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Heats of Combustion of Organic Chloro Compounds Determined by the "Quartz Wool" Method

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A determination of the heats of combustion in the calorimetric bomb of compounds containing chlorine is difficult, owing to the fact that a mixture of free chlorine and hydrogen chloride is formed during the combustion. Thus the final state is not defined. Berthelot and Matignon [1] proposed to place a solution of arsenious acid in the bomb (that is to say on its bottom), in order to reduce the formed chlorine to hydrogen chloride. This method, however, has proved to be unsatisfactory [2,3]. The surface of the arsenious solution has to be enlarged. For this purpose the inside of the bomb must be covered with some material [4] moistened with the arsenious solution.

Quartz fibers proved to be satisfactory. A string of loosely joined fibers is wound in a spiral on the upper part of the inside of the bomb. The weight of the spiral is 4 g and it retains about 4 ml of the arsenious solution, the total quantity of which is 20 ml. The total surface, covered by the string of quartz threads and its interspaces, amounts to 50—60 % of the interior surface of the bomb. The spiral can easily be put in its place. The unpractised investigator might perhaps at first moisten the fibers with water, which is afterwards evaporated in a heating box.**

The effect of the quartz spiral moistened with arsenious solution is twofold. On one hand the process of reduction is promoted. At the end of the main period — in this paper always 5 minutes after the ignition — no traces of

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* Further particulars about the collaboration on p. 67 and p. 78. D. Folkesson was my calculating assistant (p. 82).

** The name "quartz wool method" is misleading, for it is quite impossible to wind *wool* of quartz to a durable spiral.

chlorine can be detected in the gases from the combustion. On the other hand the total amount of free chlorine formed is also diminished, which is certainly due to the fact, that the moistened spiral delivers water vapor to the combustion zone, thus affecting the equilibrium [3]:

$$2\ H_2O + 2\ Cl_2 \rightleftharpoons 4\ HCl + O_2$$

By the aid of the quartz spiral method the heats of combustion of more than 130 organic chloro compounds were determined in the Department of Organic Chemistry of the University of Lund *. Most of these values were published in 3 dissertations for the degree of doctor of philosophy, namely by E. Schjånberg [4] 1934, E. Eftring [5] 1938 and K. J. Karlsson [6] 1941. Some determinations were made by others, especially by Smith and collaborators and by G. Sjöström [7] 1936.

The principal features of the quartz wool method have been described by Schjånberg [12]. Here I have reason to remind of the following details. The heat equivalent was determined in the presence of the spiral, moistened with arsenious solution (0.35 *N*, 20.0 ml). Mean error of the mean values of the heat equivalent ± 0.01 %. The bomb was lined with platinum; its volume was 280 ml. Between crucible and shield about 3 cm. Oxygen pressure 25 atm. Total heat evolved 5 000 cal. Average total rise of temperature 1.7°. Room at constant temperature, generally 20.0°, in a few cases 18.3° or 18.5°.

Schjånberg and Karlsson burned liquid compounds of relatively low volatility in open crucible with a cellophane cover, a method recommended by W. A. Roth, while Eftring — in a few cases also Schjånberg and Karlsson — for this purpose used glass ampoules, whose necks were sealed with a drop of paraffin oil.

The authors in question applied the following corrections: for paraffin oil, used as auxiliary substance, for cellophane, for the oxidation of arsenious acid (10—14 cal), for dissolved platinum and gold (1—3 cal).

The accuracy arrived at in the combustion of chloro compounds is dependent on their content of chlorine, since on one hand the necessary percentage quantity of paraffin oil rises with the chlorine content, on the other hand an increased chlorine content in a compound diminishes its heat of combustion. In the combustion of carbontetrachloride *e.g.* this compound contributes about 4 % to the total evolution of heat, in the combustion of amylchloride more than 50 %. Of course the carbontetrachloride represents an extreme case. From some figures of Schjånberg I have calculated that the mean error of a combustion rises from ± 0.01 % at 20 % of chlorine to 0.1 % at 65 %. As for the accuracy of the determination of the heat equivalent see above.

The heats of combustion of chloro compounds can also be determined by another method. The final communication on the quartz wool method was published in 1931. Two years later Popoff and Shirokich [9] described such combustions in a swinging bomb, driven by a wire; the construction of the driving device was not given. Later on we

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* (19 iodo compounds were also burned in Lund; Karlsson in his dissertation.)

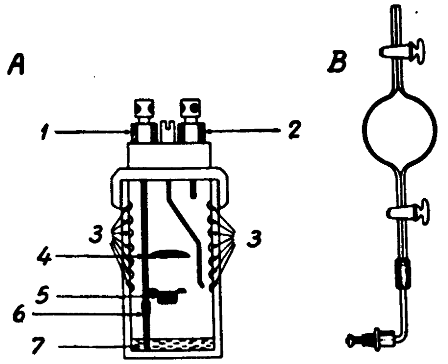

Fig. 1. A. The bomb adapted for the taking of a sample. 1) outlet valve for sample, 2) inlet valve for oxygen, 3) quartz wool coil, 4) shield, 5) platinum crucible, 6) tube extension, 7) arsenious oxide solution. B. the bulb with two stopcocks.

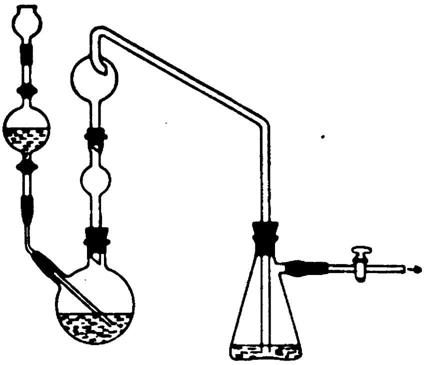

Fig. 2. The apparatus for determination of carbon dioxide.

started experiments with swinging as well as with rotating bombs [10,11] and attained by that means about the same reproducibility and the same values of combustion as with the stationary bomb.

I. FURTHER CORRECTIONS ON THE HEATS OF COMBUSTION *

As reported in a previous paper [8], the values of the above mentioned authors are not entirely correct, inasmuch as Washburn corrections have not been applied, among which the heat of solution of dissolved carbon dioxide in this case is the most important. Furthermore a correction must be applied for the heat, accompanying the dilution of the different solutions of hydrochloric acid, formed during the combustion, to a uniform final concentration.

These two corrections can not be *calculated* directly from the values communicated by the authors. Special experimental investigations were necessary for this purpose. After this the principal part of the remaining Washburn corrections may be calculated from his formulas by anyone, who has available the dissertations referred ta above **. Concerning the magnitude of these Washburn corrections see p. 80.

The determinations of the two first mentioned corrections are described below.

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* In collaboration with Sven Krook, and Henrik Westermark.

** Data necessary for these calculations are also given in the Tables 6—9 of this paper.

1. Determination of dissolved carbon dioxide. This determination must be made in the bomb solutions at the termination of the main period (5 min.) without diminishing the oxygen pressure, *i.e.* without opening the bomb previously. An approximative knowledge of the concentration of carbon dioxide after the final period (10 min.) is likewise necessary.

For this purpose we made combustions with varying quantities of carbon (paraffin oil) and with varying concentrations of hydrochloric acid (0; 0.2; 0.4 N) in the 0.35 N arsenious acid. During the combustion the bomb was immersed in a thermostat, kept at 19.0 °. As described below a sample was taken of the solution on the bottom, where about 80 % of the whole bomb liquid is to be found, and analysed. Samples were taken after 5 as well as after 10 min.

Fig. 1 A represents a schematic drawing of the bomb, adapted for our analyses. As the figure shows, the inlet tube is extended to the bottom of the bomb for this purpose. A sample of the solution on the bottom is forced by the interior pressure through a silver tube, serving as connecting joint (see Fig. 1 B), into an evacuated bulb, fitted with two gastight stopcocks. The bulb is then transferred to and connected with the distillation apparatus, shown in Fig. 2. The determination of the carbon dioxide dissolved in the sample was carried out according to Vesterberg's vacuum method [13]. The correctness of our analyses were checked by special tests. The total quantity of carbon dioxide, dissolved in other parts of the solution, was calculated by an indirect method.

After a combustion in the presence of the moistened quartz string the bomb is brought into horizontal position and slowly turned around (two rotations in one minute was deemed adequate) while swinging the bomb slightly. Hereby the differences in concentrations are equalized, and an analysis of a sample from the layer on the bottom, after the bomb is brought into vertical position, will give an average concentration of the total amount of carbon dioxide *now* dissolved.

The motion of the solution in contact with the gaseous phase brings about an increase of the concentration in the water layer, which is not yet saturated with carbon dioxide. This increase was approximately determined in the following way. We analysed the bottom layer after two combustions with *dry* quartz string (all the solution on the bottom), the first time without turning the bomb, the second turning it. — These two combustions were identical in other respects. — The difference between these two determinations will give the "rotation-increase" per g substance in the content of carbon dioxide in the solution. The subtraction of this quantity from the above mentioned total amount of carbon dioxide per g, and the multiplication by the weight of the bomb solution give the *total quantity of dissolved carbon dioxide in an ordinary combustion — in a first approximation.* For a more accurate calculation of this quantity we had also to apply two further small corrections, the determinations of which, however, may be omitted here.

Concerning our determinations of dissolved carbon dioxide I will also mention that every rotation experiment was made twice, and that it was possible to attain an accuracy of 1—3 % in the average value of parallel determinations. It will be seen from what precedes that every value of a total concentration of carbon dioxide is the result of 8 combustions, all of them with the same quantity of paraffin oil: dry quartz string, bomb turned and not turned respectively, moistened quartz with the same two alternatives and then parallel experiments. One of these last ones ("bomb not turned") served as a control.

All the concentrations *after 10 minutes* were determined in this way (Table 1).

Table 1.

Milliatoms of carbon burned	Dissolved carbon dioxide in mg. 20 ml of arsenious solutions with hydrochloric acid of the following concentrations		
	I 0.0 *N*	II 0.2 *N*	III 0.4 *N*
24.8	—	34.5	33.9
31.1	41.1	39.6	39.0
41.4	52.3	50.6	48.3
50.0	58.7		

The dissolved quantity diminishes with increasing acidity of the solutions. The decrease, however, is very small and of no importance: 1 mg carbon dioxide corresponds to only 0.1 cal. In Fig. 3 the curves for the relation between the values of the table and milliatoms of carbon burned are given. As a result of a miscalculation, discovered too late, the point for 50 milliatoms was determined only for solution I. The approximate positions for solutions II and III were found by extrapolation, as it appears from the diagram. Nevertheless this manner of proceeding may be considered satisfactory, since these "10-minutes" values are not used for the corrections of the heats of combustion, but only for the estimation of the heats of solution during the final period. It is desirable to know these values approximately because these heats may represent a systematic, though small error.

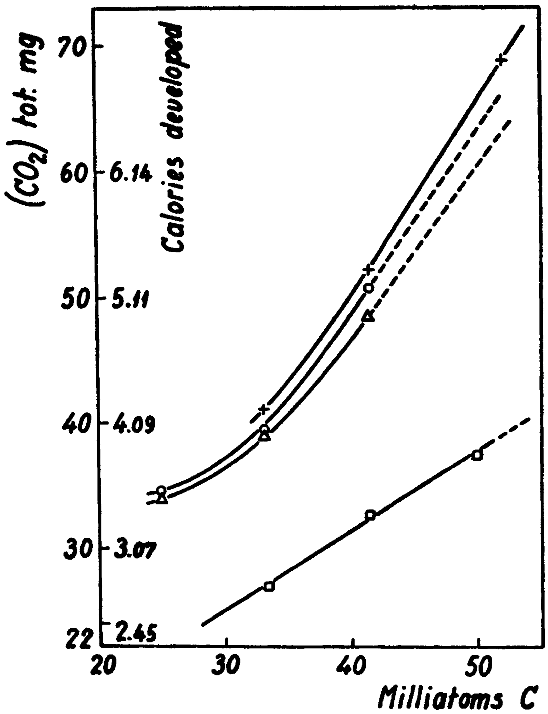

Fig. 3. Correction for dissolved carbon dioxide. CO_2 dissolved after 10 min. in solution I × ×, II ○—○, III △—△. CO_2 dissolved after 5 min., mean values □—□.

The procedure just described is circumstantial and suffers besides from an uncertainty. Since the turning of the bomb must be started one minute before the sample is to be taken, the state in the interior is not the same at this last moment as at the beginning of the rotation. At the end of the final period this uncertainty in the definition of the time must be of less importance than after the end of the main period, when the convective movements of the gases have just ceased. Hence we chose another way of proceeding for the end of the main period. For its description we need the following notations:

$[CO_2]_{tot}$ = total quantity (mg) of carbon dioxide dissolved
$[CO_2]_b$ = concentration (mg/g) of the carbon dioxide in the bottom layer (moistened spiral, without rotation)
$[CO_2]_{sp}$ = average concentration (mg/g) of carbon dioxide in the spiral and other places in the bomb than the bottom
g_{tot} = weight of the total solution, including water formed by the combustion
g_b = weight of the solution on the bottom.

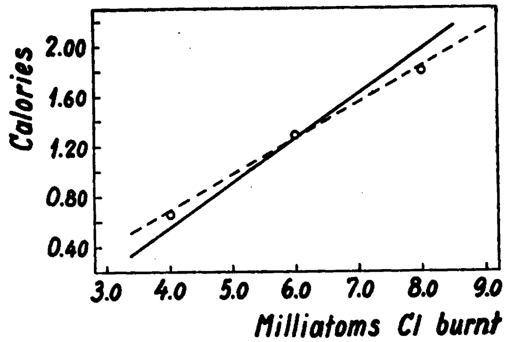

Fig. 4. Correction for HCl-dilution. (Corr$_{HCl}$). — — — *5 minutes,* ——— *10 minutes.*

Then we have:

$$[CO_2]_{tot} = g_b \cdot [CO_2]_b + (g_{tot} - g_b) \cdot [CO_2]_{sp} \qquad (1)$$

Knowing $[CO_2]_{tot}$ one can calculate $[CO_2]_{sp}$ from equation (1). We determined in the manner above described $[CO_2]_{tot}$ at 10 min and found for $[CO_2]_{sp}$ an average value of 2.2, nearly independent of the amount of carbon dioxide (we used solution II). At 6 min the value 2.0 ± 0.2 was found. The uncertainty in these determinations is of less importance, however, owing to the fact that the quantity g_b is about 4 times greater than $(g_{tot} - g_b)$. Hence we considered the value 2.2 valid also for 5-minute analyses, determined $[CO_2]_b$ (moistened spiral, without rotation) at this moment and then used equation (1). The results are found in Table 2.

Contrary to Table 1 this table shows no decided diminishing of the amount of dissolved carbon dioxide with increasing acidity of the solutions. Hence it is justified to take mean values. The connexion between these and the quantities of burned carbon is found in Fig. 3 (the lower curve). Evidently

Table 2.

Milliatoms of carbon burned	Dissolved carbon dioxide in mg. 20 ml of arsenious solutions with hydrochloric acid of the following concentrations			
	I 0.0 *N*	II 0.2 *N*	III 0.4 *N*	Mean values
33.2	26.5	28.8	25.6	27.0
41.4	32.3	33.3	32.0	32.5
49.7	38.6	37.6	35.9	37.4

the best representation is a straight line. The total amount of dissolved carbon dioxide (in mg) can be calculated by aid of the equation:

$$[CO_2]_{tot} = 0{,}632 \cdot n_C + 0{,}620 \qquad (2)$$

n_C here denotes milliatoms of carbon burned. The dissolution of 1 millimole of carbon dioxide gives a heat of 4.5 cal. In Fig. 3 the corresponding heats are also indicated *.

2. *Determination of the different concentrations of hydrogen chloride.* The hydrogen chloride formed by the combustion is mainly deposited in the quartz spiral and its interspaces, partly in other places in the bomb: in the bottom solution, on walls and cover. On the shield only very small quantities can be found. Eftring[5] examined for the first time the concentrations in these places, and calculated that a dilution of them to a common concentration would cause an appreciable production of heat: up to 3 cal for one combustion. Eftrings examination was nevertheless a little superficial and limited to two combustions.

We burned chloro compounds in quantities containing 4, 6, and 8 milliatoms of chlorine, using monochloroacetic acid, *p*-dichlorobenzene and chloral hydrate, and used paraffin oil as the auxiliary substance. The bomb was opened after 5, and 10 min. respectively as before. Even in the first case we found only small traces of hydrogen chloride in the gasphase, although the smell of this compound was easily detected.

After the opening of the bomb the quartz string was removed and washed with hot water on a suction filter. In the filtrate the chlorine was determined. The condensed liquids on cover, the lower part of the wall and under the quartz spiral (after its removing) were absorbed separately by filter paper, immediately weighed on a torsion balance and analysed. The solution on the bottom was also weighed and analysed, but we calculated the amount of water in the quartz spiral as a difference, taking into consideration also the water formed by the combustion. The concentrations of the acid under the spiral and in it are almost the same. Accordingly they are dealt with together.

The hydrogen chloride, formed by the combustion of the above mentioned quantities of chloro compounds, forms in a 20.0 ml solution as final state 0.2 *N*; 0.3 *N* and 0.4 *N* hydrochloric acid, having the molar ratios $HCl : H_2O = 1 : 282$; $1 : 188$ and $1 : 141$. The corrections in the Tables 3 and 4 are calculated on the assumption that the different solutions of hydrogen chloride found after the combustion are diluted to these molar proportions.

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* As in all papers from Lund dealing with heats of combustion of chloro compounds, developed heat is considered positive; also here.

Table 3. Correction for HCl-dilutions.

Figures for *p*-dichlorobenzene; parallel experiments nos. 1 and 2. The figures refer to the end of the main period. The heats of dilution were taken from "selected values" of Bureau of Standards and are calculated for dilution to the molar proportion 1 : 188, see above.

Exp. no. 1: $C_6H_4Cl_2$, 441.2 mg, paraffin oil 305.4 mg
» » 2: » 442.0 » » » 431.0 »

	Cover		Wall		Quartz-spiral		Bottom layer		HCl total[2]	
No.	Sol. mg	HCl mmoles	Sol. mg	HCl mmoles	Sol. g[1]	HCl mmoles	Sol. g	HCl mmoles	mmoles found	mmoles calc.
1	135	0.50	102	0.25		4.79	15.36	0.39	5.94	6.00
2	116	0.41	211	0.33		4.73	15.71	0.40	5.89	6.00
	Water mg	Corr cal	Water mg	Corr cal	Water g[1]	Corr cal	Water g	Corr cal	Total cal	mean
1	117	0.43	93	0.14	5.2	0.81	15.06	−0.06	1.32	1.28
2	101	0.34	199	0.11	4.9	0.85	15.40	−0.06	1.24	

[1] Calculated (see above)

[2] The correction for the solution in crucible and on shield is very small and for that reason neglected.

In Table 4 there is given the thermal effect (in cal) accompanying the change in concentrations of the hydrochloric acid, as it is formed in the bomb, to a uniform concentration in 20.0 ml solution.

Table 4.

milliatoms Cl in comp.		4	6	8
corr. after	5 min	0.67	1.28	1.81
	10 »	0.58	1.26	1.98
for dilution to		0.2—	0.3—	0.4—*N*

All the figures are mean values of two experiments. The deviation from the mean in the 5 min. experiments is ± 0.03—0.07 and in the 10 min. series is somewhat more. The differences between calculated milliatoms chlorine 4, 6, and 8 in the compounds and amount of hydrochloric acid found (see

Table 3) in the bomb solutions are very small: the largest difference observed is the one in Table 3.

Table 4 shows that the total corrections after the lapse of 5 and 10 min. are almost equal, which evidently is a result of the rate at which gaseous HCl goes into solution. It also follows from the table that the total correction is nearly proportional to the chlorine content of the compound burned. The very good agreement between the parallel experiments is perhaps somewhat astonishing in consideration of the fact that the concentrations of the solutions of hydrochloric acid in a definite part of the bomb (cover, wall, quartz spiral etc.) are not always easy to reproduce, *i.e.* often differ more in parallel experiments than the sum of all the corrections.

The relation between correction ($\mathrm{corr}_{\mathrm{HCl}}$) and milliatoms of chlorine in the compound (n_{Cl}) is given, as Fig. 4 shows, by straight lines represented by the following equations:

$$\text{at 5 min:}\quad \mathrm{corr}_{\mathrm{HCl}} = 0.29\ n_{\mathrm{Cl}} - 0.46\ \text{(cal)} \tag{3}$$

$$\text{at 10 min:}\quad \mathrm{corr}_{\mathrm{HCl}} = 0.36\ n_{\mathrm{Cl}} - 0.88\ \text{(cal)} \tag{4}$$

3. *Formulas for the calculation of the corrections for the dissolved carbon dioxide.* The calculation is of an elementary sort, but I think that the somewhat complicated formulas may be convenient for readers, who wish to check the following corrections. It should be observed that heat evolved is always considered positive, (see note on page 72).

The following notations are used. The unit for heat is calory.

E and E_{corr}	heat equivalent of the calorimeter, uncorr. and corr. respectively.
Q, Q_{b}, Q_{p}, Q_{cell}	heat of combustion of substance, benzoic acid, paraffin oil and cellophane.
Q_{corr}, $Q_{\mathrm{b\ corr}}$, $Q_{\mathrm{p\ corr}}$, $Q_{\mathrm{cell\ corr}}$	the same heats corr.
g, g_{b}, g_{p}, g_{cell}	weights of substance, benzoic acid etc.
Δt, Δt_{b}, Δt_{p}, Δt_{cell}	rise of temperature in combustion of substance, benzoic acid etc.
n, n_{b}, n_{p}, n_{cell}	millimoles of dissolved carbon dioxide in the combustion of substance etc.
w_{sol}	heat of solution of carbon dioxide (per millimole).
q	sum of other small amounts of heat evolved during a combustion.
corr, corr_E, $\mathrm{corr}_{\mathrm{p}}$, $\mathrm{corr}_{\mathrm{cell}}$	these quantities are defined in equations 7, 10, 11, and 13.

a. Correction for the heat equivalent.

$$E\Delta t_{\mathrm{b}} = g_{\mathrm{b}}Q_{\mathrm{b}} + q \tag{5}$$

$$E_{\mathrm{corr}}\Delta t_{\mathrm{b}} = g_{\mathrm{b}}Q_{\mathrm{b}} + n_{\mathrm{b}}w_{\mathrm{sol}} + q \tag{6}$$

$$E_{\mathrm{corr}} - E = \frac{n_{\mathrm{b}}w_{\mathrm{sol}}}{t\Delta_{\mathrm{b}}} = \mathrm{corr}_E \tag{7}$$

b. Correction for the heat of combustion of paraffin oil.

$$E\Delta t_{\mathrm{p}} = g_{\mathrm{p}}Q_{\mathrm{p}} + q \tag{8}$$

$$E_{\mathrm{corr}}\Delta t_{\mathrm{p}} = g_{\mathrm{p}}Q_{\mathrm{p\,corr}} + n_{\mathrm{p}}w_{\mathrm{sol}} + q \tag{9}$$

Then with the aid of (7) we get

$$Q_{\mathrm{p\,corr}} - Q_{\mathrm{p}} = \frac{\mathrm{corr}_E\Delta t_{\mathrm{p}} - n_{\mathrm{p}}w_{\mathrm{sol}}}{g_{\mathrm{p}}} = \mathrm{corr}_{\mathrm{p}} \tag{10}$$

c. In the same way we get for cellophane:

$$\mathrm{corr}_{\mathrm{cell}} = \frac{\mathrm{corr}_E\Delta t_{\mathrm{cell}} - n_{\mathrm{cell}}w_{\mathrm{sol}}}{g_{\mathrm{cell}}} \tag{11}$$

d. Correction for the chloro compound, burned in the presence of paraffin oil and cellophane.

$$E_{\mathrm{corr}}\Delta \mathrm{t} = gQ_{\mathrm{corr}} + g_{\mathrm{p}}Q_{\mathrm{p\,corr}} + g_{\mathrm{c}}Q_{\mathrm{c\,corr}} + q + nw_{\mathrm{so}} \tag{12}$$

Finally with the aid of equations (7), (10) and (11) we obtain:

$$Q_{\mathrm{corr}} - Q = \frac{\mathrm{corr}_E\Delta t - g_{\mathrm{p}}\mathrm{corr}_{\mathrm{p}} - g_{\mathrm{cell}}\mathrm{corr}_{\mathrm{cell}} - nw_{\mathrm{sol}}}{g} = \mathrm{corr} \tag{13}$$

This last correction thus represents the total "carbon dioxide correction" for the chloro compound. Owing to the fact that the corrections for benzoic acid, paraffin oil and cellophane, *i.e.* corr_E, $\mathrm{corr}_{\mathrm{p}}$, and $\mathrm{corr}_{\mathrm{cell}}$, are practically constant, the use of this somewhat complicated formula is considerably simplified. The correction term nw_{sol} may be taken from Fig. 3 or be calculated with the help of equation (2).

To the correction of equation (13) we then have to add the correction for the dilution of the formed hydrochloric acid ($\mathrm{corr}_{\mathrm{HCl}}$) according to Fig. 4 or equation (3).

II. COMMENTS ON THE "QUARTZ WOOL" METHOD.

1. The main feature of the "quartz wool" method is the *spiral* made of a string of fine quartzthreads. One may imagine that in laying the windings on the wall of the bomb there may arise small discrepancies between different experimenters, possibly giving *accidental* deviations in the results. Still such possible deviations are certainly less than those caused by other factors. This is shown by some combustions of paraffin oil by Schjånberg[4] and Bjellerup.

Schjånberg burned paraffin oil a) with b) without quartz spiral and found in series a) 11001 ± 3, in series b) 11001 ± 4 cal/g. Bjellerup burned paraffin oil using in series a) the rotating bomb[11], in series b) the quartz spiral method. Results in a) 10975.1 ± 0.7, in b) 10975.7 ± 1.0 cal/g. The errors in temperature readings or other factors in Bjellerups combustions[14] are very much diminished compared with those of Schjånberg but in spite of this the accuracy found by Bjellerup is about the same in series b) as in series a), which must show that neither *accidental* nor *systematic* errors are of importance even with more exact methods than those used by the first workers in this field.

2. The corrections made here for the heat of dilution of hydrochloric acid have been calculated on the assumption that the values found in the literature are valid also in the presence of some amount af arsenious acid. We made a few investigations concerning the correctness of this assumption. Mixing first water and pure hydrochloric acid solution and second water and hydrochloric acid containing arsenious oxide, we determined the rise of temperature in both cases. The final concentrations were the same as in the combustion experiments. We used a glass calorimeter in a laboratory with constant temperature (± 0.1°).

For quantities 20 times greater than the ones used in the combustions a small difference between the two types of experiments were found. This difference (0.5 cal), however, has no noticeable effect on the heat of dilution in the case in question here.

3. The heat evolved during the final period by the dissolution of carbon dioxide can be calculated with the aid of the curves in Fig. 3. We find as average values for 30 milliatoms burned carbon about 1.5 and for 50 milliatoms nearly 3 cal evolved. When determining the heat equivalent we use about 50 milliatoms carbon, when determining the heats of combustion of the chloro compounds not quite so many milliatoms. The average of the amounts found in Karlssons paper (aromatic compounds) is 42, in Schjånbergs and in Eftrings 35 milliatoms. Yet these smaller quantities of carbon cancel most of the corresponding error in the calibration experiments. The remaining part of this error we need not take into consideration.

4. It is well known that a diluted solution of arsenious acid slowly diminishes its concentration in contact with the air. The most important presumption for the use of arsenious acid for the reduction of chlorine according to Berthelot-Matignon is of course that the bomb oxygen itself does not oxidize the arsenious acid during the combustion experiment. If such an oxidation takes place, in any case it must be very slight and the error caused may be neglected *e.g.* on account of its compensation by the same error, when the heat equivalent is determined.

Karlsson observed [6, p. 3] that the concentration of the solution of the arsenious acid in the bomb does not remain quite unchanged even by combustions of compounds, containing no chlorine. The magnitude of the change observed was "very much varying" and impossible to reproduce.

On my request Sunner a few years ago carried out some experiments concerning this question. He used the above mentioned quantity of arsenious acid (20 ml 0.35 N solution) and oxygen of 25 and 35 atm. pressure and found that in the first case the arsenious acid lost about 0.1 % of its normality in half an hour (the usual time in our experiments for combustion with a main period of 5 min.). This gives a heat effect of 0.2 cal.*

Sunner, however, did not use a quartz spiral in his experiments. On that account we now moistened the quartz string with arsenious solution in the ordinary way. Then we immediately made a combustion (using paraffin oil) with oxygen of 25 atm. We found no difference between the blank and the combustion experiment as regards the consumption of permanganate, that is no change in the concentration of the arsenious solution present in the bomb during the combustion. This was the case, whether the solution contained hydrochloric acid or not. We conclude from these experiments that even in the presence of the moistened quartz string, the errors arising from oxidation by the bomb oxygen are negligible. Nor did Bjellerup, in his experiments with bromo compounds, find any oxidation of this kind (private communication).

Karlsson's results may be explained by insufficient washing of the quartz spiral after the combustion. Some arsenious acid may thus have been left behind in it.

5. In the present investigation we have for the first time taken an interest in the quantity of arsenious solution, retained in the quartz string. The authors of previous papers in this field — even Smith — had an exaggerated idea of this quantity; see *e.g.* Eftring, who writes that about half of the volume of the solution (20 ml) runs down to the bottom. As has previously been stated, in reality about 4/5 of the solution runs down and only 4 g remain in the string.

But even this small quantity is obviously sufficient to accelerate the reduction process, which may be considered to take place mainly in the quartz string. It is interesting to compare the number of milliequivalents contained in these 4 g of the solution (about 1.4) with the number totally reduced during a combustion.

Burning in a crucible brings about a greater reduction than burning in ampoules, probably owing to a faster combustion and a higher temperature. Thus Eftring's values, found by the use of ampoules, are less than 1.4 meq. with the exception of the one for tetrachloro ethylene (1.6). The highest figure for the rest is 1.25 for CCl_4. For the solid compound C_2Cl_6 (crucible) the value is 1.75. Schjånbergs crucible values for compounds with similar constitution

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* On the same occasion Sunner investigated the oxidation of hydrazine chloride and found it about 3 times as oxidable as arsenious acid.

are about twice as great as Eftring's. But only for the chloroacetic acids and some simple derivatives of them, generally containing more than 50 % of chlorine, the reduced quantity is equal to or exceeds 1.5 meq. Karlsson's crucible values are low, as may be expected with aromatic compounds. The highest one is 1.3 for the dichlorobenzenes (48 % chlorine).

From the figures quoted we may conclude that theoretically 4 g of 0.35 *N* solution would be sufficient for the reduction in most cases.

No experiments have been made by myself or the authors referred to in order to investigate the minimum of volume, necessary for a quick reduction *in the presence of a moistened quartz string*. Only a few experiments, by no means systematic, have been made *without a quartz string*.

It is a matter of course that every considerable reduction of the volume of the arsenious solution *may* be advantageous in many respects for the accuracy of the combustion, but for answering this question we must first know the corrections for the heat of solution of the carbon dioxide and the heat of dilution of the hydrogen chloride under the new conditions. For their determination special experiments are required.

III. ON THE MAGNITUDE AND RELIABILITY OF THE CORRECTIONS DETERMINED *.

The magnitude of the sum of the corrections for dissolved carbon dioxide and hydrogen chloride will, above all, depend on the content of chlorine in the burned compound. A few examples will be given to show this: the sum of corrections is given in cal/g of substance burned:

Carbon tetrachloride 6.0; chloroform 5.8; methylene chloride 5.7; 1,2,3-trichloropropane 5.0; *o*-dichlorobenzene 3.3; chlorobenzene 1.9; *n*-amyl chloride 2.7; *p*-chlorobenzoic acid 1.1.

A comparison between values, obtained by the quartz spiral and the moving bomb methods, must be of importance for the estimation of the reliability of the quartz spiral method, as it is probable that the moving bomb gives heats of combustion free from systematic errors. For such a comparison we chose some compounds in the dissertations above referred to[4-6] and calculated the corrections for "carbon dioxide" and "hydrogen chloride" and also the other corrections applied in the tables given in the following chapter (p. 79). Then Bjellerup prepared and purified respectively the compounds and determined their heats of combustion in a moving bomb, using closed ampoules for liquids.

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* In collaboration with Lars Bjellerup.

It may be observed, however, that a comparison between the methods is unreliable regarding the volatile compounds, that are burned with cellophane cover (number 1, 2 and 6 a in Table 5), because their heats of combustion often tend to be too low. This uncertainty in the cellophane method was not known to us beforehand, otherwise we should have chosen other compounds than these ones. The compounds 3 and 4 (Eftring) were burned in a glass ampoule with paraffin prop, which is a more reliable method. Number 6 b Bjellerup burned in a closed ampoule. Other details about these and other recently burned chloro compounds will be published subsequently.

Table 5.

No	Substance	Quartz spiral	Moving bomb
1	*n*-Propyl chloroacetate	4820.8 ± 2 [1]	4828.7 ± 2.6
2	*n*-Butyl chloroacetate	5406.7 ± 0.5 [1]	5419.5 ± 2.2
3	*n*-Amyl chloride	7499.3 ± 2	7499 ± 5
4	1,2,3-Trichloro propane	2800.5 ± 3	2808.4 ± 1.3
5	*p*-Chlorobenzoic acid	4681.2 ± 2	4681.2 ± 2.3
6	*o*-Dichloro benzene a)	4808.3 ± 2 [1]	4817.7 ± 2.9
	b)	4814.5 ± 3.5 [2]	

[1] with cellophane.

[2] in ampoule (Bjellerup).

The table gives evidence of the agreement of both methods for the same substance up to 50 % content of chlorine with the exception of Schjånberg's cellophane values (1 and 2). Concerning compounds with more chlorine further investigations are necessary. It should be mentioned, however, that a small correction — about 0.5 cal — is to be added to numbers 1, 2, 5 and 6 a (see below).

IV. THE CORRECTED HEATS OF COMBUSTION OF SOME ORGANIC CHLORO COMPOUNDS

The original values by Schjånberg [4], Eftring [5], Karlsson [6] and Sjöström [7]* are corrected here in the following way.

1. Corrections to weight in vacuum. This correction was not possible to carry out with Sjöström's compounds, whose densities are not known.
2. Corrections for dissolved carbon dioxide and dilution of hydrogen chloride, according to Figs. 3 and 4; both after 5 min. The sum of the corrections is given in the tables.

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* For the chlorhydrins mentioned by Smith [3] new determinations are beeing made and will be published later on.

The *heat equivalents* were also corrected for *dissolved carbon dioxide.* I consider it unnecessary to reproduce these corrections here. It appears from the original papers that no corrections on the heat equivalents to weight in vacuum need to be applied.

Concerning the reliability of the values of the standards used by the authors for determination of the heat equivalents it may be sufficient to refer to Table 5 above: Karlsson and Bjellerup have burned the *same sample of p-chlorobenzoic acid* and found the same heat of combustion for this compound. For the determination of the heat equivalent, however, Karlsson used a benzoic acid sample from Schering-Kahlbaum (standardized by Prof. W. A. Roth), while Bjellerup had a benzoic acid from Bureau of Standards. From this we may conclude that the heats of combustion of both samples are identical within the limits of errors. The standard benzoic acid samples of the other authors had likewise the signature of Roth.

3. The four original authors have used wrong values when correcting for the heat accompanying the solution of platinum and gold *. For the latter metal this error is insignificant, but for the platinum Eftring's and Sjöström's figures are altered (Tables 6 and 9). From Karlsson and Schjånberg the original metal corrections were not available any more. For Schjånberg's part this error may be estimated to be 0.5—1.0 cal/g, for Karlsson's, 0.3—0.5 cal/g. These quantities are to be added to the heats of combustion, *which has not been done in the Tables 7 and 8.*

4. The correction for the oxidation of arsenious acid by the chlorine has been calculated using the value 19.6 cal per meq. by the authors in question. In the tables recalculation is made with the new value 18.6.

5. Finally we have considered it more convenient to refer all the heats of dilution of the hydrogen chloride to a common value: the molar proportion $HCl : H_2O = 1 : 600$ (using "selected values" of Bureau of Standards).

By a mistake the corrections for carbondioxide and hydrogen chloride at 10 min. were calculated at first for *all values* in the tables of the authors. — Sjöströms measurements form an exception. — For that reason it was not necessary to compute the corrections at 5 min. for all values. Guided by the corrections at 10 min. we could get the mean correction at 5 min. by the aid of two or three values in a series of combustions.

In the tables below there are also given — for an average value of the corrections at 5 min. — the quantities of compound, paraffin oil and cellophane (with 3 figures).

The quantities just mentioned may be used for the calculation of the Washburn corrections. For this purpose the approximate initial and final temperatures are given in connexion with the tables. Concerning oxygen

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* This error was originally observed by Sunner.

Table 6. Eftring's heats of combustion. Compounds burned in glass ampoules, see p. 77. Initial temperature in nos. 47—59 18.7°, in the rest 17.2°. Rise of temperature about 1.7°.

No.	Compound	g substance	g par. oil	Heat of comb. uncorr. cal/g	Vac corr	HCl + CO_2 corr cal/g	Pt corr cal/g	As_2O_3 corr cal/g	1 : 600 corr cal/g	Heat of comb. corr. cal/g
47	CCl_4	0.321	0.442	552.1±3	0.3	6.0	1.6	4.5	3.6	567.5
48	$CHCl_3$	0.320	0.417	934.3±2	0.6	5.8	1.2	3.9	3.1	947.7
49	CH_2Cl_2	0.364	0.384	1689.4±1	1.3	5.7	1.3	3.2	3.1	1701.4
51	C_2Cl_6	0.362	0.426	718.7±2	0.3	5.9	1.3	5.1	3.7	734.4
52	C_2HCl_5	0.310	0.427	1004.7±3	0.6	5.7	1.1	3.9	2.9	1017.7
53	$C_2H_2Cl_4$ (*symm.*)	0.319	0.422	1370.1±2	0.8	5.6	1.3	3.6	3.1	1382.9
54	$C_2H_4Cl_2-1,1$	0.367	0.377	2997.0±2	2.6	5.1	0.9	2.9	2.6	3005.9
55	$C_2H_4Cl_2-1,2$	0.348	0.373	2995.9±2	2.4	4.7	0.6	3.0	2.5	3004.3
56	C_2Cl_4	0.342	0.452	1183.5±3	0.7	5.7	0.9	4.7	3.5	1197.6
57	C_2HCl_3	0.306	0.424	1738.3±2	1.2	5.4	1.0	4.0	3.1	1750.6
58	$C_2H_2Cl_2$-*trans*	0.397	0.372	2689.6±3	2.2	4.7	0.5	3.4	2.8	2698.8
59	$C_2H_2Cl_2$-*cis*	0.336	0.400	2684.3±2	2.1	4.5	0.7	3.1	2.4	2692.9
60	C_3H_7Cl-*n*	0.369	0.283	6162.7±2	7.5	3.6	0.5	1.3	0.9	6161.5
61	C_3H_7Cl-*i*	0.308	0.313	6162.4 *	7.7	3.3	0.7	1.6	0.8	6161.1
62	$C_3H_6Cl_2-2,2$	0.470	0.289	3961.0±2	3.8	4.6	1.0	2.5	2.4	3967.7
63	$C_3H_6Cl_2-1,2$	0.497	0.291	3969.2±2	3.6	4.7	1.2	2.3	2.2	3976.0
64	$C_3H_6Cl_2$-1,3	0.478	0.302	3972.5±2	3.5	4.8	1.0	2.6	2.5	3979.9
65	$C_3H_5Cl_3$-1,2,3	0.380	0.370	2790.7±3	2.0	5.0	0.8	3.1	2.9	2800.5
66	C_4H_9Cl-*n*	0.439	0.204	6971.8±2	8.4	3.3	0.7	1.1	0.7	6969.2
67	C_4H_9Cl-*i*	0.441	0.202	6943.2±2	8.5	3.3	0.5	1.2	0.8	6940.5
68	C_4H_9Cl-*sec.*	0.373	0.263	6938.9±2	8.5	3.2	0.7	1.4	0.8	6936.5
69	C_4H_9Cl-*tert.*	0.365	0.228	6898.1±2	8.8	3.0	0.5	1.3	0.6	6894.7
70	$C_5H_{11}Cl$-*n*	0.365	0.227	7503.9±2	9.1	2.7	0.3	1.1	0.4	7499.3
71	$C_5H_{11}Cl$-*i*	0.350	0.243	7496.5±2	9.1	2.7	0.4	1.1	0.4	7491.9
72	$C_5H_{11}Cl$-*tert.*	0.376	0.202	7452.4±2	9.2	2.7	0.3	1.1	0.4	7447.7

* 3 combustions; deviations from the arithmetical mean = + 3.8; — 2.6; — 1.1.

pressure, volume of the bomb and of the solution of the arsenious acid, see above. The temperature-rise was approximately 1.7° (in Table 7 generally 1.8°), the quantities of benzoic acid burned were 0.80—0.85 g.

It may be suitable here to give an idea of the approximate magnitude of the rest of the Washburn corrections. It is to assume that these corrections do not differ very much from the ones for the bromo compounds, the final state in the bomb being very similar: hydrogen chloride instead of hydrogen bromide. Bjellerup has calculated the corrections for a series of alkyl bromides and told me that the *sum* of the two gas corrections (Washburn's ΔU_{gas} and $\Delta U''_{corr}$) amounts to + 0.4 cal/g for each of these compounds and to + 0.5 for paraffin oil. Certainly these corrections are next in importance to the corrections, applied in this paper.

Table 7. Karlsson's heats of combustion. Some compounds are burned with cellophane cover. Initial temperature about 18.8°. Temperature rise usually 1.8°. Karlsson states that his correction for dissolved gold and platinum amounts to 0.6—1 cal per combustion, original values not available now. Since this correction is wrongly calculated, his statement means that 0.3—0.5 cal are to be added to the corrected values in Table 7.*

No.	Compound	g substance	g par. oil	g cellophane	Heat of comb. uncorr. cal/g	Vac. corr cal/g	HCl + CO_2 corr. cal/g	As_2O_3 corr cal/g	1 : 600 corr. cal/g	Heat of comb. corr cal/g
9	$C_6H_4Cl \cdot CO_2H$-*o*	0.693	0.210		4722.9±2	3.0	1.1	1.2	0.4	4722.6
10	$C_6H_4Cl \cdot CO_2H$-*m*	0.704	0.188		4685.0±1	3.0	1.1	1.2	0.4	4684.7
11	$C_6H_4Cl \cdot CO_2H$-*p*	0.802	0.148		4681.4±2	3.0	1.1	1.2	0.5	4681.2
12	$CH_3 \cdot C_6H_4 \cdot Cl$-*o*	0.524	0.161	0.025	7081.4±3	6.9	2.0	1.2	0.4	7078.1
13	$CH_3 \cdot C_6H_4 \cdot Cl$-*m*	0.459	0.190	0.023	7085.4±2	6.9	1.9	1.3	0.4	7082.1
14	$CH_3 \cdot C_6H_4 \cdot Cl$-*p*	0.513	0.167	0.028	7094.0±3	6.9	2.0	1.3	0.4	7090.8
15	$C_6H_4Cl_2$-*o*	0.554	0.220	0.024	4804.7±2	3.7	3.3	2.5	1.6	4808.4
16	$C_6H_4Cl_2$-*m*	0.527	0.234	0.025	4796.6±2	3.7	3.2	2.4	1.6	4800.1
17	$C_6H_4Cl_2$-*p*	0.512	0.232	0.023	4773.5±1	3.2	3.2	2.5	1.6	4777.6
18	$C_6H_4Cl \cdot CHO$-*o*	0.515	0.208	0.025	5735.8±1	4.7	1.3	1.3	0.4	5734.1
19	$C_6H_4Cl{\cdot}CHO$-*m***	0.598	0.184		5722.8±2.5	4.7	1.5	1.4	0.4	5721.4
20	$C_6H_4Cl \cdot CHO$-*p*	0.527	0.214		5688.3±1.5	4.7	1.3	1.3	0.4	5686.6
21	$C_6H_4Cl \cdot OH$-*o*	0.605	0.168	0.024	5417.9±2	4.4	1.6	1.4	0.5	5417.0
22	$C_6H_4Cl \cdot OH$-*m* pulverous	0.500	0.243		5375.8±3	4.4	1.5	1.4	0.4	5374.7
23	$CH_4Cl \cdot OH$-*m* in pieces	0.617	0.174		5376.4±2	4.4	1.6	1.2	0.5	5375.3
24	$C_6H_4Cl \cdot OH$-*m* supercooled	0.579	0.197		5407.2±0.7	4.4	1.6	1.6	0.5	5406.5
25	$C_6H_4Cl \cdot OH$-*p* in pieces	0.633	0.168		5392.2±1.5	4.4	1.6	1.4	0.5	5391.3
26	$C_6H_4Cl \cdot OH$-*p* supercooled	0.617	0.212		5422.1±2	4.4	1.7	1.1	0.6	5421.1
27	C_6H_5Cl ***	0.410	0.239		6603.6±3	6.2	1.9	1.5	0.5	6601.3
28	$C_{10}H_7Cl$-*α*	0.534	0.136		7366.8±1.8	6.4	1.2	0.8	0.2	7362.6
29	$C_{10}H_7Cl$-*β*	0.699	0.071		7366.8±4.5	5.9	1.5	0.9	0.4	7363.7

* see p. 80.

** some combustions of this substance were carried out with cellophane cover, the weight of which is not given.

*** This compound was burned in a glass ampoule.

In the Tables 6—9 there are given: in the first column the table number in the authors paper (in Table 9 only the number of the compound in this table), in the second the formula of the compound, in the following the weight of the substance, paraffin oil and in certain cases the cellophane. It may be observed that the corrections "corr Pt" and "corr As_2O_3" do not denote the total correction but supplementary corrections (see above). The final values are given without the "mean error", inasmuch as this is to be found in the column of the "orig. values" *.

With the exception of the vacuum correction all corrections are positive.

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* Almost all these numerical calculations are carried out by Mr. *D. Folkesson.*

Table 8. Schjånberg's heats of combustion. Most compounds are burned with cellophane cover. Rise of temperature about 1.7°, exceptions are no. 74 (1.2°) and no. 83 (1.4°). Initial temperature usually 17.2°, in nos. 142—147 18.7°, finally in the just mentioned nos. 74 and 83 probably 17.5°. For erroneous correction for dissolving of metal 0.5—1.0 cal/g are to be added to the final values of the table [1].

No.	Compound	g substance	g par. oil	g cellophane	Heat of comb. uncorr. cal./g	Vac. corr. cal/g	HCl + CO_2 corr. cal/g	As_2O_3 corr cal/g	1 : 600 corr cal/g	Heat of comb. corr cal/g
64	$CH_2Cl \cdot CO_2H$	0.761	0.363		1838.7±1	1.4	2.2	2.0	1.5	1843.2
65	$CH_2Cl \cdot CO_2CH_3$	0.861	0.215	0.024	3198.4±2	2.7	2.2	1.8	1.2	3200.9
66	$CH_2Cl \cdot CO_2C_2H_5$	0.777	0.178	0.022	4080.2±2	3.7	2.0	1.3	0.9	4080.7
67	$CH_2Cl \cdot CO_2C_3H_7$-*n*	0.797	0.136	0.022	4821.6±2	4.6	2.0	1.1	0.7	4820.8
68	$CH_2Cl \cdot CO_2C_4H_9$-*n*	0.711	0.140		5408.8±0.5	5.3	1.9	0.8	0.5	5406.7
69	$CH_2Cl \cdot CO_2C_3H_7$-*i*	0.792	0.126	0.022	4786.8±2	4.6	2.0	1.0	0.7	4785.9
70	$CH_2Cl \cdot CO_2C_4H_9$-*i*	0.689	0.133	0.020	5399.6±1	5.3	1.8	0.8	0.4	5397.3
71	$CH_2Cl \cdot CO_2C_5H_{11}$-*i*	0.691	0.111		5896.7±0.7	6.0	1.8	0.6	0.4	5893.5
72	$CH_2Cl \cdot CO_2C_3H_5$	0.789	0.144	0.024	4628.4±0.7	4.2	1.9	1.2	0.7	4628.0
73	$CH_2Cl \cdot CONH_2$	0.750	0.317		2663.4±1	—	2.7	2.1	1.4	2669.6*
74	$CHCl_2 \cdot CO_2H$	0.546	0.285		1149.0±1	1.7	3.1	4.1	2.1	1156.6
75	$CHCl_2 \cdot CO_2CH_3$	0.722	0.308	0.024	2194.5±1	1.6	3.3	1.7	2.3	2200.2
76	$CHCl_2 \cdot CO_2C_2H_5$	0.582	0.329	0.020	3010.1±2	2.4	3.1	2.4	1.5	3014.7
77	$CHCl_2 \cdot CO_2C_3H_7$-*n*	0.661	0.236	0.020	3680.5±0.9	3.1	3.0	2.2	1.5	3684.1
78	$CHCl_2 \cdot CO_2C_4H_9$-*n*	0.685	0.208		4238.2±1	3.7	2.9	1.9	1.3	4240.6
79	$CHCl_2 \cdot CO_2C_3H_7$-*i*	0.688	0.240	0.022	3655.4±1	3.0	3.0	2.0	1.6	3659.0
80	$CHCl_2 \cdot CO_2C_4H_9$-*i*	0.712	0.202		4233.6±1	3.7	2.9	1.6	1.3	4235.7
81	$CHCl_2 \cdot CO_2C_5H_{11}$-*i*	0.795	0.141		4725.2±2	4.3	2.8	0.7	1.3	4725.7
82	$CHCl_2 \cdot CO_2C_3H_5$	0.657	0.256	0.022	3508.1±0.8	2.8	2.9	2.5	1.5	3512.2
83	$CCl_3 \cdot CO_2H$	0.535	0.370		717.8±1		4.0	4.1	2.9	728.8*
84	$CCl_3 \cdot CO_2CH_3$	0.527	0.390	0.024	1631.9±2	1.1	3.9	3.7	2.4	1640.8
85	$CCl_3 \cdot CO_2C_2H_5$	0.480	0.334	0.024	2338.3±2	1.7	3.6	3.2	1.9	2345.3
86	$CCl_3 \cdot CO_2C_3H_7$-*n*	0.494	0.362	0.021	2928.8±2	2.2	3.6	2.8	1.8	2934.8
87	$CCl_3 \cdot CO_2C_4H_9$-*n*	0.564	0.310		3444.7±1	2.7	3.5	2.6	1.7	3449.8
88	$CCl_3 \cdot CO_2C_3H_7$-*i*	0.530	0.343	0.021	2901.1±1		3.6	2.5	1.9	2909.1*
89	$CCl_3 \cdot CO_2C_4H_9$-*i*	0.565	0.298		3437.2±2	2.8	3.4	2.2	1.7	3441.7
90	$CCl_3 \cdot CO_2C_5H_{11}$-*i*	0.628	0.261		3897.0±1	3.2	3.4	2.3	1.7	3901.2
91	$CCl_3 \cdot CO_2C_3H_5$	0.507	0.352	0.022	2761.3±0.9	2.0	3.5	3.1	1.9	2767.8
92	$CCl_3 \cdot CONH_2$	0.488	0.416		1147.3±1		4.3	4.8	2.8	1159.2*
101	$CH_3CHCl \cdot CO_2H$	0.841	0.262		3069.9±0.8	2.5	2.2	1.7	1.2	3072.5
102	$CH_3 \cdot CHCl \cdot CO_2CH_3$	0.850	0.160	0.024	4108.2±1	3.8	2.1	1.3	0.9	4108.7
103	$CH_3 \cdot CHCl \cdot CO_2C_2H_5$	0.822	0.112	0.023	4795.3±1	4.6	2.0	1.1	0.7	4794.5
104	$CH_3 \cdot CHCl \cdot CO_2C_3H_7$-*n*	0.699	0.119	0.022	5402.1±2	5.4	1.8	0.8	0.5	5399.8
105	$CH_3CHCl \cdot CO_2C_4H_9$-*n*	0.689	0.109	**	5896.3±0.6	6.1	1.8	0.7	0.4	5893.1
106	$CH_3 \cdot CHCl \cdot CO_2C_3H_7$-*i*	0.708	0.116	0.023	5345.1±0.8	5.5	1.8	0.8	0.5	5342.7
107	$CH_3 \cdot CHCl \cdot CO_2C_4H_9$-*i*	0.685	0.102	0.022	5851.0±2	6.1	1.7	0.7	0.4	5847.7
108	$CH_3 \cdot CHCl \cdot CO_2C_5H_{11}$-*i*	0.662	0.101	0.022	6267.7±0.8	6.6	1.7	0.6	0.3	6263.7
109	$CH_2Cl \cdot CH_2 \cdot CO_2H$	0.861	0.256		3011.3±1		2.1	1.5	1.2	3016.1*
110	$CH_2Cl \cdot CH_2 \cdot CO_2CH_3$	0.828	0.164	0.023	4095.4±2	3.7	2.1	1.4	0.9	4096.1
111	$CH_2Cl \cdot CH_2 \cdot CO_2C_2H_5$	0.814	0.116	0.025	4816.1±1	4.6	2.0	1.0	0.7	4815.2

[1] Schjånberg has also burned 21 chlorine free compounds [9]. The heats may be corrected "for CO_2" according to Fig. 3 in this paper.

* no corr. to vac.

** In some combustions the substance has been ignited by a small strip of cellophane (about 0.002 g), in some without this one. A strip has also been used in nos. 140 and 143—147.

Table 8 (continued).

112	$CH_2Cl \cdot CH_2 \cdot CO_2C_3H_7$-*n*	0.728	0.117	**	5422.8±1	5.3	1.9	0.8	0.5	5520.7
113	$CH_2Cl \cdot CH_2 \cdot CO_2C_4H_9$-*n*	0.710	0.097	**	5916.4±1	6.0	1.8	0.6	0.4	5913.2
114	$CH_2Cl \cdot CH_2 \cdot CO_2C_3H_7$-*i*	0.702	0.125	0.022	5394.6±2	5.4	1.8	0.8	0.5	5392.3
115	$CH_2Cl \cdot CH_2 \cdot CO_2C_4H_9$-*i*	0.687	0.109	0.020	5895.1±2	6.0	1.8	0.7	0.3	5891.9
116	$CH_2Cl \cdot CH_2 \cdot CO_2C_5H_{11}$-*i*	0.665	0.097	0.024	6312.6±0.8	6.5	1.7	0.6	0.3	6308.7
124	$C_2H_5 \cdot CHCl \cdot CO_2H$	0.821	0.182		3939.8±1	3.5	2.0	1.4	0.9	3940.6
125	$C_2H_5 \cdot CHCl \cdot CO_2CH_3$	0.828	0.119	0.021	4736.5±1	4.5	1.9	1.1	0.7	4735.7
126	$C_2H_5 \cdot CHCl \cdot CO_2C_2H_5$	0.682	0.128	0.023	5303.3±2	5.3	1.8	1.0	0.5	5301.3
127	$C_2H_5 \cdot CHCl \cdot CO_2C_3H_7$-*n*	0.701	0.098	0.023	5810.3±1	6.0	1.8	0.9	0.4	5807.4
128	$C_2H_5 \cdot CHCl \cdot CO_2C_4H_9$-*n*	0.658	0.099	0.022	6230.1±2	6.5	1.7	0.8	0.3	6226.4
129	$C_2H_5 \cdot CHCl \cdot CO_2C_3H_7$-*i*	0.716	0.105	0.022	5787.4±1	6.0	1.8	0.9	0.4	5784.5
130	$C_2H_5 \cdot CHCl \cdot CO_2C_4H_9$-*i*	0.657	0.102	0.011	6221.3±1	6.6	1.7	0.7	0.3	6217.4
131	$C_2H_5 \cdot CHCl \cdot CO_2C_5H_{11}$-*i*	0.596	0.113	0.023	6583.0±1	7.0	1.6	0.7	0.2	6578.5
132	$CH_3CHCl \cdot CH_2 \cdot CO_2H$	0.812	0.171		3977.2±1	3.4	2.0	1.4	0.9	3978.1
133	$CH_3 \cdot CHCl \cdot CH_2 \cdot CO_2CH_3$	0.797	0.117	0.020	4791.3±2	4.5	2.0	1.1	0.7	4790.6
134	$CH_3 \cdot CHCl \cdot CH_2{\cdot}CO_2C_2H_5$	0.722	0.118	0.022	5376.1±1	5.4	1.9	1.0	0.5	5374.1
135	$CH_3{\cdot}CHCl{\cdot}CH_2{\cdot}CO_2C_3H_7$-*n*	0.708	0.094	0.019	5869.5±1	6.0	1.8	0.8	0.4	5866.5
136	$CH_3{\cdot}CHCl{\cdot}CH_2{\cdot}CO_2C_4H_9$-*n*	0.668	0.094	0.019	6289.3±1	6.6	1.7	0.8	0.3	6285.5
137	$CH_3{\cdot}CHCl{\cdot}CH_2{\cdot}CO_2C_3H_7$-*i*	0.702	0.090	0.024	5844.4±0.6	6.1	1.8	0.8	0.4	5841.3
138	$CH_3{\cdot}CHCl{\cdot}CH_2{\cdot}CO_2C_4H_9$-*i*	0.660	0.095	0.019	6272.3±1	6.6	1.7	0.6	0.3	6268.3
139	$CH_3{\cdot}CHCl{\cdot}CH_2{\cdot}CO_2C_5H_{11}$-*i*	0.602	0.103	0.021	6632.4±0.7	7.1 ***	1.6	0.6	0.2	6627.7
140	$ClCH_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H$	0.763	0.201	0.002	3957.5±1	3.3	2.0	1.5	0.8	3958.5
141	$ClCH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2CH_3$	0.799	0.122	0.022	4788.2±1	4.4	2.0	1.2	0.7	4787.7
142	$ClCH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2C_2H_5$	0.715	0.120	0.023	5375.1±1	5.3	1.8	1.0	0.5	5373.1
143	$ClCH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2C_3H_7$-*n*	0.712	0.110	0.002	5867.6±2	5.9	1.8	0.9	0.4	5864.8
144	$ClCH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2C_4H_9$-*n*	0.670	0.099	0.002	6279.5±1	6.5	1.7	0.8	0.3	6275.8
145	$ClCH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2C_3H_7$-*i*	0.676	0.112	0.002	5845.1±1	6.0	1.8	1.2	0.4	5842.5
146	$ClCH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2C_4H_9$-*i*	0.658	0.096	0.002	6262.2±1	6.5	1.7	0.8	0.3	6258.5
147	$ClCH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2C_5H_{11}$-*i*	0.619	0.104	0.002	6617.0±1	6.9	1.6	0.7	0.2	6612.6

** In some combustions the substance has been ignited by a small strip of cellophane (about 0.002 g), in some without this one. A strip has also been used in nos. 140 and 143—147.

*** In the thesis there is a misprint in the density figure. This correction is estimated.

The comparison made in Table 5 certainly shows that many of Schjånberg's values must be too low owing to his use of the cellophane method. This error diminishes with rising boiling points of the compounds burned. Table 8 also shows that in a homologous series the mean errors are as a rule greater for the lower members than for the higher ones. This is more pronounced in the derivatives of the monochloro acetic acid than in those of the chloro butyric acids. Certainly the experimental skill of Schjånberg and his great capacity for uniform working is the cause of the fact that the effect of the volatility is not more noticeable. For that reason it is also probable that these "cellophane errors" disappear when calculating differences in the heats of combustions between consecutive members of a series.

Table 9. Sjöströms heats of combustion [7]*. The initial temperature is in the combustions of the compounds 1—3 in Table 9 17.0°, in the rest 18.7°. The rise of temperature is everywhere about 1.7°. The final values are corrected for erroneous heat of dissolving of metal, but not to weight in vacuum, the densities of the compounds being unknown.*

No.	Compound	g substance	g par. oil	Heat of comb. uncorr. cal/g	HCl + CO_2 corr cal/g	As_2O_3 corr cal/g	Pt corr cal/g	1 : 600 corr cal/g	Heat of comb. corr cal/g
1	monochlorobenzoquinone	0.889	0.105	4347.3±1.2	1.4	1.4	0.3	0.7	4351.1
2	trichlorobenzoquinone	0.486	0.343	2600.0±1.5	3.0	2.7	0.6	1.6	2607.9
3	trichlorohydroquinone	0.496	0.336	2702.7±0.8	3.0	2.6	0.6	1.6	2710.5
4	monochlorobenzoquinone	0.869	0.102	4346.5±1.2	1.4	1.4	0.1	0.7	4350.1
5	monochlorohydroquinone	0.895	0.101	4488.9±1.1	1.5	1.2	0.4	0.7	4492.7
6	2,6-dichlorohydroquinone	0.577	0.289	3408.9±1.3	2.4	2.1	0.3	1.2	3414.9
7	2,6-dichlorobenzoquinone	0.571	0.292	3305.0±1.2	2.3	2.0	0.3	1.2	3310.8
8	2,5-dichlorohydroquinone	0.561	0.284	3404.4±1.1	2.4	2.1	0.3	1.1	3410.3
9	2,5-dichlorobenzoquinone	0.556	0.291	3304.1±1.4	2.3	2.1	0.3	1.2	3310.0
10	2,3-dichlorohydroquinone	0.564	0.287	3418.5±1.2	2.4	2.1	0.3	1.1	3424.4
11	2,3-dichlorobenzoquinone	0.558	0.289	3299.8±1.4	2.3	2.1	0.3	1.2	3305.7
12	tetrachlorobenzoquinone	0.398	0.383	2101.0±2	3.4	3.3	0.3	1.7	2109.7
13	tetrachlorohydroquinone	0.393	0.382	2199.3±2	3.4	2.9	0.5	1.7	2207.8

SUMMARY

Experimental methods have been developed for correcting heats of combustion of chlorinated compounds, determined with the "quartzwool" method. Such corrections were applied to values published from the Institute for Organic Chemistry of the University of Lund by E. Eftring, K. J. Karlsson, E. Schjånberg and G. Sjöström. Totally 128 heat values were corrected. In order to check the reliability of the corrections applied, six of the chloro compounds were also burned in a moving bomb.

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