244. *The Heat of Decomposition of Dichlorine Heptoxide.*

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A knowledge of the heats of decomposition of the oxides of chlorine is of great value in interpreting the processes of their thermal and photochemical decomposition. The heats of decomposition of chlorine monoxide and dioxide have been determined by a number of investigators but no value has been published for dichlorine heptoxide. That of the monoxide has been deduced both from its heat of solution in potassium iodide by Berthelot ("Thermochemische Messungen," Leipzig, 1893), Thomsen ("Thermochemistry," 1908), Neumann and Müller (*Z. anorg. Chem.*, 1929, **182**, 235), and from direct measurements of its heat of explosion by Mayer (Diss., Hanover, 1924), Gunther and Wekua (*Z. physikal. Chem.*, 1931, **154**, 193), and Wallace and Goodeve (*Trans. Faraday Soc.*, 1931, **27**, 648). The heat of decomposition of chlorine dioxide was first determined directly as the heat of explosion, by Booth and Bowen (J., 1925, **127**, 342), using a carbon dioxide–chlorine dioxide mixture, and by Wallace and Goodeve (*loc. cit.*), using the pure vapour.

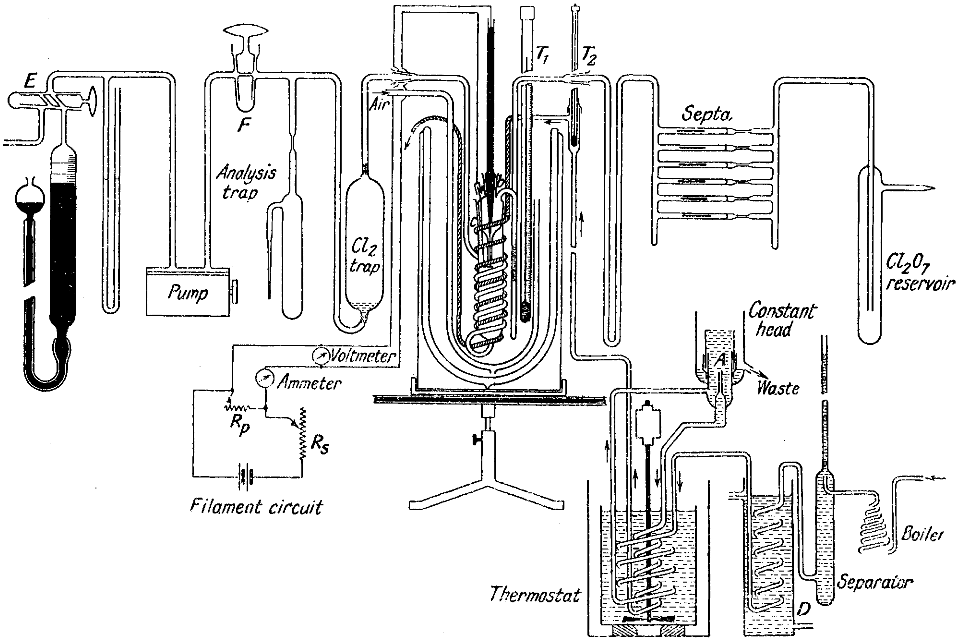
There is no convenient indirect method of measuring the heat of decomposition of chlorine heptoxide, and an indirect method has the disadvantage that experimental error is greatly magnified because the final result is obtained as a small difference between two large quantities.

In the method adopted, gaseous heptoxide was decomposed directly into its elements by streaming it continuously over a red-hot platinum filament. The decomposition could be carefully controlled to avoid lower oxides in the final products. This method has apparently not been used before for thermochemical determinations and may have wider application than that given here.

EXPERIMENTAL.

After a number of preliminary trials the final apparatus was constructed as shown in Fig. 1. The heptoxide from the reservoir passed to the decomposition chamber through a bank of septa, which took the place of a tap, and through a U-tube immersed in water to ensure that it was at the temperature of the calorimeter. The vapour was decomposed as it streamed through a fine jet, down the centre of which was the heated filament. The heat generated by this filament was compensated by means of a cooling coil of lead " Compo " tubing (shaded in the figure), through which flowed a steady stream of cold water. The chlorine resulting from the decomposition was frozen out in a liquid-air trap for subsequent analysis, and the oxygen collected in a graduated eudiometer tube.

FIG. 1.



The decomposition chamber was made entirely of Monax glass, and was connected to the rest of the apparatus (of soda glass) by two ground-glass joints. The chlorine heptoxide vapour entered through a U-tube in which was a 1·5-cm. length of fine sand fixed securely between two glass-wool plugs; this served to prevent the frequent explosions which occurred during the decomposition passing back to the heptoxide reservoir : when the length was reduced to about ¾ cm. an explosion did pass back to the reservoir. The jet was 1 mm. in bore and 2 cm long. The platinum filament (0·1 mm. in diameter and 2·5 cm. long) was connected between two thick platinum leads (1 mm. diameter) and was replaced when necessary by dissembling the apparatus at the ground-glass joints b and c. These joints were lubricated with graphite and a trace of metaphosphoric acid, and made vacuum-tight with picene wax. Several coatings of seccotine were applied to the picene owing to the solubility of the latter in the toluene, used for the calorimeter liquid. A pint-size Dewar vessel was used as a calorimeter, and stirring was effected by its rotation at constant speed (100 r.p.m.). Vertical stirring was assisted by an air pump, the air having been previously saturated with toluene at the temperature of the calorimeter. The Beckmann thermometer T_1 was read to 0·001° with a telescope. In order to prevent the mercury thread sticking, the thermometer was automatically shaken by an electromagnetic hammer, contacts being arranged on the turn-table. The shaking could be interrupted for readings by means of a tapping-key.

The chlorine trap contained a 3-mm. layer of fine sand to prevent crystals of chlorine being swept through by the oxygen stream. The sand was kept in place by a plug of glass-wool sintered into the base of the trap. A second plug sintered into the top of the trap prevented particles of sand from being blown back into the decomposition chamber on admission of air into the apparatus between experiments. The tap *F* did not come in contact with heptoxide and, therefore, graphite and metaphosphoric acid could be used as a lubricant.

The pump used was of the Gaede type, and was fitted with special gaskets of glue–glycerol composition to make it air-tight. There was a considerable volume of air above the oil in this pump, which consequently had to be turned on about an hour before an experiment was carried out in order to allow it to reach an equilibrium temperature.

The eudiometer tube was graduated in 0·2 c.c. and could be read to 0·1 c.c. A sulphuric acid differential manometer was connected to the eudiometer tube to facilitate the adjustment of the oxygen to atmospheric pressure.

Electrical Circuit for Platinum Filament.—When the apparatus was evacuated, a current of about 0·9 amp. and a potential drop of about 2 volts were sufficient to keep the filament at a bright-red heat, 800—900° (the temperature was calculated from the change of resistance). As soon as the decomposition commenced, however, the heat conducted away from the filament by the gases surrounding it was considerable, and the temperature of the filament fell to 400—500°. This fall in temperature was accompanied by a corresponding fall in the resistance of the filament, so that, if constant voltage was maintained, the wattage increased considerably. This difficulty was overcome by placing a resistance R_s in series with a 4-volt supply, and a further resistance R_p in parallel with the filament. By adjustment of R_s and R_p, the circuit could be so balanced that, when the temperature of the filament fell, the increased current was counteracted by a proportionate fall in the voltage across the filament. The values of R_s and R_p were approximately 1·5 and 20 ohms respectively. This circuit could not be perfectly adjusted, however, and readings of current and voltage had to be taken at minute intervals throughout the experiment. Standardised Weston instruments were used. By plotting the current–voltage product against the time, a correction could be applied for any slight increase or decrease of wattage.

Cooling System.—In order to ensure a steady flow of water at constant temperature through the compensating cooling coil, the water first had to be boiled to remove dissolved gases, its rate of flow controlled by a constant-head device, and its temperature thermostatically controlled just before it entered the cooling coil. Tap-water was boiled in a cone-shaped spiral of " Compo " tubing, whence it passed into the separator where the liberated gases were removed. It was then rapidly cooled to the temperature of tap-water in the vessel *D*. It now passed through the outer coil of " Compo " tubing in the thermostat, providing the necessary cooling effect for control of the latter at 13°. From this coil the water entered the constant-head device by the side-tube, the greater part of it going to waste while a constant stream passed on to the inner coil of the thermostat. Its rate of flow was roughly controlled by the narrow constriction, *A*, fine control being provided by variation of the head of water in the concentric tubes.

The thermostat consisted of a 4-litre beaker resting on an asbestos ring in a chromium-plated vessel, and the thermoregulator was made of 20 ft. of glass tubing coiled around the inside of the beaker and filled with xylene. No relay was used, a small heater in series with a 25-c. p. carbon-filament lamp being connected in parallel with the platinum contacts of the thermoregulator. The thermostat was filled with kerosene on account of its good insulating properties and low viscosity. A very fast stirrer was used.

The inner coil of the thermostat was connected to the cooling coil in the calorimeter by a short length of pressure tubing which was well lagged with asbestos-wool. The temperature of the water was observed just before it entered the cooling coil by means of the Beckmann thermometer T_2. Despite the thorough lagging of the pressure tubing, the temperature of the water was very sensitive to changes of room temperature, and consequently all experiments had to be conducted in a room the temperature of which (20°) was thermostatically controlled to within 0·1°. Calculations from heat-conductivity data showed that, at the rate of flow used (about 2 c.c./min.), the temperature of the water on leaving was equal to that of the calorimeter.

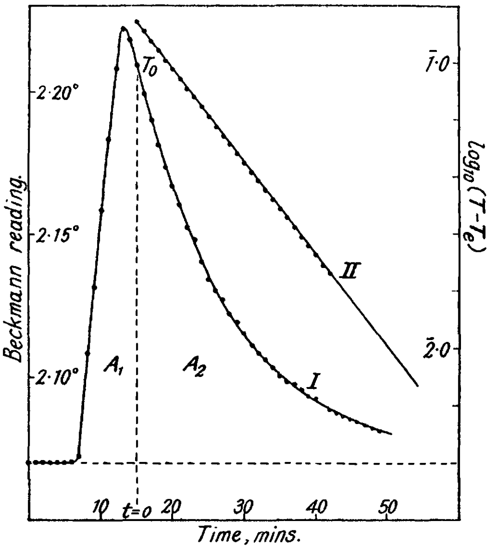
Procedure.—At the beginning of an experiment the apparatus was completely evacuated, the tap E being open to the atmosphere. Liquid air was placed round the chlorine heptoxide reservoir and on the chlorine trap, and a septum was broken. Care was taken before the experiment that the cooling system was completely free from air bubbles, these having a serious effect on the rate of flow of the water. The rotating calorimeter and its cooling system were then started. The cooling effect of the water being proportional to the difference between the temperatures of the calorimeter and cooling coil, an equilibrium temperature was reached where the cooling effect of the water was equal to the heating effect of the filament. After the preliminary experiments, the equilibrium temperature was known to within a few hundredths of a degree and could, therefore, be quickly attained by a temporary increase or decrease of the cooling effect.

As soon as equilibrium temperature had been reached, tap E was rotated, and the liquid air round the heptoxide reservoir was replaced by a water-bath at about 15° (equilibrium vapour pressure = 52 mm.). A higher reservoir temperature, causing a more rapid flow of heptoxide, resulted in only partial decomposition, and in some of the preliminary experiments a dark ring of dichlorine hexoxide was observed in the chlorine trap after the experiment. Readings of the temperatures of the calorimeter and cooling water, and of the current and voltage of the filament, were taken at minute intervals.

When sufficient heptoxide had been decomposed, the distillation was stopped by cooling the heptoxide reservoir to − 78° in carbon dioxide–alcohol for a minute and then to − 180° by liquid air. If the distillation was stopped by sudden cooling in liquid air, chlorine tended to diffuse back from the decomposition chamber, and resulted in a low chlorine analysis.

Readings were continued for a further 20 minutes, the cooling of the calorimeter being followed back almost to equilibrium temperature. At the end of an experiment, the broken septum was sealed off at the constriction, and the tap F closed. The chlorine was distilled into the analysis trap, sealed off, and subsequently determined by breaking the jet beneath potassium iodide solution and titrating the free iodine against $N/10$-sodium thiosulphate.

FIG. 2.



I. The temperature-time curve of the calorimeter for experiment B.5.
II. The corresponding $\log_{10}(T - T_e)$ curve.

The heat capacity of the calorimeter was determined electrically in the usual way, the filament being used as the heating resistance.

Theory of Method.—The temperature–time curves obtained by the above procedure were of the type shown in Fig. 2 (curve I). The temperature is dependent on the rate of heat production in the filament, the rate of removal of heat by the cooling water, and the heat produced by the decomposition of the heptoxide. The first is given by the equation

$$dq/dt = IV/4{\cdot}18, \text{ cals. per sec.} \qquad \ldots \ldots \ldots \quad (1)$$

where I is the current through the filament and V the potential across the leads. The cooling water on passing through the calorimeter is raised from T_w, its temperature just before entering, to T, the temperature of the calorimeter. " The cooling effect," *i.e.*, the heat removed from the calorimeter (per second), is proportional to the difference in temperature and is given by

$$dq/dt = -c_w(T - T_w)dm/dt \qquad \ldots \ldots \ldots \quad (2)$$

where c_w is the specific heat of water per gram, and dm/dt the rate of flow. Other heat effects, such as those from the stirrer or from conduction, were either constant or varied linearly with temperature and are included in equations (1) and (2).

In the absence of inconstant heating effects the temperature reaches an equilibrium value, T_e, given by the equation

$$dq/dt = IV/4{\cdot}18 - c_w(T_e - T_w)dm/dt = 0 \qquad \ldots \ldots \ldots \quad (3)$$

If now a quantity of heat, q_D, arising from a chemical reaction, is absorbed by the calorimeter, the temperature will rise, but as the cooling effect will also increase, it will finally be brought back to its equilibrium value as shown in Fig. 2. The quantity of heat, q_D, will then have been completely removed by the *extra* cooling effect occurring while the temperature is above the equilibrium value. This extra cooling effect is obtained by subtracting equation (3) from the generalised equation obtained by adding equations (1) and (2) :

$$dq/dt = -c_w(T - T_e)dm/dt \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

This, on integration, gives

$$q_D = -\int dq/dt = c_w dm/dt\int (T - T_e)dt = k\int (T - T_e)dt \quad . \; . \; . \; . \quad (5)$$

We thus have the heat absorbed by the calorimeter given in terms of a constant, $k = c_w(dm/dt)$, multiplied by the area under the curve.

The constant can be evaluated by making use of the equation $dq/dt = C \,.\, dT/dt$, where C is the heat capacity of the calorimeter. Equation (4) on rearrangement can be integrated for the cooling part of the curve, giving

$$\log\,(T - T_e) = -kt/C + \log\,(T_0 - T_e) \quad . \; . \; . \; . \; . \; . \quad (6)$$

where T_0 is the temperature at an arbitrary zero of time soon after the heating effect, due to the chemical reaction, has ceased. A plot of $\log_{10}\,(T - T_e)$ against t gives a straight line of slope $-k/2{\cdot}3C$ as shown in Fig. 2 (curve II). From an experimentally determined value of C and this slope, k is thus determined.

The area under the curve is divided into two sections A_1 and A_2, the division being effected at the time $t = 0$. As no simple equation fits the first part of the experimental curve, the area of section A_1 is determined by counting the squares on millimetre graph paper. The area of section A_2 is obtained from equation (6) by transformation into $T - T_e = (T_0 - T_e)e^{-kt/C}$ and integration :

$$A_2 = \int_0^\infty (T - T_e)dt = (T_0 - T_e)\int_0^\infty e^{-kt/C}\,.\,dt = (T_0 - T_e)C/k \quad . \; . \; . \quad (7)$$

On multiplying the total area $A_1 + A_2$, by k, the heat evolved by the chemical reaction is obtained. On dividing this by the fraction of a g.-mol. of heptoxide decomposed, the heat per g.-mol. is obtained. This is the value of ΔH, as the reaction is carried out at constant pressure. The temperature of the calorimeter was usually about 17°.

Results.—The results of 12 experiments on three separate preparations of heptoxide are given in the table. The values necessary for equation (5) are shown in cols. 2 and 3. The correction for changes in the wattage of the filament during the passage of the heptoxide gas is given in col. 4. This correction could be made to an accuracy of about 2% in the result. The values of ΔH calculated from both the oxygen and the chlorine analyses are given in cols. 7 and 8.

Expt. No.	Area under curve, ° C. secs.	$k \times 10$, cals./° C. sec.	$\Delta(IV)$ correction, cals.	Cl_2O_7 decomposed, millimols.		ΔH, kg.-cals./g.-mol.		Statistical weight.
				From O_2.	From Cl_2.	From O_2.	From Cl_2.	
A.1	225	1·61	−0·3	0·576	0·568	62·4	63·3	2
A.2	212	1·94	−1·4	0·579	—	68·6	—	1
A.4	119	2·30	−4·2	0·399	—	58·3	—	1
B.1	124	2·44	+0·6	0·433	0·430	71·3	71·9	3
B.2	—	—	+2·1	0·455	0·455	62·5	62·5	1
B.3	121	2·63	+1·8	0·538	0·538	62·8	62·8	4
B.4	153	1·71	−2·6	0·438	0·474	—	56·8	1
B.5	160	2·07	−2·2	0·493	0·481	62·7	64·4	2
C.1	245	1·38	−3·1	0·523	0·503	58·9	61·2	2
C.2	171	1·77	−0·6	0·506	0·511	—	59·0	3
C.3	167	1·79	0·0	0·458	0·472	—	65·9	2
C.4	136	1·84	−0·1	0·401	0·397	63·1	63·7	4

Weighted mean = 63·4

Owing to the necessary complexity of the apparatus, it was inevitable that the limits of error of the various experiments should differ considerably. The results have therefore been statistically weighted, as in the last column, on the following considerations. The calibration apparatus used for the first series was less accurate than that used for the second and third. The equilibrium temperature sometimes changed during the course of an experiment, due to permanent changes in the resistance of the filament, or to external influences. If such a change occurred during the cooling part of the experiment, the accuracy of the results was little affected; if, however, it occurred during the heating period, as in experiment B.2, results could only be obtained by an extrapolation method, leaving large limits of error. The chlorine analysis failed in experiments A.2 and A.4 for mechanical reasons, thus preventing confirmation of the complete decomposition of the heptoxide. Traces of chlorine dioxide were found in the products from experiments B.4, C.2, and C.3, but the small correction could be calculated from the difference between the oxygen and chlorine analyses and the heat of decomposition of the dioxide.

It will be seen from the theoretical treatment that the temperature of the incoming cooling water need not be known, but must, of course, be constant. The variation of the filament and capillary temperatures during the passage of the gas produces no error, as their temperatures at the time $t = 0$ have returned to their initial values. At all events, the heat capacity of these parts is negligible.

The weighted mean for the heat of decomposition has been found to be 63·4 kg.-cals. per g.-mol. of dichlorine heptoxide with a probable error of 5% or ± 3 kg.-cals.

SUMMARY.

A new calorimetric technique for the study of gaseous reactions which take place only at high temperatures has been developed and applied to a study of the heat of decomposition of dichlorine heptoxide. The value of ΔH_{17° for the reaction $Cl_2O_7 \longrightarrow Cl_2 + 3\frac{1}{2}O_2$ has been found to be — 63·4 ± 3 kg.-cals.

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

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[*Received, May* 25*th*, 1937.]