acta Physicochim.*, U. S. S. R., **9**, 681 (1938).

[2] Gorin, *J. Chem. Phys.*, **7**, 256 (1939).

[3] Blacet and Heldman, THIS JOURNAL, **64**, 889 (1942).

[4] Blacet and Loeffler, *ibid.*, **64**, 893 (1942).

[5] Melville, *Trans Faraday Soc.*, **32**, 1525 (1936).

[6] Taylor, *J. Chem. Phys.*, **2**, 377 (1934).

[7] Thomas, *Rev. Sci. Instruments*, **12**, 309 (1941).