The chain-ending step, reaction (10), would serve as a mechanism for equilibration of the N_2 and exchange with NO when the decomposition is carried out in the presence of the latter. From the experimental data one therefore would conclude that the chain length in the presence of NO must be of the order of 50–500. If there were chains of this length, then NO, when present in large concentrations such as our exchange experiment, would produce a sufficient concentration of nitrogen atoms by reaction (9) to lead to the production of N_2 by the recombination of the former. This nitrogen would necessarily come from NO, have the isotopic composition $N^{14}N^{14}$, and act as a diluent of the N_2 from the decomposition of N_2O. Since no dilution of the nitrogen product over the original N_2O is observed, this would argue for short chains. The apparent paradox argues against the above chain mechanism.[12]

(12) We are grateful to the referee of this paper for emphasizing the role of NO as a diluent for the nitrogen product.

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Low Temperature Heat Capacities of Inorganic Solids. XV. The Heat Capacity and Entropy of Red Mercuric Oxide[1]

BY THOMAS W. BAUER AND HERRICK L. JOHNSTON

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The heat capacity of red mercuric oxide was measured over the temperature range from 15°K. to room temperature. Thermodynamic functions were obtained from these values for the heat capacity, the molal entropy at 298.16°K. being 16.77 ± 0.05 e.u. Calculations were also made which confirmed the applicability of the Third Law to the entropy of red mercuric oxide.

Introduction

The question as to whether the red and yellow modifications of mercuric oxide differ only in particle size, or whether they are allotropic modifications is still undecided. The heat capacity of the red modification has been measured between 25 and 75° by Guenther,[2] and between 85 and 300°K. by Garrett.[3] The heat capacity of the yellow modification has been measured between 85° and room temperature by McDowell[4] and the results agree to within the limits of error.

Garrett and Hirschler[5] deduced from differential solubility measurements that the free energy of the yellow form was 31 cal./mole larger than that of the red form, but they were unable to decide whether this increase was due to an increase in surface energy or to a free energy of transition. Calorimetric heat of formation values for the two modifications are so inaccurate as to provide no means of ascertaining whether the two forms have different heats of formation. Even free energy of formation values calculated from cell measurements do not decide the dilemma, since the values of different investigators vary widely, and some neglected to state which modification was used in their cells, while others neglected to state the concentration of the electrolyte and failed to correct for this concentration. It was therefore decided to measure the heat capacity of red mercuric oxide over the range from 15°K. to room temperature, to get a reliable value for the entropy.

Apparatus and Material.—The mercuric oxide used was the red modification, commercial Baker Analyzed Reagent, containing the following percentage impurities: insoluble in HCl, 0.020; non-volatile matter, 0.010; Cl, 0.001; Fe, 0.004; SO_4, 0.005; total N, 0.003.

The calorimetric data were obtained with Calorimeter No. 3, whose construction and operation have been described previously.[6] Measurements were made with the calorimeter filled with 189.981 g. (0.87787 mole) of red HgO. The experimental values of the molal heat capacity in defined thermochemical calories are given in Table I. The smoothed curve through these points is believed to be accurate to within 0.2% above 45°K., but may be in error by as much as 0.5% at 20°K.

Smoothed values of the thermodynamic functions obtained from the heat capacity by graphical means are entered in Table II. The molal entropy at 298.16°K. is 16.77 ± 0.05 e.u.; of this amount 0.31 e.u. was contributed by a Debye extrapolation below 16°K., with θ equal to 126.8.

Third Law Check.—The dissociation pressures of red and yellow HgO have been measured by Taylor and Hulett,[7] who found them to be the same at all temperatures measured, and from their data Randall[8] has calculated the free energy and heat of formation of HgO (red or yellow):

$$\text{Hg (liq)} + {}^1/{}_2\text{O}_2\text{ (g)} = \text{HgO (crystalline, red or yellow)}$$

$$\Delta F^\circ_{25} = -13{,}950\text{ cal.};\quad \Delta H^\circ_{25} = -21{,}600\text{ cal.};\quad \Delta S^\circ_{25} = -25.66\text{ e.u.}$$

without giving an indication of the method of calculation or of the accuracy of the data.

Calorimetric values for the heat of formation of HgO vary widely: thus Berthelot[9] gives $\Delta H = -21{,}300$ cal., Thomsen[10] gives $-22{,}000$ cal., Nernst[11] reports $-20{,}700$ cal., and Varet[12] found $-21{,}500$ cal. The cell

$$\text{H}_2\text{, Pt} \mid \text{alkali} \mid \text{HgO(c), Hg}$$

$$\text{HgO(c)} + \text{H}_2\text{(g)} = \text{Hg(liq)} + \text{H}_2\text{O(liq)}$$

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(1) This work was supported in part by the Office of Naval Research under contract with The Ohio State University Research Foundation.

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TABLE I

HEAT CAPACITY OF RED MERCURIC OXIDE, HgO

Mol. wt. = 216.61; 0.87707 mole

$T_{av.}$, °K.	C_p, cal./deg./mole	$T_{av.}$, °K.	C_p, cal./deg./mol
14.89	0.760	114.42	7.215
17.06	1.106	124.94	7.504
19.45	1.464	136.03	7.786
22.33	1.885	142.70	7.943
25.41	2.276	147.34	8.061
28.10	2.581	150.84	8.089
30.69	2.916	158.15	8.339
33.49	3.249	169.51	8.573
37.24	3.631	180.87	8.784
41.78	4.045	210.58	9.304
46.96	4.434	216.19	9.379
52.24	4.787	227.55	9.570
57.58	5.156	240.44	9.733
58.36	5.142	240.62	9.743
64.59	5.443	250.73	9.961
69.17	5.653	250.86	9.919
74.56	5.848	262.10	10.138
80.84	6.151	268.37	10.188
87.52	6.417	278.18	10.306
95.56	6.738	291.23	10.449
104.34	6.995	298.24	10.483

TABLE II

SMOOTHED HEAT CAPACITIES AND DERIVED THERMODYNAMIC FUNCTIONS OF RED MERCURIC OXIDE, HgO

T, °K.	C^0_p, cal./deg./mole	$(H^0 - H^0_0)/T$, cal./deg./mole	S^0, e.u.	$-(F^0 - H^0_0)/T$, cal./deg./mole
16	0.934	0.234	0.311	0.077
25	2.223	0.728	1.004	0.276
50	4.641	2.148	3.382	1.234
75	5.904	3.206	5.522	2.316
100	6.796	3.997	7.349	3.352
125	7.505	4.630	8.943	4.313
150	8.125	5.161	10.367	5.206
175	8.668	5.625	11.662	6.037
200	9.123	6.035	12.850	6.815
225	9.536	6.401	13.949	7.548
250	9.907	6.733	14.973	8.240
275	10.245	7.037	15.934	8.897
298.16	10.528	7.298	16.774	9.426
300	10.551	7.318	16.839	9.521

has been investigated by numerous investigators, among them Brönsted,[13] Luther and Pokorny,[14] Donnan and Allmand,[15] Chow,[16] Miyamoto,[17] Buehrer,[18] Fried,[19] Ishikawa and Kimura,[20] and Shibata.[21,22] Brönsted did not state whether the yellow or red form of mercuric oxide had been used in his cell. His data have been recalculated by Fried,[19] who corrected them to the new value of the international volt, and for the concentration of the electrolyte. From Fried's recalculation one finds

$$E^\circ_{25} = 0.9267 \text{ int. volt}$$
$$(dE/dT)_{25} = 0.000287 \text{ int. volt/deg.}$$

Luther and Pokorny[14] give $E_{25} = 0.927$ v., without stating which modification had been used, what the concentration of the electrolyte was, and whether corrections had been made for the concentration. Donnan and Allmand[15] found

$$E^\circ_{25} = 0.9243 \text{ int. volt}$$
$$(dE/dT)_{25} = -0.0031 \text{ v./deg.}$$

without specifying the modification, the concentration of the electrolyte, and using a cell from which liquid junction potentials had not been eliminated. Chow[16] gives $E_{25} = 0.9264$ v., without specifying the modification and without correcting for the concentration of the electrolyte. Under the same circumstances Miyamoto[17] reports $E_{25} = 0.9270$ v. Buehrer[18] is quoted by the "International Critical Tables" as giving $E_{25} = 0.9264$ v., without giving any details as to how this value was obtained. Fried used very pure yellow mercuric oxide,[19] and correcting his observed e.m.f.'s to pure water, he found

$$E^\circ_{25} = 0.92598 \text{ int. volt}$$
$$(dE/dT)_{25} = -0.0002923 \text{ v./deg.}$$

Ishikawa and Kimura found for yellow mercuric oxide[19]

$$E^\circ_{25} = 0.9263 \text{ int. volt}$$

and Shibata[21,22] found for the yellow modification, corrected for the electrolyte concentration

$$E^\circ_{25} = 0.92554 \text{ int. volt}$$
$$(dE/dT)_{25} = -0.0002875 \text{ v./deg.}$$

These data show the accuracy of the e.m.f. data to be about 0.5 millivolt in E_{25} and 0.02 millivolt in dE/dT.

Ishikawa and Kimura[20] also measured a cell containing red mercuric oxide, obtaining (corrected for the concentration of the electrolyte)

$$E^\circ_{25} = 0.92565 \text{ int. volt}$$
$$(dE/dT)_{25} = -0.0002948 \text{ v./deg.}$$

Assuming the above limits of error, these values correspond to

$$HgO(c, \text{red}) + H_2(g) = Hg(\text{liq}) + H_2O(\text{liq})$$
$$\Delta F^\circ_{25} = -42{,}711 \pm 23 \text{ cal.}$$
$$\Delta H^\circ_{25} = -46{,}767 \pm 297 \text{ cal.}$$
$$\Delta S^\circ_{25} = -13.60 \pm 0.92 \text{ e.u.}$$

Using the values of the heat and free energy of formation of water reported by Wagman,[23] one finds for the heat and free energy of formation of red mercuric oxide

$$\Delta F^\circ_{25} = -13{,}979 \pm 34 \text{ cal.}$$
$$\Delta H^\circ_{25} = -21{,}626 \pm 307 \text{ cal.}$$
$$\Delta S^\circ_{25} = -25.40 \pm 0.94 \text{ e.u.}$$

The value of ΔS°_{25} computed from the calorimetric entropy of HgO and from the entropies of Hg and

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O_2 selected by Kelley,[24] is $\Delta S^\circ_{25} = -26.27 \pm 0.16$ e.u. These two values agree to just within the limits of error, and should confirm the applicability of the Third Law to the entropy of red HgO.

The values of ΔS derived from the dissociation pressures and from e.m.f. measurements are in good agreement, although it may easily be possible that they are both wrong. A part of Randall's calculations was based on doubtful data, *e.g.*, for the heat capacity of HgO he used a value at 600° derived from the measurements of Guenther between 25 and 75°K.; also, the probable error in ΔH derived from the cell measurements is large enough to account for the discrepancy.

Giving the two values of ΔF equal weight, the best value of ΔH is derived from these values, and from the calorimetric entropy of HgO

$$\mathrm{Hg(liq)} + {}^1/_2\mathrm{O_2(g)} = \mathrm{HgO(red)}$$
$$\Delta F^\circ_{25} = -13{,}965 \pm 35 \text{ cal.}$$
$$\Delta S^\circ_{25} = -26.27 \pm 0.16 \text{ e.u.}$$
$$\Delta H^\circ_{25} = -21{,}708 \pm 82 \text{ cal.}$$

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Methylchloroform: The Infrared Spectrum from 130–430 cm.$^{-1}$, the Energy Levels and Potential for Internal Rotation and the Thermodynamic Properties[1]

BY KENNETH S. PITZER AND J. L. HOLLENBERG

RECEIVED JANUARY 14, 1953

The infrared spectrum of gaseous methylchloroform has been measured in the range 130–430 cm.$^{-1}$. In addition to bands showing PQR structures at 239 and 344 cm.$^{-1}$, there is a series of absorption peaks in the range 130–180 cm.$^{-1}$. This series is interpreted as a sequence of difference bands involving internal rotation and yields values for the first three energy level separations associated with that motion. These energy levels are interpreted with a two term expansion of the potential function for internal rotation. Other vibration frequencies are discussed and the thermodynamic functions are calculated for methylchloroform.

The molecule CH_3–CCl_3, methylchloroform, has been the subject of several recent spectroscopic investigations. The most recent publications are those of Venkateswarlu,[2] El-Sabban, Meister and Cleveland,[3] and Smith, Brown, Nielsen, Smith and Liang.[4] These authors give references to earlier work. These various investigations cover both the Raman and infrared spectra except for the region of the infrared below about 250 cm.$^{-1}$. It is the purpose of this paper to present the infrared spectrum of methylchloroform in the range 130–430 cm.$^{-1}$ and to discuss the implication of our additional results with respect to the vibration frequency assignment and in particular the torsional vibration.

Experimental Method and Results

The spectrum was measured in a grating spectrometer described recently by Bohn, Freeman, Gwinn, Hollenberg and Pitzer.[5] The experimental procedures were the same as those described previously. The sample of methylchloroform was from the Eastman Kodak Co. The spectrum is shown in Fig. 1.

In the region from 300 to 400 cm.$^{-1}$ which overlaps previous investigations, we agree completely with the most recent work—that of Venkateswarlu.[2] He found the weak band at 382 cm.$^{-1}$ and the strong one at 344 cm.$^{-1}$. In each case the frequency value agrees within 1 cm.$^{-1}$.

We find no trace of a band in the gas at 411 cm.$^{-1}$, where Smith, *et al.*, found one in the liquid. Similarly we find nothing near 300 cm.$^{-1}$ where a weak Raman band has been observed. However, the fundamental at 239 cm.$^{-1}$ appears clearly with a PQR structure. The shoulder near 283 cm.$^{-1}$ is probably real but not certain. The most interesting feature of the spectrum is the series of three decreasing absorption peaks in the region 130–180 cm.$^{-1}$. While our experimental signal in this region is very small, we believe these peaks to be real. However, the exact frequency of the first peak is uncertain.

TABLE I

FUNDAMENTAL FREQUENCIES OF METHYLCHLOROFORM

Symmetry	Designation	Frequency (gas)	Symmetry	Designation	Frequency (gas)
A_1	ν_1	2954	E	ν_7	3017
	ν_2	1383		ν_8	1456
	ν_3	1075		ν_9	1089
	ν_4	526		ν_{10}	725
	ν_5	344		ν_{11}	351
A_2	ν_6	214		ν_{12}	239

Spectral Assignment.—Previous workers have come to agree on all of the fundamental frequencies shown in Table I except for numbers 3, 6 and 11. We have little new information to contribute with respect to ν_3, which is principally a C–C stretching motion. We are strongly influenced by the fact that almost all observers of the Raman spectrum have resolved a band at about 1070 cm.$^{-1}$ from the ν_9 band at 1084 cm.$^{-1}$, and by the observation of Smith, *et al.*, that the lower frequency component is moderately polarized while the higher one is fully depolarized. This pair cannot be a resonance doublet if the polarization is different for the two components, and it is then difficult to understand the intensity of the 1070 cm.$^{-1}$ band except as a fundamental. Thus we have selected this band for ν_3, the gas phase frequency being 1075 cm.$^{-1}$.

The unsymmetrical C–Cl bending motion, ν_{11}, is expected to have a frequency near that of the symmetrical bending motion, ν_5, at 344 cm.$^{-1}$. Previ-

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[1] This work was assisted by the American Petroleum Institute through Research Project 50.

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