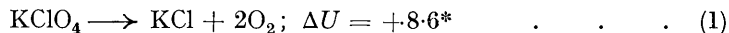


382. *The Thermochemistry of Perchloric Acid and the Perchlorates.*

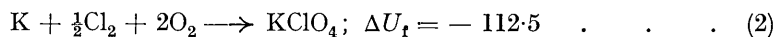
By CHARLES F. GOODEVE and ARTHUR E. L. MARSH.

The heat of solution of dichlorine heptoxide has been measured, and this, combined with the value recently obtained for its heat of formation, gives a value for the heat of formation of aqueous perchloric acid. This provides a convenient basis for the thermochemistry of the perchlorates, since reliable data exist for the heats of neutralisation of perchloric acid, and the heats of solution of its salts. The new basis is about 7.5 kg.-cals. different from that previously used.

At the commencement of this work the only available data for the heats of formation of perchloric acid and the perchlorates were those of Berthelot (*Ann. Chim. Phys.*, 1882, **27**, 214). In collaboration with Vieille (*ibid.*, p. 225) he determined the heat of reduction of potassium perchlorate as the difference between the heat of combustion of potassium picrate with pure oxygen on the one hand and with potassium perchlorate on the other. They found, for the equation



The experiment was repeated with ammonium picrate in place of the potassium salt, and a value of +6.5 obtained. The mean of the two values, +7.5, together with Thomsen's value for the heat of formation of potassium chloride, 105, was used in calculating



This value is the basis of the heats of formation of the perchlorates given in Landolt-Börnstein.

Berthelot and Vieille do not give the value they obtained for the heat of combustion of the picrate. Calculation shows, however, that it is of the order of 400/g.-mol. of per-

* All heats of reaction are given in terms of kg.-cals.

chlorate ($2O_2$) and the limits of error in determining a small difference between two such large quantities must be very high.

Whereas Berthelot and Vieille found the reduction of potassium perchlorate [equation (1)] to be endothermic, Hofmann (*Sitzungsber. Akad. Wiss. Berlin*, 1932, 448), who repeated the experiments using paraffin in place of the picrate, found the reaction to be slightly exothermic, and obtained a value of $\Delta U = -1.73 \pm 0.07$ (or $\Delta H = -0.55$). The values of the measured heats of combustion are again not given, but calculations show that they were of the order of 180/g.-mol. of perchlorate. In view of this, the accuracy claimed is unusually high.

EXPERIMENTAL.

Determination of the Heat of Solution.—Preliminary experiments revealed that the course of the reaction between dichlorine heptoxide and water consists of two stages; the first causes a rapid rise in temperature during about 2 min., and the second, a slow, steady rise for a further 5–15 mins. It was thought possible that the reaction proceeded *chemically* in two stages, with the initial formation of a fairly stable intermediate complex such as $Cl_2O_7 \cdot H_2O$. To test this point, the course of the reaction was followed in all experiments by measuring the conductivity simultaneously with the temperature.

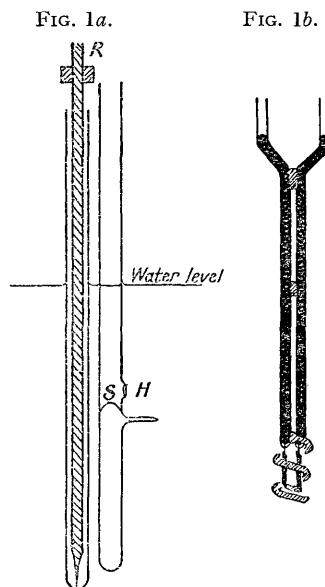
Apparatus. A simple all-glass apparatus was designed (Fig. 1a) which enabled the dichlorine heptoxide to be manipulated without coming into contact with the atmosphere. The septum *S* and the lower, closed end were made as thin as possible. About 0.4 c.c. of the heptoxide was introduced through the side arm by vacuum distillation from a main reservoir. Slight traces of high-vapour-pressure impurities, such as chlorine dioxide, were then distilled off. The colour of the heptoxide at liquid-air temperature is very sensitive to such impurities; a slight trace of any other oxide turns it yellow or orange-red. The side arm was then sealed off at the constriction. A number of such samples were prepared at a time and stored in a solid carbon dioxide–alcohol mixture until required.

The conductivity cell is shown in Fig. 1b. Two thin platinum electrodes (3 mm. \times 10 mm., and 5 mm. apart), coated with platinum-black, were sealed into Pyrex contact arms and protected by a coil of Pyrex rod. The cell was connected into the usual bridge circuit, a valve oscillator providing the source of alternating current. The heating effect of the conductivity cell was tested and found to be negligible.

A Dewar vessel of 250 c.c. capacity was used as a calorimeter. In order to protect it from draughts, it was set in a box loosely packed with asbestos wool and fitted with a lid. A very fast glass stirrer, driven by a constant-speed motor, was used to effect as rapid a dissolution of the heptoxide as possible. The temperature was observed with a Beckmann thermometer which could be read to 0.001°. In order to prevent the mercury thread sticking, the thermometer was automatically shaken by an electromagnetic hammer, as previously described (Goodeve and Marsh, this vol., p. 1161).

For each experiment the heat capacity was determined electrically in the usual way, standardised Weston instruments being used.

Procedure. At the commencement of an experiment one of the sample tubes was washed thoroughly free from alcohol and clamped in position in the calorimeter with the small hole *H* below the level of the water. Readings of temperature were taken at minute intervals, and when a steady state had been reached the glass rod *R* was quickly withdrawn and dropped down the centre of the sample tube. As soon as the septum *S* was shattered, water rushed in, and as the lower end was broken, the heptoxide fell as a large drop to the bottom of the calorimeter, just below the stirrer. Readings of temperature and conductivity were taken every minute until a steady state was again reached. The rise in temperature due to the reaction was found by plotting temperature against time and extrapolating the initial and the final steady state. This extrapolation could be made accurately, as the rate of rise of temperature in the two states was almost identical. Irregular external heat effects occurring while the heptoxide was dissolving



were shown to be absent by a comparison between the temperature rise and the conductivity. The solution of perchloric acid formed was subsequently diluted to 500 c.c., and about six 25-c.c. samples titrated against N/100-sodium hydroxide.

RESULTS AND DISCUSSION.

The values obtained for the heat of reaction of dichlorine heptoxide with excess water (final concentrations about N/100-perchloric acid) are given in Table I, together with other experimental details.

In experiments A, 1, 3, and 5, the stirring was irregular and the results are consequently less accurate. In B, 1 a different apparatus was employed for the conductivity measurements and the heating effect was found to be appreciable. The circuit was subsequently altered to eliminate this heating effect. Expts. B, 2, 3, and 4 were carried out with impure

TABLE I.

| Expt. No. | Heat capacity, cals./° C. | Cl ₂ O ₇ used, g.-mols. × 10 ³ . | ΔT. | ΔH, kg.-cals. | Statistical weight. |
|-----------|------------------------------|--|--------|---------------|------------------------|
| A, 1 | 275.0 | 1.241 | 0.228° | -50.2 | 2 † |
| A, 2 | 274.0 | 1.419 | 0.259 | -50.0 | 4 |
| A, 3 | 273.3 | 1.006 | 0.180 | -48.8 | 1 † § |
| A, 4 | 264.5 | 1.875 | 0.361 | -50.8 | 4 |
| A, 5 | 268.8 | 1.528 | 0.291 | -49.5 | 1 † § |
| A, 6 | 279.7 | 2.360 | 0.410 | -48.5 | 4 |
| B, 1 | 276.8 | 1.520 | 0.284 | -51.3 | 2 § * |
| B, 2 | 267.3 | 1.067 | 0.189 | -48.2 | 0 ‡ |
| B, 3 | 258.3 | 0.950 | 0.180 | -48.9 | 0 ‡ |
| B, 4 | 273.5 | 1.731 | 0.313 | -49.4 | 0 ‡ |
| B, 5 | 264.9 | 0.727 | 0.137 | -49.7 | 3 § |
| B, 6 | 264.9 | 1.230 | 0.232 | -50.1 | 4 |
| B, 7 | 255.5 | 1.324 | 0.262 | -50.4 | 4 |

Weighted mean = -50.0 kg.-cals.

† Stirring irregular.

‡ Impure sample.

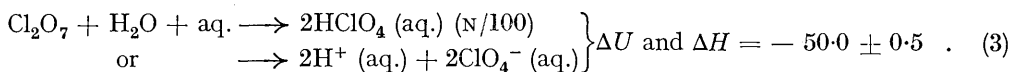
§ Steady state uncertain.

* Heating effect due to conductivity cell.

samples, and the results obtained were consequently neglected in calculating the mean value for the heat of the reaction. An approximate statistical weight, based upon the above considerations, has been given to each value in calculating the mean: $\Delta H = -50.0$ /g.-mol. of dichlorine heptoxide, with a probable error of ± 0.5 .

The formation of a fairly stable intermediate hydrate such as Cl₂O₇·H₂O has been suggested above as a possible explanation of the slow rate of solution of dichlorine heptoxide in water. Such a complex would not be ionised, and no change in the conductivity of the solution would be observed until it dissociated into perchloric acid. No such delay was observed, however, and the conductivity was found to follow the rise of temperature exactly (the conductivity is proportional to the amount of perchloric acid at the low concentrations used here).

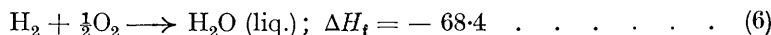
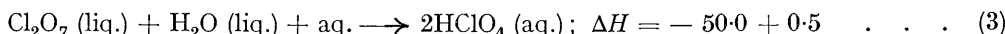
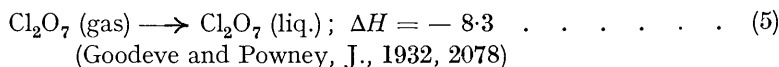
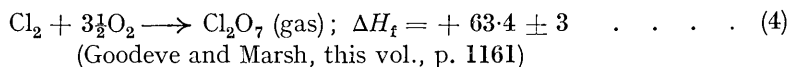
The value of ΔH measured in the experiments is, therefore, the heat of the following reaction :



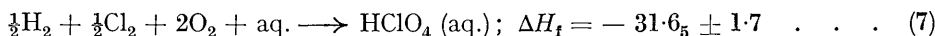
The slow rate of rise of temperature was almost certainly due to a slow rate of solution of the drop of dichlorine heptoxide. This was observed in preliminary trials in glass vessels, and confirmed the previous observations of Michael and Conn (*Amer. Chem. J.*, 1900, **23**, 444), who found that this oxide, when poured into water, sank to the bottom and dissolved slowly. The slowness of the reaction is surprising in view of the great affinity of the heptoxide for water, as shown by the instantaneous fuming of the gaseous oxide in air. The interfacial tension between liquid heptoxide and water was high and remained so throughout the dissolution of the drop. Perchloric acid is miscible with water in all proportions and if it were likewise miscible with the heptoxide it would be impossible for a boundary to be set up which could exhibit a surface tension. One concludes, therefore, that there is a limited solubility of perchloric acid in the heptoxide. The initial rapid rise of temperature can be attributed to the setting up of saturation at least in the outer parts of the drop, and

the subsequent slow rise to the gradual diffusion of water through a thin perchloric acid layer *outside* the drop. This is supported by the fact that the rate of reaction during the period of slow rise in temperature was directly proportional to the calculated surface area of the drop.

Thermochemical Data.—By means of the following heats of reaction :



one obtains the heat of formation of aqueous perchloric acid,



The value calculated by Berthelot was $- 39.1$.

In Table II the heats of formation of the crystalline perchlorates, calculated on the basis of equation (7), are given, together with the other thermochemical data employed. The concentrations of perchloric acid used by Berthelot in determining its heats of neutral-

TABLE II.

| | $\Delta H_f\text{MOH(aq.)}$, kg.-cals. | ΔH neutralisation, kg.-cals. | $\Delta H_f\text{MClO}_4\text{(aq.)}$, kg.-cals. | $\Delta H_s\text{MClO}_4$, kg.-cals. | $\Delta H_f\text{MClO}_4$, kg.-cals. |
|------------------------------------|--|---|--|--|--|
| MClO ₄ . | | | | | |
| NaClO ₄ | -112.05 (0.166N) | -14.25 | - 89.5 (0.08N) | + 3.5 (0.215* and 0.005N †) | - 93.0 |
| KClO ₄ | -114.83 (0.083N) | -14.25 | - 92.3 (0.04N) | +12.1 (0.32 ‡ and 0.03N §) | -104.4 |
| NH ₄ ClO ₄ | - 87.72 (0.25N) | -12.90 | - 63.8 (0.10N) | + 6.36 (0.2N ‡) | - 70.2 |
| Ba(ClO ₄) ₂ | -237.50 (0.166N) | -28.94 | -192.8 (0.08N) | + 1.42 (0.126N *) | -194.3 |

* Smeets (*Natuurwetensch. Tijds.*, 1933, **15**, 105).

† Askew *et al.* (J., 1934, 1368).

‡ Berthelot (*loc. cit.*).

§ Latimer and Ahlberg (*J. Amer. Chem. Soc.*, 1930, **52**, 539).

isation (given in col. 3) are greater than those attained in the present work on the heat of solution of the heptoxide. Consideration of Berthelot's data for the heat of dilution of aqueous perchloric acid, however, shows that the correction is negligible.

The values used for the heats of formation of the aqueous hydroxides (col. 2) are those given by Bichowsky and Rossini ("Thermochemistry of Chemical Substances," 1936). Values for the heats of solution (ΔH_s) of the perchlorates, and the corresponding normality of the solutions, are given in col. 5.

The new value for equation (2) leads to a value of $\Delta H = + 0.2 \pm 1.7$ for equation (1), on the basis of $\Delta H_f\text{KCl} = - 104.2$ (Landolt-Börnstein). Despite its high limits of error, arising out of possible errors in equation (4), the new value is in good agreement with the result of Hofmann, who found for equation (1) $\Delta H = - 0.55$. This agreement justifies a reduction in the limits of error of equation (4) from ± 3 to ± 1.5 , giving to equation (7) and to the heats of formation of the perchlorates a limit of error of less than ± 1 .

Berthelot determined the heat of dilution of pure perchloric acid and obtained a value of $\Delta H = - 20$. This is not very reliable, however, for, as he remarks, "the experiments were difficult owing to the rapidity with which the acid attracted moisture during weighing, and the violence of the reaction with water when the experiment was carried out." The heat of formation of pure perchloric acid has not, therefore, been calculated here.

The authors are indebted to the Department of Scientific and Industrial Research for a grant in aid of this research.