Reduction to Standard Heat of Combustion of Bomb Calorimetric Data for Organic Bromine Compounds

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The rigorous Washburn reduction of combustion calorimetric data for organic bromine compounds is discussed and applied to a recent high-precision moving-bomb method.

The general scheme for the reduction is treated in two respects: (i) The accuracy of the reduction is improved by presentation of experimental data for the auxiliary numerical quantities entering some of the more important corrections. For $As_2O_3 - As_2O_5 - HBr$ solutions of various composition, data are thus given for, (a) the density at 20 and 25°C, (b) the heat capacity at 25°C, and (c) the solubility of carbon dioxide at 20 and 25°C. (ii) The general scheme is modified to apply specifically to the above-mentioned bomb calorimetric method.

A combustion-bomb calorimetric method for organic bromine compounds has recently been described [1] by which results of an immediate precision [2] slightly better than 0.01 % can be obtained. To take full advantage of this high precision in order to obtain high-accuracy standard heats of combustion for organic bromine compounds, the application of rigorous Washburn corrections [3] to the calorimetric data obtained is required. The original Washburn reduction [3] treated data obtained on compounds containing only carbon, hydrogen and oxygen. Later, the Washburn reduction was extended to apply to nitrogen compounds of the formula $C_aH_bO_cN_d$[4,5] and to sulfur compounds of the formula $C_aH_bO_cS_d$[7-9]. In Ref. [9] a complete and rigorous treatment was given not only of those corrections usually described as the "Washburn corrections", but of all other corrections that must be applied to the original calorimetric data from combustion experiments with organic sulfur compounds in order to obtain the energy of the idealized combustion reaction, *i.e.* the standard heat of combustion of the compound investigated. The corrections were treated separately and presented in a systematic computation form in which the various terms were kept separate. This mode of presentation had several advantages. One was that many of the terms, either unchanged or modified, enter into reductions to standard heat of combustion of calorimetric data obtained on organic compounds containing other elements instead of sulfur. This was illustrated by discussion of the modifications to the general computation form for sulfur compounds that had to be made to apply it to

organic nitrogen, chlorine, bromine and iodine compounds, respectively. For chlorine and bromine compounds, however, no critical selection could be made of the numerical quantities that enter into some of the more important corrections, because reliable experimental data were not available for these quantities cf. Refs.[9] (p. 126—127), [10] (p. 217—218) Through recent work in this laboratory, data have been obtained for the more important of these auxiliary quantities. Part of this work has been reported elsewhere [11] and the remainder is given here.

More specifically, the aim of this paper is to describe the modifications and additions that have to be made to the treatment, given in Ref.[9] (p. 114—119), of the reduction to standard heat of combustion of bomb calorimetric data for bromine compounds, to make the reduction applicable to and commensurate in accuracy with the experimental method described in Ref.[1]
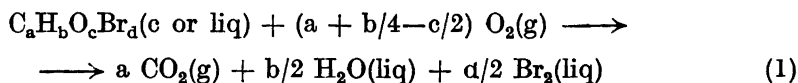
MODE OF PRESENTATION. NOTATION

For convenience the same presentation and notation as in Ref.[9] is used in this paper. On only a few points, which are clearly indicated in the text, is the treatment and the notation of this paper different from those of Ref.[9]

ACTUAL BOMB PROCESS AND IDEALIZED COMBUSTION REACTION

The actual process occurring in the bomb in combustion experiments with organic bromine compounds, using the method given in Ref.[1], was discussed in detail in the cited paper.

The idealized combustion reaction, to which the standard heat of combustion of the compound is referred, is defined by eqn. 1, where reactants and products are in their thermodynamic standard states [12].

$$C_aH_bO_cBr_d(c \text{ or } liq) + (a + b/4 - c/2)\ O_2(g) \longrightarrow$$
$$\longrightarrow a\ CO_2(g) + b/2\ H_2O(liq) + d/2\ Br_2(liq) \qquad (1)$$

It should be noted that this idealized combustion reaction is the same as that given in Refs. [9] (p. 118), [10] (p. 211, eqn. 3)

CALCULATION OF THE CORRECTIONS

The calculation of the standard heat of combustion from the original calorimetric data was described in Ref.[1] * Some of the corrections were treated in detail and the rest, mainly those usually described as the Washburn corrections, are discussed here. These are presented as modifications to the various items of the computation form for bromine compounds given in Ref. [9] (p. 114—119) and make the reduction applicable to data obtained with the experimental method described in Ref.[1]

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* There are two obvious misprints in eqn. 29 of Ref. [1]. The equation should read:

$$-\Delta Ec°/M(\text{Compound}) = \frac{1}{m'}\Big\{-\Delta E_{\text{I.B.P.}} -\Big[-\Delta E(\text{As}) - \Delta E(\text{Oil}) - \Delta E(\text{Fuse}) - \Delta E(\text{CO}_2) -$$
$$- \Delta E(\text{HNO}_3) - \Delta E(\text{Au}) - \Delta E(\text{Pt})\Big] - \Delta E(\text{HBr}) - \Delta E\Sigma\Big\}$$

Initial and final states

(1) $C_aH_{b'}O_{c'}Br_{d'}$; (2)—(6) unchanged; (7) $C_{a''}H_{b'}O_{c''}Br_{d''}$; (8)—(12) unchanged; (13) $C_{a'''}H_{b'''}O_{c'''}Br_{d'''}$; (14)—(23) unchanged; (24)—(25) these two items are entirely formal. They can be deleted and the following treatment accordingly modified; (26)—(29b) unchanged;

(29c) g^i, the ratio of the vapor pressure of H_2O over the initial solution to that over pure water. Experimental data are not available for the lowering of the vapor pressure by arsenious oxide. From data [13] (p. 294) on comparable compounds (boric acid) however, g^i for the 0.0625 M As_2O_3 solution, used in Ref.[1], can be estimated at 0.998;
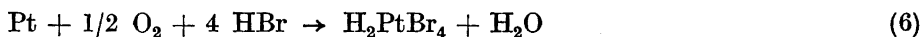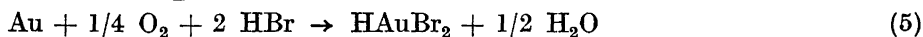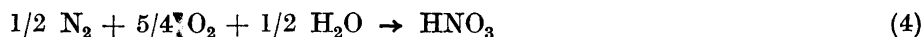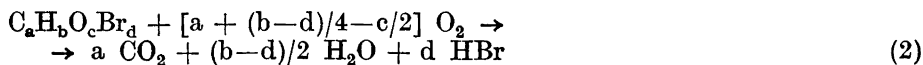
(29d) $K^{*i}(O_2)$ the solubility of O_2 in the initial bomb solution in moles per liter of solution per atm O_2 pressure. Since no data on the solubility of O_2 in aqueous As_2O_3 solutions are available the values of the solubility in pure water, given in the table on p. 84 in Ref.[9], will be used as an approximation;

(30)—(34) unchanged;

(35) $n^i(O_2$ diss.$) = K^{*i}(O_2)V^i(\text{soln.})[P^i(\text{gas.}) - P^i(H_2O \text{ vap.})]$. Since, in combustion experiments with bromine compounds, N_2 is present only as a small impurity in the O_2 and since it can be treated as though it were O_2, except for the formation of HNO_3, the notation $(O_2 + N_2)$ used in Ref.[9] has been changed to (O_2) in this paper;

(36) $n^i(O_2$ tot.$) = n^i(\text{gas.}) - n^i(H_2O \text{ vap.}) + n^i(O_2 \text{ diss.})$.

The stoichiometry of the isothermal bomb process can be described by the following set of equations [1]:

$$C_aH_bO_cBr_d + [a + (b-d)/4 - c/2]\, O_2 \rightarrow$$
$$\rightarrow a\ CO_2 + (b-d)/2\ H_2O + d\ HBr \qquad (2)$$

$$As_2O_3 + O_2 \rightarrow As_2O_5 \qquad (3)$$

$$1/2\ N_2 + 5/4\ O_2 + 1/2\ H_2O \rightarrow HNO_3 \qquad (4)$$

$$Au + 1/4\ O_2 + 2\ HBr \rightarrow HAuBr_2 + 1/2\ H_2O \qquad (5)$$

$$Pt + 1/2\ O_2 + 4\ HBr \rightarrow H_2PtBr_4 + H_2O \qquad (6)$$

The amounts of HNO_3, $HAuBr_2$ and H_2PtBr_4 present in the final bomb solution are listed in the items:

(37) $n^f(HNO_3)$; (37a) $n^f(HAuBr_2)$; (37b) $n^f(H_2PtBr_4)$. Under the conditions of the experimental technique described in Ref.[1] these quantities are small enough to permit decomposition, as outlined in Ref.[9] (p. 122-123), of the corresponding substances under actual bomb conditions immediately after Step 12 without significant loss in accuracy. This means that all terms involving $n^f(HNO_3)$, $n^f(HAuBr_2)$ and $n^f(H_2PtBr_4)$, except in items 86a, 86b and 86c, can be left out from the subsequent discussion.

(38)—(38a) unchanged; (39) $n^f(HBr) = d$; (40) $n^f(H_2O$ liq.$) = n^i(H_2O$ tot.$) + (b-d)/2 - n^i(H_2O$ vap.$)$; (41) $m^f(\text{soln.}) = 18.016 n^f(H_2O$ liq.$) +$

$+ 197.82 n^f(As_2O_3) + 229.82 n^f(As_2O_5) + 80.924 n^f(HBr)$; (42) wt.%$(As_2O_3) =$
$= 19\ 782 n^f(As_2O_3)/m^f(soln.)$; (42a) wt.%$(As_2O_5) = 22\ 982 n^f(As_2O_5)/m^f(soln.)$;
(42b) wt.%$(HBr) = 8092 n^f(HBr)/m^f(soln.)$; (43) delete;

(44) $\varrho^f(soln.) = \varrho(H_2O) + 0.00785$ wt.%$(As_2O_3) + 0.00808$ wt.%$(As_2O_5) +$
$+ 0.00710$ wt.%(HBr) g/ml. This equation has been found to represent, within an uncertainty of $\pm$ 0.0001 g/ml, experimental data [14] on the densities at 20 and 25°C of seven aqueous As_2O_3—As_2O_5—HBr solutions of various compositions within the concentration ranges 0—1.23 wt.% of As_2O_3, 0—1.28 wt.% of As_2O_5 and 0—1.79 wt.% of HBr, which are the ranges of interest in the given method [1].

(45) unchanged; (46)—(47) delete; (48)—(49) unchanged;

(50) $n^f(CO_2\ tot.) = a$;

(51) $K(CO_2) = 0.0383_5$ and 0.0336 mole/liter atm at 20 and 25°C, respectively. The solubility of CO_2 in aqueous As_2O_3—As_2O_5—HBr solutions, similar in composition to those obtained in combustion experiments, has been measured * by use of the method given in Ref.[7] (p. 85) It was found that the solubility of CO_2 was the same in each of three investigated solutions, which had the following compositions:
(A) 0.0633 M As_2O_3; (B) 0.0475 M As_2O_3—0.0158 M As_2O_5—0.0671 M HBr;
(C) 0.0317 M As_2O_3—0.0316 M As_2O_5—0.122 M HBr. Therefore the solubility values given above can be used in all combustion experiments irrespective of the HBr concentration in the final bomb solution.

(52)—(55) unchanged;

(56) $n^i(O_2\ tot.) = n^i(O_2\ tot.) - [a + (b-d)/4 - c/2] - n^f(As_2O_5)$;

(57) $K^f(O_2)$, the solubility of O_2 in the final bomb solution in moles per liter of solution at unit fugacity (in atm) of O_2 gas. Since no data on the solubility of O_2 in As_2O_3—As_2O_5—HBr solutions are available the values of the solubility in pure water, given in Ref.[9] (p. 88), will be used as an approximation;

(58) unchanged; (59) $K^{*f}(O_2) = D(O_2)K^f(O_2)$;

(60) $n^f(O_2\ diss.) = \dfrac{0.082054(t_h + 273.2)K^{*f}(O_2)V^f(soln.)/V^f(gas.)}{1 + 0.082054(t_h + 273.2)K^{*f}(O_2)V^f(soln.)/V^f(gas.)}\ n^f(O_2\ tot.)$;

(61) $n^f(O_2\ gas.) = n^f(O_2\ tot.) - n^f(O_2\ diss.)$; (62) $n^f(gas.) = n^f(O_2\ gas.) +$
$+ n^f(CO_2\ gas.) + n^i(H_2O\ vap.)$; (63)—(65) unchanged;

(66) g^f, the ratio of the vapor pressure of H_2O over the final solution to that over pure H_2O. Experimental data are not available for the vapor pressure lowering of water by the mixture of As_2O_3, As_2O_5 and HBr present in the final bomb solution. As in item 29c, however, g^f for an average final bomb solution, having the composition 0.02 M As_2O_3—0.04 M As_2O_5—0.16 M HBr, was estimated at 0.993 from data [13] (p. 293—294) on comparable compounds;

(67) $n^f(H_2O\ vap.) =$
$g^f[C_0 + \{a(O_2) + [a(CO_2) - a(O_2)]x(CO_2)\}P^f(gas.)]\ V^f(gas.)/18.016$.

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Energy factors and calorimetric data

(68)—(69) unchanged. For the 0.0625 M As_2O_3 solution, used as initial bomb solution in Ref.[1], a value for $(\delta V/\delta T)_P$ of 2.57×10^{-7} liter/g deg was obtained from experimental density data. In the same way $(\delta V/\delta T)_P$ values were obtained for various As_2O_3—As_2O_5—HBr solutions having compositions corresponding to combustion experiments with samples containing from 4 to 7 mgatoms of bromine. In all cases the value of $(\delta V/\delta T)_P$ was found to be virtually the same and equal to 2.35×10^{-7} liter/g deg. Therefore the following values can be used at 25°C for all combustion experiments with the method of Ref.[1]: $(\delta E/\delta P)_T^i(\text{soln.}) = -0.00186$ cal/g atm and $(\delta E/\delta P)_T^f(\text{soln.}) = -0.00170$ cal/g atm;

(70) delete;

(71) $\Delta E'_{\text{soln.}}(O_2)$ and (71a) $\Delta E''_{\text{soln.}}(O_2)$, the change of internal energy in cal/mole at t_h for the solution of O_2 in the initial and final bomb solution, respectively. Since no data are available for the heat of solution of O_2 in aqueous As_2O_3 and As_2O_3—As_2O_5—HBr solutions, the corresponding values for pure water, given in Ref.[9] (p. 100), will be used as an approximation;

(71b) $\Delta E''_{\text{soln.}}(CO_2)$, the change of internal energy in cal/mole at t_h for the solution of CO_2 in the final bomb solution. From the solubility data given above in item 51 a value for $\Delta E_{\text{soln.}}(CO_2)$ of $-4\,000$ cal/mole at 22.5°C was obtained for the pertinent final bomb solutions. By the use of a temperature coefficient of $+44$ cal/mole deg [9] (p. 99),[15] the following values were obtained for $\Delta E''_{\text{soln.}}(CO_2)$: $-4\,110$ and $-3\,890$ cal/mole at 20 and 25°C;

(71c) $\Delta E_{\text{oxid.}}(HBr)$, the change of internal energy in cal/mole at t_h for the oxidation of HBr in Soln. I (under a pressure of 1 atm) with O_2 (in its standard state) to water and bromine (both in their standard states) according to the equation $d(HBr \cdot nH_2O)(\text{in Soln. I}) + d/4\,O_2(g) \rightarrow d(n+1/2)\,H_2O(\text{liq}) + d/2\,Br_2(\text{liq})$. No experimental values have been obtained for the energy of this reaction and since no data are available for the energy of formation of HBr in aqueous As_2O_3—As_2O_5 solutions, it is not possible to calculate values for $\Delta E_{\text{oxid.}}(HBr)$. However, the values of $\Delta E^{\circ}_{\text{oxid.}}(HBr)$, given in Ref.[9] (p. 119) can be used as a satisfactory approximation since the error introduced thereby is almost entirely cancelled by the introduction of the same error, but with opposite sign, in the $\Delta E_{\text{decomp.}}(As_2O_5)$ value given in the following item;

(71d) unchanged. From experimental data reported [11] for the heat of the reaction $[As_2O_3 + 2\,H_2O](aq) + 2\,Br_2(\text{liq}) \rightarrow [As_2O_5 + 4\,HBr](aq)$ a value of $-(77.4 \pm 0.1) \times 10^3$ cal/mole was calculated for the change of internal energy, $\Delta E_{\text{oxid.}}[As_2O_3(aq)]$, for the reaction $As_2O_3(aq) + O_2(g) \rightarrow As_2O_5(aq)$. In this calculation, it was assumed that the energy of formation of HBr in aqueous As_2O_3—As_2O_5 solution is the same as that in pure water [12]. Thus, by using $\Delta E_{\text{oxid.}}[As_2O_3(aq)]$ for $-\Delta E_{\text{decomp.}}(As_2O_5)$, the error introduced by the approximation is almost entirely cancelled by an analogous error introduced in item 71c. The value 77.4×10^3 cal/mole will therefore be used for $\Delta E_{\text{decomp.}}(As_2O_5)$ at 25°C;

(71e) unchanged. No heat of dilution data for $As_2O_3 \cdot nH_2O$ are available and therefore the corresponding correction in item 92b has to be neglected.

Since C^i(Soln.) is rather small and since the difference in concentration of As_2O_3 in Soln. III and in the initial bomb solution is also small, the error introduced by neglecting the correction in item 92b certainly will be barely significant;

(72)—(73) unchanged;

(74) ε^o(Calor.), the energy equivalent of "the standard calorimetric system". As described in Ref.[1] the energy equivalent of the calorimetric system is divided in three parts: (i) ε^o(Calor.), the energy equivalent of the whole system as assembled for a fictive experiment with no contents in the bomb ("the standard calorimetric system"), (ii) $C_P(H_2O)m^i$(Cont.), the energy equivalent of an amount of water equal in mass to the contents of the bomb (*cf.* item 74a and 74b), and (iii) ε(Cont.), the energy equivalent of the contents of the bomb, by which is understood all removable matter in the interior of the bomb, including the platinum combustion crucible and its suspension ring (*cf.* item 75 and 76);

(74a) m^i(Cont.), the mass of the contents of the bomb, is obtained from the relation m^i(Cont.) = $32.00 n^i(O_2$ tot.) + V^i(soln.)ϱ^i(soln.) + m(Sub.) + + m(Pt) + m(glass);

(74b) ε(Calor.) = ε^o(Calor.) — $C_P(H_2O)m^i$(Cont.);

(75) ε^i(Cont.) = $C_V(O_2)n^i(O_2$ tot.) + $A^i V^i$(soln.)ϱ^i(soln.) + $Bn^i(H_2O$ vap.) + + $C'_P m' + C''_P m'' + C'''_P m''' + 0.0317 m$(Pt) + $0.17 m$(glass). For 0.0624 M As_2O_3 solution under a pressure of 1 atm the heat capacity, C_P, has been found [11] to be 0.988 cal/g deg at 25°C. This value will be used as an approximation for A^i. For C_P(Pt) the value 0.0317 cal/g deg at 25°C is given in Ref.[16]

(76) ε^f(Cont.) = $C_V(O_2)n^f(O_2$ tot.) + $C_V(CO_2)n^f(CO_2$ tot.) + $A^f[m^f$(soln.)+ + $18 n^f(H_2O$ vap.)] + $Bn^f(H_2O$ vap.) + $0.0317 m$(Pt) + 0.17 m(glass). As in the preceding item, C_P values for final bomb solutions under a pressure of 1 atm will be used as approximations for A^f. For As_2O_3—As_2O_5—HBr solutions having compositions corresponding to combustion experiments with samples containing 5 and 6 mgatoms of bromine the heat capacities, C_P, at 1 atm and 25°C have been found * to be 0.969 and 0.964 cal/g deg, respectively;

(77) unchanged. With the method of Ref.[1] $\Delta E_{ign.}$ is incorporated into the value of ε^o(Calor.). Therefore it is formally put equal to zero in the calculations;

(78)—(79) unchanged;

(80) $\Delta t_{ex.}$. This symbol was used in Ref.[1] for "the heat exchange correction" and it will be retained here. It represents the same quantity as does the symbol $\Delta t_{corr.}$ in Ref.[9]

Changes in internal energy

(81)—(83) unchanged; (84) $\Delta E^i_{soln.}(O_2) = \Delta E'_{soln.}(O_2)n^i(O_2$ diss.); (85) unchanged; (86) $\Delta E_{I.B.P.} = \varepsilon$(Calor.)$(t_i - t_f + \Delta t_{ex.}) + \varepsilon^i$(Cont.)$(t_i - t_h) + + \varepsilon^f$(Cont.)$(t_h - t_f + \Delta t_{ex.}) + \Delta E_{ign.}$;

Step 12a. The HNO_3, $HAuBr_2$ and H_2PtBr_4 are decomposed under final bomb conditions according to the reactions $HNO_3(aq) \rightarrow 1/2\ N_2(g) + 5/4$ $O_2(g) + 1/2\ H_2O(liq)$, $HAuBr_2(aq) + 1/2\ H_2O(liq.) \rightarrow Au(c) + 1/4\ O_2(g) +$ $2HBr(aq)$ and $H_2PtBr_4(aq) + H_2O(liq) \rightarrow Pt(c) + 1/2\ O_2(g) + 4\ HBr(aq)$. As discussed in Ref.[1] the following values of ΔE, at 25°C, can be used for these reactions: $\Delta E_{decomp.}(HNO_3) = 14.18 \times 10^3$, $\Delta E_{decomp.}(HAuBr_2) = 8 \times 10^3$ and $\Delta E_{decomp.}(H_2PtBr_4) = 43.4 \times 10^3$ cal/mole. The change of energy associated with this step is the sum of the following three items:

(86a) $\Delta E^f_{decomp.}(HNO_3) = \Delta E_{decomp.}(HNO_3)n^f(HNO_3)$;

(86b) $\Delta E^f_{decomp.}(HAuBr_2) = \Delta E_{decomp.}(HAuBr_2)n^f(HAuBr_2)$;

(86c) $\Delta E^f_{decomp.}(H_2PtBr_4) = \Delta E_{decomp.}(H_2PtBr_4)n^f(H_2PtBr_4)$;

(87) unchanged; (88) $\Delta E^f_{soln.}(O_2) = -\Delta E''_{soln.}(O_2)n^f(O_2 \text{ diss.})$; (89) unchanged; (90)—(91b) delete;

Step 19. The HBr is oxidized with O_2 (in its standard state) according to the reaction d $(HBr \cdot nH_2O)(\text{in Soln. I}) + d/4\ O_2(g) \rightarrow d(n + 1/2)\ H_2O(liq) +$ $+ d/2\ Br_2(liq)$. The water and the bromine are brought to their standard states.

(92) $\Delta E^f_{oxid.}(HBr) = \Delta E_{oxid.}(HBr)n^f(HBr)$;

Step 19a. The As_2O_5 in Soln. II is decomposed to As_2O_3 in Soln. III and O_2 gas in its standard state.

(92a) $\Delta E^f_{decomp.}(As_2O_5) = \Delta E_{decomp.}(As_2O_5)n^f(As_2O_5)$;

Step 19b. Water (in its standard state) is removed from Soln. III to bring the concentration of As_2O_3 to $C^i(soln.)$.

(92b) $\Delta E^f_{diln.}(As_2O_3) = \Delta E_{diln.}(As_2O_3)n^i(As_2O_3)$;

(93) $\Delta E^f(gas.)]^{o}_{P^f(gas.)} = -(\delta E/\delta P)_T(O_2\ gas.)\{1 + 1.69x(CO_2)[1 + x(CO_2)]\}$ $P^f(gas.)n^f(gas.)$;

(94)—(98) unchanged;

(99) $\Delta Ec^o/M(\text{Compound}) = n'\Delta Ec^o(\text{Compound})/m'$;

(100) $\Delta Ec^o(\text{Compound}) = M'\Delta Ec^o/M(\text{Compound})/1\ 000$;

By definition of the quantities $\Delta E_B/M(\text{Compound})$ and ΔE_Σ as follows: $\Delta E_B/M(\text{Compound}) = [\text{items } 86+86a+86b+86c+87+92+92a-96-97]/m'$ $\Delta E_\Sigma = \text{items}\ 81 + 82 + 83 + 84 + 85 + 88 + 89 + 92b + 93 + 94$, item 99 becomes

(99) $\Delta Ec^o/M(\text{Compound}) = \Delta E_B/M(\text{Compound}) + \Delta E_\Sigma/m'$. The reason for this operation is given in Ref.[9] (p. 102-103)

It is seen that the symbols $\Delta Ec^o/M(\text{Compound})$, $\Delta E_{I.B.P.}$ and ΔE_Σ denote the same quantities in this paper as in Ref.[1], and the symbols $\Delta E^f_{decomp.}(HNO_3)$, $\Delta E^f_{decomp.}(HAuBr_2)$, $\Delta E^f_{decomp.}(H_2PtBr_4)$, $\Delta E^f_{soln.}(CO_2)$, $\Delta E^f_{oxid.}$ (HBr), $\Delta E^f_{decomp.}(As_2O_5)$, $n''\Delta Ec^o(\text{Auxiliary material})$ and $n'''\Delta Ec^o(\text{Fuse})$ of this paper correspond with the symbols $-\Delta E(HNO_3)$, $-\Delta E(Au)$, $-\Delta E(Pt)$, $-\Delta E(CO_2)$, $+\Delta E(HBr)$, $-\Delta E(As)$, $+\Delta E(Oil)$ and $+\Delta E(Fuse)$, respectively, in Ref.[1]

The numerical ΔE_Σ values reported in Ref.[1] were calculated according to the scheme given in this paper.

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