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Heat of Decomposition of Sodium and Potassium Chlorate

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The heats of decomposition of sodium and potassium chlorate into their respective chlorides have been determined in a bomb calorimeter. The processes may be represented by the equations:

 $\begin{array}{l} {\rm NaClO_3(c) = NaCl(c) + 3/2 \ O_2(g)} \\ \Delta H^\circ \ (25 \ ^\circ{\rm C}) = - \ 45.76 \ \pm 0.17 \ {\rm kJ/mole} \\ = - \ 10.94 \ \pm 0.04 \ {\rm kcal/mole} \\ {\rm KclO_3(c) = KCl(c) + 3/2 \ O_2(g)} \\ \Delta H^\circ \ (25 \ ^\circ{\rm C}) = - \ 38.25 \ \pm 0.30 \ {\rm kJ/mole} \\ = - \ 9.16 \ \pm 0.07 \ {\rm kcal/mole}. \end{array}$

Combination of these data with the heats of formation of NaCl(c) and KCl(c) gives -87.33 ± 0.07 kcal/mole and -95.23 ± 0.10 kcal/mole for the standard heats of formation of NaClO₃(c) and KClO₃(c), respectively, at 25° C.

1. Introduction

This investigation was carried out in the Thermochemistry Section of the National Bureau of Standards, as part of a program currently in progress on the determination of the thermodynamic properties of the "light element" compounds. Although sodium and potassium chlorate are well known, considerable uncertainty exists in the values of the heats and free energies of formation.

2. Materials

The sodium chlorate and potassium chlorate were reagent-grade materials which were twice recrystallized from water. They were dried at 120 °C, ground, and stored in a desiccator over magnesium perchlorate. Tests for chloride ion in the recrystallized samples were negative.

The benzoic acid was NBS Standard Sample 39h. Samples of the same material were used for both the calibration and decomposition experiments.

The oxygen was freed from traces of combustible materials and of carbon dioxide by passing it successively though (1) a tube packed with copper oxide and heated to 600 °C, and (2) an absorber containing Ascarite. No attempt was made to remove traces of nitrogen.

3. Units of Energy and Molecular Weights

The unit of energy is the joule; for conversion to the conventional thermochemical calorie, one calorie is taken as 4.1840 J.

All atomic weights were taken from the 1961 International Table of Atomic Weights [1].¹

4. Apparatus and Procedure

The calorimeter was of the Dickinson isothermaljacket type which has been previously described [2, 3]. The temperature of the calorimeter jacket was controlled within ± 0.002 °C at about 25 °C by means of a thermostat. The calorimeter temperatures were measured by means of a platinum resistance thermometer and a Mueller-type bridge; timing of the experiments was made by reference to the NBS standard second signals.

The bomb was of the NBS twin-valve type, similar to that which has been described [3]; its volume was 365.9 ml. It was modified slightly for the NaClO₃ and KClO₃ decomposition experiments in that two crucibles were used, one being mounted about 1 mm directly above the other. The sample of chlorate was weighed into the upper crucible, while the benzoic acid pellet, approximately 0.5 g, was weighed into the lower crucible. Ignition was accomplished by means of an electrically heated iron-wire fuse which was placed in contact with the benzoic acid pellet. Care had to be taken to ensure that the iron-wire fuse was not shorted out by contact with either of the platinum crucibles. One milliliter of water was placed in the bomb, which was then sealed, flushed with oxygen, and filled with oxygen to a pressure of 30 atm at 25 °C.

The details of the calorimetric procedure have been described [3, 4]. The heat evolved by burning the benzoic acid was sufficient to decompose the NaClO₃ and KClO₃ samples, leaving a mass of fused NaCl or KCl in the crucible. In each case the combustion products were analyzed, to determine how completely the chlorate had decomposed to the chloride. The total mass of carbon dioxide was determined by collecting the dry gas in a weighed absorption tube containing Ascarite. The material remaining

¹ Figures in brackets indicate the literature references at the end of this paper.

in the bomb was washed into a flask, and the amount of chloride ion determined by titration with standard $AgNO_3$, using fluorescein as the indicator [5]. The reaction went to completion, except for two cases indicated in the tables.

The calorimeter system was calibrated by a series of combustion experiments with benzoic acid, NBS Standard Sample 39h. The mass of benzoic acid (about 0.52 g) was chosen because it was sufficient for the NaClO₃ and KClO₃ decomposition experiments, and it was desirable to duplicate as nearly as possible the initial and final calorimeter temperatures.

5. Results and Calculations

The results of the calibration experiments with benzoic acid are given in table 1, where ΔRc is the corrected rise in temperature of the calorimetric system [6], (as measured on the particular thermometer and bridge), m_s is the mass of benzoic acid corrected to weigh in vacuo, q_i is the ignition energy from combustion of the iron-wire fuse, and q_N is the energy evolved by the formation of nitric acid from traces of nitrogen in the bomb. The quantity WC is the Washburn correction [6, 7] applied here to convert the reactants and products from their thermodynamic standard states into the actual conditions of the bomb process. The quantity Δe is the deviation in energy equivalent of the actual calorimeter system from that of the "standard" system, which in this instance was taken to include 0.515 g of benzoic acid.

Expt. No.	$\triangle R_c$	q_{i}	q_N	m_s	WC	E_s
	Ohm	J	J		J	J/ohm
1	0.101535	34.0	4.4	0.51560	9.2	134, 593
2	. 101860	33.1	5.8	. 51708	9.3	134, 55
3	.101796	35.3	4.2	. 51665	9.3	134, 530
4	. 101121	34.8	4.6	. 51361	9.2	134,63
5	. 101531	34.4	4.4	. 51557	9.2	134, 59
<u>6</u>	. 101369	35.3	6.0	. 51461	9.2	134, 58
1	. 101957	34.0	5.2	. 51759	9.3	134, 56
Mean						134,58

TADLE 1

The heat of combustion of benzoic acid for the standard bomb process, $-\Delta E_B(25 \text{ °C})$ was taken as 26434.0 J/g. This value was corrected to give $-\Delta E^{\circ}(25 \text{ °C}) = 26413.3$ J/g for the heat of combustion at constant volume, for the reactants and products in their thermodynamic standard states.

The energy equivalent of the "standard" calorimetric system for the temperature interval of 24 to 25 °C is obtained by:

$$E_s(25~^{\mathrm{o}\mathrm{C}}) = rac{(26,413.3~m_s+ ilde{q}_i+ extsf{q}_n+ extsf{WC})-\Delta e}{\Delta R c}.$$

The results of the experiments on the decomposition of NaClO₃ are given in table 2, for KClO₃ in table 3. The value obtained for the standard

Expt. No.	$\triangle Rc$	$\triangle e$	q_i	<i>q</i> _N	<i>Q в а</i>	WC	NaClO ₃	$-\triangle E^{\circ}$ (25 °C)
$\begin{array}{c}1\\2\\3\\4\\5\\6\end{array}$	$\begin{array}{c} Ohm \\ 0, 110907 \\ .110380 \\ .111061 \\ .111263 \\ .110561 \\ .111243 \end{array}$	$\begin{matrix} J/ohm \\ 26.2 \\ 26.6 \\ 26.6 \\ 26.6 \\ 26.5 \\ 26.6 \end{matrix}$	$\begin{matrix} J \\ 33.6 \\ 33.6 \\ 33.1 \\ 43.3 \\ 44.3 \\ 42.7 \end{matrix}$	$egin{array}{c} J \ 4.9 \ 4.9 \ 1.3 \ 1.$	$\begin{matrix} J \\ 13, 613, 2 \\ 13, 609, 7 \\ 13, 635, 3 \\ 13, 648, 0 \\ 13, 545, 3 \\ 13, 642, 5 \end{matrix}$	$\begin{matrix} J \\ 24. 2 \\ 23. 9 \\ 24. 5 \\ 25. 0 \\ 24. 6 \\ 24. 7 \end{matrix}$	$\begin{array}{c} Mole\\ 0.\ 0251582\\ .\ 02400^{*}\\ .\ 0255067\\ .\ 0255270\\ .\ 0255452\\ .\ 0255149 \end{array}$	$\begin{array}{c} kJ/mole\\ 49,805\\ 49,412\\ 49,222\\ 49,332\\ 49,594\\ 49,500\\ \end{array}$
Jean							49.478 ± 0.168	

TABLE 2

*By analysis.

Table 3

Expt. No.	$\triangle Rc$	$\triangle e$	q_i	<i>QN</i>	Q B A	WC	$KClO_3$	$-\triangle E^{\circ} (25 \ ^{\circ}\mathrm{C})$
$ \begin{array}{c} 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \\ 7 \end{array} $	$\begin{array}{c} Ohm \\ 0.\ 107426 \\ .\ 107643 \\ .\ 107543 \\ .\ 108517 \\ .\ 105985 \\ .\ 108117 \\ .\ 109033 \end{array}$	$\begin{matrix} {J}/{ohm} \\ 19.1 \\ 20.0 \\ 20.1 \\ 20.5 \\ 18.0 \\ 23.6 \\ 22.5 \end{matrix}$	$\begin{matrix} J \\ 34.8 \\ 36.4 \\ 35.0 \\ 36.8 \\ 35.1 \\ 34.8 \\ 35.1 \end{matrix}$	$J \\ 4.9 \\ $	$\begin{matrix} J \\ 13, 593, 6 \\ 13, 583, 3 \\ 13, 565, 9 \\ 13, 766, 3 \\ 13, 514, 1 \\ 13, 585, 4 \\ 13, 751, 3 \end{matrix}$	$\begin{matrix} \boldsymbol{J} \\ 20, 9 \\ 21, 5 \\ 21, 9 \\ 20, 9 \\ 19, 2 \\ 22, 8 \\ 22, 1 \end{matrix}$	$\begin{array}{c} Mole\\ 0,0190032\\ ,0199302\\ ,0200348\\ ,0187698\\ ,0164333\\ ,02172^*\\ ,0207571\end{array}$	
Mean Standard deviation of the mean							41.967 ± 0.300	

*By analysis.

constant-volume process at 25 °C is given by the relationship:

$$-\Delta E^{\circ}(25 \ ^{\circ}C) = \frac{(Es + \Delta e)\Delta Rc - q_i - q_n - q_{BA} - WC}{\text{mole NaClO}_3}$$

and may be represented by the equation:

$$NaClO_3(c) = NaCl(c) + 3/2 O_2(g)$$

 $\Delta E^{\circ}(25 \ ^{\circ}C) = -49.48 \pm 0.17 \text{ kJ/mole.}$ (1)

For $KClO_3$, the same relationship applies for the standard constant-volume process and for the equation:

$$KClO_{3}(c) = KCl(c) + 3/2 O_{2}(g)$$
$$\Delta E^{\circ}(25 \ ^{\circ}C) = -41.97 \pm 0.30 \text{ kJ/mole.}$$
(2)

The results of eqs (1) and (2) were corrected to constant pressure at 25 °C, with R=8.3143 J/deg mole:

$$\Delta H^{\circ}(25 \text{ °C}) = \Delta E^{\circ} + P \Delta V = \Delta E^{\circ} + \Delta n R T$$

for eq (1) $\Delta H^{\circ}(25 \text{ °C}) = -45.76 \pm 0.28 \text{ kJ/mole}$,

 $=-10.94\pm0.07$ kcal/mole,

for eq (2)

 $= -9.16 \pm 0.10$ kcal/mole.

= -38.25 \pm 0.42 kJ/mole,

The uncertainty intervals for the measured heats have been taken as twice the overall standard deviation of the mean, based on the sum of the variances from the calibration and reaction experiments and reasonable estimates for other errors.

The heat of formation of NaCl(c) has been taken as -98.232 kcal/mole [8] and the heat of formation of KCl(c) has been taken as -104.175 kcal/mole [8]. From these values and the heats of decomposition corresponding to eqs (1) and (2) the following values have been obtained:

NaClO₃(c),
$$\Delta H f^{\circ}(25 \ ^{\circ}C) = -87.29 \pm 0.07 \ \text{kcal/mole};$$

KClO₃(c),
$$\Delta H f^{\circ}(25 \ ^{\circ}C) = -95.02 \pm 0.10 \text{ kcal/mole.}$$

6. Discussion

The heat of decomposition of $KClO_3(c)$ has been measured by Thomsen [10]; Frankland [11]; Hofmann and Marin [12]; Wöhler and Schuff [13]; and Vorob'ev, Privalova, and Huang Li-Tao [14]. Thomsen obtained the decomposition by burning H_2 in O_2 in the presence of KClO₃, while Hofmann and Marin produced decomposition in a bomb by burning paraffin oil. Vorob'ev et al., produced decomposition by electrical heating of a bomb containing KClO₃ to which MnO_2 had been added to facilitate decom- the various combined experimental data.

position. No details of Wöhler and Schuff's procedure are available.

Thomsen [10] and Berthelot [9] determined the heat of formation of $HClO_3(aq)$ by measuring the heat of reaction of $SO_2(aq)$ with $HClO_3(aq)$ to form $H_2SO_4(aq) + HCl(aq)$. These data yield values of $\Delta H f^{\circ}$ for $HClO_3(aq) = -32.5$ and -27.4 kcal/mole, respectively. Taking the heat of neutralization of $HClO_3(aq)$ to be the same as that for $HNO_3(aq)$ (see Thomsen [10]) and the heat of solution of $KClO_3(c)$ to be +9.9 kcal [16] we obtain -102.5 and -97.4kcal/mole for the heat of formation of $KClO_3(c)$. The results of the various investigations on $KClO_3$ are compared with present work in table 4.

The only measurements on NaClO₃(c) are those of Vorob'ev et al., who reported a heat of decomposition of -12.5 kcal/mole. From this we compute the heat of formation to be -88.94 kcal/mole, whereas the value obtained here is -87.38 kcal/mole.

TABLE 4

Decomposition of KClO₃(c), kcal/mole

Investigator	$\Delta H_{\rm decomp}(25~^{\circ}{\rm C})$	$\Delta H f^{\circ}(25 \ ^{\circ}\mathrm{C})$
Berthelot		-97.4
Thomsen	-9.71	-94.67
Thomsen		-102.5
Frankland	-4.3	-100.8
Hofmann et al	-11.2	-93.0
Wöhler et al	-10.2	-94.0
Vorob'ev et al	-11.6	-97.69
This work	-9.16	-95.25

Brönsted [15], from EMF data, obtained for the following reaction:

$$\begin{array}{l} \operatorname{NaClO_3(c)} + \operatorname{KCl(c)} \to \operatorname{NaCl(c)} + \operatorname{KClO_3(c)} \\ \Delta H = -1.52 \ \mathrm{kcal/mole.} \end{array}$$

Using the recently selected values for NaCl(c) and KCl(c) [17], -98.27 and -104.39 kcal/mole, we obtain:

$$\Delta H f^{\circ} \text{KClO}_3(c) - \Delta H f^{\circ} \text{ NaClO}_3(c) = -7.64 \text{ kcal/mole.}$$

The result of our present investigation yields -7.73kcal/mole for this difference.

The consistency of the present results may also be demonstrated by calculation of the heat of formation of ClO_3^{-} (aq) ion from the heats of solution of the chlorates [16] and the values of $\Delta H f^{\circ}$ for Na⁺(aq) and K⁺(aq) [17], -57.39 and -60.32 kcal/mole, respectively. We calculate the following:

$$\begin{array}{l} \mathrm{NaClO_3(c)} \rightarrow \mathrm{NaClO_3(aq, inf diln)} \\ \Delta H^\circ = 5.191 \ \mathrm{kcal/mole} \\ \Delta H f^\circ \mathrm{ClO_3^-(aq)} = -24.71 \ \mathrm{kcal/mole} \\ \mathrm{KClO_3(c)} \rightarrow \mathrm{KClO_3(aq, inf diln)} \\ \Delta H^\circ = 9.89 \ \mathrm{kcal/mole} \\ \Delta H f^\circ \mathrm{ClO_3^-(aq)} = -24.81 \ \mathrm{kcal/mole}. \end{array}$$

This agreement is well within the uncertainties of

7. References

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