

558. An All-glass Calorimeter, and the Heat of Combustion of Ethyl Chloride.

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An all-glass calorimeter is described, suitable for determination of the heats of combustion of gases containing halogens. The heat of combustion of ethyl chloride vapour was determined as 341 ± 2.5 kcals./g.-mol. at 20° .

THE work described below was started because engineering calculations required a value of the heat of combustion of ethyl chloride accurate to about 2 kcals./g.-mol. The first attempts at measurement were made with a bomb calorimeter, the ethyl chloride being sealed under low pressure into containers made first of glass and later of Polythene. These experiments were terminated when corrosion of the bomb by hydrochloric acid was observed. Trials were then made with a combustion calorimeter, but ignition was difficult and combustion incomplete, and on one occasion a gas explosion occurred. It was then decided to design an all-glass calorimeter for further measurements.

EXPERIMENTAL.

All-glass Calorimeter.—The principle adopted was to burn the gas in a stream of air or oxygen and bubble the products directly through water in the calorimeter. The apparatus is illustrated in the figure. The calorimeter vessel of glass was separated from a copper jacket by a 1-cm. air gap, and the whole was immersed in a thermostat at 20° . All gases were brought to 20° before being introduced into the calorimeter.

Gas to be burnt was displaced from the storage vessel by a steady stream of mercury, and passed through capillary tubing to a hard-glass combustion jet. Air or oxygen for combustion was drawn through the apparatus by suction and was introduced saturated with water at 20° at a steady rate observed on a flowmeter between the calorimeter and the pump. Attempts to employ spark ignition were unsuccessful and a platinum-wire spiral was used, the energy dissipated being kept independent of the temperature of the wire to a first approximation, by electrical heating from accumulators, with a total circuit resistance equal to twice that of the spiral.

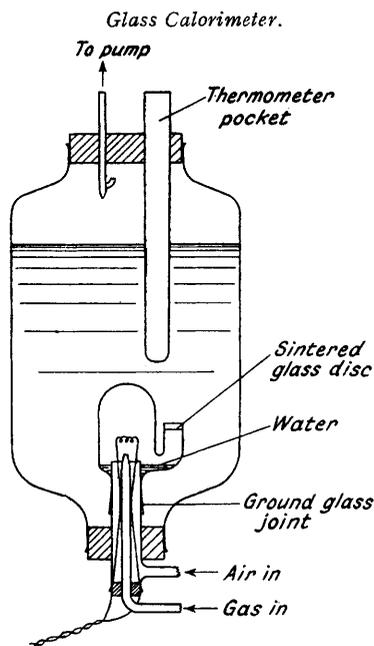
The combustion chamber had a short vertical side arm, closed at the top by a sintered glass disc. Ingress of the water in which the chamber was immersed was prevented by coating the sintered glass lightly with Apiezon M grease from benzene solution. The bottom of the combustion chamber was shaped to hold about 5 c.c. of water, and in practice about 2 c.c. were introduced before the beginning of any combustion involving chlorides so as to ensure adequate dilution of any aqueous hydrochloric acid condensate.

Temperatures were measured in early experiments with a Beckmann thermometer to $\pm 0.001^\circ$ and later to a higher accuracy with a platinum resistance thermometer and a Smith difference bridge. Temperature rises were derived graphically in the usual way and were of the order of 1° . Calibration was effected by burning known volumes (about 160 c.c.) of pure hydrogen, prepared from pure zinc and hydrochloric acid and washed and dried before use. The calorimeter held about 500 c.c. of water, the total water equivalent after filling being about 600 g.

In calculation of the results, the major allowance necessary is for the heat set free in the platinum spiral, which was kept hot during all combustion. This allowance was determined separately for each experiment. It accounted for nearly 30% of the observed temperature rises in most experiments but did not constitute a source of error as it could be measured accurately. A correction was made for the gas which remained unburnt in the capillary connection between the reservoir and the jet, and a further small correction was also made for the water vapour condensed from the oxygen used in combustion of hydrogen.

Difficulty was sometimes experienced in maintaining combustion of gases containing halogens, even after dilution with hydrogen. This was cured empirically when necessary by adjusting the jet size and gas velocity. Under the conditions described above and in the latter portion of this paper, the accuracy achieved in the measurement of heat liberated was considered to be approximately $\pm 0.5\%$.

Heat of Combustion of Ethyl Chloride.—To ensure adequate combustion without liberation of free halogen, ethyl chloride was burnt as a dry mixture containing 90% by volume of hydrogen. The



proportions of gases needed were measured by volume, the ethyl chloride used having been purified by repeated distillation, and the hydrogen having been prepared from zinc and hydrochloric acid.

The procedure adopted was the following. The calorimeter was set up, air flow was adjusted, and conditions were allowed to become stable. From then on temperature readings were taken at suitable regular intervals, usually of 1 minute. First the correction due to the ignition coil was determined by passing the current for a known period. Then the calorimeter was standardised by burning a known volume of hydrogen, the ignition coil being kept hot for a known period, longer than the actual combustion. The hydrogen and ethyl chloride were then burnt in a similar manner. It was then usual to repeat the standardisation with hydrogen and the determination of the correction due to the ignition coil.

The gases from the combustion were tested for carbon monoxide, and the water in the calorimeter was tested for hypochlorite, but in no case was a positive result obtained.

The following data for a single run illustrate the results obtained and the method of calculation :

Vol. of hydrogen for standardisation	158 ml. at 16°/781 mm.
Mixture for combustion { ethyl chloride	16.2 ml. "
{ hydrogen	138.8 ml. "

(The above volumes are corrected for gas unburnt in the leads.)

Standardisation of calorimeter :

- (1) Temp. rise 1.176°; duration of heating of ignition coil 140 sec.
 (2) " " 1.249°; " " " " 165 sec.

Heating effect of ignition coil 0.174°/min.

Combustion of ethyl chloride-hydrogen mixture :

Temp. rise 1.480°; duration of heating of ignition coil 135 sec.

Temp. rise, corr. for heating of ignition coil :

Hydrogen (1) 0.770°, (2) 0.771°.

Mixture 1.088°.

The heat of combustion of hydrogen was taken to be 68.38 kcals./g.-mol.

Heat evolved by combustion of hydrogen for standardisation	= 468.2 cal.
Heat evolved by combustion of mixture	= 661.6 "
Heat evolved by combustion of hydrogen in mixture	= 411.0 "
Heat of combustion of 0.0470 g. of ethyl chloride	= 250.6 "
Heat of combustion of ethyl chloride	= 343 kcals./g.-mol.

The correction for moisture condensed from oxygen used in combustion amounts to less than 0.1% and has therefore been neglected.

The results obtained are given in the table. The mean value of the heat of combustion of ethyl chloride obtained was 341 kcals./g.-mol. and, on the assumption that there is no systematic error, this has a 95% probability of being within ± 2.5 of the true value. This figure relates to gaseous ethyl

Heat of combustion of ethyl chloride.

Expt. no. :	I	II	III	IV
Corrected temperature rises :				
(i) hydrogen, 1	0.774°	0.770°	0.769°	0.880°
(ii) hydrogen, 2	0.774°	0.771°	—	0.869°
(iii) ethyl chloride mixture	1.086°	1.088°	1.215°	1.197°
Heat of combustion of hydrogen used, cal.	470.1	468.2	470.7	448.7
Heat given by combustion of mixture, cal.	660	662	744	614
Portion due to hydrogen	412	411	394	398
Portion due to ethyl chloride	248	251	350	216
Mass of ethyl chloride combusted, g.	0.0472	0.0470	0.0660	0.0409
Heat of combustion of ethyl chloride, kcals./g.-mol.	338	343	342	341

chloride at 20° with products of combustion carbon dioxide (g.), hydrochloric acid (dil. aq.), and liquid water. The corresponding heat of formation of the gas is 24 kcals./g.-mol., if the heat of formation of carbon dioxide is assumed to be 94.38 kcals./g.-mol. and that of dilute aqueous hydrochloric acid 39.46 kcals./g.-mol.

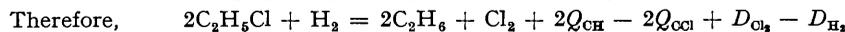
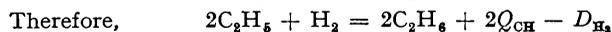
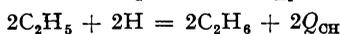
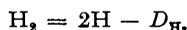
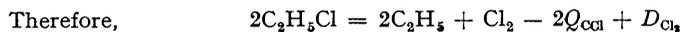
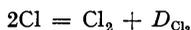
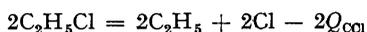
DISCUSSION.

The following figures have been converted when necessary to gaseous ethyl chloride at 20°, the products of combustion being gaseous carbon dioxide, dilute aqueous hydrochloric acid, and liquid water.

Berthelot ("Essai de Mécanique Chimique," Dunos, Paris, 1879, p. 107) and Thomsen

("Thermochemistry," Longmans Green, 1908, p. 370) measured the heat of combustion of ethyl chloride directly and obtained values of 334 and 326 kcal./g.-mol. respectively. Rudkowski, Trifel, and Frost (*Ukrain. Chem. J.*, 1935, **10**, 277) studied the equilibrium $C_2H_4 + HCl \rightleftharpoons C_2H_5Cl$ in the temperature range 170—230° and their values for the equilibrium constant give a mean heat of reaction in this temperature range of 13.4 kcal. This was converted to 20° by means of known specific-heat data and used in conjunction with the heat of formation of ethylene given by Rossini and Prosen (*J. Res. Nat. Bur. Stand.*, 1946, **36**, 269). The heat of combustion of ethyl chloride thus determined was 342 kcal./g.-mol.

Less direct estimates of the heat of combustion of ethyl chloride may be obtained from bond-energy data. The energy of the C-Cl bond is, for example, often derived from results with compounds such as methyl chloride containing a single C-Cl bond and these values may be used directly, provided that care is taken to avoid confusion owing to the assumption of different heats of sublimation of graphite (Long and Norrish, *Proc. Roy. Soc.*, 1946, *A*, **187**, 337). In order to limit errors as far as possible, the heat of formation of ethane given by Bichowsky and Rossini ("The Thermochemistry of Chemical Substances," Rheinhold, 1936) has been adopted (21 kcal./g.-mol.), so that only the difference in the energies of the C-Cl and C-H bonds needs to be used, together with the heats of dissociation of hydrogen and chlorine. The following scheme represents the method, bond energies being represented by Q and dissociation energies by D .



The heat of formation thus deduced may be converted into the heat of combustion in the usual way. The heats of dissociation of chlorine and hydrogen were taken as 57.4 and 100.8 respectively.

Pauling ("Nature of the Chemical Bond," Cornell, 2nd Edn., 1944, p. 53) gives the mean energies of the C-Cl and C-H bonds as 66.5 and 87.3 kcal. respectively, from which the heat of combustion may be calculated as 343 kcal./g.-mol. (a complete summation of the molecules using Pauling's values for bond energies and dissociation energies gives 339 kcal./g.-mol.). A further approach is possible along the lines indicated by Barton and Howlett (*J.*, 1949, 155). The heat of addition of chlorine to ethylene at 355° K. has been determined as 43.7 kcal. by Conn, Kistiakowsky, and Smith (*J. Amer. Chem. Soc.*, 1938, **60**, 2764), corresponding to 43.9 kcal. at 20°. The heat of hydrogenation of ethylene has been measured by Conant and Kistiakowsky (*Chem. Reviews*, 1937, **20**, 181) as 32.8 kcal./g.-mol. The corresponding difference between the energies of the C-Cl and C-H bonds is 16.2 kcal., the above heats of dissociation being assumed, and this leads to a heat of combustion of ethyl chloride of 338 kcal./g.-mol. A direct deduction from the figures given by Bichowsky and Rossini (*op. cit.*) for methane, methyl chloride, and ethane gives a heat of combustion for ethyl chloride of 342 kcal./g.-mol.

The results of the present work do not agree with the earlier direct measurements by Berthelot and Thomsen, but do agree with the work of Rudkowski, Trifel, and Frost on the equilibrium between ethylene and gaseous hydrogen chloride. The agreement with the mean bond energies deduced by Pauling is also satisfactory, although these may not in fact have been deduced from compounds of type relevant to the present work. The agreement between the methyl and the ethyl system is also satisfactory.

It is interesting to note that the heat of combustion of ethyl chloride determined in this work differs somewhat from that deduced above from the heats of hydrogenation and chlorination of ethylene. Conn, Kistiakowsky, and Smith (*loc. cit.*) have discussed this in a different way, by calculating from their data the heat of hydrochlorination of ethylene. They deduce 15.9 kcal. at 25°, whereas they calculate 14.6 kcal. from the heat of formation of ethyl chloride, quoted by Bichowsky and Rossini (*op. cit.*) as 25.7 kcal./g.-mol. (the origin of this figure is not stated by Bichowsky and Rossini, and a literature search failed to reveal determinations other than those given above). By use of the present value for the heat of formation of ethyl chloride,

the heat of hydrochlorination is calculated to be 13 kcals., other thermochemical data used being unchanged. The energy of the C-Cl bond in ethyl chloride is thus about 3 kcals. less than the mean C-Cl bond energy in ethylene dichloride, a rather unexpected result which suggests that the configuration of the latter compound is rather more favourable to stability than is that of the former. The difference is, however, on the borderline of experimental accuracy.

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