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Thermochemistry of Haloethanes

V.P.Kolesov and T.S.Papina

Data on the thermochemistry of haloethanes are surveyed. The most reliable standard enthalpies of formation of 37 haloethanes are recommended on the basis of a critical analysis of the experimental results published up to 1980 inclusive (and partly in 1981). The constants of a computational scheme for the estimation of the enthalpies of formation of hitherto uninvestigated haloethanes have been evaluated by the method of least squares. The enthalpies of formation of 210 haloethanes containing H, F, Cl, and Br have been calculated with the aid of these constants.
The bibliography includes 131 references.

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I. INTRODUCTION

Organohalogen compounds are widely used in many branches of the national economy. The study of their thermochemical properties is of great practical and theoretical importance[1,2]. Studies[3,4] in which the available experimental data were analysed and recommendations were made concerning the estimation of the standard enthalpies of formation of hitherto uninvestigated compounds were devoted to the thermochemistry of halomethanes and also organofluorine compounds with three or more carbon atoms. No similar investigations have been published on the thermochemistry of haloethanes.

However, haloethanes occupy a very important place in modern chemistry and technology. They are used as cooling agents, aerosol propellants, flame inhibitors, solvents, etc. Some of them have found applications in medicine and as effective anaesthetics. Many representatives of the haloethanes are the final or intermediate products in large-scale manufacturing processes (CF_2ClCF_2Cl, C_2F_5Cl, CH_3CHF_2, CF_2BrCF_2Br, etc.[5]). In this connection detailed analysis of the present state of the thermochemistry of haloethanes is urgently required. Its practical value is determined primarily by the need to have reliable thermochemical data for calculations on technological processes. The study of the influence of the nature and number of substituent atoms on the energetic properties of molecules with similar compositions and structures is of theoretical interest.

There are few experimental enthalpies of formation of haloethanes and they are frequently contradictory. While the total number of known haloethanes is 630, the enthalpies of formation of only 30 compounds of this class can be found in the handbooks published in recent years[6-9]. Furthermore, the discrepancies between the values of ΔH_f° adopted from different sources (for example, for CF_2ClCF_2Cl and $CF_2Br.CHFCl$) reach up to 50–60 kJ mol^{-1}.

During recent years many new data, which have not yet been incorporated in handbooks, have been published on the enthalpies of formation of haloethanes. Thus the enthalpies of formation of 9 compounds which had not been investigated previously were determined: CH_2ClCCl_3, CH_2CF_2Cl, $CH_3CF_2.Br$, $CF_3CH_2.Br$, $CH_3CHClBr$, CH_2ClCH_2Br, $CF_3CHClBr$, $CF_2.ICF_2I$, CH_3CF_2I. The enthalpies of formation of certain substances for which previous data had been contradictory were redetermined (CF_2ClCF_2Cl, $CF_2ClCFCl_2$, $CF_2BrCHFCl$). Significant errors in the results of previous studies were discovered and eliminated in these measurements. New determinations of the enthalpies of formation of certain haloethanes (CH_3CH_2Cl, CH_3CHCl_2, $CH_2ClCHCl_2$, $CHCl_2CHCl_2$) made it possible to revise previous recommendations.

In addition the values of ΔH_f° for a whole series of haloethanes should be recalculated and significantly modified because their calculation involves the use of the ΔH_f° for compounds whose values have been fundamentally redetermined in recent years. For example, a new determination of the enthalpy of formation of chlorotrifluoroethylene[10] led to a sharp change in the values of ΔH_f° for CH_2FCHF_2 and $CF_2.BrCFClBr$, which were calculated from the enthalpies of hydrogenation[11] and bromination[12] of $CF_2=CFCl$. Certain enthalpies of formation of substances in the gaseous state have been revised as a result of new determinations of the enthalpies of vaporisation.

The publication in recent years of a large number of experimental ΔH_f° makes it timely and necessary to re-examine the set of enthalpies of formation of haloethanes. This paper surveys the present state of the thermochemistry of haloethanes. The methods of experimental determination and the possibility of the approximate calculation of the enthalpies of formation of haloethanes are briefly characterised. All the available experimental literature data for the ΔH_f° for haloethanes published up to 1980 inclusive (and partly in 1981) are examined and analysed. The most reliable ΔH_f° for 37 compounds are recommended on the basis of this analysis. The enthalpies of formation of all the 210 possible bromochlorofluoroethanes have been calculated by Bernstein's method[13,14] from the selected experimental ΔH_f° for haloethanes containing H, F, Cl, and Br atoms. The inadequate number of experimental enthalpies of formation of iodoethanes at present precludes a similar calculation for all haloethanes including the iodo-derivatives.

II. UNITS OF MEASUREMENT AND KEY AND AUXILIARY QUANTITIES

In conformity with the International System of Units ("SI"), all the thermodynamic quantities in the present review are expressed in joules. The initial data and the data in handbooks expressed in kcal were recalculated on the basis of the relation 1 cal = 4.1840 J.[15] The atomic weights were adopted

in accordance with a IUPAC publication[16]. The enthalpies of formation of haloethanes were calculated using the following ΔH_f° (kJ mol^{-1})[17] included in the unique system of key quantities adopted by the Committee on Numerical Data for Science and Engineering (CODATA):

Compound	CO_2 (gas)	H_2O (liq.)	F^- (aq.)	Cl^- (aq.)	Br_2 (gas)
ΔH^0_f	−393.51±0.13	−285.830±±0.042	−335.35±0.65	−167.08±0.088	30.91±0.11
Compound	I_2(gas)	HCl (gas)	HBr (gas)	HI (gas)	
ΔH^0_f	62.421±0.08	−92.31±0.13	−36.38±0.17	26.36±0.8	

All the values of ΔH_f° indicated in this review and derived from handbooks or original communications have been recalculated on the basis of these key quantities. The enthalpies of dilution of HF solutions were taken from Johnson et al.[18] and the enthalpies of dilution of HCl solutions were taken from the Tables of Cox et al.[19] The heat capacities of the pure substances (except where stipulated otherwise) were taken from a handbook[7] and the heat capacities of solutions were taken from Parker[20].

In the calculation of the enthalpies of reaction from the equilibrium constants, the thermodynamic functions quoted by Glushko[21] were used. Apart from the above key quantities, in the calculation of the ΔH_f° for certain haloethanes it is also necessary to know the enthalpies of formation of ethylene or its halogeno-derivatives.

The enthalpy of formation of chlorotrifluoroethylene, $\Delta H_f^\circ[C_2F_3Cl(gas)] = -515.1 \pm 3.4$ kJ mol^{-1}, was taken from a recent study[10]; the reasons for its selection are given below (in Section III). The enthalpy of formation of vinyl bromide, $\Delta H_f^\circ[C_2H_3Br(gas)] = 79.3 \pm 1.9$ kJ mol^{-1}, was taken from a handbook[9] where it was recommended on the basis of the enthalpy of hydrogenation of C_2H_3Br to C_2H_6 measured by Lacher et al.[22] The enthalpies of formation of all the remaining haloethylenes were taken from Glushko's handbook[21]. All the recommended values in two handbooks[9,21] were calculated on the basis of the same system of key quantities which was adopted in the present study and their employment does not therefore impair the mutual consistency of the enthalpies of formation. The values $\Delta H_f^\circ[C_2H_4(gas)] = 52.4 \pm 0.5$ kJ mol^{-1} and $\Delta H_f^\circ[C_2F_4(gas)] = -659.5 \pm 2.5$ kJ mol^{-1} have been recommended[21] on the basis of reliable experimental data of several workers. The quantity $\Delta H_f^\circ[C_2H_3Cl(gas)] = 23.0 \pm 2.1$ kJ mol^{-1} was adopted on the basis of measurements of the enthalpy of polymerisation of liquid C_2H_3Cl,[23] the enthalpy of formation of the polymer[24], and the enthalpy of vaporisation of $CH_2 = CHCl$ quoted by Glushko[7]. The quantity $\Delta H_f^\circ[1,1\text{-}C_2H_2Cl_2(gas)] = 2.3 \pm 1.4$ kJ mol^{-1} is based on precise calorimetric measurements of the enthalpy of formation[24,25] and the enthalpy of vaporisation[26].

The enthalpies of formation of *cis*- and *trans*-1,2-$C_2H_2Cl_2$. .(gas) have been found[21] by adjusting the enthalpies of formation of the liquid isomers[27] for consistency with the enthalpies of vaporisation measured in several studies and on the basis of an investigation of the *cis*–*trans* isomerisation equilibrium[28–30]. This led to $\Delta H_f^\circ = 4.1 \pm 1.0$ and 6.1 ± 1.0 kJ mol^{-1} for *cis*- and *trans*-$C_2H_2Cl_2$(gas) respectively. The enthalpies of formation of tri- and tetra-chloroethylenes have been calculated[21] from measurements[27] of their enthalpies of combustion in the liquid state using the enthalpies of vaporisation measured calorimetrically[31]: $\Delta H_f^\circ[C_2HCl_3(gas)] = -4.1 \pm 1.2$ kJ mol^{-1} and $\Delta H_f^\circ[C_2Cl_4(gas)] = -11.0 \pm 2.1$ kJ mol^{-1}. The quantity $\Delta H_f^\circ[1,1\text{-}C_2F_2Cl_2(gas)] = -338 \pm 11$ kJ mol^{-1} has been recommended on the basis of measurements[11] of the enthalpies of hydrogenation of 1,1-$C_2F_2Cl_2$ to 1,1-$C_2H_4F_2$ in the gas phase and the enthalpy of formation of gaseous 1,1-$C_2H_4F_2$ determined by Kolesov et al.[32]

Among the ΔH_f° for haloethylenes indicated, the most reliable are those for C_2H_4, C_2F_4, 1,1-$C_2H_2Cl_2$, and C_2F_3Cl. The majority of other ΔH_f° for haloethylenes have been determined with a relatively low accuracy and their use for the calculation of the ΔH_f° for haloethanes therefore introduces a considerable additional error and is as a rule undesirable.

III. METHODS FOR THE DETERMINATION OF THE ENTHALPIES OF FORMATION OF HALOETHANES

All the experimental methods for the determination of the enthalpies of formation of haloethanes described in the literature can be divided, with very rare exceptions, into two large groups: calorimetric measurements and determination of equilibrium constants. The most important results for this range of substances have been undoubtedly obtained by calorimetric methods, among which the most universal is the method of combustion in a bomb calorimeter. When it is used to determine the ΔH_f° for organohalogen compounds, particularly those with a high halogen content, complications arise due to the low specific energy of combustion of the substances, the complex composition and high corrosion activity of the combustion products, and the occurrence of side reactions. These complications can be partly overcome by employing special apparatus (for example, calorimeters with rotating bombs lined with platinum), auxiliary substances, reductants, careful analysis of the combustion products, etc.; however, all these procedures undoubtedly complicate the method and have an unfavourable effect on the accuracy of the measurements[33,34]. Furthermore, in view of the low specific energy of the combustion of many haloethanes, more stringent requirements must be imposed on the purity of the test specimens.

However, despite these complications, the method of combustion in a bomb has many valuable advantages (in the first place the fact that the apparatus and method have been thoroughly developed and comprehensively tested, the high accuracy of the calorimetric measurements, and the possibility of careful analysis of the combustion products in both gaseous and condensed phases). The fact that the method of determination of the combustion energies in calorimeters with a rotating bomb has been significantly improved in recent years is also important.

In the Laboratory of Thermochemistry at Moscow State University, the method was modernised by increasing the accuracy of the measurement of the temperature and temperature control, by careful study of the processes occurring in the bomb, and partly by employing new more accurate methods of analysis of the combustion products. The changes introduced into the method have already been described[35,36].

The improvements in the method of determination of the energy of combustion in rotating bomb calorimeters made it possible to apply it to the study of new groups of haloethanes: compounds containing different halogen atoms (for example, $CF_3CHClBr$ and $CF_2BrCHFCl$), gaseous and volatile Freons (CF_2ClCF_2Cl and $CF_2ClCFCl_2$), etc.

The determination of the energies of combustion of gaseous haloethanes in a bomb calorimeter involves additional complications, since, as usual, the entire gas does not react and the amount of combusted substance can be determined only from the results of the analysis of the combustion products[37]. The method of combustion of gases in a calorimeter with a burner at a pressure close to atmospheric yields more accurate results[38,39]. However, this method is applicable only to compounds with a low halogen content, mainly to monochloroalkanes[38]. At the present time the majority of enthalpies of combustion of gaseous haloethanes have been obtained by combustion in a bomb.

The method of combustion in the liquefied state in a bomb calorimeter of substances which are gaseous at room temperature, developed recently, is extremely valuable for the

investigation of haloethanes[10,36]. Its principal advantage is almost complete combustion of the test substances. A specially designed crucible container has been used for the liquefaction and combustion of such substances. The method has been developed in a series of calorimetric experiments on the determination of the energies of combustion of chlorotrifluoroethylene[10]. $\Delta H_f^\circ[CF_2 = CFCl(gas)] = -515.1 \pm 3.4$ kJ mol^{-1} has been obtained. Previous determinations of this quantity by measuring the enthalpies of reactions with alkali metals yielded markedly divergent results: -502.3,[40] -549.1,[41] and -565.5 kJ mol^{-1}.[42] The reliability of the determination of $\Delta H_f^\circ[CF_2 = CFCl(gas)]$ obtained in the above study[10] is confirmed by the similarity of the values found by two other procedures: on the basis of the experimental[43] enthalpy of combustion of $CF_2ClCFCl_2$ using the enthalpies of chlorination[44] of chlorotrifluoroethylene, which yielded $\Delta H_f^\circ[CF_2 = CFCl(gas)] = -522.0 \pm 3.4$ kJ mol^{-1}, and also the experimental[45] enthalpy of combustion of $CF_2BrCHFCl$ and the experimental[46] enthalpy of hydrobromination of chlorotrifluoroethylene, which yielded $\Delta H_f^\circ[CF_2 = CFCl(gas)] = -509.5 \pm 5.6$ kJ mol^{-1}. The method developed by Erastov and Kolesov[10] leads to extensive possibilities for the investigation of the thermochemical properties of substances which are not fully combusted in the bomb in the gaseous state.

The results of measurements of the enthalpies of the catalytic halogenation, hydrohalogenation, and hydrogenation of ethylene and its halogeno-derivatives in the gaseous state are frequently used for the calculation of the ΔH_f° of haloethanes. A whole series of such measurements have been carried out by Lacher and co-workers[11,12,22,44,46-50] in a specially designed isothermal calorimeter of the compensation type. In these investigations a fairly high reproducibility of the experimental results was achieved (usually to within ~ 0.5–1.0 kJ mol^{-1}). However, significant systematic discrepancies with data obtained by other methods were also observed in certain cases and it was therefore suggested that the catalyst employed is insufficiently inert[39]. Calculation of ΔH_f° for haloethanes from the data of Lacher and co-workers as a rule requires the knowledge of the ΔH_f° for other organohalogen compounds (for example, haloethylenes).

In order to determine the enthalpies of formation of gaseous chlorofluorocarbons (including chlorofluoroethanes), the method of measurement of the enthalpies of reaction of these compounds with alkali metals has been frequently used[3,40-42]. The reactions are initiated by an electric arc whose energy has to be measured accurately. This method is less accurate than the determination of the heats of combustion owing to the complexity of the composition of the products formed and the need to introduce numerous corrections[3]. The ΔH_f° for haloethanes have been sometimes determined by measuring the enthalpies of reactions which can be achieved only for a few compounds. Thus $\Delta H_f^\circ(C_2F_6)$ has been determined by measuring the enthalpy of the reaction of hexafluoroethane with nitrogen trifluoride[51]. Other cases are examined in Section IV.

Numerous enthalpies of formation of haloethanes have been obtained by measuring the equilibrium constants. The enthalpy of reaction is related to the equilibrium constant by the familiar expression

$$\Delta H_T^0 = -RT \ln K_p + T\Delta S_T^0 \ . \qquad (1)$$

Having measured K_p at several temperatures and having assumed that ΔH_T° and ΔS_T° are constant in the experimental temperature range, it is possible to find the ΔH_T° from the temperature variation of ln K_p (the method of the Second Law of Thermodynamics). If the entropies of the reactants are known, a more accurate calculation of ΔH_T° by the direct substitution of ΔS_T° in Eqn.(1) is possible (the method of the Third Law of Thermodynamics); in principle, it is then sufficient to measure the equilibrium constant at a single temperature. The similarity of the values of ΔH° found on the basis of the Second and Third Laws of Thermodynamics usually indicates the absence of systematic errors from the experimental data. The necessary conditions for the determination of reliable enthalpies of reaction from the study of equilibria are an accurate measurement of the concentrations and (or) pressures of the reactants, careful monitoring of the attainment of the state of equilibrium and, in calculations based on the Second Law, also a fairly wide temperature range of the measurements. In a highly sophisticated experiment, the results of the determination of the enthalpies of reaction by measuring the equilibrium constants are frequently not inferior in their accuracy and reliability to the results of calorimetric measurements.

IV. ANALYSIS OF EXPERIMENTAL DATA AND SELECTION OF THE RECOMMENDED ENTHALPIES OF FORMATION

Ethane

The bibliography of studies on the determination of ΔH_f° for ethane has already been published[7,21]. The most reliable measurements of the enthalpies of combustion of gaseous ethane in a flow calorimeter were carried out by Rossini[52] and Pittam and Pilcher[53]. The amount of combusted ethane was determined by analysing the combustion products for H_2O[52] and CO_2.[53] The values of $\Delta H_f^\circ[C_2H_6(gas)]$ obtained are similar: -84.73 ± 0.48 kJ mol^{-1} [52] and -83.87 ± 0.24 kJ mol^{-1},[55] but the difference between them is nevertheless outside the limits of error. Pittam and Pilcher[53] used a purer specimen than that in Rossini's investigation[52]. However, in the latter study[52] the heat capacity of the calorimeter was determined by measuring the electrical energy, while Pittam and Pilcher found it from the heat of combustion of hydrogen, which renders their results dependent on their latter quantity; it was taken from Rossini's determinations. $\Delta H_f^\circ[C_2H_6.(gas)] = -84.0 \pm 0.4$ kJ mol^{-1} is recommended. It agrees with the value adopted by Glushko[21] as a result of the joint treatment of Rossini's[52] and Pittam and Pilcher's[53] data and the results of studies[54-56] in which the enthalpies of formation and hydrogenation of ethylene were measured.

Hexafluoroethane

The enthalpy of formation of hexafluoroethane has been determined by different methods: by measuring the enthalpy of the reaction of C_2F_6 with potassium[51] or nitrogen trifluoride[51]:

$$C_2F_6\,(gas) + {}^2/_3NF_3\,(gas) \rightarrow 2CF_4\,(gas) + {}^1/_2N_2\,(gas) \qquad (2)$$

and by investigating the equilibria in the reactions[57]

$$C_2F_6\,(gas) + Br_2\,(gas) \rightleftarrows 2CF_3Br\,(gas) \qquad (3)$$

or[58]

$$2CF_3CN\,(gas) \rightleftarrows C_2F_6\,(gas) + C_2N_2\,(gas)\ . \qquad (4)$$

The result obtained by Kirkbride and Davidson[41] is doubtful, since they did not characterise the purity of the substances and did not introduce all the necessary corrections for side reactions. The most reliable value has been obtained[21] by adjusting for mutual consistency the thermochemical data for reactions involving C_2F_6, CF_3Br, CF_3I, CF_3Cl, and CHF_3, including reactions (2)–(4): $\Delta H_f^\circ[C_2F_6(gas)] = -1344.0 \pm 4.0$ kJ mol^{-1}.

1,1-Difluoroethane

The enthalpy of combustion of gaseous CH_3CHF_2 in a bomb calorimeter has been determined[32]: $\Delta H_C^\circ = -1219.6 \pm 8.4$ kJ mol^{-1}. Mass-spectrometric analysis of the combustion products failed to reveal the presence of any fluoro-derivatives, except for a small amount of CH_3CHF_2 which had not reacted. Calculation of the enthalpy of formation using the key quantities adopted above leads to $\Delta H_f^\circ[CH_3CHF_2(gas)] = -497.0 \pm 8.5$ kJ mol^{-1}. Lacher et al.[11] measured ΔH° for the hydrogenation of $CF_2 = CCl_2$ with formation of CH_3CHF_2. However, these data were not used to calculate $\Delta H_f^\circ(CF_2 = CCl_2)$ (see Section II).

1,1,1-Trifluoroethane

The enthalpy of combustion of gaseous 1,1,1-trifluoroethane has been measured[59]: $\Delta H_C^\circ[CH_3CF_3(gas)] = -1008.3 \pm 1.7$ kJ mol^{-1}. A correction for adjustment to the standard state was not applied[59]; we calculated it on the basis of the calorimetric experimental data presented in the above study[59] and found it to be 4 ± 2 kJ mol^{-1}. When account is taken of this correction, we obtain $\Delta H_f^\circ[CH_3CF_3(gas)] = -748.7 \pm 3.2$ kJ mol^{-1}. A very similar value was obtained[60] by calculation from the dissociation energy of the C–C bond in 1,1,1-trifluoroethane found from kinetic data for the dehydrofluorination of CH_3CF_3: $\Delta H_f^\circ[CH_3CF_3(gas)] = -747.3$ kJ mol^{-1}. This method is much less accurate than that employed by Kolesov and Martynov[59].

1,1,2-Trifluoroethane

Lacher et al.[11] measured the enthalpy of hydrogenation of chlorotrifluoroethylene at 401 K:

$$CF_2 = CFCl\,(gas) + 2H_2\,(gas) \rightarrow CH_2FCHF_2\,(gas) + HCl\,(gas). \qquad (5)$$

They found $\Delta H_{401}^\circ(5) = -271.6$ kJ. After adjustment to the standard temperature, we obtain $\Delta H_{298}^\circ(5) = -268.2$ kJ, whence $\Delta H_f^\circ[CH_2FCHF_2(gas)] = -691 \pm 10$ kJ mol^{-1}. The error was estimated approximately in view of the lack of the necessary information in the above study[11] for its calculation.

Hexachloroethane

Berthelot[61] determined the enthalpy of combustion of hexachloroethane by an obsolete method which did not ensure the complete reduction of chlorine. Smith et al.[27] used the "quartz spiral" method and showed that it makes it possible to measure the heats of combustion of organochlorine compounds with an accuracy close to that of measurements in a rotating bomb calorimeter. They recalculated the results obtained previously by this method after introducing a series of necessary corrections. However, an important disadvantage of the study of Smith et al.,[27] which lowers the reliability of the determinations, is the absence of data on the purities of the test substances. Furthermore, the influence of impurities on the measurements of ΔH_C° is particularly marked for compounds with a high chlorine content. The data of Smith et al.[27]† for hexachloroethane yield $\Delta H_f^\circ[C_2Cl_6(cryst.,$ orthorhomb.$)] = -198.4 \pm 2$ kJ mol^{-1}. Taking into account the enthalpy of sublimation ($\Delta H_{s,298}^\circ = 60.7 \pm 4.2$ kJ mol^{-1}[7,21]), we find $\Delta H_f^\circ[C_2Cl_6(gas)] = -137.7 \pm 4.7$ kJ mol^{-1}. The accuracy of the enthalpy of sublimation of hexachloroethane is likewise low. The value of $\Delta H_{s,298}^\circ$ was calculated by Glushko[7,21] as the sum of three experimental quantities: the enthalpy of vaporisation of C_2Cl_6(cryst.,triclin.) and the enthalpies of fusion of the triclinic and orthorhombic modifications. Thus the value of $\Delta H_f^\circ[C_2Cl_6(gas)]$ found from the data of Smith et al.[27] cannot be regarded as sufficiently reliable.

Kirkbride[63] measured the enthalpy of chlorination of liquid tetrachloroethylene and the enthalpy of solution of C_2Cl_6 in C_2Cl_4, whence he found $\Delta H_{298}^\circ(6) = -155.2$ kJ for the reaction

$$C_2Cl_4\,(liq.) + Cl_2\,(gas) = C_2Cl_6\,(cryst.). \qquad (6)$$

$\Delta H_f^\circ[C_2Cl_6(gas)] = -145.2$ kJ mol^{-1} corresponds to the value. Kirkbride's study[63] was not precise; the slowness of the chlorination reaction made it necessary to introduce several large corrections which were not determined with adequate accuracy. His result must therefore be regarded as merely approximate.

The equilibrium in the gas-phase catalytic reaction

$$C_2Cl_4\,(gas) + Cl_2\,(gas) \rightleftarrows C_2Cl_6\,(gas). \qquad (7)$$

has been investigated[64–67]. We calculated $\Delta H_{298}^\circ(7) = -127.0$ kJ in accordance with the Third Law of Thermodynamics from the equilibrium constant measured[64,65] at 776 K, whence $\Delta H_f^\circ[C_2Cl_6(gas)] = -138.0$ kJ mol^{-1}. The equilibrium constants were measured[66,67] at three temperatures in the range 773–873 K and the enthalpy of reaction (7) has been found from the temperature variation of K_p: $\Delta H_{853}^\circ(7) = -130.5$ kJ. Adjustment to the standard temperature leads to $\Delta H_{298}^\circ(7) = -136.9$ kJ. Calculation of the enthalpy of reaction (7) in accordance with the Third Law of Thermodynamics yields three similar values: −139.7, −140.0, and −140.1 kJ. Using the average $\Delta H_{298}^\circ(7) = -139.9$ kJ, we obtain $\Delta H_f^\circ[C_2Cl_6(gas)] = -150.9$ kJ mol^{-1}. The results of the calculation of $\Delta H_{298}(7)$ by two methods from the data of Bushneva and co-workers[66,67] agree satisfactorily. However, in the calculation of $\Delta H_f^\circ(C_2Cl_6)$ it is necessary to employ the value of $\Delta H_f^\circ(C_2Cl_4)$ determined by Smith et al.,[27] the deficiencies of whose work were mentioned above.

Thus it is difficult to recommend a reliable value of $\Delta H_f^\circ[C_2Cl_6(gas)]$ on the basis of the available experimental data. Its calculated value is presented below (Section VI).

Chloroethane

Several workers[39,68–70] determined ΔH_C° for gaseous chloroethane in a calorimeter with a burner. Studies of Berthelot[68] and Thomsen[69] are only of historical interest. The precision of the method used by Casey and Fordham[70] was not high: the calorimeter was calibrated against the heat of combustion of a known volume of hydrogen; there is a large fraction of ballast heat due to the combustion of hydrogen in the mixture with chloroethane; quantitative characteristics of the purity of the reactants are not given. Casey and Fordham[70] obtained $\Delta H_f^\circ[C_2H_5Cl(gas)] = -100 \pm 10$ kJ mol^{-1}. The most reliable data are those of Fletcher and Pilcher[39] who used pure specimens and carried out a careful analysis of the combustion products. They obtained $\Delta H_C^\circ[C_2H_5Cl(gas)] = -1413.05 \pm 0.59$ kJ mol^{-1}, which corresponds to $\Delta H_f^\circ[C_2H_5Cl.(gas)] = 112.2 \pm 0.7$ kJ mol^{-1}.

Similar results were obtained from the results of a study of the equilibrium reaction

$$C_2H_4\,(gas) + HCl\,(gas) \rightleftarrows C_2H_5Cl\,(gas) \qquad (8)$$

† All the values of ΔH_C° for chloroethanes quoted by Smith et al.[27] were measured at 292 K; in the present review they have been adjusted to the standard temperature. The heat capacity of C_2Cl_6 was taken from Rossini et al.[62] and those of all the remaining substances were taken from Glushko's handbook[7].

by Lane et al.[71] (at 722–754 K) and Howlett[72] (at 448–528 K). Lane et al.[71] obtained $\Delta H^\circ_{743}(8) = 74.98$ kJ on the basis of the Third Law of Thermodynamics and Howlett[72] obtained $\Delta H^\circ_{463}(8) = -72.97$ kJ on the basis of the Second Law of Thermodynamics. Hence, after adjustment to 298 K, we obtain $\Delta H^\circ_f[C_2H_5Cl(gas)] = -110.8 \pm 2$ and -111.1 ± 2 kJ mol^{-1} respectively. An earlier and less accurate study[73] of equilibrium (8) yielded $\Delta H^\circ_f[C_2H_5Cl(gas)] = -96.0$ kJ mol^{-1}. Measurements of Lacher and co-workers[7,48] of the enthalpy of hydrogenation of chloroethane at 521 K ($\Delta H_r = -71.80$ kJ mol^{-1}) lead to $\Delta H^\circ_f[C_2H_5Cl(gas)] = 106.7$ kJ mol^{-1} after adjustment to the standard temperature. The value obtained by Fletcher and Pilcher[39] is recommended: $\Delta H^\circ_f[C_2H_5Cl.(gas)] = -112.2 \pm 0.7$ kJ mol^{-1}.

1,1-Dichloroethane

Thomsen's study[69] involving the measurement of the enthalpy of combustion of CH_3CHCl_2 is merely of historical interest. Later measurements of ΔH°_C yielded $\Delta H^\circ_f[CH_3CHCl_2.(liq.)] = 158.3 \pm 0.9$ kJ mol^{-1} or (when account is taken of the enthalpy of evaporation $\Delta H^\circ_{v,298} = 31.00 \pm 0.04$ kJ mol^{-1} [7]), $\Delta H^\circ_f[CH_3CHCl_2(gas)] = -127.3 \pm 0.9$ kJ mol^{-1} were obtained[27]. Lacher et al.[50] determined ΔH for reaction

$$CH_3CHCl_2\,(gas) + 2H_2\,(gas) \rightarrow C_2H_6\,(gas) + 2HCl\,(gas) \qquad (9)$$

at 523 K. Their data yield $\Delta H^\circ_{298}(9) = -139.9 \pm 2.5$ kJ and $\Delta H^\circ_f[CH_3CHCl_2(gas)] = -128.8 \pm 2.6$ kJ mol^{-1}. The results of Smith et al.[27] and Lacher et al.[50] are similar and yet it is difficult to regard them as reliable. Thus the sign of ΔH for the isomerisation of dichloroethane which follows from the values of $\Delta H^\circ_f[C_2H_4Cl_2(gas)]$ found in the above studies[27,50] conflicts with that determined directly[74] (see below). The purity of the CH_3CHCl_2 specimen used by Lacher et al.[50] was low (99% according to chromatographic analysis); the method used to check that the reaction proceeds unambiguously is not indicated. Smith et al.[27] totally fail to give any information about the purity of the specimen.

More reliable data were obtained by Levanova et al.[75] in the study of the equilibria

$$CH_3CHCl_2\,(gas) \rightleftarrows CH_2{=}CHCl\,(gas) + HCl\,(gas) \qquad (10)$$

and

$$CH_2{=}CHCl\,(gas) + HCl\,(gas) \rightleftarrows CH_3CHCl_2\,(liq.) \qquad (11)$$

in the temperature ranges 403–438 K and 293–323 K respectively. They calculated $\Delta H^\circ_{420}(10) = 61.7$ kJ and $\Delta H^\circ_{308}(11) = -92.7$ kJ on the basis of the Second Law of Thermodynamics; $\Delta S^\circ_{420}(10) = 144.3$ kJ mol^{-1} K^{-1} and $\Delta S^\circ_{308}(11) = -238.9$ J mol^{-1} K^{-1}. Adjustment to the standard temperature yields $\Delta H^\circ_{298}(10) = 60.9$ kJ, whence follows $\Delta H^\circ_f[CH_3CHCl_2(gas)] = -130.2$ kJ mol^{-1}; $\Delta H^\circ_f[CH_3CHCl_2(gas)] = -131.0$ kJ mol^{-1} corresponds to $\Delta H^\circ_{298}(11)$. The similarity of the ΔH°_f found from the ΔH for reactions (10) and (11) indicates the absence of significant systematic errors.

Another confirmation of the validity of the results of Levanova et al.[75] is the satisfactory agreement between the experimental $\Delta S^\circ(10)$ and $\Delta S^\circ(11)$ and those calculated from the data in Glushko's handbook[7]: $\Delta S^\circ_{420}(10) = 148.4$ J mol^{-1} K^{-1} and $\Delta S^\circ_{298}(11) = -239.0$ J mol^{-1} K^{-1}. The average of the two values of ΔH°_f found by Levanova et al.[75] is recommended, i.e. $\Delta H^\circ_f[CH_3CHCl_2(gas)] = -130.6 \pm 3.0$ kJ mol^{-1}. The error was estimated by analogy with the results of the study of equilibria in other investigations by the same workers.

1,2-Dichloroethane

The values of ΔH°_C for 1,2-dichloroethane have been determined[69,76] but their accuracy is low. The enthalpies of combustion of liquid CH_2ClCH_2Cl found by Smith et al.[27] lead to $\Delta H^\circ_f[CH_2ClCH_2Cl(liq.)] = -158.9 \pm 0.8$ kJ mol^{-1}. When account is taken of the enthalpy of evaporation $\Delta H^\circ_{v,298} = 35.4 \pm 0.4$ kJ mol^{-1},[7] we obtain $\Delta H^\circ_f[CH_3CHCl_2(gas)] = 123.5 \pm 0.9$ kJ mol^{-1}. Later determinations[24,77] of $\Delta H^\circ_C(CH_2ClCH_2Cl)$ lead to $\Delta H^\circ_f[CH_2ClCH_2Cl(gas)] = -129.5 \pm 1.6$ and -134.1 ± 1.2 kJ mol^{-1} respectively.

The enthalpy of the reaction

$$CH_2ClCH_2Cl\,(gas) + 2H_2\,(gas) \rightarrow C_2H_6\,(gas) + 2HCl\,(gas) \qquad (12)$$

found by Lacher et al.[50] at 523 K leads to $\Delta H^\circ_{298}(12) = -142.1 \pm 2.5$ kJ and $\Delta H^\circ_f[CH_2ClCH_2Cl(gas)] = -126.6 \pm 2.6$ kJ mol^{-1} after adjustment to the standard temperature. As in the hydrogenation of 1,1-dichloroethane (see above), the specimen employed by Lacher et al.[50] was not highly pure (99%) and the absence of side reactions was not confirmed.

Conn et al.[78] determined ΔH° for the chlorination of ethylene in the gas phase at 355 K: $\Delta H^\circ_r = -182.6 \pm 0.6$ kJ mol^{-1}. After adjustment to 298 K, their data lead to $\Delta H^\circ_f[CH_2ClCH_2.Cl(gas)] = -130.4 \pm 0.8$ kJ mol^{-1}. The studies of Sinke and Stull[24], Hu and Sinke[77], and Conn et al.[78] were carried out by well tested methods using fairly pure specimens. However, one must note that the results of Hu and Sinke[24] and Conn et al.,[78] like those of Smith et al.[27] and Lacher et al.,[50] conflict with the determination[74] of ΔH for the isomerisation reaction

$$CH_3CHCl_2 \rightleftarrows CH_2ClCH_2Cl \qquad (13)$$

[$\Delta H^\circ_{385}(13) = -9.6 \pm 1.4$ kJ was obtained]. The latter value was found by the joint treatment of the results of measurements of K_p in the liquid and gas phases and is only approximate. Nevertheless its sign and approximate value must be taken into account in selecting the ΔH°_f for 1,2-dichloroethane. On the basis of these considerations, preference must be given to the data of Hu and Sinke[77], who determined ΔH°_C by the most reliable method—in a rotating bomb calorimeter, and $\Delta H^\circ_f[CH_2ClCH_2Cl(gas)] = -134.1 \pm 1.2$ kJ mol^{-1} must be adopted.

1,1,1-Trichloroethane

The enthalpy of combustion of 1,1,1-trichloroethane in rotating bomb calorimeters has been measured by a number of workers[25,77,79]. It has been shown[79] that the result obtained previously, namely $\Delta H^\circ_f[CH_3CCl_3(gas)] = -138.3$ kJ mol^{-1},[77] was erroneous owing to the inadequate purity of the specimen. In two investigations[25,79] the purities of the specimens were extremely high (99.99 and 99.96 mole % respectively). Both studies were carried out using a thoroughly tested method. The values of ΔH°_C from the above investigations[25,79] together with $\Delta H^\circ_{v,298}(CH_3CCl_3) = 32.47 \pm 0.07$[80] yield $\Delta H^\circ_f[CH_3CCl_3(gas)] = -142.1 \pm 1.4$ kJ mol^{-1}[25] and -146.1 ± 1.1 kJ mol^{-1}.[79] Hu et al.[79] also investigated the equilibrium

$$CH_2{=}CCl_2\,(gas) + HCl\,(gas) \rightleftarrows CH_3CCl_3\,(gas) \qquad (14)$$

at 348–399 K and obtained $\Delta H^\circ_{298}(14) = -54.6 \pm 8$ kJ on the basis of the Third Law of Thermodynamics. Hence we find $\Delta H^\circ_f[CH_3CCl_3(gas)] = -144.6 \pm 1.7$ kJ mol^{-1}.

The equilibrium in the hydrochlorination of 1,1-dichloroethylene in chlorobenzene at 293–353 K has been studied by Levanova et al.[81] They found $\Delta H^\circ_{323} = -56.9 \pm 2$ kJ mol^{-1}, from which follows $\Delta H^\circ_f[CH_3CCl_3(gas)] = -141.0 \pm 2.4$ kJ

mol^{-1}, its accuracy being lower than that of the results of other investigations[25,79], since no account has been taken of the enthalpy of solution of $CH_2=CCl_2$ and CH_3CCl_3 in chlorobenzene.

The weighted average of the most reliable results[25,79] presented above is recommended: $\Delta H_f^\circ[CH_3CCl_3(gas)] = -144.6 \pm 0.8$ kJ mol^{-1}.

1,1,2-Trichloroethane

Kirkbride[63] measured the enthalpy of the reaction

$$CH_2ClCH_2Cl\ (liq.) + Cl_2\ (gas) \rightarrow CH_2ClCHCl_2\ (liq.) + HCl\ (gas) \qquad (15)$$

and found $\Delta H_{298}^\circ(15) = -116.3$ kJ. Using the value of $\Delta H_f^\circ(CH_2ClCH_2Cl)$ adopted above, we obtain $\Delta H_f^\circ[CH_2ClCHCl_2.(liq.)] = -193.5$ kJ mol^{-1}. Kirkbride[63] introduced fairly large corrections for the dissolution of HCl, the evaporation of dichloroethane, etc., which had not been measured with adequate accuracy; no check was made to make sure that side reactions do not occur. His result must therefore be regarded as only approximate.

Levanova et al.[82] investigated the equilibria in the hydrochlorination of *cis*- and *trans*-dichloroethylenes in solution in tetrachloroethane. Without taking into account the heats of solution, we obtain from these results $\Delta H_f^\circ[CH_2ClCHCl_2.(liq.)] = -179.9$ and -181.9 kJ mol^{-1}. The result based on the study of the equilibrium in the isomerisation reaction

$$CH_2ClCHCl_2\ (liq.) \rightleftarrows CH_3CCl_3\ (liq.) \qquad (16)$$

at 373–473 K is more reliable[82]. Calculation based on the Second Law of Thermodynamics yielded $\Delta H_{423}^\circ(16) = 8.4 \pm 1.7$ kJ. Hence, having adopted $\Delta C_p(liq.) = \Delta C_p(gas) = 3.8$ J mol^{-1} K^{-1}[17]# in view of the lack of data for $C_p[CH_2.ClCHCl_2(liq.)]$, we find $\Delta H_{298}^\circ(16) = 7.9 \pm 1.7$ kJ and $\Delta H_f^\circ.[CH_2ClCHCl_2(liq.)] = -185.0 \pm 1.9$ kJ mol^{-1}. Taking into account the enthalpy of evaporation $\Delta H_{v,298}^\circ = 40.28 \pm 0.06$ kJ mol^{-1},[80] we have $\Delta H_f^\circ[CH_2ClCHCl_2(gas)] = -144.7 \pm 1.9$ kJ mol^{-1}.

1,1,1,2-Tetrachloroethane

The enthalpy of combustion of liquid CH_2ClCCl_3 (purity 99.95 mole %) has been measured[83] in a tantalum rotating bomb calorimeter and $\Delta H_c^\circ[CH_2ClCCl_3(liq.)] = -973.90 \pm 1.28$ kJ mol^{-1} was obtained. This leads to $\Delta H_f^\circ[CH_2ClCCl_3(liq.)] = -193.45 \pm 1.35$ kJ mol^{-1}; taking into account $\Delta H_{v,298}^\circ = 41.1 \pm 0.2$ kJ mol^{-1},[83] we find that $\Delta H_f^\circ[CH_2ClClCCl_3(gas)] = 152.3 \pm 1.4$ kJ mol^{-1}.

Levanova et al.[84] found $\Delta H_{333}^\circ = 45.4 \pm 0.4$ kJ mol^{-1} from the temperature variation of the equilibrium constants for the dehydrochlorination of 1,1,1,2-tetrachloroethane. Hence we obtain $\Delta H_{r,298}^\circ = 44.0 \pm 0.4$ kJ mol^{-1} and $\Delta H_f^\circ[CH_2ClCCl_3.(gas)] = -133.3$ kJ mol^{-1}. This result is less accurate than the data of Gundry and Head[83].

1,1,2,2-Tetrachloroethane

Smith et al.[27] determined the enthalpy of combustion of 1,1,2,2-tetrachloroethane: $\Delta H_c^\circ = -970.0 \pm 1.4$ kJ mol^{-1}. From this data, we obtain $\Delta H_f^\circ[CHCl_2CHCl_2(liq.)] = 193.0 \pm 1.5$ kJ mol^{-1} or (taking into account the enthalpy of evaporation $\Delta H_{v,298}^\circ = 45.78 \pm 0.16$ kJ mol^{-1} [80]) $\Delta H_f^\circ[CHCl_2CHCl_2.(gas)] = -147.2 \pm 1.5$ kJ mol^{-1}. The ΔH° for the chlorination of *cis*-dichloroethylene measured by Kirkbride[63] leads to a similar value: $\Delta H_f^\circ[CHCl_2CHCl_2(gas)] = -148.2$ kJ mol^{-1}. More reliable results were obtained in a study[67] where the equilibrium constants of the isomerisation reaction

$$CHCl_2CHCl_2\ (liq.) \rightleftarrows CH_2ClCCl_3\ (liq.) \qquad (17)$$

were measured at three temperatures in the range 453–493 K and the enthalpy of reaction (17) was calculated on the basis of the Second Law of Thermodynamics; $\Delta H_{473}^\circ(17) = 10.0 \pm 2.6$ kJ was obtained. Having adopted $\Delta C_p(liq.) = \Delta C_p(gas) = 2.1$ J mol^{-1} K^{-1} [7] for adjustment to 298 K (in view of the lack of the heat capacity of liquid CH_2ClCCl_3), we obtain $\Delta H_{298}^\circ(17) = 9.7 \pm 2.6$ kJ. Together with the value of $\Delta H_f^\circ.[CH_2ClCl_3(liq.)]$ quoted above, this yields $\Delta H_f^\circ[CHCl_2CHCl_2.(liq.)] = -203.1 \pm 3.0$ kJ mol^{-1} or $\Delta H_f^\circ[CHCl_2CHCl_2(gas)] = -157.3 \pm 3.0$ kJ mol^{-1}.

Pentachloroethane

The enthalpy of combustion of pentachloroethane measured by Smith et al.,[27] namely $\Delta H_c^\circ = -858.9 \pm 2.5$ kJ mol^{-1}, leads to $\Delta H_f^\circ[C_2HCl_5(liq.)] = -183.5 \pm 2.6$ kJ mol^{-1}. The enthalpy of chlorination of trichloroethylene $\Delta H_r = -150.6$ kJ mol^{-1} obtained by Kirkbride[63] leads to $\Delta H_f^\circ[C_2HCl_5(liq.)] = -188.7$ kJ mol^{-1}.

Bushneva[67] and Levanova et al.[85] determined the equilibrium constants of the catalytic reaction

$$C_2HCl_5\ (soln) \rightleftarrows HCl\ (gas) + C_2Cl_4\ (soln) \qquad (18)$$

at 363–383 K and found $\Delta H_{373}^\circ(18) = 45.1 \pm 4.5$ kJ on the basis of the Second Law of Thermodynamics. Adjustment to the standard temperature yields $\Delta H_{298}^\circ(18) = 48.1 \pm 4.5$ kJ, whence $\Delta H_f^\circ[C_2HCl_5(liq.)] = -191.4 \pm 5$ kJ mol^{-1}.

The deficiencies of the studies of Smith et al.[27] and Kirkbride[63] were already noted above [see the discussion of the value of $\Delta H_f^\circ(C_2Cl_6)$]. The accuracy of the determination of $\Delta H_f^\circ[C_2HCl_5(liq.)]$ in the above investigations[67,85] is also low as a consequence of the narrow temperature range in the measurements of K_p, the lack of enthalpies of solution for C_2Cl_4 and C_2HCl_5, and the use of an insufficiently reliable value of $\Delta H_f^\circ[C_2Cl_4(gas)]$, determined from the data of Smith et al. (see Section II).

The ΔH_f° for gaseous pentachloroethane were found to be -137.9 kJ mol^{-1},[27] -143.1 kJ mol^{-1},[63] and -145.8 kJ mol^{-1}.[67,85] Their reliability is reduced also as a consequence of the use of $\Delta H_{v,298}^\circ(C_2HCl_5) = 45.6$ kJ mol^{-1}, quoted by Kirkbride without indicating the error and the method of measurement. The calculated $\Delta H_f^\circ[C_2HCl_5(gas)]$ is therefore recommended below (see Section VI).

1,2-Dichlorotetrafluoroethane

The values of $\Delta H_f^\circ[CF_2ClCF_2Cl(gas)]$ calculated from the ΔH° for the reactions of CF_2ClCF_2Cl with potassium[41] or sodium[86] are -920.8 and -968.5 kJ mol^{-1} respectively. This discrepancy is probably due to complications arising in the determination of ΔH for reactions with alkali metals.

The measurements of the enthalpy of chlorination of tetrafluoroethylene by Lacher et al.[47] lead to $\Delta H_f^\circ[CF_2ClCF_2Cl.(gas)] = -899.4$ kJ mol^{-1}. The recommended value is based on the enthalpy of combustion of gaseous 1,2-dichlorotetrafluoroethane measured in a rotating bomb calorimeter[87]. The purity of the specimen was 99.8 mole %; a correction was

$\Delta C_p(liq.)$ and $\Delta C_p(gas)$ for dichloroethane isomers do not differ within the limits of experimental errors[7].

applied for the 0.2 mole % C_2F_5Cl impurity. $\Delta H_c^\circ[CF_2ClCF_2Cl.(gas)] = -624.7 \pm 3.6$ kJ mol^{-1} was obtained, whence follows $\Delta H_f^\circ[CF_2ClCF_2Cl(gas)] = -925.5 \pm 4.3$ kJ mol^{-1}.

1,1,2-Trichlorotrifluoroethane

The enthalpy of combustion of $CF_2ClCFCl_2$ was determined by Erastov et al.[43] The measurements were performed in two rotating bomb calorimeters, three specimens with purities of 99.60, 99.85, and 99.91 mole % were used, and the combustion products were carefully analysed. $\Delta H_f^\circ[CF_2Cl.CFCl_2(liq.)] = -755.0 \pm 2.8$ kJ mol^{-1} corresponds to the $\Delta H_c^\circ[CF_2ClCFCl_2(liq.)] = -641.6 \pm 1.9$ kJ mol^{-1} measured[43]. When account is taken of the enthalpy of evaporation $\Delta H_{v,298}^\circ = 28.2 \pm 0.4$ kJ mol^{-1},[88] we find $\Delta H_f^\circ[CF_2ClCFCl_2(gas)] = -726.8 \pm 2.8$ kJ mol^{-1}. When the enthalpy of formation $\Delta H_f^\circ.[CF_2=CFCl(gas)]$ quoted above is used, the result of Erastov et al.[43] agree satisfactorily with the enthalpy of chlorination of chlorotrifluoroethylene obtained by Lacher et al.[44]

The quantity $\Delta H_f^\circ[CF_2ClCFCl_2(gas)] = -781.9$ kJ mol^{-1}, calculated from the measurements of ΔH° for the reaction of $CF_2ClCFCl_2$ with sodium[86], is less reliable.

Tetrachloro-1,1-difluoroethane

The enthalpy of chlorination of 1,1-dichlorodifluoroethylene $\Delta H_{363} = -171.9$ kJ mol^{-1}, to which corresponds $\Delta H_f^\circ[CF_2Cl.CCl_3(gas)] = 510$ kJ mol^{-1}, has been measured[44]. It is noteworthy that the value of $\Delta H_f^\circ[CF_2=CCl_2(gas)] = -338 \pm 11$ kJ mol^{-1} (see Section II) employed in this calculation is not very reliable. The value of ΔH° obtained[44] for the chlorination reaction also gives rise to some doubts, since it deviates from the general relations for the ΔH° for the chlorination of fluoro- and chloro-ethylenes[89].

The value based on the measurement of the enthalpy of combustion of tetrachloro-1,1-difluoroethane (purity 99.6 mole %) in a rotating bomb calorimeter is more reliable[90]; it amounts to $\Delta H_c^\circ[CF_2ClCCl_2(cryst.)] = -670.5 \pm 3.5$ kJ mol^{-1}, whence follows $\Delta H_f^\circ[CF_2ClCCl_3(cryst.)] = -569.8 \pm 3.8$ kJ mol^{-1}. When account is taken of the enthalpy of fusion ($\Delta H_{m,298}^\circ = 3.3 \pm 0.4$ kJ mol^{-1} [90]) and the enthalpy of evaporation ($\Delta H_{v,298}^\circ = 40.7 \pm 1.9$ kJ mol^{-1}) of tetrachloro-1,1-difluoroethane, we obtain $\Delta H_f^\circ[CF_2ClCCl_3(gas)] = -525.8 \pm 4.3$ kJ mol^{-1}.

1-Chloro-1-fluoroethane

The enthalpy of combustion of two specimens of gaseous CH_3CHFCl (with purities of 99.78 and 99.93 mole %) were measured[91] in a rotating bomb calorimeter. $\Delta H_f^\circ[CH_3CHFCl.(gas)] = -313.4 \pm 2.6$ kJ mol^{-1} corresponds to the $\Delta H_c^\circ = -1247.75 \pm 2.5$ kJ mol^{-1} obtained.

1-Chloro-1,1-difluoroethane

The enthalpy of combustion of gaseous CH_3CF_2Cl (99.90 mole % pure) has been measured[92] in a rotating bomb calorimeter: $\Delta H_c^\circ = -1061.1 \pm 5.0$ kJ mol^{-1}. Hence follows $\Delta H_f^\circ.[CH_3CF_2Cl(gas)] = -536.2 \pm 5.2$ kJ mol^{-1}.

Bromoethane

The early determinations[68,69] of ΔH° for the combustion of bromoethane are of only historical interest. Lane et al.[71] investigated the equilibrium in the hydrobromination of ethylene at 515–573 K and calculated $\Delta H_{r,544}^\circ = -80.3 \pm 1.3$ kJ mol^{-1} on the basis of the Second Law of Thermodynamics. After adjustment to the standard temperature, we obtain $\Delta H_{r,298}^\circ = -78.2 \pm 1.3$ kJ mol^{-1} and $\Delta H_f^\circ[C_2H_5Br(gas)] = -62.2 \pm 1.4$ kJ mol^{-1}. The enthalpy of hydrogenation of bromoethane has been measured[49] at 523 K; it amounts to $\Delta H_r^\circ = -62.05 \pm 1.1$ kJ mol^{-1}, whence $\Delta H_{r,298} = -59.51 \pm 1.1$ kJ mol^{-1}. Using the value of $\Delta H_f^\circ[C_2H_6(gas)]$ recommended above, we obtain $\Delta H_f^\circ[C_2H_5Br(gas)] = -60.9 \pm 1.2$ kJ mol^{-1}. The values of ΔH_f° derived from the investigations of Fowell et al.[49] and Lane et al.[71] agree satisfactorily; their weighted mean, i.e. $\Delta H_f^\circ[C_2H_5Br(gas)] = -61.5 \pm 1.0$ kJ mol^{-1}, can be adopted as the most probable.

Ashcroft et al.[93] determined ΔH° for the reaction of C_2H_5Br with lithium hydride and found that the heat of the reaction

$$C_2H_5Br\,(liq.) + {}^1/_2H_2\,(gas) \rightarrow C_2H_6\,(gas) + {}^1/_2Br_2\,(liq.) \qquad (19)$$

is $\Delta H_{328}^\circ(19) = 11.7 \pm 6.3$ kJ. Hence follows $\Delta H_f^\circ[C_2H_5Br.(liq.)] = -95.7 \pm 6.3$ kJ mol^{-1}; bearing in mind that $\Delta H_{v,298}^\circ = 27.91 \pm 0.21$ kJ mol^{-1},[7] we obtain $\Delta H_f^\circ[C_2H_5Br(gas)] = -67.8 \pm 6.3$ kJ mol^{-1}. This value does not conflict with that recommended above but is less accurate.

1,1- and 1,2-Dibromoethanes

Berthelot's data[94] for the enthalpy of bromination of ethylene and also those of Kablukov and Perel'man[76] for the enthalpy of combustion of 1,2-dibromoethane in a static bomb calorimeter are now obsolete.

Measurements of the enthalpy of combustion of liquid CH_2BrCH_2Br in rocking[95] and rotating[96] bomb calorimeters lead to $\Delta H_f^\circ[CH_2BrCH_2Br(gas)] = -52.3$ and -22.4 kJ mol^{-1} respectively when account is taken of $\Delta H_{v,298}^\circ(CH_2BrCH_2Br) = 41.8 \pm 0.4$ kJ mol^{-1}.[7] The large discrepancy between them may be explained by the presence of impurities in the test specimens whose purities were not characterised in the above investigations[95,96].

Conn et al.[78] determined the enthalpy of bromination of ethylene (with a purity of 99.98 mole %) in the gas phase at 355 K; it proved to be -121.6 ± 1.3 kJ mol^{-1}. After adjustment to 298 K, we obtain $\Delta H_{r,298}^\circ = 121.9 \pm 1.3$ kJ mol^{-1}, whence follows $\Delta H_f^\circ[CH_2BrCH_2Br(gas)] = -38.6 \pm 1.4$ kJ mol^{-1}.

Levanova et al.[97] measured the equilibrium constants of the reactions

$$CH_3CHBr_2\,(gas) \rightleftarrows CH_2=CHBr\,(gas) + HBr\,(gas), \qquad (20)$$

$$CH_2BrCH_2Br\,(gas) \rightleftarrows CH_2=CHBr\,(gas) + HBr\,(gas), \qquad (21)$$

$$CH_3CHBr_2\,(gas) \rightleftarrows CH_2BrCH_2Br\,(gas) \qquad (22)$$

at temperatures in the range 404–520 K and calculated the following values on the basis of the Second Law of Thermodynamics: $\Delta H_{425}^\circ(20) = 70.3 \pm 2.5$ kJ, $\Delta H_{448}^\circ(21) = 79.9 \pm 1.7$ kJ, and $\Delta H_{485}^\circ(22) = -12.1 \pm 1.3$ kJ. Adopting $\Delta C_p = 0$ in reactions (20)–(22) owing to the lack of data for $C_p(CH_3.CHBr_2)$ and also in view of the low value of $\Delta C_p(21) = 0.1$ J mol^{-1} K^{-1},[7] we obtain $\Delta H_f^\circ[CH_3CHBr_2(gas)] = -27.4 \pm 3.2$ kJ mol^{-1} and $\Delta H_f^\circ[CH_2BrCH_2Br(gas)] = -37.0 \pm 6$ kJ mol^{-1} from the ΔH° for reactions (20) and (21).

Izmailov et al.[98] investigated the equilibrium in the isomerisation of dibromoethane in the liquid phase at 363–698 K and calculated the enthalpy of isomerisation as 528 K on the basis

of the Second Law of Thermodynamics, which proved to be -13.0 ± 0.5 kJ mol^{-1}. Adopting $\Delta C_p = 0$ and using the value of $\Delta H^\circ_{v,298}(CH_2BrCH_2Br)$[7] quoted above as well as the value $\Delta H^\circ_{v,298}(CH_3CHBr_2) = 39.3$ kJ mol^{-1} calculated by the Klages equation[99], we obtain $\Delta H^\circ_{298}(22) = -10.5 \pm 5.0$ kJ for the gas phase. The error takes into account the approximate nature of the calculation. The results of the determination of the enthalpies of formation of 1,1- and 1,2-dibromoethanes as well as the enthalpies of their isomerisation found in a number of studies[78,97,98] agree with one another (within the limits of the errors). Joint least squares treatment of the five results indicated, taking into account their statistical weights, yielded the following recommended values: $\Delta H^\circ_f[CH_3CHBr_2.(gas)] = -26.7 \pm 1.9$ kJ mol^{-1} and $\Delta H^\circ_f[CH_2BrCH_2Br(gas)] = -38.3 \pm 1.2$ kJ mol^{-1}.

1,2-Dibromotetrafluoroethane

Lacher et al.[12] measured the enthalpy of bromination of gaseous tetrafluoroethylene at 376 K and found it to be -161.0 ± 3.0 kJ mol^{-1}. Using $C_p[CF_2BrCF_2Br(gas)] = 119.8$ J mol^{-1} K^{-1}, estimated from the heat capacities[7] of C_2F_6 and C_2Br_6, we obtain $\Delta H_{r,298} = -161.3 \pm 3.0$ kJ mol^{-1}, whence follows $\Delta H^\circ_f[CF_2BrCF_2Br(gas)] = -789.9 \pm 4.0$ kJ mol^{-1}.

1-Bromo-1,1-difluoroethane

Pickard and Rodgers[100] measured the equilibrium constant of the reaction

$$CH_3CF_2Br\ (gas) + I_2\ (gas) \rightleftarrows CH_3CF_2I\ (gas) + IBr\ (gas) \qquad (23)$$

at 581–622 K and found [having estimated $\Delta S^\circ(23)$ and $\Delta C_p(23)$ by the method of group contributions] $\Delta H^\circ_{298}(23) = 42.7 \pm 0.8$ kJ. Adopting $\Delta H^\circ_f[IBr(gas)] = 40.80 \pm 0.14$ kJ mol^{-1} [21] and $\Delta H^\circ_f[CH_3CF_2I(gas)] = -410.0 \pm 8.5$ kJ mol^{-1} (see below), we obtain $\Delta H^\circ_f[CH_3CF_2Br(gas)] = -474.3 \pm 8.5$ kJ mol^{-1}.

Bromo-1,1,1-trifluoroethane

Buckley et al.[101] investigated the equilibrium

$$CF_3CH_2Br\ (gas) + I_2\ (gas) \rightleftarrows CF_3CH_2I\ (gas) + IBr\ (gas) \qquad (24)$$

in the range 614–726 K and calculated $\Delta H^\circ_{298}(24) = 27.6 \pm 2.1$ kJ on the basis of the Third Law of Thermodynamics using the thermodynamic functions of haloethanes taken from Ford[102]. Taking into account $\Delta H^\circ_f[CF_3CH_2I(gas)] = -648.6 \pm 3.9$ kJ mol^{-1} (see below), we obtain $\Delta H^\circ_f[CF_3CH_2Br(gas)] = -697.8 \pm 4.4$ kJ mol^{-1}.

Bromo-1,1,2,2-Tetrafluoroethane

Lacher et al.[46] measured the enthalpy of hydrobromination of gaseous perfluoroethylene and found $\Delta H^\circ_{r,367} = -137.7 \pm 0.9$ kJ mol^{-1}. Adopting $C_p[CHF_2CF_2Br(gas)] = 104.2$ J mol^{-1} K^{-1}, we find $\Delta H^\circ_{r,298} = -137.3 \pm 1$ kJ mol^{-1} and $\Delta H^\circ_f[CHF_2.CF_2Br(gas)] = -833.2 \pm 2.7$ kJ mol^{-1} from a comparison of the C_p for C_2H_6, C_2F_6, and C_2Br_6.[7]

1-Bromo-1-chloroethane

Bushneva et al.[103] investigated the equilibria in the thermocatalytic reactions of 1-bromo-1-chloroethane in the gas phase at 443–523 K and calculated the enthalpies of the following three reactions on the basis of the Second Law of Thermodynamics:

$$2CH_3CHClBr \rightleftarrows CH_3CHCl_2 + CH_3CHBr_2, \qquad (25)$$

$$CH_3CHClBr \rightleftarrows CH_2{=}CHCl + HBr, \qquad (26)$$

$$CH_3CHClBr \rightleftarrows CH_2{=}CHBr + HCl. \qquad (27)$$

They obtained $\Delta H^\circ_{483}(25) = 8.0 \pm 0.4$ kJ, $\Delta H^\circ_{483}(26) = 70.7 \pm 0.8$ kJ, and $\Delta H^\circ_{483}(27) = 66.1 \pm 1.7$ kJ. The above values were not adjusted to 298 K because of the lack of data for $C_p(CH_3CHClBr)$, but an approximate estimate of ΔC_p in reactions (25)–(27) showed that the difference between the values of ΔH°_{298} and ΔH°_{483} is less than the experimental error. Using the enthalpies of formation of chloro- and bromo-ethylenes quoted in Section II of the present review and also the ΔH°_f recommended above for CH_3CHCl_2 and CH_3CHBr_2, we obtain three values of $\Delta H^\circ_f[CH_3CHClBr(gas)]$: -82.6 ± 3.6, -84.1 ± 2.3, and -79.1 ± 3.4 kJ mol^{-1}. Their mean is recommended: $\Delta H^\circ_f[CH_3CHClBr(gas)] = -82.5$ kJ mol^{-1}. The error indicated takes into account the complexity of the composition of the equilibrium mixture and the actual discrepancies between the three results obtained[103].

1-Bromo-2-chloroethane

Bushneva et al.[104] found the enthalpies of the following reactions from measurements of their K_p at 483–523 K:

$$2CH_2ClCH_2Br\ (gas) \rightleftarrows CH_2ClCH_2Cl\ (gas) + CH_2BrCH_2Br\ (gas), \qquad (28)$$

$$CH_2ClCH_2Br\ (gas) \rightleftarrows CH_2{=}CHCl\ (gas) + HBr\ (gas), \qquad (29)$$

$$CH_2ClCH_2Br\ (gas) \rightleftarrows CH_2{=}CHBr\ (gas) + HCl\ (gas). \qquad (30)$$

They obtained $\Delta H^\circ_{503}(28) = 3.7 \pm 0.4$ kJ, $\Delta H^\circ_{503}(29) = 77.8 \pm 2.5$ kJ, and $\Delta H^\circ_{503}(30) = 69.0 \pm 2.1$ kJ. Neglecting the adjustment to the standard temperature, we obtain from these enthalpies three values of $\Delta H^\circ_f[CH_2ClCH_2Br(gas)]$: -88.1 ± 1.7, -91.2 ± 3.3, and -82.0 ± 2.8 kJ mol^{-1}. As in the case of 1-bromo-1-chloroethane, their average is recommended: $\Delta H^\circ_f[CH_2ClCH_2Br(gas)] = -87 \pm 5$ kJ mol^{-1}.

1,2-Dibromo-1,2-dichloroethane

Müller and Schumacher[105] determined the enthalpy of bromination of gaseous *trans*-dichloroethylene from the temperature dependence of the equilibrium constant in the range 343–373 K and obtained $\Delta H_{r,358} = -72.4 \pm 6$ kJ mol^{-1}. Using $C_p(CHClBrCHClBr) = 112.3$ J mol^{-1} K^{-1} estimated from the heat capacities of C_2H_6, C_2Cl_6, and C_2Br_6 quoted by Glushko[7], we find $\Delta H^\circ_{r,298} = -73.0 \pm 6$ kJ mol^{-1}, whence $\Delta H^\circ_f[CHClBr.CHClBr(gas)] = -36 \pm 6$ kJ mol^{-1}.

1,2-Dibromo-2-chloro-1,1,2-trifluoroethane

Lacher et al.[12] measured the enthalpy of bromination of gaseous chlorotrifluoroethylene: $\Delta H^\circ_{r,376} = -132.2 \pm 1.3$ kJ mol^{-1}. $C_p(CF_2BrCFClBr) = 124.9$ J mol^{-1} K^{-1} was adopted (from a comparison of the heat capacities of C_2F_6, C_2Cl_6, and C_2Br_6 quoted by Glushko[7]) in order to adjust the above quantities to 298 K. This yields $\Delta H^\circ_{r,298} = -132.6 \pm 1.3$ kJ mol^{-1}, whence follows $\Delta H^\circ_f[CF_2BrCFClBr(gas)] = -616.8 \pm 3.7$ kJ mol^{-1}.

1-Bromo-1-chloro-2,2,2-trifluoroethane

The enthalpy of combustion of 1-bromo-1-chloro-2,2,2-trifluoroethane, measured in a rotating bomb calorimeter[45], amounts to $\Delta H_c^\circ = -761.6 \pm 3.2$ kJ mol^{-1}. Hence ΔH_f°[CF_3.$CHClBr$(liq.)] $= -729.6 \pm 3.8$ kJ mol^{-1}. Taking into account the enthalpy of evaporation $\Delta H_{v,298}(CF_3CHClBr) = 29.69 \pm 0.1$ kJ mol^{-1} (the mean of two calorimetric determinations[45,106]), we obtain ΔH_f°[$CF_3CHClBr$(gas)] $= -699.9 \pm 3.8$ kJ mol^{-1}.

1-Bromo-2-chloro-1,1,2-trifluoroethane

The enthalpy of combustion of $CF_2BrCHFCl$ has been determined in a rotating bomb calorimeter at $\Delta H_c^\circ = -806.3 \pm 5.2$ kJ mol^{-1}.[45] Hence ΔH_f°[$CF_2BrCHFCl$(liq.)] $= -684.8 \pm 5.6$ kJ mol^{-1} or, when account is taken of the enthalpy of evaporation $\Delta H_{v,298}^\circ(CF_2BrCHFCl) = 30.15 \pm 0.1$ kJ mol^{-1},[107] one can obtain ΔH_f°[$CF_2BrCHFCl$(gas)] $= -654.7 \pm 5.6$ kJ mol^{-1}. The value found agrees with the measured[46] enthalpy of hydrobromination of chlorotrifluoroethylene when ΔH_f°.[$CF_2=CFCl$(gas)] $= 515.1 \pm 3.4$ kJ mol^{-1}, taken from Erastov and Kolesov[10], is used.

1-Bromo-2,2-dichloro-1,1-difluoroethane

Lacher et al.[46] measured the enthalpy of hydrobromination of 1,1-dichloro-2,2-difluoroethylene and obtained $\Delta H_{r,367} = 96.4 \pm 0.5$ kJ mol^{-1}. Having estimated $C_p(CF_2BrCHCl_2) = 114.1$ J mol^{-1} K^{-1} (from a comparison of the C_p for C_2H_6, C_2F_6, C_2Cl_6, and C_2Br_6 quoted by Glushko[7]), we find $\Delta H_{r,298}^\circ = -96.3$ kJ mol^{-1} and ΔH_f°[$CF_2BrCHCl_2$(gas)] $= -471 \pm 11$ kJ mol^{-1}.

The Difference between the Enthalpies of Formation of Bromoperfluoroethane and Pentafluoroethane

The equilibrium in the gas-phase reaction

$$C_2HF_5 + Br_2 \rightleftarrows C_2F_5Br + HBr \qquad (31)$$

was investigated[108,109] at temperatures in the range 632–860 K and $\Delta H_{746}^\circ(31) = -24.2 \pm 0.7$ kJ was found from the temperature variation of K_p. Buckley et al.[110] calculated $\Delta H_{298}^\circ(31) = -31.4 \pm 0.4$ kJ from the data of Coomber and Whittle[108] and Ferguson and Whittle[109] on the basis of the Third Law of Thermodynamics using the thermodynamic functions of C_2HF_5 and C_2F_5Br from Ford's dissertation[102]. The difference ΔH_f°[C_2F_5Br(gas)] $- \Delta H_f^\circ$[C_2HF_5(gas)] $= 35.9 \pm 0.5$ kJ mol^{-1} corresponds to the above value.

The Difference between the Enthalpies of Formation of Bromo- and Chloro-Perfluoroethanes

Coomber and Whittle[111] investigated the equilibrium

$$C_2F_5Br\,(gas) + Cl_2\,(gas) \rightleftarrows C_2F_5Cl\,(gas) + BrCl\,(gas) \qquad (32)$$

at 738–833 K and calculated $\Delta H_{785}^\circ(32) = -43.3 \pm 1.1$ kJ on the basis of the Second Law of Thermodynamics. Buckley et al.[110] calculated from the same data $\Delta H_{298}^\circ(32) = -39.75 \pm 0.4$ kJ on the basis of the Third Law of Thermodynamics. Hence we find the difference ΔH_f°[C_2F_5Br(gas)] $- \Delta H_f^\circ$[C_2F_5Cl.(gas)] $= 54.5 \pm 0.4$ kJ mol^{-1}.

Iodoethane

Measurements of the enthalpy of combustion of iodoethane by Thomsen[69] and Berthelot[112] as well as the determination of the ΔH of the substitution of iodine by bromine in iodoethane[68] are at present only of historical interest. Springall and White[113] determined the enthalpy of combustion of liquid iodoethane and obtained $\Delta H_c^\circ = -1466.5 \pm 2.1$ kJ mol^{-1}; hence ΔH_f°[C_2H_5I(liq.)] $= -35.1 \pm 2.1$ kJ mol^{-1} and, when account is taken of $\Delta H_{v,298}^\circ(C_2H_5I) = 32.2 \pm 0.4$ kJ mol^{-1},[7] we obtain ΔH_f°[C_2H_5I(gas)] $= -2.9 \pm 2.1$ kJ mol^{-1}. One should note that Springall and White[113] give no information about the purity of the specimen, the results of the analysis of the combustion products, and the number of experiments.

Carson et al.[114] measured the enthalpies of iodination of solutions of diethylzinc and diethylcadmium in benzene and ether respectively and also the enthalpies of solution of iodine in benzene and ether. Neglecting the enthalpies of solution of iodoethane in benzene and ether and using the values of ΔH_f° for diethylzinc, diethylcadmium, and the corresponding metal iodides adopted by Glushko[7], we obtain from these data two values of ΔH_f°[C_2H_5I(liq.)], which are respectively -40.6 and -39.7 kJ mol^{-1}. Their reliability is reduced owing to the inadequately rigorous allowance for the heats of side reactions.

Ashcroft et al.[93] measured the enthalpy of reduction of ethyl iodide by lithium hydride in an ethereal solution of lithium tetrahydroaluminate, whence the heat of the reaction

$$C_2H_5I\,(liq.) + {}^1/_2H_2\,(gas) = C_2H_6\,(gas) + {}^1/_2I_2\,(cryst.) \qquad (33)$$

was found to be $\Delta H_{298}^\circ(33) = -44.3 \pm 0.7$ kJ. This value leads to ΔH_f°[C_2H_5I(liq.)] $= -39.7 \pm 0.8$ kJ mol^{-1} and ΔH_f°.[C_2H_5I(gas)] $= -7.5 \pm 0.9$ kJ mol^{-1}. We believe that this latter value is the most reliable.

1,2-Di-iodoethane

The equilibrium constants of the reaction

$$CH_2ICH_2I\,(gas) \rightleftarrows C_2H_4\,(gas) + I_2\,(gas) \qquad (34)$$

have been measured[115–118] at 282–476 K). The results of Mooney and Ludlam[115] are doubtful, since their measurements were performed at I_2 and $C_2H_4I_2$ concentrations close to saturation. The other data[116–118] agree satisfactorily. Benson and Amano[118] subjected them to a joint treatment on the basis of the Second Law of Thermodynamics and obtained $\Delta H_{380}^\circ(34) = 48.12 \pm 0.84$ kJ. Adjustment to the standard temperature leads to $\Delta H_{298}^\circ(34) = 48.16 \pm 0.84$ kJ, whence ΔH_f°[CH_2ICH_2I(gas)] $= 66.7 \pm 1.0$ kJ mol^{-1}.

Tetrafluoro-1,2-di-iodoethane

Wu and Rodgers[119] investigated the equilibrium

$$CF_2=CF_2\,(gas) + I_2\,(gas) \rightleftarrows CF_2ICF_2I\,(gas) \qquad (35)$$

at 477–562 K and calculated $\Delta H_{520}^\circ(35) = -66.5 \pm 2.1$ kJ on the basis of the Second Law of Thermodynamics. Adjustment to 298 K, which the authors carried out themselves[119], led to $\Delta H_{298}^\circ(35) = -69.5 \pm 2.1$ kJ. Hence it follows that ΔH_f°[CF_2I.CF_2I(gas)] $= -666.6 \pm 3.3$ kJ mol^{-1}.

1,1-Difluoro-1-iodoethane

Pickard and Rodgers[100] quote the difference between the enthalpies of formation of 1,1-difluoro-1-iodoethane and 1,1-difluoroethane given previously in Pickard's dissertation[120]:

$[\Delta H_f^0(CH_3CF_2I\,(gas)) - \Delta H_f^0(CH_3CHF_2\,(gas))]_{298} = 87.0 \pm 0.8$ kJ mol^{-1}

Using the value of $\Delta H_f^\circ(CH_3CHF_2)$ recommended above, we find $\Delta H_f^\circ[CH_3CF_2I(gas)] = -410.0 \pm 8.5$ kJ mol^{-1}.

1,1,1-Trifluoroiodoethane

Wu and Rodgers[121] measured the equilibrium constant of the reaction

$$CF_3CH_3\,(r) + I_2\,(r) \rightleftarrows CF_3CH_2I\,(r) + HI\,(r) \qquad (36)$$

at 730–775 K. Having estimated the entropies of haloethanes, the above workers[121] calculated $\Delta H_{298}^\circ(36) = 64.0 \pm 2.1$ kJ on the basis of the Third Law of Thermodynamics. Hence, taking into account the value of $\Delta H_f^\circ[CH_3CF_3(gas)]$ recommended above, we obtain $\Delta H_f^\circ[CF_3CH_2I(gas)] = -648.6 \pm 3.9$ kJ mol^{-1}.

1-Bromo-2-Iodoethane

Berthelot[68] measured the enthalpy of the reaction

$$CH_2ICH_2I\,(cryst.) + Br_2\,(liq.) = CH_2BrCH_2I\,(cryst.) + BrI\,(cryst.) \qquad (37)$$

and obtained $\Delta H(37) = -58.2$ kJ. In view of the lack of more accurate measurements of $\Delta H_f^\circ(CH_2BrCH_2I)$, we calculated this quantity from Berthelot's data[68]. Using $\Delta H_f^\circ[IBr(cryst.)] = -10.33$ kJ mol^{-1} and $\Delta H_{S,298}^\circ(CH_2ICH_2I) = 66.9$ kJ mol^{-1} taken from Glushko's handbook[7] as well as the value of $\Delta H_f^\circ[CH_2I.\,.CH_2I(gas)]$ recommended above, we find $\Delta H_f^\circ[CH_2ICH_2Br.\,.(cryst.)] = -48.1$ kJ mol^{-1}. Adopting $\Delta H_{S,298}^\circ(CH_2BrCH_2I) = 60.3$ kJ mol^{-1} [the mean of the two values of $\Delta H_{S,298}^\circ(CH_2I.\,.CH_2I)$ presented above and $\Delta H_{S,283}^\circ(CH_2BrCH_2Br) = 53.6$ kJ mol^{-1}[7]], we obtain $\Delta H_f^\circ[CH_2BrCH_2I(gas)] = 12.2$ kJ mol^{-1}; this value is only approximate.

The Difference between the Enthalpies of Formation of Iodo- and Bromo-perfluoroethanes

Buckley et al.[110] studied the equilibrium

$$C_2F_5Br + I_2 \rightleftarrows C_2F_5I + IBr \qquad (38)$$

in the gas phase at 618–667 K. Using the thermodynamic functions of haloethanes calculated by Ford[102], Buckley et al.[110] obtained $\Delta H_{298}^\circ(38) = 38.5 \pm 0.8$ kJ. Hence we obtain the difference $\Delta H_f^\circ[C_2F_5I(gas)] - \Delta H_f^\circ[C_2F_5Br(gas)] = 60.1 \pm 0.8$ kJ mol^{-1}.

V. ESTIMATION OF THE ENTHALPIES OF FORMATION OF HALOETHANES

Among the numerous additive methods whereby the enthalpies of formation of organic compounds can be calculated approximately, only a few have been used to estimate the ΔH_f° of haloethanes. The enthalpies of formation were usually estimated only for a small number of haloethanes. All the haloethanes were never embraced by a single computational scheme sufficiently accurate in relation to this particular group of substances.

Rodgers[122] used Zahn's method[123] for the calculation of the enthalpies of formation of chlorofluorocarbons and evaluated six constants of the additive scheme whereby it is possible to calculate the ΔH_f° for only ten haloethanes. Furthermore some of the experimental ΔH_f° used by Rodgers[122] to calculate the constants are now obsolete. The attempt by Lacher and Skinner[124] to apply Allen's scheme[125] to fluoro- and chloro-derivatives of methane and ethane did not yield satisfactory results owing to the small number of experimental data available at the time. Later Gasteiger et al.[126] used Allen's scheme to estimate the enthalpies of formation of haloalkanes having at their disposal more extensive experimental data. Constants were found for the calculation of the ΔH_f° for mono- and poly-chloro-substituted hydrocarbons and also mono-fluoro-, monobromo-, and monoiodo-derivatives; only a small proportion of the haloethanes are included in the above groups of substances.

The "incremental" method used by Andreevskii et al.[127] for fluoroalkanes makes it possible to calculate the enthalpies of formation of substances containing substituent atoms of only two types. Benson et al.[128], who proposed the method of "group contributions" for the calculation of ΔH_f°, evaluated the contributions of 12 halogen-containing groups with the aid of which it is possible in principle to find the enthalpies of formation of 78 haloethanes. However, it has been noted by several workers[60,128] that the method of group contributions leads to highly distorted estimates for compounds containing adjacent groups with sharply different polarities, which is in fact a characteristic feature of a large number of haloethanes.

According to the scheme developed by Somayajulu and Zwolinski[129,130], the enthalpies of formation of haloethanes are calculated as sums of contributions corresponding to the interactions in sets of three atoms linked to a single carbon atom and to "excess" vicinal interactions. Somayajulu and Zwolinskii[130] quote constants whereby it is possible to estimate the ΔH_f° for 78 haloethanes, but some of the experimental ΔH_f° used in their study have now been modified. The calculation of the constants of the scheme of Somayajulu and Zwolinski constitutes a fairly cumbersome procedure in view of the need to calculate the number of sets of three atoms and vicinal interactions.

Bernstein[13,14] proposed a method for the estimation of the enthalpies of formation based on the allowance for the pair interactions of all the atoms in the molecule both linked and not linked by chemical bonds. In the estimation of the ΔH_f° for haloethanes in Bernstein's later study[14], the initial scheme was simplified: the group $-CH_3$ was regarded as one of the substituents in methane and the enthalpies of formation of haloethanes not containing the CH_3 group were calculated as the sums of the contributions of two substituted methyl groups. In this approach no account was taken of the fairly intense interactions of the substituents in haloethanes located at different carbon atoms. This simplification, made in view of the limited number of experimental data, led to a significant decrease of the accuracy of the estimate. Discrepancies are particularly large between the ΔH_f° calculated by Bernstein[14] and subsequently determined experimentally for fluoroethanes.

Nevertheless the method proposed by Bernstein is in principle extremely promising for compounds with a short carbon chain and different substituents, since it makes it possible to estimate the enthalpies of formation with a satisfactory accuracy using a comparatively small number of constants in the computational formulae. In combination with modern experimental data, this method has been applied successfully to the estimation of ΔH_f° for halomethanes[3,21] and fluoroethylenes[21].

In the present review Bernstein's method was used for the approximate calculation of the enthalpies of formation of haloethanes. Since the experimental data accumulated at the present time make it possible to take into account all the pair interactions of the atoms in haloethanes (except in the case of iodo-derivatives) and in order to facilitate calculations,

the computational formulae were modified compared with those proposed by Bernstein[13,14].

The enthalpy of formation of a haloethane containing substituents of only two types (X and Y) can be represented, according to Bernstein, by the sum of the following contributions: $P(CC)_1$, $P(CX)_1$, $P(CY)_1$, $P(CX)_2$, $P(CY)_2$, $P(XX)_2$, $P(YY)_2$, $P(XY)_2$, $P(XX)_3$, $P(YY)_3$, and $P(XY)_3$. Subscript 1 refers to a pair of atoms connected by chemical bond, subscript 2 refers to atoms linked by two bonds, and subscript 3 refers to atoms joined by three bonds. Since the numbers of contributions are not linearly independent, they can be reduced to the following four constants of the computational scheme:

$$[CX]_1 = {}^1/_6 P(CC)_1 + P(CX)_1 + P(CX)_2 + P(XX)_2 + {}^3/_2 P(XX)_3 , \quad (39)$$

$$[CY]_1 = {}^1/_6 P(CC)_1 + P(CY)_1 + P(CY)_2 + P(YY)_2 + {}^3/_2 P(YY)_3 , \quad (40)$$

$$[XY]_2 = P(XY)_2 - {}^1/_2 [P(XX)_2 + P(YY)_2] , \quad (41)$$

$$[XY]_3 = P(XY)_3 - {}^1/_2 [P(XX)_3 + P(YY)_3] . \quad (42)$$

The linear combinations (39–(42) were selected so that the evaluation of ΔH_f° requires the calculation of only the number of bonds between carbon atoms and substituents and the number of interactions between unlike substituent atoms.

Table 1. Experimental and calculated enthalpies of formation of haloethanes at 298.15 K.

No.	Compound	$-\Delta H_f^0$ (gas), kJ mol^{-1}		Refs.*
		expt.	calc.	
1	CH_3CH_3	84.0±0.4	83.2	[52, 53]
2	CF_3CF_3	1344.0±4.0	1345.1	[21]
3	CH_3CHF_2	497.0±8.5	502.6	[32]
4	CH_3CF_3	748.7±3.2	744.8	[59]
5	CH_2FCHF_2	691±10	688.0	[11]
6	CCl_3CCl_3	(137.7; 145.2; 138; 150.9)**	149.5	—
7	CH_3CH_2Cl	112.2±0.7	111.1	[39]
8	CH_3CHCl_2	130.6±3.0	131.1	[75]
9	CH_2ClCH_2Cl	134.1±1.2	133.2	[77]
10	CH_3CCl_3	144.6±0.8	142.9	[25, 79]
11	$CH_2ClCHCl_2$	144.7±1.9	147.2	[82]
12	CH_2ClCCl_3	152.3±1.4	153.2	[83]
13	$CHCl_2CHCl_2$	157.3±3.0	155.3	[67]
14	$CHCl_2CCl_3$	(137.9; 143.1; 145.8)	155.4	—
15	CF_2ClCF_2Cl	925.5±4.3	925.8	[87]
16	$CF_2ClCFCl_2$	726.8±2.8	724.1	[43]
17	CF_2ClCCl_3	525.8±4.3	527.9	[90]
18	CH_3CHFCl	313.4±2.6	314.1	[91]
19	CH_3CF_2Cl	536.2±5.2	538.6	[92]
20	CH_3CH_2Br	61.5±1.0	63.7	[49, 71]
21	CH_3CHBr_2	26.7±1.9	26.7	[97, 98]
22	CH_2BrCH_2Br	38.3±1.2	33.1	[78, 97, 98]
23	CF_2BrCF_2Br	789.9±4.0	800.7	[12]
24	CH_3CF_2Br	474.3±8.5	472.8	[100]
25	CF_3CH_2Br	697.8±4.4	703.7	[101]
26	CHF_2CF_2Br	833.2±2.7	846.2	[46]
27	$CH_3CHClBr$	82±5	80.9	[103]
28	CH_2ClCH_2Br	87±5	82.1	[104]
29	$CHClBrCHClBr$	36±6	44.6	[105]
30	$CF_2BrCFClBr$	616.8±3.7	602.5	[12]
31	$CF_3CHClBr$	699.9±3.8	698.1	[45]
32	$CF_2BrCHFCl$	654.7±5.6	655.9	[45]
33	$CF_2BrCHCl_2$	471±11	471.4	[46]
34	$[\Delta H_f^0(C_2F_5Br) - \Delta H_f^0(C_2HF_5)]$	35.9±0.5	43.9	[108, 109]
35	$[\Delta H_f^0(C_2F_5Br) - \Delta H_f^0(C_2F_5Cl)]$	54.5±0.4	59.8	[111]
36	CH_3CH_2I	7.5±0.9	—	[93]
37	CH_2ICH_2I	−66.7±1.0	—	[116–118]
38	CF_2ICF_2I	666.6±3.3	—	[119]
39	CH_3CF_2I	410.0±8.5	—	[100]
40	CF_3CH_2I	648.6±3.9	—	[121]
41	CH_2BrCH_2I	(−12.2)	—	[68]
42	$[\Delta H_f^0(C_2F_5I) - \Delta H_f^0(C_2F_5Br)]$	60.1±0.8	—	[110]

* References are given only to studies which served as a basis for the recommended ΔH_f°.

** Here and henceforth the experimental values regarded as unreliable are given in brackets.

For example, the enthalpy of formation of 1,1,2-trifluoroethane can be represented by the following sum:

$$\Delta H_f^\circ(CH_2FCHF_2) = 3[CH]_1 + 3[CF]_1 + 4[HF]_2 + 5[HF]_3 .$$

Thus, in order to calculate the ΔH_f° for ten haloethanes having the composition $C_2X_{6-n}Y_n$ (where $0 \leq n \leq 6$), it is necessary to know four constants. When a third substituent (Z) is introduced, a further five constants must be added: $[CZ]_1$, $[XZ]_2$, $[XZ]_3$, $[YZ]_2$, and $[YZ]_3$, which are defined by relations analogous to Eqns.(39)–(42); having calculated them, it is possible to evaluate the enthalpies of formation of 55 haloethanes having the composition $C_2X_{6-m-n}Y_mZ_n$. When there are substituents of four types, 16 constants are necessary to estimate the ΔH_f° for 210 compounds. When a fifth substituent is introduced, the number of haloethanes increases to 630 and the number of constants rises to 25.

The available set of experimental data makes it possible to calculate the 16 constants necessary to estimate the ΔH_f° for ethanes containing H, F, Cl, and Br. The following numerical constants (in kJ mol^{-1}) were found by the method of least squares from the recommended experimental values listed in Table 1 (with the exception of ΔH_f° for C_2Cl_6 and C_2HCl_5 as well as iodoethanes): $[CH]_1 = -14.488$, $[CF]_1 = -223.266$, $[CCl]_1 = -23.897$, $[CBr]_1 = +33.523$, $[HF]_2 = +12.858$, $[HF]_3 = -3.444$, $[HCl]_2 = -3.916$, $[HCl]_3 = -3.151$, $[HBr]_2 = -6.880$, $[HBr]_3 = -3.672$, $[FCl]_2 = +2.920$, $[FCl]_3 = +1.018$, $[FBr]_2 = +7.675$, $[FBr]_3 = -1.351$, $[ClBr]_2 = -1.273$, and $[ClBr]_3 = +1.448$. These constants were used to estimate the enthalpies of formation of bromoethanes listed in Tables 1 and 2.

It is noteworthy that the recommended values of ΔH_f° for haloethanes containing only H, F, and Cl are as a rule the most reliable: the availability of numerous experimental data made it possible to select the most accurate values confirmed by several workers. In this connection, it is possible to obtain also more accurate estimates of ΔH_f° for ethanes containing H, F, and Cl. For this purpose, 17 experimental values of ΔH_f° for ethanes containing H, F, and Cl (except for C_2Cl_6 and C_2HCl_5) were treated by the method of least squares, which yielded the following nine constants (in kJ): $[CH]_1 = -13.859$, $[CF]_1 = -224.190$, $[CCl]_1 = -24.915$, $[HF]_2 = +10.786$, $[HF]_3 = -3.401$, $[HCl]_2 = -4.038$, $[HCl]_3 = -2.952$, $[FCl]_2 = +2.753$, and $[FCl]_3 = +2.444$. The enthalpies of formation of chlorofluoroethanes listed in Tables 1 and 3 were calculated with the aid of the above constants.

The nine constants for the estimation of ΔH_f° for ethanes containing H, F, and I or the 16 constants for the estimation of ΔH_f° for ethanes with H, F, Br, and I can also be found in principle from the available experimental data (Table 1). However, the number of experimental values of ΔH_f° for iodoethanes which serve as reference values for the calculation of constants referring to interactions of the iodine atom with other atoms, namely $[CI]_1$, $[HI]_2$, $[HI]_3$, $[FI]_2$, etc., is equal to the number of the required constants and such a system of equations would be ill-founded. Further accumulation of experimental data is therefore necessary for the estimation of the unknown ΔH_f° for iodoethanes.

VI. CONCLUSION

The calculated ΔH_f° for haloethanes are compared in Table 1 with the recommended experimental values. The average discrepancy between the experimental and calculated values for chlorofluoroethanes is 1.9 kJ mol^{-1}, while for the bromo-derivatives it is much higher (5.3 kJ mol^{-1}), which was to be expected in view of the lower accuracy of the experimental

data. Comparison of the experimental and calculated values (Table 1) suggests that the errors of the estimated ΔH_f° for ethanes containing H, F, and Cl (Table 3) do not exceed 5–10 kJ mol^{-1}, while those for bromine-containing ethanes (Table 2) are not more than 20–25 kJ mol^{-1}.

Table 2. Calculated enthalpies of formation of bromoethanes (kJ mol^{-1}) at 298.15 K.

No.	Compound	$-\Delta H_f^0$ (gas)	No.	Compound	$-\Delta H_f^0$ (gas)
1	CBr_3CBr_3	—201.1	27	CH_2FCBr_3	152.0
2	CH_3CBr_3	—24.1	28	$CHBr_2CHFBr$	168.9
3	$CH_2BrCHBr_2$	—11.2	29	$CFBr_2CH_2Br$	173.0
4	CH_2BrCBr_3	—69.3	30	$CHFBrCF_3$	874.8
5	$CHBr_2CHBr_2$	—62.9	31	CHF_2CFBr_2	592.4
6	$CHBr_2CBr_3$	—128.4	32	$CHFBrCF_2Br$	602.9
7	CF_3CF_2Br	1071.5	33	CF_3CHBr_2	649.4
8	CF_3CFBr_2	818.8	34	$CHBr_2CF_2Br$	374.8
9	CF_3CBr_3	581.4	35	$CHFBrCFBr_2$	346.3
10	$CF_2BrCFBr_2$	545.3	36	CBr_3CHF_2	353.9
11	CF_2BrCBr_3	305.2	37	$CHBr_2CFBr_2$	115.6
12	$CFBr_2CFBr_2$	287.1	38	$CHFBrCBr_3$	105.1
13	$CFBr_2CBr_3$	44.4	39	CCl_3CCl_2Br	84.2
14	CH_3CHFBr	255.4	40	CCl_3CClBr_2	22.4
15	CH_2FCH_2Br	251.3	41	CCl_2BrCCl_2Br	27.8
16	$CH_2FCHFBr$	436.1	42	CCl_3CBr_3	—41.9
17	CH_2BrCHF_2	464.7	43	$CCl_2BrCClBr_2$	—31.0
18	CH_3CFBr_2	216.7	44	CCl_2BrCBr_3	—92.4
19	CH_2FCHBr_2	208.6	45	$CClBr_2CClBr_2$	—87.0
20	$CH_2BrCHFBr$	219.0	46	$CClBr_2CBr_3$	—145.5
21	CHF_2CHFBr	642.6	47	CH_3CCl_2Br	90.2
22	CF_2BrCH_2F	646.7	48	$CH_2ClCHClBr$	93.0
23	CH_2FCFBr_2	391.7	49	$CH_2BrCHCl_2$	92.7
24	CH_2BrCF_2Br	430.7	50	CH_3CClBr_2	34.3
25	$CHFBrCHFBr$	398.1	51	$CH_2ClCHBr_2$	36.9
26	CHF_2CHBr_2	416.1	52	$CH_2BrCHClBr$	42.0
53	CCl_3CH_2Br	95.5	79	CCl_3CF_2Br	458.9
54	$CHCl_2CHClBr$	97.3	80	$CFCl_2CFClBr$	464.9
55	CCl_2BrCH_2Cl	96.0	81	CCl_2BrCF_2Cl	478.6
56	$CH_2ClCClBr_2$	38.2	82	$CF_2ClCClBr_2$	424.5
57	CH_2BrCCl_2Br	43.1	83	CF_2BrCCl_2Br	410.2
58	$CHCl_2CHBr_2$	39.2	84	$CFClBrCFClBr$	406.4
59	CH_2ClCBr_3	—22.2	85	$CFCl_2CFBr_2$	401.0
60	$CHBr_2CHClBr$	—10.6	86	CF_2ClCBr_3	367.8
61	$CClBr_2CH_2Br$	—11.8	87	$CFBr_2CFClBr$	345.3
62	$CHCl_2CCl_2Br$	94.0	88	$CClBr_2CF_2Br$	359.0
63	$CHClBrCCl_3$	93.7	89	$CFCl_2CCl_2Br$	278.5
64	$CHCl_2CClBr_2$	34.2	90	$CFClBrCCl_3$	268.6
65	$CHClBrCCl_2Br$	39.4	91	$CFCl_2CClBr_2$	220.5
66	CCl_3CHBr_2	33.7	92	$CFClBrCCl_2Br$	216.1
67	$CHBr_2CCl_2Br$	—17.8	93	CCl_3CFBr_2	200.8
68	$CHClBrCClBr_2$	—17.5	94	$CFBr_2CCl_2Br$	151.2
69	CBr_3CHCl_2	—28.1	95	$CFClBrCClBr_2$	161.1
70	$CHBr_2CClBr_2$	—71.8	96	CBr_3CFCl_2	160.0
71	$CHClBrCBr_3$	—77.0	97	$CFBr_2CClBr_2$	99.1
72	$CF_3CFClBr$	875.1	98	$CFClBrCBr_3$	103.5
73	CF_2ClCF_2Br	861.5	99	$CH_3CFClBr$	278.6
74	CF_3CCl_2Br	684.6	100	$CH_2FCHClBr$	260.9
75	$CF_2ClCFClBr$	667.1	101	$CH_2ClCHFBr$	266.2
76	$CF_2BrCFCl_2$	657.3	102	$CH_2BrCHFCl$	275.8
77	CF_3CClBr_2	634.2	103	$CH_2FCFClBr$	451.7
78	$CF_2ClCFBr_2$	606.9	104	CH_2ClCF_2Br	482.4
105	CH_2BrCF_2Cl	495.1	124	CHF_2CClBr_2	408.5
106	$CHF_2CHClBr$	466.6	125	$CHFClCFBr_2$	400.2
107	$CHFClCHFBr$	453.0	126	$CHFBrCFClBr$	405.4
108	CH_2FCCl_2Br	262.6	127	$CHClBrCF_2Br$	424.4
109	$CH_2ClCFClBr$	283.1	128	$CHBr_2CF_2Cl$	438.3
110	$CH_2BrCFCl_2$	292.4	129	$CHFClCCl_2Br$	274.4
111	$CHClBrCHFCl$	20.79	130	$CHFBrCCl_3$	264.3
112	$CHFBrCHCl_2$	278.2	131	$CHClBrCFCl_2$	289.3
113	$CH_2FCClBr_2$	203.2	132	$CFClBrCHCl_2$	279.8
114	$CH_2ClCFBr_2$	219.2	133	$CHFClCClBr_2$	218.5
115	$CH_2BrCFClBr$	234.0	134	$CHFBrCCl_2Br$	213.0
116	$CHFClCHBr_2$	224.7	135	$CHClBrCFClBr$	229.0
117	$CHFBrCHClBr$	220.3	136	$CHCl_2CFBr_2$	213.9
118	$CHF_2CFClBr$	650.6	137	$CHBr_2CFCl_2$	236.9
119	$CHFBrCF_2Cl$	665.4	138	$CHFClCBr_3$	159.9
120	CHF_2CCl_2Br	460.7	139	$CHFBrCClBr_2$	160.7
121	$CHFClCFClBr$	462.2	140	$CHClBrCFBr_2$	166.0
122	$CHFBrCFCl_2$	462.0	141	$CHBr_2CFClBr$	175.6
123	$CHClBrCF_2Cl$	490.8			

The calculated ΔH_f° obey certain relations noted previously. Thus there is a sharp increase of $|\Delta H_f^\circ|$ in the series $C_2H_{6-n}F_n$, $C_2Cl_{6-n}F_n$, $C_2Br_{6-n}F_n$ as fluorine atoms accumulate at the same carbon atom, as in the case of other organofluorine compounds[3,89,131]. In the $C_2H_{6-n}Cl_n$ series there is also an increase of ΔH_f° with increase of n, but there is a maximum at $n = 4$. A similar picture has been noted for chloromethanes where the maximum value of $|\Delta H_f^\circ|$ corresponds to $CHCl_3$.[3]

On successive replacement of hydrogen by bromine in the $C_2H_{6-n}Br_n$ series, a more rapid increase of ΔH_f° is observed than would have been the case for a linear relation between ΔH_f° and n. This is also characteristic of bromomethanes[3].

Table 3. Calculated enthalpies of formation of chlorofluoroethanes (kJ mol^{-1}) at 298.15 K.

No.	Compound	$-\Delta H_f^0$ (gas)	No.	Compound	$-\Delta H_f^0$ (gas)
1	CH_3CH_2F	282.1	20	CHF_2CHFCl	702.4
2	CH_2FCH_2F	474.3	21	CF_2ClCH_2F	715.2
3	CH_2FCF_3	923.3	22	CH_2FCFCl_2	512.6
4	CHF_2CHF_2	894.9	23	CH_2ClCF_2Cl	543.1
5	CHF_2CF_3	1123.4	24	$CHFClCHFCl$	514.7
6	CCl_3CCl_3	149.5	25	CHF_2CHCl_2	515.4
7	$CHCl_2CCl_3$	155.4	26	CCl_3CH_2F	315.5
8	CF_3CF_2Cl	1133.0	27	$CHCl_2CHFCl$	332.6
9	CF_3CFCl_2	926.4	28	$CFCl_2CH_2Cl$	345.4
10	CF_3CCl_3	725.3	29	CHF_2CF_2Cl	913.3
11	$CFCl_2CFCl_2$	527.3	30	$CHFClCF_3$	928.8
12	$CFCl_2CCl_3$	336.0	31	CHF_2CFCl_2	708.7
13	CH_2FCH_2Cl	301.3	32	$CHFClCF_2Cl$	723.7
14	$CH_2FCHFCl$	497.5	33	CF_3CHCl_2	739.9
15	CH_2ClCHF_2	513.0	34	$CHCl_2CF_2Cl$	539.5
16	CH_3CFCl_2	338.0	35	$CHFClCFCl_2$	524.0
17	CH_3FCHCl_2	312.4	36	CCl_3CHF_2	509.6
18	$CH_2ClCHFCl$	327.4	37	$CHCl_2CFCl_2$	344.7
19	CF_3CH_2Cl	746.4	38	$CHFClCCl_3$	329.7

Further development of the thermochemistry of haloethanes involves the accumulation of reliable experimental data. Thus very few values of ΔH_f° are available at present for iodoethanes and there are no data whatever for haloethanes containing Cl and I. The number of known values of ΔH_f° for bromoethanes is clearly inadequate and the reliability of some of the available data is low. As regards the haloethanes containing H, F, and C atoms, which are of greatest importance in practice, some of the values measured previously (for example, for C_2Cl_6, and C_2HCl_5) must also be checked experimentally and the number of reliable experimental data must be increased. All these considerations will permit an improvement in the accuracy of the estimates of ΔH_f° and will give rise to more reliable thermochemical parameters for all haloethanes.

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Faculty of Chemistry,
Lomonosov Moscow State University