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Thermochemistry of Halogenomethanes

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Data on the thermochemistry of halogenomethanes are surveyed. The most reliable enthalpies of formation of 17 compounds have been selected by analysing the literature results and the "key" values adopted in recent years. The scope of modern methods for the approximate calculation of the enthalpies of formation of halogenomethanes is examined. Values are recommended for the enthalpies of formation of all 70 halogenomethanes and their reliability is estimated.
The bibliography includes 111 references.

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I. INTRODUCTION

The great importance of organic halogeno-compounds in modern chemistry and technology is due to their extensive and rapidly growing applications. Halogeno-derivatives of lower aliphatic hydrocarbons, particularly those of methane, occupy an especially important place among such substances.

The thermochemistry of halogenomethanes is of great interest from both theoretical and practical points of view. The theoretical interest is related to the specific influence of the successive introduction of halogen atoms on the energetic properties of the molecule, which is manifested, for example, by unusual thermochemical reactions [1,2]. The practical interest arises primarily from the necessity to carry out thermodynamic calculations for technical purposes.

Nevertheless the thermochemistry of halogenomethanes has been investigated inadequately and the published data for the enthalpies of formation are contradictory [3-9]. This is caused primarily by the difficulty of the experimental determination of the enthalpies of formation of organic halogeno-compounds, particularly polysubstituted compounds [2,5]. Critical analysis of the available data has shown that this is why reliable enthalpies of formation

have been obtained experimentally only for a comparatively small number of halogenomethanes. In many cases the results obtained by different investigators or by different methods show appreciable discrepancies and the choice between them is difficult. Frequently, having at their disposal the same set of initial data, different workers selected "best" values differing by 10–15 kcal mol^{-1}.[5,9,10] Another source of the contradictions in the recommended enthalpies of formation is associated with the necessity to employ methods of approximate calculation, because among the 70 halogenomethanes experimental data are available for a comparatively small number of compounds (not more than 20).

Thus using 17 "reference" values of ΔH_f° which they selected, Yudin and Khachkuruzov[5] estimated the enthalpies of formation of other halogenomethanes by approximate methods. A handbook[3] quoted data for 46 compounds based on their investigation, and still constitutes the most complete compilation of thermochemical constants in the field under consideration. Bernstein[9] estimated the enthalpies of formation of 35 compounds having the composition $CH_nCl_mBr_pF_{4-m-n-p}$ by the method which he proposed. However estimates of the enthalpies of formation by approximate methods involve an even greater arbitrary factor than the choice between experimental values. The results of such estimates generally depend both on the selection of "reference" ΔH_f° values and on the choice of the method of estimation. The estimates of the enthalpies of formation of halogenomethanes by Yudin and Khachkuruzov[5] and Bernstein[9] cannot be regarded as successful for certain groups of compounds. Thus Yudin and Khachkuruzov's[5] enthalpies of formation of chlorofluoromethanes (CH_2FCl, $CHFCl_2$, and CHF_2Cl) proved to deviate appreciably from the true values mainly as a result of the incorrect selection of "reference" ΔH_f° values for fluoromethanes (CH_3F, CH_2F_2, and CHF_3) and also owing to a non-critical application of computational methods[10]. The choice of ΔH_f° in Bernstein's paper[9] for CBr_4, which serves as a basis for the calculation of the enthalpies of formation of other bromo-derivatives, gives rise to appreciable doubts.

The handbooks published in recent years[4,7,8,11] contain carefully selected enthalpies of formation of halogenomethanes, but they include only a comparatively small number of results found experimentally.

This review presents a compilation of the enthalpies of formation of all 70 halogenomethanes. Different experimental methods are described concisely and their possibilities are compared; the difficulties arising in the study of this group of compounds and the methods which can be used to overcome them are discussed. The experimental data are analysed and a value is recommended for each substance. The regularities in the enthalpies of formation of halogenomethanes are considered. The literature methods for the approximate calculation of the enthalpies of formation of halogenomethanes and their theoretical foundations are analysed; recommendations are made concerning the use of these methods.

The enthalpies of formation of the 70 halogenomethanes are recommended on the basis of critically selected most reliable available enthalpies of formation (17 values), the complete set of methods of approximate calculation, and the observed regularities in ΔH_f°. All the recommended values of ΔH_f° have been recalculated on the basis of the key data adopted in 1972–1975 by the International CODATA Commission[12,13].

II. METHODS FOR THE DETERMINATION OF THE ENTHALPIES OF FORMATION OF HALOGENOMETHANES

The most general method for determining the enthalpies of formation of solid and liquid organic compounds is based on the measurement of their enthalpies of combustion in oxygen at an elevated pressure[14,15]. This procedure, developed by Berthelot and known as the bomb calorimetric method, is the most reliable for very many organic compounds of comparatively simple combustion ($C_aH_bO_cN_d$), but its application to organic halogeno-compounds involves considerable difficulties, associated mainly with the complex composition of the combustion products and their highly corrosive nature[2,14,15]. These difficulties may be overcome by employing rotating bombs, auxiliary reducing agents (for organic chloro- and bromo-compounds) and other complications and improvements in the method[14,15]. In the determination of the enthalpies of combustion of liquid and solid organic halogeno-compounds an accuracy to within approximately ±0.01–0.02% can be achieved nowadays, which usually corresponds to the determination of the standard enthalpy of formation with an error not exceeding several tenths of kcal mol^{-1}.[14,15] However, this accuracy can be achieved only when many additional conditions are observed; high purity of the test substances, rapid and complete reduction of the free halogens to hydrogen halides, careful analysis of the solution in the bomb calorimeter and of the gaseous reaction products with subsequent application of reliably determined thermal corrections, etc. The actual discrepancies between the results obtained by different workers amount in many instances to several kcal mol^{-1} and the choice between such values is frequently not evident.

The method involving the determination of enthalpies of combustion in a stream of oxygen under a pressure close to atmospheric has been used successfully for gaseous organic compounds[14,16]. The method is applicable to halogeno-derivatives with a low halogen content, as a rule to monohalogeno-derivatives[16]. The determination of the enthalpies of formation of gaseous compounds with a high halogen content or compounds containing different halogens is more difficult. Their enthalpies of formation are sometimes determined by combustion in oxygen in a bomb calorimeter[2,17,18]. In this case careful analysis of the combustion products is necessary, because the combustion of the gases in the bomb does not as a rule go to completion.

The experimental difficulties encountered in the determination of the enthalpies of combustion of halogenomethanes in oxygen led to the development of many new procedures, usually less universal but having definite advantages in the study of individual groups of compounds. In order to determine the ΔH_f° for gas-phase catalytic reactions, Lacher and coworkers designed a novel isothermal calorimeter of the compensation type[14,19,20]. They used it most often to measure the enthalpies of reactions involving addition to a double bond (chlorination, bromination, hydrobromination, etc.). However, in certain cases, the enthalpies of hydrogenation of organic halogeno-compounds with complete or partial substitution of the halogen by hydrogen were determined[21–23]. These studies made it possible to calculate the standard enthalpies of formation of individual halogenoalkanes, particularly halogenomethanes.

The choice of the catalyst and the reaction conditions is very important for the determination of the enthalpies of gas-phase reactions. The reproducibility of the results of

measurements is as a rule fairly high (0.1–0.2 kcal mol^{-1}), but in certain cases there are significant discrepancies with data obtained by other methods [16]. Thus the discrepancy for methyl chloride amounts to ~1 kcal mol^{-1} and is probably associated with failure to take into account the systematic errors in the determination of ΔH° for the catalytic reaction (for example, owing to the insufficient inertness of the catalyst [16]).

In order to determine the enthalpies of formation of chlorofluorocarbons, particularly chlorofluoromethanes, a method [24–30] based on the measurement of the enthalpies of the reactions of these compounds with alkali metals has been used:

$$CF_nCl_{4-n} + 4M \rightarrow C + n\,MF + (4-n)\,MCl\ ; \quad M = Na \text{ or } K. \qquad (1)$$

This reaction is initiated by an electric arc, the energy of which must therefore be accurately measured. It usually results in the formation of amorphous highly dispersed carbon. Since the enthalpies of formation of different specimens of amorphous carbon may differ, it is desirable to determine them experimentally for each series of experiments. In order to prevent side reactions, it is very important to make sure that, when reaction (1) is carried out in a calorimeter, the gaseous substance investigated reacts in its entirety [31]. To make sure that the reaction goes to completion and proceeds unambiguously, it is necessary to carry out numerous measurements and analyses: measurement of the residual pressure in the bomb, analysis of the contents of the bomb for fluoride and chloride ions, weighing of the initial gas, weighing of the alkali metal, and determination of the amount of metal which has not reacted. The accuracy of the results is determined ultimately by the accuracy of these measurements and analyses and also by the accuracy of the measurement of the energy of the arc and of the enthalpy of combustion of the carbon. The enthalpies of reactions with alkali metals can be determined only for a limited range of substances. In terms of accuracy, this method is much inferior to the determination of the enthalpies of combustion in oxygen. Its use for chlorofluoromethanes is justified by the fact that more accurate thermochemical procedures are as a rule inapplicable to this group of compounds [31].

Other methods are still more specific. The application of the method of combustion in fluorine, which has been used successfully in recent years to determine the enthalpies of formation of fluorides and certain other classes of compounds, is restricted in the case of halogenomethanes by the need to determine the enthalpy of formation of carbon tetrafluoride [32,33].

The method based on the measurement of the enthalpies of reduction of halogeno-derivatives by lithium tetrahydroaluminate has been used successfully for certain methane derivatives [34]. The reduction is carried out in ethereal solution in the presence of an excess of lithium hydride. Lithium tetrahydroaluminate is regenerated under these conditions and the reaction may be represented by the equation

$$RX + LiH \xrightarrow[\text{in ethereal soln.}]{LiAlH_4} RH + LiX\ , \qquad (2)$$

where X is the halogen (bromine or iodine). The enthalpies of formation of LiH, RH, and LiX are known, so that the calculation of the enthalpies of formation of RX presents no difficulties. The method is mainly applicable to monohalogeno-derivatives. In certain cases the enthalpies of formation of halogenomethanes were determined by measuring the enthalpies of their thermal decomposition reactions [17,35]. The enthalpies of formation of certain chlorofluoromethanes have been measured by the method involving explosion in a spherical bomb [37,38]. The last three methods are applicable solely to a small group of substances and has not as yet been adequately investigated. Their use must be accompanied by particularly careful chemical control of the relevant process.

Apart from the procedures described, there exist also calorimetric methods which have been used only in individual and exceptional cases. Their possibilities are briefly described below in connection with the assessment of specific literature data.

Together with direct measurements, the method involving the determination of the enthalpies of reaction from chemical equilibrium data is frequently used in the thermochemistry of halogenomethanes. Measurement of the equilibrium constants makes it possible to calculate the Gibbs free energy of reaction:

$$\Delta G^\circ_T = -RT \ln K_p,$$

or the enthalpy of reaction may be calculated from the equation

$$\Delta H^\circ_T = -RT \ln K_p + T\Delta S^\circ_T. \qquad (3)$$

ΔH°_T may be calculated from Eqn. (3) by two procedures. Usually ΔH°_T is calculated from the temperature dependence of K_p assuming that ΔS°_T is constant. On the other hand, when the values of ΔS°_T for the given reaction may be calculated by an independent method, it is possible to evaluate ΔH°_T directly. The latter method is more accurate, but is applicable only when the entropies of all the reactants are known (for example, have been calculated on the basis of the Third Law of Thermodynamics).

The calculation of the enthalpies of reaction from equilibrium data does not always lead to reliable results. An essential condition for the successful application of this method is a high accuracy of the measurement of K_p, the attainment of equilibrium over the entire temperature range, and the absence of side reactions. This is particularly important in the calculation of ΔH°_T from the temperature variation of K_p.

In a series of careful studies in recent years [39–46], undertaken to investigate equilibria involving halogenomethanes, a high accuracy of the measurement of K_p was achieved as a result of the employment of sensitive instruments for the measurements of pressure and concentration and careful investigation of the equilibrium conditions over a wide temperature range. In terms of the accuracy of the calculation of ΔH°_T, some of these studies can compete successfully with the measurements of ΔH°_T by direct calorimetric methods.

Apart from the equilibrium method, other non-calorimetric procedures are sometimes used. Thus enthalpies of formation have been estimated [5] using the results of the experimental determination of the bond dissociation energies (for example, by the electron impact method). However, this method is much less accurate than those described above. The determination of dissociation energies is usually associated with the measurement of the appearance and ionisation potentials and the accuracy of such measurements is comparatively low (see Yudin and Khachkuruzov [5], Table 3). Furthermore, in order to calculate ΔH°_f for compounds in terms of the dissociation energy, it is necessary to know the ΔH°_f for the groups involved; these values are also as a rule not accurate. For this reason, the calculation of ΔH°_f in

terms of dissociation energies can be usefully employed only in the absence of more accurate data and only in those cases where even a rough estimate of the thermochemical quantities is sufficient.

III. KEY VALUES AND UNITS OF MEASUREMENT

To ensure the mutual consistency of all the recommended thermochemical data, the single system of key values developed and adopted by the Committee on Data for Science and Technology (CODATA) is used in the present review. In calculating the enthalpies of formation of halogenomethanes, the following key values of ΔH_f°(kcal mol^{-1}) were used: -68.315 ± 0.010 (H_2O, liq.); -94.051 ± 0.031 (CO_2, gas); -80.15 ± 0.16 (F^-_{aq}); -39.933 ± 0.021 (Cl^-_{aq}); -29.039 ± 0.35 (Br^-_{aq}); 7.388 ± 0.026 (Br_2, gas); -8.695 ± 0.041 (HBr, gas); -57.433 ± 0.015 (Na^+_{aq}); -60.271 ± 0.025 (K^+_{aq}); -22.063 ± 0.031 (HCl, gas); 6.30 ± 0.19 (HI, gas); 14.919 ± 0.019 (I_2, gas).[12,13,47] All the values of ΔH_f° quoted in this review refer to the standard states of the substances and 298.15 K.

The most significant difference between the adopted system of key values and those employed in the most widely used handbooks[4,7] consists in the revision of ΔH_f° (F^-_{aq}). The remaining quantities have remained unchanged or have been changed very insignificantly.

In many instances, apart from the quantities listed above, others (enthalpy of evaporation, enthalpy of dilution, etc.) are needed to calculate the enthalpies of formation of halogenomethanes. These auxiliary quantities were taken from handbooks[4,7] and other publications[48,49]. In calculating the enthalpies of reaction from equilibrium constants, revised values of the thermodynamic functions were used[50].

The enthalpies of formation of compounds in the vast majority of thermochemical studies are expressed in kcal mol^{-1}. To facilitate the comparison of the results, these units were used also in the present review. However, the final data in the Table of recommended values are also expressed in kJ mol^{-1}, which corresponds to the International "SI" system of units adopted by the XIth General Conference on Weights and Measures in 1960.[51,52]. These units are related: 1 cal = 4.184 J.[14] The atomic weights were adopted from Ref. 53.

IV. ANALYSIS OF EXPERIMENTAL THERMOCHEMICAL DATA FOR HALOGENOMETHANES AND SELECTION OF RECOMMENDED ENTHALPIES OF FORMATION

Methane

The bibliography of the determinations of the enthalpy of combustion of methane up to 1970 is given by Glushko[4]. Rossini's study[54] is the most accurate. After applying corrections for the adjustment of the gas to the ideal state[55] and for the modification of atomic weights, these data[54] lead to ΔH_f° (CH_4, gas) = -17.88 ± 0.08 kcal mol^{-1}.[3,4] In 1972 Pittam and Pilcher[56] redetermined the enthalpy of combustion of gaseous methane in an improved calorimeter with a burner[16] and obtained ΔH_f° (CH_4, gas) = -17.80 ± 0.10 kcal mol^{-1}. Pittam and Pilcher had at their disposal a purer methane specimen than in Rossini's work, but, since they calibrated the calorimeter on the basis of the heat of combustion of hydrogen, their results depend on the latter. Since the discrepancy between the values in Refs. 54 and 56 is small, it is desirable to adopt the mean as the recommended value of ΔH_f° (CH_4, gas), i.e.

$$\Delta H_f^\circ(CH_4, \text{gas}) = -17.85 \pm 0.06 \text{ kcal mol}^{-1}.$$

Difluoromethane

Neugebauer and Margrave[57] determined the enthalpy of combustion of difluoromethane in a rotating bomb calorimeter. Since the solubilities and heats of solution of CO_2 and O_2 in HF solution were unknown, the calorimeter was calibrated in three series of experiments: under standardised conditions, with the bomb containing 50 cm^3 of water, and with the bomb containing 50 cm^3 of the HF solution. This procedure enabled the authors[57] to apply a correction for the standard state and also to exclude a secondary thermal effect associated with the corrosion of the walls of the bomb. Mass-spectrometric analysis of the combustion products showed that no substance other than CO_2 and HF were obtained on combustion. Only a small amount of uncombusted difluoromethane was detected. The enthalpy of combustion of CH_2F_2 via the reaction

$$CH_2F_2(\text{gas}) + O_2(\text{gas}) \rightarrow CO_2(\text{gas}) + 2HF\ (\text{soln};\ 2.4\ N)$$

which the present author calculated from the results of individual experiments quoted by Neugebauer and Margrave[57], is -139.83 ± 0.20 kcal mol^{-1}. ΔH_f° (CH_2F_2, gas) = -108.09 ± 0.42 kcal mol^{-1} corresponds to this value.

Trifluoromethane

Neugebauer and Margrave[57] determined the enthalpy of combustion of CHF_3 by the same method as for CH_2F_2 (see above). Their results lead to the following value when account is taken of the key quantities adopted above: ΔH_f° (CHF_3, gas) = -166.47 ± 0.90 kcal mol^{-1}.

The equilibrium in the reaction

$$Br_2 + CHF_3 \rightleftarrows HBr + CBrF_3 \qquad (4)$$

has been investigated[42,58]. Calculation based on the Third Law of Thermodynamics using revised values of thermodynamic functions[50] yielded $\Delta H^\circ(4) = -4.26 \pm 0.11$ kcal mol^{-1} for this reaction. Coomber and Whittle[41] also investigated the equilibrium in the reaction

$$C_2F_6 + Br_2 \rightleftarrows 2CF_3Br \qquad (5)$$

and their results lead to $\Delta H^\circ(5) = 3.287 \pm 0.075$ kcal mol^{-1}.

The equilibria in reactions (4) and (5) were attained from both directions. The results of the measurement of $\Delta H(4)$ and $\Delta H(5)$ make it possible to establish the relation $\Delta H_f^\circ(C_2F_6) - 2\Delta H_f^\circ(CHF_3) = 12.193 \pm 1.2$ kcal mol^{-1}, whence, using $\Delta H_f^\circ(C_2F_6$, gas) = -321.03 ± 1.30 kcal mol^{-1},[50] we obtain ΔH_f° (CHF_3, gas) = -166.97 ± 0.90 kcal mol^{-1}.

The values of ΔH_f° obtained by the two different methods agree within the limits of experimental error. The recommended value is the weighted mean of those quoted above:

$$\Delta H_f^\circ(CHF_3, \text{gas}) = -166.72 \pm 0.64 \text{ kcal mol}^{-1}.$$

Carbon Tetrafluoride

The example of CF_4 shows particularly clearly how difficult is a reliable determination of the enthalpies of formation of organic halogeno-compounds with a high

halogen content. In the 15 studies carried out during the period between 1933 and 1965 different methods were used to determine ΔH_f°: combustion of carbon in fluoride[59,60], combustion of methane in fluorine[61], reaction between CF_4 and potassium[24,25] and sodium[27], thermal decomposition of tetrafluoroethylene[17,35], combustion of polytetrafluoroethylene[62,63] and docosafluorobicyclohexyl[64] in oxygen under conditions leading to markedly different CF_4 contents in the combustion product, explosion in a spherical bomb[37,38], etc. However, the results were not very accurate and the maximum discrepancy between them reached more than 70 kcal mol^{-1} (the results range from −162 kcal mol^{-1} [59] to −235 kcal mol^{-1} [24]).

The most reliable results were obtained in recent years by the direct measurement of the enthalpy of fluorination of graphite[32,33]. Domalski and Armstrong[32] combusted a mixture of graphite and Teflon in fluorine. Greenberg and Hubbard[33] achieved a high degree of combustion of graphite by a successful choice of the reaction initiator (silicon powder). The combustion products were carefully analysed in both cases; the amounts of the C_2F_6 and C_3F_8 admixtures in the products were very small and the values of $\Delta H_f^\circ(CF_4, gas)$ obtained agree extremely well: −222.87 ± 0.38 kcal mol^{-1} [32] and −223.05 ± 0.20 kcal mol^{-1}.[33] Similar results were also obtained[65] from the measurement of the heat of combustion of Teflon in fluorine: $\Delta H_f^\circ(CF_4, gas) = -222.0$ kcal mol^{-1}, and from a determination[66] of the enthalpy of reaction between dicyanogen and nitrogen trifluoride: $\Delta H_f^\circ(CF_4, gas) = -223.23 \pm 0.5$ kcal mol^{-1}. The following value has been adopted[4] on the basis of the results in Refs. 32 and 33:

$$\Delta H_f^\circ(CF_4, gas) = -223.0 \pm 0.4 \text{ kcal mol}^{-1},$$

This is a key value in the thermochemistry of organic fluoro-compounds and one of the most reliable among the known enthalpies of formation of halogenomethanes.

Chloromethane

The enthalpy of combustion of gaseous chloromethane was determined by Berthelot[67] and Thomsen[68], but the accuracy of their results is low. The enthalpy of the hydrogenation of CH_3Cl to methane was determined in later investigations[21-23], the results leading to $\Delta H_f^\circ(CH_3Cl, gas) = -20.6$ kcal mol^{-1}.[4] Very similar values of ΔH_f° were obtained in a number of compilations[3,6,8] from the results in Refs. 21 and 22. Somewhat later Fletcher and Pilcher[69] determined the enthalpy of combustion of chloromethane in a calorimeter with a heater. Their results lead to the following value:

$$\Delta H_f^\circ(CH_3Cl, gas) = -19.58 \pm 0.16 \text{ kcal mol}^{-1},$$

which we recommend bearing in mind the reliability of the apparatus and method used[69]. A similar value, $\Delta H_f^\circ(CH_3Cl, gas) = -19.32$ kcal mol^{-1}, was adopted in Ref. 7.

Dichloromethane

The determination of the enthalpy of combustion of CH_2Cl_2 by Berthelot and Ogier[70] is only of historical interest. Smith et al.[71] determined the enthalpy of combustion of CH_2Cl_2 in a stationery bomb calorimeter. Their value of ΔH_C°, adjusted to 25°C, corresponds to $\Delta H_f^\circ(CH_2Cl_2, liq.) = -28.74$ kcal mol^{-1}. Taking into account the enthalpy of evaporation, which is 6.90 ± 0.03 kcal mol^{-1},[4] we find $\Delta H_f^\circ(CH_2Cl_2, gas) = -21.84$ kcal mol^{-1}. Lacher et al.[72] measured the enthalpy of the gas-phase hydrogenation of dichloromethane to methane and hydrogen chloride at 250°C. After adjustment to 25°C, their data leads to $\Delta H_f^\circ((CH_2Cl_2, gas) = -22.92$ kcal mol^{-1}. Hu and Sinke[73] redetermined in 1969 the enthalpy of combustion of liquid dichloromethane using a rotating bomb calorimeter and a very pure CH_2Cl_2 specimen. Their results yield $\Delta H_f^\circ(CH_2Cl_2, liq.) = -29.66 \pm 0.07$ kcal mol^{-1} or $\Delta H_f^\circ(CH_2Cl_2, gas) = -22.76 \pm 0.08$ kcal mol^{-1}. The last value is the most reliable and agrees very well with the data of Lacher et al.[72].

Trichloromethane

The accuracy of the determinations of the enthalpy of combustion of trichloromethane in Refs. 68, 74, and 75 is not high. The data of Smith et al.[71] for the enthalpy of combustion of $CHCl_3$ lead to $\Delta H_f^\circ(CHCl_3, liq.) = -31.65$ kcal mol^{-1} after adjustment to 25°C. Kirkbride[76] measured the enthalpy of the reaction between liquid trichloromethane and gaseous chlorine and his result makes it possible to establish only the relation $\Delta H_f^\circ(CHCl_3, liq.) = \Delta H_f^\circ(CCl_4, liq.) + 0.24$ kcal mol^{-1}. The most reliable data are those of Hu and Sinke[73], who determined the enthalpy of combustion of an extremely pure trichloromethane specimen in a rotating bomb calorimeter. Their results[73] lead to $\Delta H_f^\circ(CHCl_3, liq.) = -32.04 \pm 0.35$ kcal mol^{-1} or, taking into account $\Delta H^\circ_{V298,15}(CHCl_3, liq.) = 7.5 \pm 0.1$ kcal mol^{-1},[4] to $\Delta H_f^\circ(CHCl_3, gas) = -24.54 \pm 0.37$ kcal mol^{-1}.

Carbon Tetrachloride

The determination of the enthalpy of combustion carried out by Berthelot[74] and Thomsen[68] are less accurate than the values obtained in later studies. Bodenstein et al.[77] determined the enthalpy of the gas-phase reaction of CCl_4 with hydrogen involving the formation of hydrogen chloride and amorphous carbon. ΔH_f° for amorphous carbon may vary appreciably; having adopted its value from the paper of Neugebauer and Margrave[17], Yudin and Khachkuruzov[5] obtained the following value from the data of Bodenstein et al.[77]: $\Delta H_f^\circ(CCl_4, gas) = -24.7$ kcal mol^{-1}. Baibuz and Medvedev[37,38] found $\Delta H_f^\circ(CCl_4, gas) = -24.6 \pm 1.9$ kcal mol^{-1} by an explosion method. Neugebauer[78] measured the enthalpy of the reaction of carbon tetrachloride with magnesium and obtained $\Delta H_f^\circ(CCl_4, liq.) = -32.3 \pm 1.5$ kcal mol^{-1}. Smith et al.[71] determined the enthalpy of combustion of CCl_4 in oxygen in the presence of a large amount of an auxiliary substance—only 4% of the measured heat corresponded to CCl_4. After adjustment to 25°C, their data lead to $\Delta H_f^\circ(CCl_4, liq.) = -29.03$ kcal mol^{-1}. Lord and Pritchard[79] studied the equilibrium

$$CO_2(gas) + CCl_4(gas) \rightarrow 2COCl_2(gas) \quad (6)$$

and found $\Delta H^\circ_{298}(6) = 16.8 \pm 0.5$ kcal mol^{-1}. Depending on the enthalpy of formation of phosgene adopted, this value leads to $\Delta H_f^\circ(CCl_4, gas) = -29.75 \pm 1.1$ or $\Delta H_f^\circ(CCl_4, gas) = -27.4 \pm 0.7$ kcal mol^{-1}. In their study of the equilibrium

$$Br_2 + CCl_4 \rightleftarrows BrCl + CBrCl_3, \quad (7)$$

Mendenhall et al.[43] obtained $\Delta H^\circ_{298}(7) = 8.84 \pm 0.3$ kcal mol^{-1}; recalculation of this value using revised thermodynamic functions[50] yields $\Delta H^\circ_{298}(7) = 8.37 \pm 0.30$ kcal mol^{-1}. Sullivan and Davidson[80] found $\Delta H^\circ_{298}(8) = -1.44 \pm 0.10$ kcal mol^{-1} for the reaction

$$Br_2 + CHCl_3 \rightleftarrows HBr + CBrCl_3 \quad , \qquad (8)$$

which, together with the previous result, yields the difference $\Delta H^\circ_f(CCl_4, gas) - \Delta H^\circ_f(CHCl_3, gas) = 2.44 \pm 0.35$ kcal mol^{-1}. Using the value $\Delta H^\circ_f(CHCl_3, gas) = -24.54 \pm 0.37$ kcal mol^{-1} adopted above, we obtain $\Delta H^\circ_f(CCl_4, gas) = -22.10 \pm 0.51$ kcal mol^{-1}.

The most reliable study is that of Hu and Sinke[73], who determined ΔH° for the combustion of a pure carbon tetrachloride specimen in a rotating bomb calorimeter. Their data lead to $\Delta H^\circ_f(CCl_4, liq.) = -30.61 \pm 0.16$ kcal mol^{-1} or, taking into account the enthalpy of evaporation $\Delta H^\circ_{V298.15}(CCl_4, liq.) = 7.75 \pm 0.01$ kcal mol^{-1},[4] the result is $\Delta H^\circ_f(CCl_4, gas) = -22.86 \pm 0.16$ kcal mol^{-1}.

Chlorotrifluoromethane

The values of $\Delta H^\circ_f(CF_3Cl, gas)$ calculated from ΔH° for the reactions of CF_3Cl with potassium[25,26] or sodium[29,30] diverge appreciably: -176.2 kcal mol^{-1} [25]; -167.0 kcal mol^{-1} [26]; -176.7 kcal mol^{-1}.[29,30] These discrepancies are probably a consequence of numerous complications arising in the determination of the heats of reaction with alkali metals (see above). Mears and Stahl's measurements[81] of the enthalpy of the disproportionation reaction lead to -20.85 kcal mol^{-1} for the reaction

$$3HF + CCl_4 \rightarrow CF_3Cl + 3HCl$$

at 573 K, which on recalculation yields $\Delta H^\circ_f(CF_3Cl, gas) = -172.6$ kcal mol^{-1}. Baibuz and Medvedev[37,38] found $\Delta H^\circ_f(CF_3Cl, gas) = -167.7 \pm 2.2$ kcal mol^{-1} by an explosion method in a spherical bomb. Lord and coworkers[82,83] studied the equilibria

$$CF_3Cl + I_2 \rightleftarrows CF_3I + ICl \quad , \qquad (9)$$

$$CF_3H + I_2 \rightleftarrows CF_3I + HI \quad . \qquad (10)$$

When revised thermodynamic functions[50] are used, their data lead to $\Delta H^\circ_{298}(9) = 17.22 \pm 0.11$ kcal mol^{-1} and $\Delta H^\circ_{298}(10) = 17.29 \pm 0.15$ kcal mol^{-1}.[82] Hence we obtain $\Delta(\Delta H) = \Delta H^\circ_f(CF_3Cl, gas) - \Delta H^\circ_f(CF_3H, gas) = -2.07 \pm 0.30$ kcal mol^{-1}. The quantity $\Delta(\Delta H)$ may also be calculated from Coomber and Whittle's data[42,84] for the equilibria

$$CF_3Br + Cl_2 \rightleftarrows CF_3Cl + BrCl \quad , \qquad (11)$$

$$CF_3Cl + Br_2 \rightleftarrows CF_3Br + BrCl \quad , \qquad (12)$$

$$CF_3H + Br_2 \rightleftarrows CF_3Br + HBr \quad . \qquad (13)$$

They obtained $\Delta H^\circ_{298}(11) = -10.69 \pm 0.30$ kcal mol^{-1}, $\Delta H^\circ_{298}(12) = 10.49 \pm 0.40$ kcal mol^{-1}, and $\Delta H^\circ_{298}(13) = -4.26 \pm 0.11$ kcal mol^{-1}. $\Delta(\Delta H) = -2.75 \pm 0.50$ kcal mol^{-1} when $\Delta H^\circ(11)$ and $\Delta H^\circ(13)$ are used, and $\Delta(\Delta H) = -2.84 \pm 0.53$ kcal mol^{-1} follows from $\Delta H^\circ(12)$ and $\Delta H^\circ(13)$. The average value of the difference $\Delta(\Delta H)$ based on the results in Refs. 42 and 82–84 is -2.55 ± 0.50 kcal mol^{-1}. Since $\Delta H^\circ_f(CHF_3, gas) = -166.72 \pm 0.64$ kcal mol^{-1}, we obtain

$$\Delta H^\circ_f(CF_3Cl, gas) = -169.27 \pm 0.81 \text{ kcal mol}^{-1}.$$

Bearing in mind the satisfactory agreement between the three values of $\Delta(\Delta H)$, the last value of the enthalpy of formation appears to be the most reliable.

Dichlorodifluoromethane

The values of $\Delta H^\circ_f(CF_2Cl_2, gas)$ calculated from the ΔH° for the reactions of CF_2Cl_2 with potassium[25,26] or sodium[29,30] agree satisfactorily: -115.6 kcal mol^{-1} [25]; -114.6 kcal mol^{-1} [26]; -115.0 kcal mol^{-1}.[29,30] Mears and Stahl[81] quote $\Delta H^\circ_{573}(14) = -10.97$ kcal mol^{-1} for the reaction

$$2HF + CCl_4 \rightarrow CF_2Cl_2 + 2HCl \, , \qquad (14)$$

which leads to $\Delta H^\circ_f(CF_2Cl_2, gas) = -119.8$ kcal mol^{-1}. Petersen and Pitzer[85] measured K_p for the reaction

$$2CF_3Cl + CCl_4 \rightleftarrows 3CF_2Cl_2 \quad . \qquad (15)$$

According to their data, $\Delta H^\circ_{298}(15) = 7.64$ kcal mol^{-1} and $\Delta H^\circ_f(CF_2Cl_2, gas) = -117.9$ kcal mol^{-1}. Mears and Stahl[81] published no information about the experiment and Petersen and Pitzer[85] noted the occurrence of side reactions. We therefore recommend the mean of the three values obtained in Refs. 25, 26, 29, and 30, i.e. $\Delta H^\circ_f(CF_2Cl_2, gas) = -115.1$ kcal mol^{-1}. The error of this quantity probably does not exceed ± 2 kcal mol^{-1}.

Trichlorofluoromethane

The values of $\Delta H^\circ_f(CFCl_3, gas)$ calculated from the ΔH° for the reaction of $CFCl_3$ with potassium differ significantly: -72.0 kcal mol^{-1} [25] and -64.6 kcal mol^{-1}.[26] Mears and Stahl's data[81] lead to values which vary from -64.7 to -70.2 kcal mol^{-1} depending on the selected method of calculation. Petersen and Pitzer[85] measured K_p for the reaction

$$CF_3Cl + 2CCl_4 \rightleftarrows 3CFCl_3 \, , \qquad (16)$$

and according to their data $\Delta H^\circ_{298}(16) = 10.56$ kcal mol^{-1} and $\Delta H^\circ_f(CFCl_3, gas) = -68.1$ kcal mol^{-1}. They noted the occurrence of side reactions between chlorofluoromethanes and the catalyst ($AlCl_3$). Baibuz and Medvedev[37,38] found $\Delta H^\circ_f(CFCl_3, gas) = -67.5$ kcal mol^{-1} by an explosion method in a spherical bomb. Neugebauer[36] measured ΔH° for the reaction of $CFCl_3$ with magnesium and obtained $\Delta H^\circ_f(CFCl_3, gas) = -66.2$ kcal mol^{-1}. Recalculation of this result on the basis of the system of key quantities adopted in the present review is impossible owing to the lack of information about the experiment in Neugebauer paper[36]. The choice of the recommended value of ΔH°_f is difficult, but the available set of data suggests that it lies in the range between -65 and -70 kcal mol^{-1}. The average value $\Delta H^\circ_f(CFCl_3, gas) = -67.5 \pm 2.5$ kcal mol^{-1} is recommended.

Bromomethane

Berthelot[67] and Thomsen[68] measured ΔH° for the combustion of bromomethane, but the accuracy of their measurements is low. Bak[86] investigated the equilibrium

in the gas-phase reaction

$$CH_3Br + HCl \rightleftarrows CH_3Cl + HBr \quad (17)$$

and $\Delta H^\circ_{298}(17) = -2.41 \pm 0.10$ kcal mol^{-1} and $\Delta H^\circ_f(CH_3Br, gas) = -8.62 \pm 0.19$ kcal mol^{-1} were calculated from his data. Hartley et al.[87] determined the enthalpy of the reaction

$$Hg(CH_3)_2(liq.) + 2Br_2(liq.) \rightarrow HgBr_2(cryst.) + 2CH_3Br\ (gas) \quad (18)$$

and found $\Delta H^\circ_{298}(18) = -72.15 \pm 0.61$ kcal mol^{-1}. Together with the ΔH° for the combustion of dimethylmercury,[88] these data lead to $\Delta H^\circ_f(CH_3Br, gas) = -8.6$ kcal mol^{-1}. Fowell et al.[23] determined the enthalpy of the hydrogenation of CH_3Br to methane and their results yield $\Delta H^\circ_f(CH_3Br, gas) = -8.97 \pm 0.34$ kcal mol^{-1}.

Adams et al.[89] determined the energy of the reaction of bromomethane with lithium hydride in lithium tetrahydroaluminate, whence they found $\Delta H^\circ_{298}(19) = -3.3 \pm 0.3$ kcal mol^{-1} for the reaction

$$CH_3Br(liq.) + \tfrac{1}{2}H_2(gas) \rightarrow CH_4(gas) + \tfrac{1}{2}Br_2(liq.). \quad (19)$$

We obtain from these data $\Delta H^\circ_f(CH_3Br, liq.) = -14.55 \pm 0.31$ kcal mol^{-1} or, taking into account the enthalpy of evaporation $\Delta H^\circ_{V298}(CH_3Br, liq.) = 5.64 \pm 0.10$ kcal mol^{-1}, we have $\Delta H^\circ_f(CH_3Br, gas) = -8.91 \pm 0.32$ kcal mol^{-1}. Ferguson et al.[90] investigated the equilibrium in the gas-phase bromination of methane with formation of HBr and CH_3Br; calculation from their results based on the Second Law of Thermodynamics yields $\Delta H^\circ_{298} = -8.63$ kcal mol^{-1} for the bromination reaction, while calculation based on the Third Law gives rise to $\Delta H^\circ_{298} = -6.26 \pm 0.10$ kcal mol^{-1}. The latter result corresponds to $\Delta H^\circ_f(CH_3Br, gas) = -8.03 \pm 0.12$ kcal mol^{-1}, but conflicts with the results of the majority of other studies. The most probable value is the mean of those obtained in Refs. 23 and 89, i.e. $\Delta H^\circ_f(CH_3Br, gas) = -8.94 \pm 0.30$ kcal mol^{-1}.

Bromotrifluoromethane

The enthalpy of reaction (4) and the value of $\Delta H_f(CHF_3, gas)$ adopted above lead to $\Delta H^\circ_f(CF_3Br, gas) = -155.22 \pm 0.65$ kcal mol^{-1}. Lord et al.[82] investigated the equilibrium

$$CF_3Br + I_2 \rightleftarrows CF_3I + BrI \quad (20)$$

and according to their data $\Delta H^\circ_{298}(20) = 9.55 \pm 0.04$ kcal mol^{-1}. Together with the enthalpy of reaction (10), this yields $\Delta H^\circ_f(CF_3Br, gas) = -155.55 \pm 0.70$ kcal mol^{-1}. The following average value is recommended:

$$\Delta H^\circ_f(CF_3Br, gas) = -155.38 \pm 0.65 \text{ kcal mol}^{-1}.$$

Bromotrichloromethane

Equilibrium (8) was investigated by Sullivan and Davidson[80] and their results made it possible to calculate $\Delta H^\circ_f(CCl_3Br, gas) = -9.90 \pm 0.40$ kcal mol^{-1}. The data of Mendenhall et al.[43] for reaction (7) lead to $\Delta H^\circ_f(CCl_3Br, gas) = -10.65 \pm 0.35$ kcal mol^{-1}. The mean of the two values quoted, i.e. $\Delta H^\circ_f(CCl_3Br, gas) = -10.28 \pm 0.35$ kcal mol^{-1}, may be adopted as the most probable value.

Iodomethane

Berthelot[67,91] and Thomsen[68] measured ΔH° for the combustion of iodomethane, but these studies are only of historical interest. Carson et al.[92,93] determined ΔH° for the reaction of dimethylcadmium with iodine in ether and their results lead to $\Delta H^\circ_f(CH_3I, liq.) = -3.4 \pm 0.8$ kcal mol^{-1}.[87] Hartley et al.[87] determined the enthalpy of the reaction

$$Hg(CH_3)_2(liq.) + 2I_2(cryst.) \rightarrow HgI_2(cryst.) + 2CH_3I(liq.) \quad (21)$$

and obtained $\Delta H^\circ_{298}(21) = 44.11 \pm 0.44$ kcal mol^{-1}. These data, together with ΔH° for the combustion of dimethylmercury[88], lead to $\Delta H^\circ_f(CH_3I, liq.) = -2.3$ kcal mol^{-1}. Mackle and Ubbelohde[94] and later Nichol and Ubbelohde[95] measured ΔH° for the reaction of the Grignard reagent with I_2 and HI in solutions in ether and *p*-xylene; the data[95] for the reaction

$$CH_3I(gas) + HI(gas) \rightarrow CH_4(gas) + I_2(gas) \quad (22)$$

lead to $\Delta H^\circ_{291}(22) = -11.04 \pm 1.33$ kcal mol^{-1}, whence it follows that $\Delta H^\circ_f(CH_3I, gas) = -1.7$ kcal mol^{-1}. Carson et al.[34] measured ΔH° for the reduction of iodomethane by lithium tetrahydroaluminate in ether and obtained $\Delta H^\circ_{298}(23) = -15.0 \pm 0.4$ kcal mol^{-1} for the reaction

$$CH_3I(liq.) + \tfrac{1}{2}H_2(gas) \rightarrow CH_4(gas) + \tfrac{1}{2}I_2(cryst.), \quad (23)$$

whence it follows that $\Delta H^\circ_f(CH_3I, liq.) = -2.85 \pm 0.4$ kcal mol^{-1}; these are apparently the most accurate measurements for liquid iodomethane.

The most accurate studies on gaseous iodomethane were those of Goy and Pritchard[39] and Golden et al.[40]. They dealt with the equilibrium in the reacton

$$CH_4(gas) + I_2(gas) \rightleftharpoons CH_3I(gas) + HI(gas), \quad (24)$$

and led to $\Delta H^\circ_{298}(24) = 12.61 \pm 0.04$ kcal mol^{-1} [40] and 12.63 ± 0.03 kcal mol^{-1}.[39] These values correspond to $\Delta H^\circ_f(CH_3I, gas) = 3.38 \pm 0.21$ kcal mol^{-1} [40] and 3.40 ± 0.21 kcal mol^{-1},[39] which agree very well, but those of Goy and Pritchard[39] are somewhat superior, since the latter investigated a wider temperature range, the reproducibility of the values of K_p was more satisfactory, and the enthalpies ΔH° calculated on the basis of the Second and Third Laws of Thermodynamics agree better. Taking into account the enthalpy of evaporation $\Delta H^\circ_{V298}(CH_3I, liq.) = 6.6 \pm 0.3$ kcal mol^{-1}, we obtain $\Delta H^\circ_f(CH_3I, liq.) = -3.16 \pm 0.37$ kcal mol^{-1}, in satisfactory agreement with the results of Carson et al.[34] Bearing in mind the difficulty of accurate thermochemical measurements using lithium tetrahydroaluminate, preference must be given to the value of $\Delta H^\circ_f(CH_3I, liq.)$, calculated from Goy and Pritchard's data[39] and ΔH°_V.

Di-iodomethane

Berthelot[91] measured ΔH° for the combustion of di-iodomethane and on the basis of his results Glushko[4] obtained $\Delta H^\circ_f(CH_2I_2, gas) = 28.5$ kcal mol^{-1}. More reliable data were obtained by Furuyama et al.[44], who investigated the equilibrium in the reaction

$$2CH_3I \rightleftarrows CH_4 + CH_2I_2 \quad (25)$$

and obtained $\Delta H^\circ_{298}(25) = 4.24 \pm 0.63$ kcal mol^{-1}. This result leads to $\Delta H^\circ_f(CH_2I_2, gas) = 28.9 \pm 0.7$ kcal mol^{-1}.

Trifluoroiodomethane

It follows from $\Delta H^\circ_{298}(10)$ that $\Delta H^\circ_f(CF_3I, gas) = -140.8 \pm 0.7$ kcal mol^{-1}.

V. METHODS FOR THE APPROXIMATE ESTIMATION OF THE ENTHALPIES OF FORMATION OF HALOGENOMETHANES

A whole series of methods have been proposed for the estimation of the enthalpies of formation of organic compounds; a fairly complete bibliography is given in Refs. 96–101. Most of the methods are based on the representation of the energy of formation of the molecule by the sum of the contributions due to its structural elements.

One of the simplest and most widely used additive computational schemes is based on the hypothesis that the average thermochemical bond energies are constant[5,10]. When this procedure is applied to a series of halogenomethanes of the type $CX_{4-n}Y_n$, where X and Y are hydrogen or a halogen, a linear relation between ΔH°_f and n is postulated. Generally speaking, bond energies can vary markedly, particularly in those cases where there is a sharp alteration in the environment of the bond. For this reason, the method of average bond energies as a rule makes it possible to estimate the required quantities only to a rough approximation. This is seen also in relation to certain series of the type $CX_{4-n}Y_n$; thus the experimental enthalpies of formation of compounds of the $CH_{4-n}F_n$ or $CH_{4-n}I_n$ series can be in no way represented by a linear function of n. However, the method of average bond energies may yield entirely satisfactory results when it is used for comparatively small groups of substances of a similar type or for series where the dependence of the bond energies on their environment is believed to be small.

The method proposed by Kharasch[107] also leads to a linear relation between ΔH°_f and n in series of the type $CX_{4-n}Y_n$.[10]

Among the methods where account is taken of the bond environment, only Bernstein's method[9,102], in which account is taken of the interaction of all the atoms, both linked directly and not linked at all, may be widely applied to halogenomethanes. Allowance for pair interactions only leads to a quadratic relation between $\Delta H^\circ_f(CX_{4-n}Y_n)$ and n.[102] On the other hand, the introduction of triple as well as pair interactions leads to a cubic relation[9]. Thus, in order to calculate the enthalpies of formation of compounds in the $CX_{4-n}Y_n$ series, it is necessary to know three[102] or four[9] constants, i.e. to know three or four quantities of the five to be determined.

Other computational schemes taking into account the interactions of bonds or atoms cannot be used owing to the insufficiency of experimental data. Some of these, for example Allen's scheme[98], are used in a few instances to establish relations between the enthalpies of formation of related compounds[103].

Apart from additive schemes, other approximate methods are frequently used, for example, the methods of comparative calculation developed by Karapet'yants[97]. Here it is most convenient to employ the equation

$$F_{II} = AF_I + B, \qquad (26)$$

which establishes the relation between the numerical values of the parameter F (for example, ΔH°_f) in two similar series of compounds (I) and (II). The methods of comparative calculation usually yield satisfactory results[97]; in the case of halogenomethanes the greatest difficulty is associated with the selection of the appropriate reference series. Where it is necessary to take into account the structural analogy of the series, the chemical similarity of the fragments by which they differ, and the observed thermochemical regularities (the increase of the C–F bond energy as H is substituted by F,[1,2] the decrease of the C–I bond energy in the analogous substitution, etc.), i.e. series (I) and (II), resembling one another as regards the dependence of ΔH°_f on composition, must be selected.

Estimates of the enthalpies of formation of halogenomethanes by approximate methods are given below. In those cases where the amount of experimental data was sufficient, an additive scheme taking into account the bond environment was used (Bernstein's method[9,102]; Allen's scheme[98,103]). In other cases the ΔH°_f were estimated by methods of comparative calculation[97] using variable reference series, and the method of average bond energies was used for individual small groups of substances.

VI. ESTIMATION OF THE ENTHALPIES OF FORMATION OF HALOGENOMETHANES

Fluoromethanes

No calorimetric determinations have been made for this substance. The accuracy of the mass-spectrometric determinations of $\Delta H^\circ_f(CH_3F, gas)$ in terms of the appearance potential of the CH_3^+ ion or the ionisation potential of the CH_3 radical[104,105] is very low; the results vary from −59 to −79 kcal mol^{-1}.[3]

A more reliable result may be obtained by calculation. Since reliable values of ΔH°_f are available for all the compounds of the $CH_{4-n}F_n$ series except CH_3F, the relevant quantity may be calculated using comparatively accurate computational methods: Allen's scheme[98] and Bernstein's cubic equation[9].

Application of Allen's scheme leads to the relation[103]

$$\Delta H^0_f(CH_3F) = 1/4\,[\Delta H^0_f(CH_4) + \Delta H^0_f(CF_4)] + 3/2\Delta H^0_f(CH_2F_2) - \Delta H^0_f(CHF_3),$$

which yields $\Delta H^\circ_f(CH_3F, gas) = -55.6$ kcal mol^{-1}. Bernstein's cubic equation gives the same result.

The $CH_{4-n}Br_n$ Series

Reliable values of ΔH°_f are available for CH_4 and CH_3Br in this series. Kaboukov and Perel'man[75] determined ΔH° for the combustion of liquid $CHBr_3$, but their results are very unreliable owing to the incomplete reduction of free bromine, poor reproducibility of the experimental data, and insufficient purity of the specimen.

The difference between the enthalpies of formation of gaseous $CHBr_3$ and CBr_4 may ve calculated from the results of the study of the equilibrium

$$Br_2 + CHBr_3 \rightleftarrows CBr_4 + HBr\,. \qquad (27)$$

Strong and Pease[106] obtained $\Delta H^\circ_{298}(27) = -1.0$ kcal mol^{-1} for reaction (27). More accurate measurements[45] lead to $\Delta H^\circ_{298}(27) = -1.66 \pm 0.09$ kcal mol^{-1}. $\Delta H^\circ_f(CBr_4, gas) - \Delta H^\circ_f(CHBr_3, gas) = 14.42 \pm 0.10$ kcal mol^{-1} follows from these data.

The available set of data makes it possible to apply Bernstein's quadratic equation, which takes into account the pair interactions between atoms[102], to the calculation of ΔH°_f in the $CH_{4-n}Br_n$ series. The calculation leads to

the following values: $\Delta H_f^\circ(CH_2Br_2, gas) = 1.77$ kcal mol^{-1}, $\Delta H_f^\circ(CHBr_3, gas) = 14.33$ kcal mol^{-1}, and $\Delta H_f^\circ(CBr_4, gas) = 28.73$ kcal mol^{-1}. These results are larger than the values adopted in the literature[3,4], because the latter estimates were based on the average bond energies without taking into account the interaction of non-bonded atoms.

The $CH_{4-n}I_n$ Series

The experimental values of ΔH_f° for CH_4, CH_3I, and CH_2I_2 are quoted above. The enthalpy of combustion of crystalline iodoform was determined by Berthelot in 1900[91]; these data were adopted as the basis for the calculation of $\Delta H_f^\circ(CHI_3)$ in a number of compilations[3,4,6,7]. When account is taken of the enthalpies of sublimation, they lead to a value of $\Delta H_f^\circ(CHI_3, gas)$ between 50.3 and 51 kcal mol^{-1}. However, this value appears to be too low: if it is adopted, it is found that the enthalpy of formation varies non-systematically in the $CH_{4-n}I_n$ series and, on passing from CH_2I_2 to CHI_3, the second difference between the ΔH_f° changes sign.

Calculation by Bernstein's quadratic equation[102] using the CH_4, CH_3I, and CH_2I_2 data leads to a significantly different result: $\Delta H_f^\circ(CHI_3, gas) = 58.7$ kcal mol^{-1}. Analogous calculation for CI_4 yields $\Delta H_f^\circ(CI_4, gas) = 92.7$ kcal mol^{-1}. The values of $\Delta H_f^\circ(CI_4, gas)$ estimated[3,4] from the average bond energies are approximately 20 kcal mol^{-1} lower. However, comparison of the ΔH_f° data adopted above for CH_4, CH_3I, and CH_2I_2 shows clearly that the dependence of ΔH_f° on n in the $CH_{4-n}I_n$ series is non-linear; for this reason, calculation based on the average bond energies is unjustified in this instance[44].

The $CBr_{4-n}F_n$ Series

Three values of ΔH_f° are known in this series; for CF_4, CF_3Br, and CBr_4 (see above). This makes it possible to use Bernstein's equation[102] for the calculation of the enthalpies of formation of the remaining two compounds. The calculation yields

$$\Delta H_f^\circ(CF_2Br_2, gas) = -90.9 \text{ kcal mol}^{-1};$$
$$\Delta H_f^\circ(CFBr_3, gas) = -29.5 \text{ kcal mol}^{-1}.$$

The $CI_{4-n}F_n$ Series

Three values of ΔH_f° are also known in this series: for CF_4, CF_3I, and CI_4. Calculation by Bernstein's equation[102] leads to

$$\Delta H_f^\circ(CF_2I_2, gas) = -60.8 \text{ kcal mol}^{-1};$$
$$\Delta H_f^\circ(CFI_3, gas) = 17.0 \text{ kcal mol}^{-1}.$$

The $CBr_{4-n}Cl_n$ Series

Three values of ΔH_f° are known in the CCl_4–CBr series: for CCl_4, CCl_3Br, and CBr_4 (see above). Calculation by Bernstein's equation[102] leads to

$$\Delta H_f^\circ(CCl_2Br_2, gas) = 2.5 \text{ kcal mol}^{-1};$$
$$\Delta H_f^\circ(CClBr_3, gas) = 15.5 \text{ kcal mol}^{-1}.$$

The $CCl_{4-n}I_n$ Series

Since only two values of ΔH_f° are known in this series (for CCl_4 and CI_4), it is impossible to estimate the missing quantities by Bernstein's method. They can be estimated from the average bond energies or by the method of comparative calculation[97]. Calculation based on average bond energies yields

$$\Delta H_f^\circ(CCl_3I, gas) = 6.0 \text{ kcal mol}^{-1};$$
$$\Delta H_f^\circ(CCl_2I_2, gas) = 34.9 \text{ kcal mol}^{-1};$$
$$\Delta H_f^\circ(CClI_3, gas) = 63.8 \text{ kcal mol}^{-1}.$$

When the method of comparative calculation is used, it is possible, in principle, to select as a reference any of the eight series of the type $CX_{4-n}Y_n$ examined above; the numerical data obtained for three compounds of the $CCl_{4-n}I_n$ series vary appreciably under these conditions (in the range from 6 to 9 kcal mol^{-1}). The $CH_{4-n}I_n$ and $CH_{4-n}Br_n$ series are probably closest to the $CCl_{4-n}I_n$ series as regards their thermochemical properties. This can be justified as follows: (1) the replacement of an H atom by Cl entails a very small thermochemical effect—thus the first differences between the ΔH_f° in the $CH_{4-n}Cl_n$ series is only approximately 2 kcal mol^{-1}; (2) the non-linear dependence of ΔH_f° on n in the $CH_{4-n}I_n$ and $CH_{4-n}Br_n$ series is probably due to some destabilisation of the compound as the I or Br atoms accumulate (for example, owing to steric hindrance). Presumably this effect also persists in the $CCl_{4-n}I_n$ series. The method of comparative calculation using the $CH_{4-n}I_n$ and $CH_{4-n}Br_n$ series yields very similar results. Data obtained with the aid of the $CH_{4-n}I_n$ reference series are listed below:

$$\Delta H_f^\circ(CCl_3I, gas) = -0.6 \text{ kcal mol}^{-1};$$
$$\Delta H_f^\circ(CCl_2I_2, gas) = 26.0 \text{ kcal mol}^{-1};$$
$$\Delta H_f^\circ(CClI_3, gas) = 57.1 \text{ kcal mol}^{-1}.$$

If a reference series is chosen in which the dependence of ΔH_f° on n is close to linearity, for example $CCl_{4-n}Br_n$, then the result naturally agrees with that calculated from the average bond energies. Since by virtue of the causes mentioned above there are no grounds for the hypothesis that there is a linear relation for the $CCl_{4-n}I_n$ series, preference must be given to the calculation by the comparative method based on the $CH_{4-n}I_n$ series.

The $CBr_{4-n}I_n$ Series

In this series too only two values of ΔH_f° were selected: for CBr_4 and CI_4. The difference between the ΔH_f° for CBr_4 and CI_4 is much smaller than in the case of CCl_4 and CI_4. The choice of a reference series for the calculation of ΔH_f° in the $CBr_{4-n}I_n$ series is therefore less important than in the $CCl_{4-n}I_n$ series. The values of ΔH_f° for the three missing compounds, calculated from the average bond energies and by the comparative method (four reference series), vary in the range of 4 to 5 kcal mol^{-1}. In view of the similarity of the properties of Br and I atoms, the dependence of ΔH_f° on n in the $CBr_{4-n}I_n$ series should presumably be closer to linearity than in the $CH_{4-n}I_n$ and $CH_{4-n}Br_n$ series. The best of the calculated values should therefore lie in the range between those obtained by the Karapet'yants method[97], based on series with a distinct quadratic relation, and those found from the average bond energies. It is useful to employ a reference series in which the quadratic relation is weak,

for example $CBr_{4-n}F_n$. Then the method of comparative calculation yields the following data:

$$\Delta H_f^\circ(CBr_3I, \text{gas}) = 43.5 \text{ kcal mol}^{-1};$$
$$\Delta H_f^\circ(CBr_2I_2, \text{gas}) = 59.1 \text{ kcal mol}^{-1};$$
$$\Delta H_f^\circ(CBrI_3, \text{gas}) = 75.5 \text{ kcal mol}^{-1}.$$

Chlorofluoromethane, Chlorodifluoromethane, and Dichlorofluoromethane

Among these compounds, experimental data are available only for CHF_2Cl. Edwards and Small[108] investigated the equilibrium

$$2CHF_2Cl \rightleftarrows C_2F_4 + 2HCl \quad (28)$$

by measuring the pressures of the components at 600°C. They noted the formation of side products and obtained K_p by extrapolation. It follows from their data that $\Delta H_{298}^\circ(28) = 28.75$ kcal mol^{-1} [11] and $\Delta H_f^\circ(CHF_2Cl, \text{gas}) = -115.5$ kcal mol^{-1}. A more reliable value of ΔH_f° may be obtained by the method of comparative calculation based on the $CF_2H_{2-n}Cl_n$ and $CF_{4-n}Cl_n$ (reference) series, where $0 \leqslant n \leqslant 2$:

$$\Delta H_f^\circ(CHF_2Cl, \text{gas}) = -111.6 \text{ kcal mol}^{-1}.$$

The compounds CH_2FCl and $CHFCl_2$ may be regarded as members of the $CFH_{3-n}Cl_n$ series, where the enthalpies of formation of the extreme members are known. Calculation by the comparative method using the $CH_{4-n}Cl_n$ reference series (where $0 \leqslant n \leqslant 3$) yields the following results:

$$\Delta H_f^\circ(CH_2FCl, \text{gas}) = -58.8 \text{ kcal mol}^{-1};$$
$$\Delta H_f^\circ(CHFCl_2, \text{gas}) = -64.7 \text{ kcal mol}^{-1}.$$

In both series considered, $CF_2H_{2-n}Cl_n$ and $CFH_{3-n}Cl_n$, the difference between the values of ΔH_f° for the extreme members of the series is very small, so that the result of the calculation by the comparative method is relatively insensitive to the selection of the reference series. Similar results are also obtained if the constancy of the bond energies in the given series is assumed.

Bromofluoromethane, Bromodifluoromethane, and Dibromofluoromethane

The compounds CH_2BrF and $CHBr_2F$ may be regarded as members of the $CFH_{3-n}Br_n$ series in which the values of ΔH_f° for CFH_3 and $CFBr_3$ are known. Calculation by the comparative method using the $CH_{4-n}Br_n$ reference series (where $0 \leqslant n \leqslant 3$) yields

$$\Delta H_f^\circ(CH_2FBr, \text{gas}) = -48.4 \text{ kcal mol}^{-1};$$
$$\Delta H_f^\circ(CHFBr_2, \text{gas}) = -39.7 \text{ kcal mol}^{-1}.$$

The value of $\Delta H_f^\circ(CHF_2Br, \text{gas})$ may be obtained by the method of comparative calculation based on the $CF_2H_{2-n}Br_n$ and $CBr_{2-n}F_{2+n}$ (reference) series:

$$\Delta H_f^\circ(CHF_2Br, \text{gas}) = -99.7 \text{ kcal mol}^{-1}.$$

Fluoroiodomethane, Difluoroiodomethane, and Fluorodiiodomethane

The choice of the reference series in the calculation of ΔH_f° for the above three substances by the comparative method is particularly important, because the enthalpies of formation of fluoroiodomethanes vary very markedly with composition. Presumably the dependence of ΔH_f° on n for series of the type $CF_{4-m-n}I_nH_m$ with constant m should be close to the variation of these quantities in the $CF_{4-n}I_n$ series. The compounds CHF_2I and $CHFI_2$ may be regarded as members of the $CHF_{3-n}I_n$ series in which the values of ΔH_f° for CHF_3 and CHI_3 are known. Calculation by the comparative method using the $CF_{4-n}I_n$ reference series (where $0 \leqslant n \leqslant 3$) yields

$$\Delta H_f^\circ(CHF_2I, \text{gas}) = -89.5 \text{ kcal mol}^{-1};$$
$$\Delta H_f^\circ(CHFI_2, \text{gas}) = -14.4 \text{ kcal mol}^{-1}.$$

The value of $\Delta H_f^\circ(CH_2FI, \text{gas})$ may be obtained by the method of comparative calculation involving comparison of the $CH_2F_{2-n}I_n$ and $CF_{4-n}I_n$ (reference) series, where $0 \leqslant n \leqslant 2$:

$$\Delta H_f^\circ(CH_2FI, \text{gas}) = -38.7 \text{ kcal mol}^{-1}.$$

Bromochloromethane, Dibromochloromethane, and Bromodichloromethane

By considering the $CBrH_{3-n}Cl_n$ series, in which the values of ΔH_f° for CH_3Br and CCl_3Br are known, and the $CH_{3-n}Cl_{1+n}$ reference series, we obtain

$$\Delta H_f^\circ(CH_2ClBr, \text{gas}) = -10.2 \text{ kcal mol}^{-1};$$
$$\Delta H_f^\circ(CHCl_2Br, \text{gas}) = -11.0 \text{ kcal mol}^{-1}.$$

The values of ΔH_f° for CH_2Br_2 and CCl_2Br_2 in the $CBr_2H_{2-n}Cl_n$ series are known. Using the $CBr_{4-n}Cl_n$ reference series, where $0 \leqslant n \leqslant 2$, we find

$$\Delta H_f^\circ(CHClBr_2, \text{gas}) = 2.1 \text{ kcal mol}^{-1}.$$

We may note that the replacement of H by Cl in the $CBrH_{3-n}Cl_n$ and $CBr_2H_{2-n}Cl_n$ series entails a very slight change in the values of ΔH_f°. Within the limits of these series, it is possible to use successfully the method of average bond energies; the values of ΔH_f° calculated by this method are very close to those quoted above.

Chloroiodomethane, Dichloroiodomethane, and Chlorodiiodomethane

By considering the $CClH_{3-n}I_n$ series, in which the values of ΔH_f° for CH_3Cl and CI_3Cl are known, and the $CH_{4-n}I_n$ reference series, where $0 \leqslant n \leqslant 3$, we obtain

$$\Delta H_f^\circ(CH_2ClI, \text{gas}) = 1.7 \text{ kcal mol}^{-1};$$
$$\Delta H_f^\circ(CHClI_2, \text{gas}) = 27.2 \text{ kcal mol}^{-1}.$$

The quantity $\Delta H_f^\circ(CHCl_2I, \text{gas})$ can be readily obtained by considering the $CCl_2H_{2-n}I_n$ series, in which the values of ΔH_f° for CH_2Cl_2 and CI_2Cl_2 are known. Using the $CH_{4-n}I_n$ reference series, where $0 \leqslant n \leqslant 2$, we find

$$\Delta H_f^\circ(CHCl_2I, \text{gas}) = -0.6 \text{ kcal mol}^{-1}.$$

In the case under consideration the difference between the enthalpies of formation of the corresponding compounds in the test and reference series is comparatively

small (only 2–4 kcal mol^{-1}), which ensures a fairly accurate estimate of ΔH_f° by the comparative method.

Bromoiodomethane, Bromodi-iodomethane, and Dibromoiodomethane

The values of ΔH_f° for CH_3I and CBr_3I are known in the $CIH_{3-n}Br_n$ series. Using the $CH_{3-n}Br_{1+n}$ reference series, we obtain the following values for CH_2BrI and $CHBr_2I$:

$$\Delta H_f^\circ(CH_2BrI, gas) = 14.8 \text{ kcal mol}^{-1};$$
$$\Delta H_f^\circ(CHBr_2I, gas) = 28.2 \text{ kcal mol}^{-1}.$$

The value of $\Delta H_f^\circ(CHBrI_2, gas)$ may be obtained by comparing the $CI_2H_{2-n}Br_n$ series with the $CH_{2-n}Br_{2+n}$ reference series:

$$\Delta H_f^\circ(CHBrI_2, gas) = 43.0 \text{ kcal mol}^{-1}.$$

The selection of the reference series for the estimation of the ΔH_f° for the three compounds considered is determined by the similarity of the properties of the Br and I atoms. The latter is manifested particularly in the similarity of the dependence of ΔH_f° on n in the $CH_{4-n}I_n$ and $CH_{4-n}Br_n$ series.

Bromochlorodifluoromethane, Bromodichlorofluoromethane, and Dibromochlorofluoromethane

The enthalpies of formation of $CFCl_2Br$ and $CFClBr_2$ may be calculated by considering the $CFCl_{3-n}Br_n$ and $CCl_{4-n}Br_n$ (reference) series, where $0 \leq n \leq 3$:

$$\Delta H_f^\circ(CFCl_2Br, gas) = -55.0 \text{ kcal mol}^{-1};$$
$$\Delta H_f^\circ(CFClBr_2, gas) = -42.4 \text{ kcal mol}^{-1}.$$

The value of $\Delta H_f^\circ(CF_2ClBr, gas)$ can be obtained by comparing the $CF_2Cl_{2-n}Br_n$ series with the $CCl_{4-n}Br_n$ reference series, where $0 \leq n \leq 3$:

$$\Delta H_f^\circ(CF_2ClBr, gas) = -103.1 \text{ kcal mol}^{-1}.$$

Similar values of ΔH_f° are obtained, for example, also by considering the $CClF_{3-n}Br_n$ and CF_3Br_{1+n} (reference) series or the $CBrF_{3-n}Cl_n$ and $CF_{4-n}Cl_n$ (reference) series for $0 \leq n \leq 3$.

Bromodifluoroiodomethane, Dibromofluoroiodomethane, and Bromofluorodi-iodomethane

By comparing the $CIF_{3-n}Br_n$ series, in which the values of ΔH_f° for CF_3I and CBr_3I are known, with the $CF_{3-n}Br_{1+n}$ reference series, we obtain:

$$\Delta H_f^\circ(CF_2BrI, gas) = -76.3 \text{ kcal mol}^{-1};$$
$$\Delta H_f^\circ(CFBr_2I, gas) = -14.8 \text{ kcal mol}^{-1}.$$

The value of $\Delta H_f^\circ(CFBrI_2, gas)$ can be obtained by considering the $CI_2F_{2-n}Br_n$ and $CF_{2-n}BR_{2+n}$ (reference) series:

$$\Delta H_f^\circ(CFBrI_2, gas) = 0.7 \text{ kcal mol}^{-1}.$$

Similar values of ΔH_f° are obtained also, for example, by comparing the $CBrF_{3-n}I_n$ and $CF_{3-n}I_{1+n}$ (reference) series or the $CFBr_{3-n}I_n$ and $CBr_{4-n}I_n$ (reference) series, where $0 \leq n \leq 3$.

Chlorodifluoroiodomethane, Dichlorofluoroiodomethane, and Chlorofluorodi-iodomethane

The values of ΔH_f° for CF_2ClI and $CFClI_2$ can be found by considering the $CClF_{3-n}I_n$ and $CF_{4-n}I_n$ (reference) series, where $0 \leq n \leq 3$:

$$\Delta H_f^\circ(CF_2ClI, gas) = -91.7 \text{ kcal mol}^{-1};$$
$$\Delta H_f^\circ(CFlI_2, gas) = -16.3 \text{ kcal mol}^{-1}.$$

Comparison of the $CCl_2F_{2-n}I_n$ and $CCl_{2+n}F_{2+n}$ series yields

$$\Delta H_f^\circ(CFCl_2I, gas) = -42.3 \text{ kcal mol}^{-1}.$$

Similar values of ΔH_f° are obtained by comparing other similar series, for example, the $CIF_{3-n}Cl_n$ and $CF_{4-n}Cl_n$ (reference) series or the $CFCl_{3-n}I_n$ and $CCl_{4-n}I_n$ (reference) series, where $0 \leq n \leq 3$.

Bromodichloroiodomethane, Dibromochloroiodomethane, and Bromochlorodi-iodomethane

The values of ΔH_f° for CCl_2BrI and $CClBr_2I$ are obtained by comparing the $CICl_{3-n}Br_n$ and $CCl_{3-n}Br_{1+n}$ (reference series):

$$\Delta H_f^\circ(CCl_2BrI, gas) = 13.8 \text{ kcal mol}^{-1};$$
$$\Delta H_f^\circ(CClBr_2I, gas) = 28.5 \text{ kcal mol}^{-1}.$$

By comparing the $CI_2Cl_{2-n}Br_n$ and $CCl_{2-n}Br_{2+n}$ (reference) series, we find

$$\Delta H_f^\circ(CClBrI_2, gas) = 42.4 \text{ kcal mol}^{-1}.$$

Similar values of ΔH_f° are also obtained by comparing the $CICl_{3-n}Br_n$ and $CCl_{4-n}Br_n$ (reference) series, where $0 \leq n \leq 3$, or the $CI_2Cl_{2-n}Br_n$ and $CI_{2+n}Cl_{2-n}$ (reference) series, where $0 \leq n \leq 2$.

Bromochlorofluoromethanes

By considering the $CFClH_{2-n}Br_n$ and $CH_{4-n}Br_n$ (reference) series, where $0 \leq n \leq 2$, we find

$$\Delta H_f^\circ(CHFClBr, gas) = -51.4 \text{ kcal mol}^{-1}.$$

A similar value of ΔH_f° (CHFClBr, gas) is obtained by applying the method of average bond energies to the $CFBrH_{2-n}Cl_n$ series, in which the replacement of H by Cl entails a comparatively small alteration of the enthalpies of formation.

Chlorofluoroiodomethane

Application of the method of comparative calculation to the $CFIH_{2-n}Cl_n$ and $CH_{4-n}Cl_n$ (reference) series, where $0 \leq n \leq 2$, yields

$$\Delta H_f^\circ(CHFClI, gas) = -40.0 \text{ kcal mol}^{-1}.$$

The replacement of an H atom by Cl in the $CFIH_{2-n}Cl_n$ series entails a comparatively small change in ΔH_f°, so that the result of the calculation of ΔH_f°(CHFClI, gas) depends little on the choice of the reference series. Application of the method of average bond energies to the $CFIH_{2-n}Cl_n$ series also yields a similar value.

Bromofluoroiodomethane

By considering the $CFIH_{2-n}Br_n$ and $CH_{4-n}Br_n$ (reference) series, where $0 \leq n \leq 2$, we obtain

$$\Delta H_f^\circ(CHFBrI, gas) = -27.8 \text{ kcal mol}^{-1}.$$

Similar values are obtained using the $CIH_{3-n}Br_n$ or $CFH_{3-n}Br_n$ (for $0 \leq n \leq 2$) reference series.

Bromochloroiodomethane

The variation of ΔH_f° in the $CBrIH_{2-n}Cl_n$ series is very slight: $\Delta H_f^\circ(CH_2BrI, gas) = 14.8$ kcal mol^{-1} and $\Delta H_f^\circ(CCl_2.BrI, gas) = 13.8$ kcal mol^{-1}. Using the $CBr_2H_{2-n}Cl_n$ reference series, we obtain the following value for the middle member of the series:

$$\Delta H_f^\circ(CHClBrI, gas) = 14.3 \text{ kcal mol}^{-1}.$$

The use of other reference series as well as the method of average bond energies leads to very similar results.

Bromochlorofluoroiodomethane

Comparison of the $CClBrI_{2-n}F_n$ and $CHBrI_{2-n}F_n$ (reference) series leads to the following value:

$$\Delta H_f^\circ(CFClBrI, gas) = -29.8 \text{ kcal mol}^{-1}.$$

In this case the differences between the ΔH_f° for the corresponding members of two similar series are very slight, which improves the reliability of the estimate of ΔH_f° by the comparative method. Similar results are also obtained when other series are used, for example, $CBr.ICl_{2-n}F_n$ and $CI_2Cl_{2-n}F_n$ (reference) series.

VII. CONCLUSION

The recommended enthalpies of formation of all 70 halogenomethanes are listed in the Table. The error of the values chosen as the most reliable experimental data is expressed in terms of 95% confidence intervals (in addition, account was taken of the errors of the determination of all the auxiliary quantities). The only exceptions are CF_2Cl_2 and $CFCl_3$, for which the errors were estimated using the entire set of experimental data obtained and the estimate has no rigorous statistical basis owing to the inadequacy of the experimental methods employed.

The errors of the quantities found by methods of approximate estimation are not quoted in the Table. For the majority of the compounds, they probably do not exceed 3–5 kcal mol^{-1}, which may be supported by the following arguments:

1. The estimates were made by different methods and the discrepancies between the results were comparatively small, as stated above.

2. For certain series of experimental data it was found sufficient to employ additive schemes taking into account the environment of the atoms (Allen's[98] and Bernstein's[9,102] schemes).

3. In calculations by the comparative method, both the test and reference series were varied widely. For each quantity estimated, apart from that quoted in the text, a further 6–8 versions of the calculation were performed; when the series compared were sufficiently "similar", the results differed insignificantly.

4. The calculations by the method of average bond energies were performed only for narrow groups of compounds—mainly in series comprising three members and with a not unduly great variation of the enthalpy of formation. Under such conditions, even estimates carried out by this comparatively rough method could not lead to major errors.

Enthalpies of formation of halogenomethanes.

Compound	$\Delta H_{f,298,15}^0$ (gas)		Compound	$\Delta H_{f,298,15}^0$ (gas)	
	kcal mol^{-1}	kJ mol^{-1}		kcal mol^{-1}	kJ mol^{-1}
Experimental data			$CBrI_3$	75.5	315.9
CH_4	−17.85±0.06	−74.68±0.25	CH_2FCl	−58.8	−246.0
CH_2F_2	−108.09±0.42	−452.2±1.8	CHF_2Cl	−111.6	−466.9
CHF_3	−166.72±0.64	−697.6±2.7	$CHFCl_2$	−64.7	−270.7
CF_4	−223.0±0.4	−933.0±1.7	CH_2FBr	−48.4	−202.5
CH_3Cl	−19.58±0.16	−81.9±0.7	CHF_2Br	−99.7	−417.1
CH_2Cl_2	−22.76±0.08	−95.23±0.33	$CHFBr_2$	−39.7	−166.1
$CHCl_3$	−24.54±0.37	−102.7±1.5	CH_2FI	−38.7	−161.9
CCl_4	−22.86±0.16	−95.6±0.7	CHF_2I	−89.5	−374.5
CF_3Cl	−169.27±0.81	−708.2±3.4	$CHFI_2$	−14.4	−60.2
CF_2Cl_2	−115.1±2.0	−481.6±8.4	CH_2ClBr	−10.2	−42.7
$CFCl_3$	−67.5±2.5	−282.4±10.5	$CHClBr_2$	−11.0	−46.0
CH_3Br	−8.94±0.30	−37.4±1.3	$CHClBr_2$	2.1	8.8
CF_3Br	−155.38±0.65	−650.1±2.7	CH_2ClI	1.7	7.1
CCl_3Br	−10.28±0.35	−43.0±1.5	$CHCl_2I$	−0.6	−2.5
CH_3I	3.40±0.21	14.2±0.9	$CHClI_2$	27.2	113.8
CH_2I_2	28.9±0.7	120.9±2.9	CH_2BrI	14.8	61.9
CF_3I	−140.8±0.7	−589.1±2.9	$CHBr_2I$	28.2	118.0
Estimated data			$CHBrI_2$	43.0	179.9
CH_3F	−55.6	−232.6	CF_2ClBr	−103.1	−431.4
CH_2Br_2	1.77	7.4	$CFCl_2Br$	−55.0	−230.1
$CHBr_3$	14.33	60.0	$CFClBr_2$	−42.4	−177.4
CBr_4	28.73	120.2	CF_2ClI	−91.7	−383.4
CHI_3	58.7	245.6	$CFCl_2I$	−42.3	−177.0
CI_4	92.7	387.9	$CFClI_2$	−16.3	−68.2
CF_2Br_2	−90.9	−380.3	CF_2BrI	−76.3	−319.2
$CFBr_3$	−29.5	−123.4	$CFBr_2I$	−14.8	−61.9
CF_2I_2	−60.8	−254.4	$CFBrI_2$	0.7	2.9
CFI_3	17.0	71.1	CCl_2BrI	13.8	57.7
CCl_2Br_2	2.5	10.5	$CClBr_2I$	28.5	119.2
$CClBr_3$	15.5	64.9	$CClBrI_2$	42.4	177.4
CCl_3I	−0.6	−2.5	$CHFClBr$	−51.4	−215.1
CCl_2I_2	26.0	108.8	$CHFClI$	−40.0	−167.4
$CClI_3$	57.1	238.9	$CHFBrI$	−27.8	−116.3
CBr_3I	43.5	182.0	$CHClBrI$	14.3	59.8
CBr_2I_2	59.1	247.3	$CFClBrI$	−29.8	−124.7

However, in certain instances the error of the estimated ΔH_f° may be much greater. This applies particularly to carbon tetraiodide whose enthalpy of formation was obtained by the extrapolation of the experimental data available for the first three numbers of the $CH_{4-n}I_n$ series. Owing to the accumulation of errors, the error in the estimated $\Delta H_f^\circ(CI_4, gas)$ may be 10–12 kcal mol^{-1}. For the same reasons, the error in the calculated value of $\Delta H_f^\circ(CBr_4, gas)$ may reach 5–6 kcal mol^{-1}. The foregoing applies to a lesser extent to all the tri-iodo- and tribromo-substituted methanes whose enthalpies of formation were estimated.

Although experimental data are available only for a comparatively small number of halogenomethanes and the reliability of the estimated values is limited, nevertheless certain thermochemical regularities are evident for this type of compound. In the first place there is no doubt that in the general case the dependence of the enthalpy of formation of n in series of the type $CX_{4-n}Y_n$ is not linear. For the $CH_{4-n}F_n$ series, an increase of n entails a faster increase of this function compared with the increase that would be expected on the basis of a linear equation. Within the framework of the model of atom—atom interactions,

this implies that the bond energies are not constant in the $CH_{4-n}F_n$ series. The additional stabilisation of the molecules arising when the H atoms are replaced successively by F may be associated, for example, with the interaction of fluorine atoms which are not bonded directly[9,102]. Stabilisation as fluorine atoms accumulate is also observed in the $CF_{4-n}Cl_n$, $CF_{4-n}Br$, and $CF_{4-n}I_n$ series, but it is less marked.

In the $CH_{4-n}Cl_n$ series trichloromethane has the maximum absolute enthalpy of formation. Thus in this instance the experimental data cannot be described correctly by any of the proposed computational schemes. Since the experimental enthalpies of formation of all the five compounds in this series are fairly reliable, presumably the computational schemes[9,98,102] take into account inadequately the interaction of the non-bonded atoms. We may note that a similar behaviour is observed also in other organic chloro-compounds, for example, among the chloroethanes investigated the absolute enthalpy is a maximum for 1,1,2,2-tetrachloroethane[4]. It appears that, as the chlorine atoms accumulate at a single carbon atom, the energy of the interaction of the non-bonded atoms does not remain constant; as a result, the slight stabilisation of the chloromethanes which are the first members of the $CH_{4-n}Cl_n$ series is replaced by destabilisation after complete chlorination.

In certain studies it was concluded previously that in the series of halogenomethanes the enthalpy of formation varies linearly with composition[109,110]. This conclusion is a natural consequence of the unsuccessful selection of reference quantities. Papulov and coworkers[109,110] used the most reliable experimental determinations and the data from Glushko's handbook[3] as such quantities; computational methods based on a linear relation were used widely to obtain data of this kind[10].

Analysis of the data obtained by Stull et al.[6] leads to the conclusion that they are frequently mutually contradictory. As an example, it is sufficient to quote the following series[6]:

	CH_2F_2	$CHClF_2$	CCl_2F_2
ΔH_f°, kcal mol	—108.24	— 119.9	—115.0

The contradictory nature of certain numerical data in the above book[6] is due to the fact that the authors used without recalculation a fairly large number of ΔH_f° values obtained by Maslov[111]. The value of $\Delta H_f^\circ(CHClF_2, gas)$, which deviates strongly in the above series, was also taken from Maslov's work[111]. Maslov and Maslov[111] estimated ΔH_f° solely on the basis of a simple additive scheme in which the bond energies in all halogenomethanes were assumed to be constant and equal to the bond energies in the tetrahalogeno-derivatives. The choice of reference data in their study[111] is now obsolete and differs strongly from that in the book by Stull et al.[6]

In order to refine further the thermochemical properties of halogenomethanes, it is necessary to increase the number of reliable ΔH_f° reference data. On the one hand, this would make it possible to revise the estimates of ΔH_f° based on the existing computational schemes and, on the other, one could investigate in greater detail the dependence of ΔH_f° for halogenomethanes on composition and the real possibilities of the computational schemes.

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