# Evaluated Enthalpies of Formation of the Stable Closed Shell C1 and C2 Chlorinated Hydrocarbons

**Jeffrey A. Manion**[a)]
*National Institute of Standards and Technology, Physical and Chemical Properties Division, Gaithersburg, Maryland 20899*

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Experimental data on the enthalpies of formation of chloromethanes, chloroethynes, chloroethenes, and chloroethanes are critically reviewed. Enthalpy of formation values for the C1 and C2 chlorinated hydrocarbons are highly cross-linked by various measured reaction equilibria and currently available sets of values are not internally self-consistent. It is shown that the early static bomb combustion calorimetry studies on highly chlorinated compounds generally give enthalpies of formation that are systematically more positive than later values derivable from rotating bomb combustion or equilibria studies. Those previously recommended values which were based mainly on the early static bomb work therefore need substantial revision. On the basis of more recent literature data obtained with rotating bomb combustion calorimetry, together with analyses of literature data on other reaction enthalpies and equilibria involving chlorinated hydrocarbons, an updated self-consistent set of $\Delta_f H^o[298.15\,\mathrm{K}]$ values for closed shell chlorinated C1 and C2 hydrocarbons (25 compounds) is recommended. Data on the enthalpies of vaporization are also reviewed and values of $\Delta_{vap}H[298.15\,\mathrm{K}]$ and $\Delta_{vap}H^o[298.15\,\mathrm{K}]$ are recommended. The presently suggested enthalpies of formation for highly chlorinated alkenes and alkanes (particularly $C_2Cl_4$, $C_2HCl_3$, $C_2HCl_5$, and $C_2Cl_6$) are significantly (8–15 $\mathrm{kJ\,mol^{-1}}$) more negative than given by most previous evaluators. Values for the chloroethynes are 10–25 $\mathrm{kJ\,mol^{-1}}$ more positive than given in previous reviews and more limited changes are suggested for other compounds in the series. *© 2002 by the U.S. Secretary of Commerce on behalf of the United States. All rights reserved.*

Key words: chloroethanes; chloroethenes; chloroethynes; chloromethanes; enthalpy of formation; enthalpy of vaporization; ethane; ethene; ethyne; heat capacity of vaporization; heat of formation; heat of vaporization; methane.

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[a)] Electronic mail: jeffrey.manion@nist.gov

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# 1. Background

## 1.1. Introduction

Chlorinated hydrocarbons are widely utilized throughout the chemical industry, both as end products and as precursors for a wide variety of useful products, including plastics, solvents, pesticides, refrigerants, and other products. Attempts to understand and model the chemistry associated with the production, disposal, and atmospheric fate of chlorinated materials require reliable values for the standard gas phase thermodynamic properties of these compounds. In general entropies and heat capacities can be predicted very accurately using statistical mechanical methods and measured molecular properties. If measured properties are not available, group additivity methods provide reasonable accuracy and *ab initio* methods can generally result in even better estimates.

On the other hand, accurate enthalpies of formation are more difficult to predict via *a priori* methods, although great strides are being made in that area as well [1998IF]. Both for kinetic modeling of species for which data exist, and to aid in the development of accurate predictive methods for unstudied compounds, it is important to have a reliable database of evaluated values of the chlorinated hydrocarbons. The present report reviews and makes recommendations regarding the best values currently available for stable C1 and C2 chlorinated closed shell species. Unstable species such as radicals and carbenes are not considered in the present work.

As will be seen, the present recommendations for highly chlorinated compounds are significantly (8–12 kJ mol$^{-1}$) more negative than most previous evaluations.

### 1.2. Experimental Methods

Enthalpies of formation of chlorinated compounds have been determined by a number of methods. Combustion bomb calorimetry offers the most ‘‘absolute’’ measurement method in the sense that enthalpies of formation are determined relative to the well-known values for $CO_2$, $H_2O$, and HCl. The presence of chlorine, however, engenders a number of issues that make this technique substantially more difficult than with hydrocarbons. A particularly difficult problem is the adequate determination of the final state of the chlorine combustion products. Other difficulties are the need for very pure samples, problems associated with the corrosive nature of the products, and the need to introduce relatively large amounts of burnable co-material to assure complete combustion. Newer studies using platinum-lined rotating-bomb calorimeters, reducing agents, and careful product analysis are generally more accurate than the earlier work. More discussion of the difficulties involved can be found in Sunner and Månsson [1979SM], Kolesov and Papina [1983KP], Cox and Pilcher [1970CP], Rossini [1956R], Smith *et al.* [1953SBK] and the more recent papers in which this technique was used.

The calorimetric measurement of the enthalpy of a reaction other than combustion, such as that for chlorination or hydrogenation is another useful technique. Carefully done, this method sets the relative enthalpies of formation of, for example, a chloroalkene and chloroalkane, but an accurate value of one of the species must be independently known. Similarly, the measurement of reaction equilibria including isomerizations, and addition of $H_2$ (hydrogenation), HCl (hydrochlorination), or $Cl_2$ (chlorination) to chloroethenes provide further information on the relative stabilities of many chlorinated species. In principle, equilibrium measurements can provide very accurate relative values. In ‘‘Second Law’’ analyses, values of the equilibrium constant, $K_{eq}$, are determined over a range of temperatures and a plot of $\ln K_{eq}$ vs. $1/T$ yields a line with a slope equal to $\Delta_r H/\mathrm{R}$, where $\Delta_r H$ is the enthalpy of reaction and R is the gas constant. Accurate values from Second Law analyses generally require data over a wide temperature range and that no systematic experimental errors are present. Third Law analyses are more forgiving, but require accurate entropy and heat capacity data. In this case one needs only a single value of $K_{eq}$ and knowledge of the entropy change for the reaction to calculate the enthalpy change from the relation $\Delta H - T\Delta S = -\mathrm{RT}\ln K_{eq}$. The required entropy data can generally be calculated quite accurately from statistical mechanics and the molecular properties of the species involved. For the chlorinated hydrocarbons the molecular properties are generally well known, with the most significant uncertainties relating to the torsional modes in the C2 compounds. Even with a 50% uncertainty in $K_{eq}$ and $\Delta_r S$ known to only 4 J mol K$^{-1}$, at 350 K the Third Law method affords a propagated uncertainty in $\Delta_r H$ of 2.6 kJ mol$^{-1}$. The major uncertainty with equilibrium experiments is usually proof that equilibrium has truly been reached. Agreement between Second and Third Law analyses suggests that no major errors are present.

### 1.3. Sources of Data

Experiments performed at Lund University between 1934 and 1941 are the largest single source of data on the enthalpies of combustion of chlorinated species. Discussion of these data and the application of some corrections can be found in the 1953 review by Smith *et al.* [1953SBK]. More limited experiments have since been performed by various researchers. Many of the data have been conveniently compiled by Pedley *et al.* [1986PNK]. This source lists thermochemical data on a wide variety of organic compounds and includes data on some chlorinated compounds not listed in the other reviews. In the compilations of Pedley *et al.* [1986PNK], the older enthalpy of combustion data have generally been taken from Cox and Pilcher [1970CP] and then recalculated based on a slightly newer value for the enthalpy of dilution of HCl. While Pedley *et al.* [1986PNK] select best values and list uncertainties, there is no individual discussion of how these quantities were chosen. The later update to this work [1994P] has the same limitations. A wide range of data on chlorinated compounds are compiled in the DIPPR Database [2001DIP] and NIST Webbook [2001LM] but these sources do not provide detailed evaluations of the data. Evaluations of a few chlorinated organic compounds are available in the NIST-JANAF Thermochemical Tables [1998C] and, while generally thorough, these evaluations have not been updated since the late 1960s. The most recent critical evaluation of the chloroethanes is that of Kolesov and Papina [1983KP]. Kolesov and Papina pointed out some inconsistencies in the existing data and their review makes use of some liquid and gas phase equilibrium data from the Russian literature that do not appear in the other sources. In 1981 Chao published recommended values for the chloroethanes in the TRC Tables [1981C]. This source contains no discussion of uncertainties or how best values were derived, but appears to be an update to the 1974 critical evaluation of the ideal gas thermodynamic properties of six chloroethanes by Chao *et al.* [1974CRW]. The TRC data have subsequently been compiled by Frenkel *et al.* [1994FKM]. Slayden *et al.* [1995SLM] have recently presented a broad overview of the thermochemistry of halogenated compounds, but have focused on interhalogen trends rather than a detailed review of the primary data. Older critical evaluations include those of Cox and Pilcher [1970CP] and Stull, Westrum, and Sinke [1969SWS]. These latter works consider the chloroalkenes as well as chloroalkanes.

More recent evaluations of the chloroalkenes are scarce. The most recently published critical review is that of Gurvich *et al.* [1991GVA] who evaluated the thermodynamic properties of some of the C1 and C2 chlorocarbons. The 1991 English Edition is a revised and updated version of the Third Russian Edition [1979G]. While this work describes how the enthalpy of formation values were derived, the dates of the actual evaluations are not recorded. With the exception of trichloroethene, the values for the chloroethenes in [1991GVA] are the same as in [1979G] and are the same as those used by Kolesov and Papina [1983KP], who included very limited discussion in their 1983 review of the haloethanes. Alternate values are available from Rodgers [1982R] who evaluated the data on the chloroethenes for the TRC Tables in 1982 (the entropy data for a few species were corrected in 1985). This source contains no discussion of uncertainties or how best values were derived. The TRC data have later been compiled by Frenkel *et al.* [1994FKM]. As with the chloroalkanes, Pedley and co-workers [1986PNK], [1994P] selected recommended values together with an estimated uncertainty, but there is no individual discussion of how these values were chosen.

Since the above reviews and compilations there have been additional combustion calorimetry studies involving key chlorinated species for which data were lacking or were suspect. *It is very important to note that because many values for chloroethanes and chloroethenes are related by various measurements, new combustion calorimetry studies on one compound often provide information on other species as well. In order to achieve a self-consistent data set it is therefore necessary to propagate any proposed change in an enthalpy of formation through the entire data set*. The present evaluation seeks to do this. In addition to purely experimental data, in a few instances where there was contradictory information, we have made use of high level *ab initio* calculations to help choose between the conflicting experimental data.

## 1.4. Auxiliary Enthalpies of Formation

Many enthalpies of formation are obtained from the enthalpy of combustion, which, for chlorinated compounds, is usually specified as the enthalpy for the reaction: $C_aH_bCl_c + dO_2(g) + eH_2O(l) \rightarrow aCO_2(g) + c\,HCl(aq{:}600) + fH_2O(l)$. The dilution state HCl (aq: 600) was adopted by Smith *et al.* in their 1953 review [1953SBK] and has since been used by most researchers. In our calculations we used the values $\Delta_f H^o[CO_2(g),298.15\,K] = -(393.51 \pm 0.13)$ kJ/mol and $\Delta_f H^o[H_2O(l),298.15\,K] = -(285.830 \pm 0.040)$ kJ/mol, which are the 1989 CODATA-recommended values [1989CWM]. Essentially the same values for $CO_2$ and $H_2O$ have been used by all modern reviewers. For the value of HCl (aq:600), we have combined the value of $\Delta_f H^o[Cl(aq),298.15\,K] = -(167.080 \pm 0.10)$ kJ/mol from the 1989 CODATA evaluation [1989CWM], together with the enthalpies of dilution from the 1965 NSRDS evaluation [1965P]. CODATA does not specify $\Delta H_{\mathrm{dilution}}$ values for HCl, but appears to have used the 1965 NSRDS values in the dilution corrections for determining the enthalpy of solution at infinite dilution (see Table II-1 in Annex II of [1989CWM]). This yields $\Delta_f H^o[HCl(aq{:}600),298.15\,K] = -(166.540 \pm 0.10)$ kJ/mol. This newer value is slightly different from that used by Cox and Pilcher [1970CP] in their 1970 evaluation, $\Delta_f H^o[HCl(aq{:}600),298.15\,K] = -166.619$ kJ/mol. Test calculations show it to be consistent with that used by Pedley *et al.* [1986PNK] and the TRC Tables, however. This same value has also been used in the more recent combustion calorimetry work [1979GH], [1987PK].

Papers which report enthalpies of combustion always include small corrections for various side reactions that occur during the combustion, e.g., oxidation of $As_2O_3$, formation of $H_2PtCl_6$, $HAuCl_4$, etc. The nature of these corrections vary somewhat with the specific apparatus. More discussion can be found in the original papers and in previous works [1970CP], [1953SBK]. Early experimental and auxiliary data have been reexamined and updated by Smith *et al.* [1953SBK] and later by Cox and Pilcher [1970CP]. At present it does not appear to be necessary to further revise or update these corrections to the primary data and we have not attempted to do so.

The enthalpy of formation values for the C1 and C2 hydrocarbons are well established. Values from several frequently cited sources are listed in Table 1. We have adopted the enthalpy of formation values of Gurvich *et al.* [1991GVA] (see Discussion), but the values from other common sources are not significantly different. The values used here are $\Delta_f H^o[CH_4(g),298.15\,K] = -(74.6 \pm 0.3)$ kJ mol$^{-1}$, $\Delta_f H^o[C_2H_6(g),298.15\,K] = (84.0 \pm 0.4)$ kJ mol$^{-1}$, $\Delta_f H^o[C_2H_4(g),298.15\,K] = (52.4 \pm 0.5)$ kJ mol$^{-1}$, and $\Delta_f H^o[C_2H_2(g),298.15\,K] = (227.4 \pm 0.8)$ kJ mol$^{-1}$. The value $\Delta_f H^o[HCl(g),298.15\,K] = -(92.31 \pm 0.10)$ kJ mol$^{-1}$ is the 1989 CODATA-recommended value [1989CWM]. Values for other compounds were occasionally used and sources are detailed in the specific evaluations.

## 1.5. Enthalpies of Vaporization

Since experimental enthalpy of formation data frequently pertain to the liquid state, the enthalpy of vaporization is needed to derive the ideal gas value. In the course of this work we found it necessary to compile and evaluate these data as well. These are presented in a separate section for each of the chlorinated species considered in this work. The C1 and C2 hydrocarbons are gases at standard temperature and pressure and have critical temperatures near or below 298.15 K [2001DIP]. Enthalpies of vaporization for these species are not presently considered.

In the past literature, ideal gas enthalpies of formation were frequently derived directly from the liquid phase value and the experimental enthalpy of vaporization. Although rarely discussed, this tacitly assumes that $\Delta_{\mathrm{vap}}H = \Delta_{\mathrm{vap}}H^o$, which is not strictly true. While the correction is small if the temperature of interest is significantly below the boiling point, it is often larger than the uncertainty in $\Delta_{\mathrm{vap}}H$ and can become significant for compounds with low boiling points.

The correction for non-ideality of the gas can be written $\Delta_{\mathrm{vap}}H^o = \Delta_{\mathrm{vap}}H + (H^o - H)$, where $(H^o - H)$ is the enthalpic departure function. We have calculated this quantity from the expression [1985MS]:

$$(H^o - H) = P_{\mathrm{sat}}[(T\,dB/dT) - B], \tag{1}$$

TABLE 1. Recommended enthalpies of formation of C1 and C2 hydrocarbons from several commonly cited sources. Uncertainties (if given) are those of the cited source. We have selected the values of Gurvich *et al.* [1991GVA] (in bold, see also text in Secs. 3.1, 4.1, 5.1, and 6.1)

| Reference | $\Delta_f H^o$[$CH_4$ (g), 298.15 K] (kJ mol$^{-1}$) | $\Delta_f H^o$[$C_2H_2$ (g), 298.15 K] (kJ mol$^{-1}$) | $\Delta_f H^o$[$C_2H_4$ (g), 298.15 K] (kJ mol$^{-1}$) | $\Delta_f H^o$[$C_2H_6$ (g), 298.15 K] (kJ mol$^{-1}$) |
|---|---|---|---|---|
| [2001B] | −74.60 | 227.4 | 52.3 | −83.85 |
| [2001DIP] | −74.52 | 228.2 | 52.51 | −83.82 |
| [1998C] | −74.873±0.34[a] | 226.73±0.79[a] | 52.467±0.29[b] | — |
| [1994FKM][c] | −74.5 | 228.2 | 52.5 | −83.8 |
| [1992ABC] | −74.81 | 228.0 | 52.2 | −84.0 |
| **[1991GVA] (selected values)** | **−74.6±0.3**[d] | **227.4±0.8**[d] | **52.4±0.50**[d] | **−84.0±0.40**[d] |
| [1986PNK] | −74.40±0.40 | 228.20±0.70 | 52.5±0.4 | −83.80±0.40 |
| [1985TRC] | −74.475[e] | 228.2[f] | 52.51[g] | −83.85[e] |
| [1982PRS] | −74.48±0.42 | — | — | −83.85±0.09 |
| [1975CZ] | — | — | 52.51±0.63 | — |
| [1970CP] | −74.85±0.29 | 227.36±0.79 | 52.09±0.42 | −84.68±0.50 |
| [1969SWS] | −74.85 | 226.73 | 52.45 | −84.68 |

[a] Evaluation date 1961.

[b] Evaluation date 1965.

[c] This is a compilation of the data sheets of the TRC Tables, as detailed in footnotes c, d, and e.

[d] Evaluation date uncertain, value is unchanged from previous edition, [1979G].

[e] Data sheet 1010, Evaluation date 1981, Ref. [1981C].

[f] Data sheet 3040, Evaluation date 1993, Ref. [1993KWD].

[g] Data sheet 2500, Evaluation date 1981, Ref. [1981C].

where $P_{sat}$, $T$, and $B$ are the saturated vapor pressure, temperature in Kelvin, and second virial coefficients, respectively. The vapor pressures and second virial coefficients were taken from the DIPPR Tables [2001DIP]. Where possible we have checked our estimates with previous calculations by Majer and Svoboda, [1985MS], although they do not report values for all compounds of present interest. Our calculated values and those of Majer and Svoboda are plotted versus the normal boiling point in Fig. 1. The values for chloroethene and trichloroethene calculated from the DIPPR data appear to be incorrect and were not used. Additional details can be found in the evaluations and at the NIST Kinetics Database website [2001KIN].

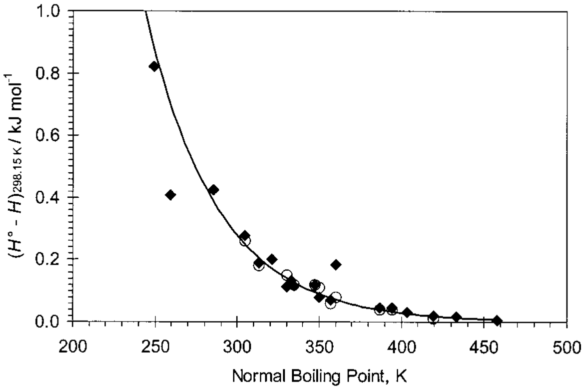

FIG. 1. The enthalpic departure function [from Eq. (1)] at 298.15 K vs the normal boiling point $T_b$ for the C1 and C2 chlorinated hydrocarbons. Filled symbols are values calculated by us taking data on the saturated vapor pressure and second virial coefficients from [2001DIP]. Open symbols are from [1985MS]. Two values calculated from the DIPPR data, those of chloroethene and trichloroethene, do not fall on the curve indicated by the other points. We were unable to determine an obvious reason for this, but these data were not used. The empirical fit to the data is given by $(H^o - H)_{298} = 250.35\,\exp(-0.227\,T_b)$.

A second issue has to do with the extrapolation of values of $\Delta_{vap}H$ at a particular temperature to the temperature of interest. There are numerous methodologies [1987RPP] for doing this that require knowledge of the critical pressure and temperature of the relevant species. Such data are not always available and we examine an alternative approach applicable to the limited range of compounds and temperatures considered herein. The general thermodynamic relation is:

$$\Delta_{vap}H(T_2) = \Delta_{vap}H(T_1) + \int_{T_1}^{T_2} \Delta_{vap}C_p \mathrm{d}T,$$

where $\Delta_{vap}C_p$ is the change in the heat capacity in going from the condensed to the gas phase. Over the moderate ranges of temperature typically encountered, $\Delta_{vap}C_p$ is usually approximately constant for a given molecule (*vide infra*, see Fig. 8 in Section 6.9). Its value is sometimes taken to be near $\Delta_{vap}C_p = -54.4\,\mathrm{J\,mol^{-1}\,K^{-1}}$ [1970CP] and further assumed to be independent of the chemical structure. In actuality there are no compelling reasons for this quantity to be constant across a series of molecules. Chikos *et al.*, [1993CHH] for example, examined the data on a variety of compounds and concluded that $\Delta_{vap}C_p$ increased with molecular size.

In a related approach, for the chlorinated hydrocarbons we have correlated this property with the normal boiling points of the compounds. Figure 2 shows clearly that the value of $\Delta_{vap}C_p$ increases with the normal boiling point of the species. A good straight line is obtained for the chloroalkanes with an intercept of very close to zero. The intercept can be rationalized since $\Delta_{vap}C_p$ should be related to the intermolecular forces in the condensed phase and those forces must

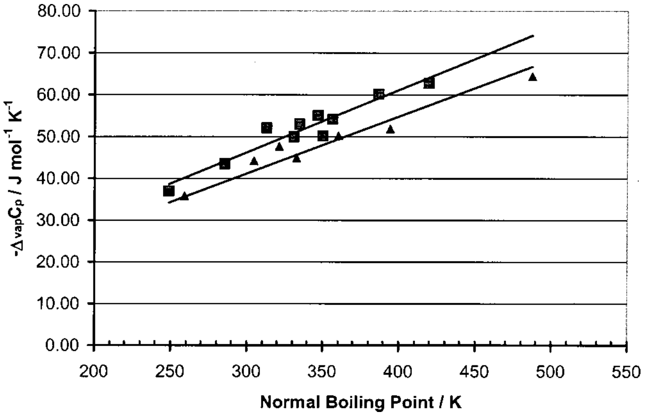

FIG. 2. Correlation of $\Delta_{\mathrm{vap}}C_{\mathrm{p}}$ with the normal boiling point for chloroalkanes and chloroalkenes. Symbols: Squares, chloroalkanes; triangles, chloroalkenes. Data are as given in evaluations. For the chloroalkenes we have also included the value $\Delta_{\mathrm{vap}}C_{\mathrm{p}}(\mathrm{C_3Cl_6}) = -64.4\ \mathrm{J\ mol^{-1}\ K^{-1}}$ derived from the temperature dependence of the enthalpy of vaporization reported by [1997SCK]. The lines are least squares fits forced through the origin (see text) and are given by: $\Delta_{\mathrm{vap}}C_{\mathrm{p}}(\mathrm{chloroalkanes})/\mathrm{J\ mol^{-1}\ K} = 0.1532(T_{\mathrm{bp}})$; $\Delta_{\mathrm{vap}}C_{\mathrm{p}}(\mathrm{chloroalkenes})/\mathrm{J\ mol^{-1}\ K} = 0.1372\ (T_{\mathrm{bp}})$. In the absence of other information, these fits were used for the estimation of $\Delta_{\mathrm{vap}}C_{\mathrm{p}}$ for purposes of extrapolating values of $\Delta_{\mathrm{vap}}H$ to the temperature of interest.

be absent in the limit of a boiling point of 0 K. The data on chloroalkenes appear to fall on a line slightly below that of the chloroalkanes. In the end we have forced both lines through zero and have used the equations so determined in instances where it was necessary to estimate $\Delta_{\mathrm{vap}}C_{\mathrm{p}}$. For all compounds the maximum deviations of the fits for $\Delta_{\mathrm{vap}}C_{\mathrm{p}}$ are less than 4 $\mathrm{J\,mol^{-1}\,K^{-1}}$. It should be noted that significant extrapolation of these empirical relations is specifically not recommended and that the above approach will obviously not be valid near the critical temperature of a compound. This latter point is not presently a concern for the determination of $\Delta_{\mathrm{vap}}H[298.15]$, since even the lowest boiling chlorinated species considered herein are expected to have $T_{\mathrm{c}}$ greater than 400 K [1987RPP], [2001DIP]. Also, since the temperature corrections to $\Delta_{\mathrm{vap}}H$ are generally small, the precise values used for $\Delta_{\mathrm{vap}}C_{\mathrm{p}}$ have a limited effect.

### 1.6. Uncertainties

The assignment of a consistent set of uncertainties is particularly important as it allows one to set limits on quantities associated with or derived from the quantities listed herein (e.g., certain rate constants, equilibrium constants, etc.). In the inevitable cases where future experimental data are not perfectly consistent with listed values, these data can also suggest where the error is most likely to lie. Our methodology for the assignment of uncertainties is based on the 1994 edition of NIST Technical Note 1297 [1994TK]. NIST Technical Note 1297 is in turn based on the approach to expressing uncertainty recommended by the International Committee for Weights and Measures (CIPM) in 1981 [1981CIPM], [1981G], [1981K], [1982G], and further elaborated upon by Technical Advisory Group 4, Working Group 3, of the International Organization for Standardization in 1993 [1993ISO]. Further details can be found in the above referenced publications. In no way is the present summary intended to modify or supplant any of the information or procedures presented in those documents. More detailed discussion can be found at the NIST Kinetics Database website [2001KIN].

*Uncertainties associated with individual experimental measurements*. For experimental measurements associated with a particular paper, unless otherwise stated, the listed uncertainties should be considered to be statistical uncertainties equal to *twice the standard deviation of the mean*. Note that this should not be confused with the *standard deviation of the sample*, a very different and much larger quantity. These values are usually taken directly from the original papers, which do not always specify the meaning of their stated uncertainties or provide enough information to repeat the statistical analysis. In such cases we have necessarily had to make judgements as to the intent of the original authors. In cases where we have derived uncertainties from the original data or propagated uncertainties by combining more than one measurement, we have used the standard statistical formulas. In the language of NIST Technical Note 1297 these are generally Type A assessments.

*Uncertainties associated with estimated or calculated quantities*. In some instances we have estimated or calculated quantities of interest. In such cases we have attempted to specify the uncertainty range such that the value has a level of confidence of approximately 95%. That is, in 19 out of 20 cases, the true value of the quantity should lie within the stated range. This range is derived by comparing the success of analogous calculations in related cases where good experimental values exist. Similarly, if an empirical estimation procedure is used, the consideration is the success of the procedure in related cases where experimental determinations exist. Unless otherwise noted, in our evaluations of such uncertainties, we have assumed a normal (Gaussian) probability distribution. Although derived in a different manner, such estimates are *approximately equivalent to statistically derived values of twice the standard deviation of the mean*.

*Uncertainties associated with final recommended quantities*. The uncertainties reported in the literature often reflect only the reproducibility of the measurement as carried out by the particular investigator using their particular apparatus. However, even a cursory perusal of the data on enthalpies of formation of the chlorinated compounds shows that frequently the uncertainties of different determinations do even come close to overlapping. Obviously not all systematic or random effects were always taken into account. If many determinations are available and all quoted uncertainties have comparable meanings, one can nonetheless derive a reasonable statistical value of the uncertainty. However this is rarely the case. More often only a single determination is available and, in consideration of related systems, the stated uncertainty is unrealistically small. To deal with this problem, rather than simply quote statistical uncertainties, wehave used our scientific judgement to assign what we feel are more realistic uncertainty limits in the final enthalpy values.

TABLE 2. Summary of recommended values for the C1 and C2 chlorinated hydrocarbons from this work

| Compound | Chemical formula | $\Delta_f H^o(\mathrm{l})$, 298.15 K (kJ mol$^{-1}$) | $\Delta_{vap}H$ 298.15 K (kJ mol$^{-1}$) | $\Delta_{vap}H^{o\ a}$ 298.15 K (kJ mol$^{-1}$) | $\Delta_f H^o(\mathrm{g})$, 298.15 K (kJ mol$^{-1}$) |
|---|---|---|---|---|---|
| Methanes | | | | | |
| methane | $CH_4$ | — | — | — | $-74.6\pm0.3$ |
| chloromethane | $CH_3Cl$ | $-102.4\pm1.5^{b}$ | $19.7\pm0.3$ | $20.5\pm0.3^{b}$ | $-81.9\pm1.5$ |
| dichloromethane | $CH_2Cl_2$ | $-124.1\pm2.5$ | $28.85\pm0.07$ | $29.03\pm0.08$ | $-95.1\pm2.5$ |
| trichloromethane | $CHCl_3$ | $-134.1\pm2.5$ | $31.20\pm0.08$ | $31.32\pm0.08$ | $-102.9\pm2.5$ |
| tetrachloromethane | $CCl_4$ | $-128.1\pm2.5$ | $32.44\pm0.06$ | $32.55\pm0.07$ | $-95.6\pm2.5$ |
| Ethynes | | | | | |
| ethyne | $C_2H_2$ | — | — | — | $227.4\pm0.8$ |
| chloroethyne | $C_2HCl$ | $206.5\pm10^{b}$ | $18.9\pm1.0$ | $19.9\pm1.0^{b}$ | $226.4\pm10$ |
| dichloroethyne | $C_2Cl_2$ | $199.2\pm14$ | $27.2\pm1.2$ | $27.4\pm1.2$ | $226.6\pm14$ |
| Ethenes | | | | | |
| ethene | $C_2H_4$ | — | — | — | $52.4\pm0.5$ |
| chloroethene | $C_2H_3Cl$ | $0.9\pm3.2^{b}$ | $20.4\pm1.0$ | $21.1\pm1.0^{b}$ | $22.0\pm3.0$ |
| 1,1-dichloroethene | $C_2H_2Cl_2$ | $-24.3\pm2.0$ | $26.48\pm0.09$ | $26.74\pm0.09$ | $2.4\pm2.0$ |
| *Z*-1,2-dichloroethene | $C_2H_2Cl_2$ | $-34.1\pm2.2$ | $31.0\pm1.0$ | $31.1\pm1.0$ | $-3.0\pm2.0$ |
| *E*-1,2-dichloroethene | $C_2H_2Cl_2$ | $-30.0\pm2.2$ | $29.3\pm1.0$ | $29.5\pm1.0$ | $-0.5\pm2.0$ |
| trichloroethene | $C_2HCl_3$ | $-52.1\pm3.0$ | $34.49\pm0.09$ | $34.57\pm0.09$ | $-17.5\pm3.0$ |
| tetrachloroethene | $C_2Cl_4$ | $-63.9\pm4.0$ | $39.68\pm0.05$ | $39.72\pm0.05$ | $-24.2\pm4.0$ |
| Ethanes | | | | | |
| Ethane | $C_2H_6$ | — | — | — | $-84.0\pm0.4$ |
| chloroethane | $C_2H_5Cl$ | $-136.7\pm1.0^{b}$ | $24.2\pm0.3$ | $24.6\pm0.3^{b}$ | $-112.1\pm0.7$ |
| 1,1-dichloroethane | $C_2H_4Cl_2$ | $-163.3\pm3.5$ | $30.68\pm0.08$ | $30.83\pm0.08$ | $-132.5\pm3.5$ |
| 1,2-dichloroethane | $C_2H_4Cl_2$ | $-167.2\pm3.5$ | $35.15\pm0.05$ | $35.21\pm0.05$ | $-132.0\pm3.5$ |
| 1,1,1-trichloroethane | $C_2H_3Cl_3$ | $-177.2\pm2.0$ | $32.47\pm0.07$ | $32.59\pm0.07$ | $-144.6\pm2.0$ |
| 1,1,2-trichloroethane | $C_2H_3Cl_3$ | $-188.3\pm4.0$ | $40.26\pm0.07$ | $40.30\pm0.07$ | $-148.0\pm4.0$ |
| 1,1,1,2-tetrachloroethane | $C_2H_2Cl_4$ | $-193.4\pm2.3$ | $41.1\pm0.5$ | $41.1\pm0.5$ | $-152.3\pm2.4$ |
| 1,1,2,2,-tetrachloroethane | $C_2H_2Cl_4$ | $-202.4\pm3.5$ | $45.72\pm0.09$ | $45.73\pm0.09$ | $-156.7\pm3.5$ |
| pentachloroethane | $C_2HCl_5$ | $-203.3\pm4.0$ | $47.4\pm1.5$ | $47.4\pm1.5$ | $-155.9\pm4.3$ |
| hexachloroethane | $C_2Cl_6$ | $-199.2\pm6.1^{c}$ | $^{c}$ | $51.0\pm2.3^{c}$ | $-148.2\pm5.7$ |

[a] These values are equal to $\Delta_{vap}H(298.15\,\mathrm{K})$ plus a calculated correction for non-ideality (see text).

[b] This compound is a gas at standard temperature and pressure. The quoted value refers to the hypothetical liquid under standard conditions.

[c] Hexachloroethane is a solid at standard temperature and pressure. The quoted value refers to the hypothetical liquid under standard conditions. Our relevant values for the crystal are $\Delta_f H^o[C_2Cl_6(s), 298.15\,\mathrm{K}] = -(217.2\pm7.0)$ kJ mol$^{-1}$ and $\Delta_{sub1}H^o[C_2Cl_6(s), 298.15\,\mathrm{K}] = (69.0\pm4.0)$ kJ mol$^{-1}$.

These limits represent an attempt to specify intervals which have a level of confidence of approximately 95%. These assignments take into account a variety of auxiliary information, including, for example, the past success and reliability of a particular technique, the past success and reliability of the investigators, the thoroughness with which potential systematic errors were considered by the investigators, if and how the instrument was calibrated, etc. In the language of NIST Technical Note 1297, the uncertainties associated with final recommended quantities are generally derived from Type B evaluations. They are purely statistical Type A evaluations only if we feel that such an analysis is sufficient to account for all non-negligible sources of error. Again, such estimates are approximately equivalent to statistically-derived values of twice the standard deviation of the mean.

*Uncertainties associated with key auxiliary thermodynamic quantities*. The enthalpy values for some relevant compounds (e.g., $CO_2$, HCl) have values that have been considered by expert committees and have internationally agreed upon ‘‘best’’ values. Where we quote such values we have not altered the uncertainties specified by the source. In such cases we believe the quoted uncertainties to be comparable to those used in our own evaluations, but the reader is referred to the specific references for details.

## 2. Overview of Results

### 2.1. Tabulation of Final Values

For convenience, the final numbers are tabulated and summarized in Table 2. The discussion will be organized as follows. We will begin with some general comments and a discussion of trends in the results. Thereafter will be the individual evaluations.

### 2.2. General Comments

When examined globally, the most striking feature of the data on C1 and C2 chlorinated hydrocarbons is that existing sets of recommended values cannot be reconciled with large portions of the available data on highly chlorinated compounds. In particular, the *relative* ethalpies of formation of many of these species are interrelated by measured reaction enthalpies of various chlorination, hydrochlorination, hydrogenation, and isomerization reactions. In many cases one has to assume that these relative measurements are not even approximately correct if currently accepted values are to be utilized. Further examination of the data makes it clear, however, that a generally consistent set of values *can* be derived if one makes the assumption that enthalpies of formation of the highly chlorinated C2 compounds are generally more negative than held by most previous evaluators. Kolesov and Papina [1983KP] pointed this out for some specific chloroethanes in their 1983 review, but did not reevaluate the data for the chloroalkenes at that time. Because of the cross-linking of the values for the chloroalkenes and chloroalkenes we believe it is necessary to consider all of the data together.

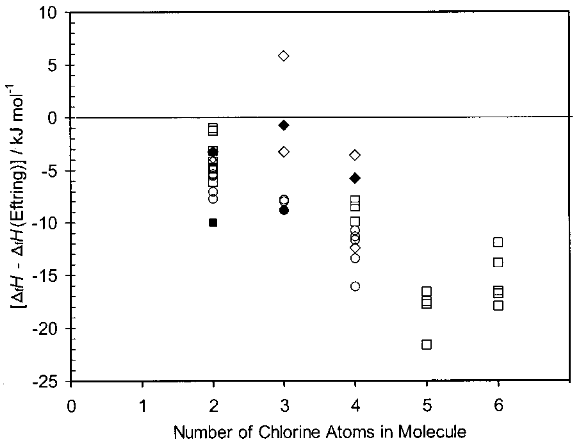

FIG. 3. Comparison of Eftring's [1938E] $\Delta_f H^o$[298.15] for chloromethanes, chloroethenes, and chloroethanes with determinations using other methods. Data of Eftring are the revised values as detailed in [1953SBK] and [1970CP], and compiled in [1986PNK]. Symbols: ◇, Chloromethanes; ○, chloroethenes; □, chloroethanes. Filled symbols indicate the newer value is from rotating bomb calorimetry, open symbols are from other methods. Data are from our evaluations. A few values, shown in our evaluations to be obviously incorrect, are not included for clarity.

We believe there is very good evidence for the more negative enthalpies of formation for the highly chlorinated compounds. Most previous evaluations have heavily weighted results from early combustion calorimetry to derive recommended values. This is understandable and reasonable in cases where there are multiple high quality studies using established techniques. However, for the highly chlorinated compounds there are relatively few combustion values. Most of the data on these species are from Lund University, particularly the 1938 thesis work of Eftring [1938E]. Eftring himself placed relatively high uncertainties of typically ±8.4 kJ mol$^{-1}$ on the accuracy of his measurements. These experiments also utilized static bomb calorimetry and the many problems related to the difficult combustion of highly chlorinated compounds were not fully appreciated at that time. In addition there is little information on the purity of the substances burned. Although some attempts to correct the original data from Lund University have been made, [1953SBK], [1970CP], the success of these attempts is questionable and this still does not address sample purity issues. Sample purity can have substantial effects as demonstrated for, e.g., 1,1,1-trichloroethane. In that case, even when utilizing a rotating bomb method, later studies by the same investigators using carefully purified material [1972HSM] produced an enthalpy of formation some 8 kJ mol$^{-1}$ more negative than the original value [1969HS]. In this case the latter result has been verified by independent methods involving gas-phase hydrochlorination (see Sec. 6.5 for details).

Of particular relevance are more recent studies on moderately chlorinated compounds that have been performed since the early work of Eftring [1938E]. Many of the later studies utilize rotating bombs, better bomb materials less subject to corrosion, and more careful techniques to assure complete reduction of the chlorine. Most of the later work has concentrated on C1 and C2 chlorinated species not studied by Eftring. A few compounds have been directly repeated, however, and the general result of the later work has been to obtain enthalpies of formation more negative than found by Eftring. Further, the species studied by other investigators are often linked to the values of Eftring by various measured enthalpies of chlorination, hydrochlorination, etc. Figure 3 shows a comparison of the results of Eftring with newer data, where we have plotted the relative $\Delta_f H^o$[298.15 K] values versus the number of chlorine atoms in the molecule. Eftring stated his uncertainties to be about ±8.4 kJ mol$^{-1}$, while Fig. 3 suggests a somewhat larger range. More important, it is immediately apparent that differences with newer data are systematic. Almost all newer data result in more negative enthalpy of formation values and the deviation increases with chlorine content of the molecule. This is not particularly surprising, since to the extent that there are systematic problems with the early combustion calorimetry work, the difficulties are expected to be greater as the chlorine content increases and the molecule becomes increasingly difficult to burn. There are no combustion studies other than those of Eftring on pentachloroethane and hexachloroethane. Although most previous reviewers have heavily weighted the values of Eftring, Fig. 3 makes it clear that his values are probably too positive. Note also that we make use of some key data that were not available to previous evaluators.

In the present work, the more negative values selected by us are largely based on three sets of data:

(i) The first of these is the combustion calorimetry work of Papina and Kolesov from the 1980s on a few select compounds [1987PK], [1985PK]. The most important of these is trichloroethene [1985PK], which can be related to several other compounds through various measurements, and for which a much more negative enthalpy of formation was determined in comparison to the value of Eftring.

(ii) Second is the work of Rozhnov *et al.* [1974RLD] on the dichloroethene equilibria, which firmly establishes their values and creates reliable links to some chlorinated ethanes through chlorination and hydrochlorination studies.

(iii) Third are the high temperature equilibration reactions of the perchloro compounds $C_2Cl_6$, $C_2Cl_4$, and $CCl_4$. Equilibria involving the first two compounds were studied in 1950 by Dainton and Ivin [1950DI], in the early 1960s by Puyo *et al.* [1963PBM], [1962PMN], and recently reexamined in the mid 1990s by Huybrechts *et al.* [1996HNMa]. This latter work is particularly important as it also contains information on the equilibria involving $CCl_4$. These experiments establish relative values of the perchloro compounds. To place the data on an absolute scale, the enthalpy of formation of $CCl_4$ is chosen as the reference, as it is by far the best determined of these species. Taken together, the high temperature data, the more recent combustion calorimetry experiments, and the enthalpy measurements of additional chlorination, hydrochlorination, and isomerization reactions can be used to construct a self-consistent set of values for the C1 and C2 chlorinated hydrocarbons.

High level *ab initio* calculations carried out at NIST [2001BAM] also seem to broadly support the enthalpy of formation values proposed here. Although there is a danger of circular arguments, the *ab initio* calculations appear to be of sufficient general accuracy that gross errors in our suggested values would be apparent. The theoretical studies will be published and discussed in a separate article. *It is important to note that, with the exceptions given below, the present set of values was derived entirely from experimental data independent of the theoretical work.* For the dichloroethanes, calculations were used to help choose between conflicting experimental results, but the selected values are still based on experimental work. In the case of the chloroethynes, no experimental data were available. For these compounds we have used the *ab initio* values rather than possible empirical methods of estimation (see Secs. 4.1 and 4.2, respectively).

## 2.3. Trends in Some Reaction Enthalpies

Figure 4 shows the enthalpy values at 298.15 K of addition of $Cl_2$, HCl, and $H_2$ to the C2 alkenes that are derivable using our final set of values. A similar plot for the C2 alkynes is shown in Fig. 5. For the alkenes, the most noticeable feature is the large decrease in the enthalpies of addition of $Cl_2$ as the ethene becomes more chlorinated. Also striking is the very weak trend in the enthalpies of addition of $H_2$ for the same alkenes. In general terms, these trends can be rationalized by the high electronegativity of chlorine. In the case of $Cl_2$, the addition of $Cl_2$ to $C_2H_4$ is even more favorable than addition of $H_2$. However, as the ethene becomes more chlorinated, the electron densities of the carbon atoms are progressively more depleted by other chlorines, and the net reaction becomes ever less favorable. One could also make arguments based on increasing steric crowding within the molecule. Whatever the reason, this destabilization is responsible for the inability of unmodified group additivity to accurately predict the enthalpies of formation of these compounds. In contrast with $Cl_2$ addition, the enthalpy of addition of the small, electropositive $H_2$ seems to vary little over the entire series. As would be expected, the observed trend for HCl addition is intermediate. The smooth trends observed for these reactions are suggestive that there are no major outliers in the set of recommended values.

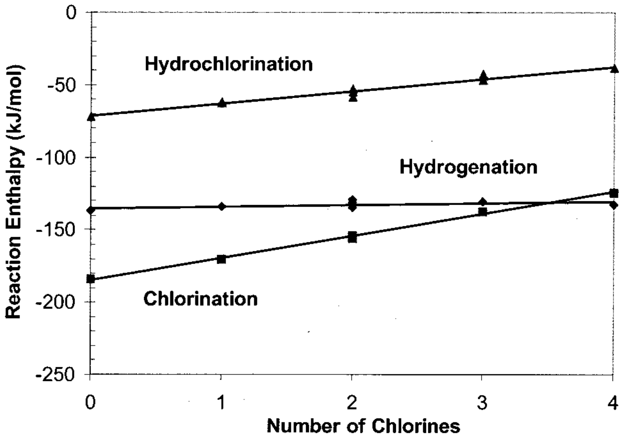

FIG. 4. Plot of the enthalpies of chlorination, hydrogenation, and hydrochlorination for the chloroethenes. Least squares analyses are: $\Delta_r H$(chlorination)/kJ mol$^{-1}$ = $15.3N - 185.0$; $\Delta_r H$(hydrogenation)/kJ mol$^{-1}$ = $1.14N - 135.0$; $\Delta_r H$(hydrochlorination)/kJ mol$^{-1}$ = $8.46N - 71.4$, where $N$ is the number of chlorines in the ethene. Data are derived from our recommended values.

It is interesting that the trends for the alkynes are different from those observed for the alkenes. Thus for the alkynes, both chlorination and hydrogenation are increasingly exothermic as the molecule becomes more chlorinated. However, it should be noted that the trends for the alkenes and alkynes are the same in the sense that the *change* in the reaction enthalpy with chlorine content of the molecule is always more favorable for hydrogenation than for chlorination (i.e., the slopes of the lines for hydrogenation are always more negative than for chlorination—see Figs. 4 and 5). This is in keeping with the electronic and steric arguments presented above. (It should further be borne in mind that the electronegativity of carbon itself changes significantly with hybridization, thus making such comparisons problematic.) That the sign of the slope changes for chlorination of alkynes and alkenes is particularly interesting. This could be rationalized in terms of steric effects being more important in the transition from alkene to alkane than from the alkyne to alkene. Alternatively, it could suggest a particular instability of the chloroalkynes, which are known to be unstable in air [1967STS]. Our calculations [2001BAM] suggest a very substantial depletion of the electron density of the carbon–carbon bond in going from $C_2H_2$ to $C_2Cl_2$, which would be consistent with a significant destabilization of the latter molecule.

Whatever the ultimate explanations for the trends apparent in Figs. 4 and 5, it would be desirable to have better experimental confirmation of the enthalpy of formation values selected herein. Experimental values for the chloroethynes would be of particular interest, but are difficult to obtain because of the general difficulties in handling these species [1967STS]. More easily accomplished would be modern combustion calorimetric determinations of the values of

$\Delta_f H(C_2Cl_4)$, $\Delta_f H(C_2HCl_5)$, and $\Delta_f H(C_2Cl_6)$. However, the cost of such experiments, together with the worldwide erosion in the necessary expertise, make this unlikely to occur in the near future.

### 2.4. Organization of the Evaluations

The organization of the subsequent evaluations is as follows. Each species is discussed separately, although in cases where the data are linked it may be necessary to refer to details given in other evaluations. For each compound the available experimental data are collected and summarized in a separate table. The tables contain a brief description of the experimental methodology along with select notes. More detailed information on each experiment is given in a section of linked Comments following each table. For easy comparison, in each table all results are presented as gas phase values. Any experimental data on liquids have thus been converted using the appropriate evaluated enthalpy of vaporization. In such cases the Comments section will contain the unconverted value. Note that the experimentally derived enthalpy values in the tables are not necessarily the values listed in the original papers as we may have used updated thermodynamic quantities and may have reanalyzed the original data. Any such changes are detailed in the Comments section as appropriate. Finally, for comparison, in a separate table section we have collected and list the values from previous evaluations.

The layout of the species is by increasing number of carbon and chlorine atoms, with subdivision of the C2s into alkynes, alkenes, and alkenes, in that order.

## 3. Evaluated Enthalpies of Formation and Vaporization of the (Chloro)methanes

### 3.1. Methane

*Enthalpy of Formation. Recommendation.* Many evaluations of the enthalpy of formation of methane exist. There are no recent experimental determinations of its value and there is no serious controversy regarding the correct value. The evaluations from a number of commonly cited sources are listed in Table 1 and the recommended $\Delta_f H^o[CH_4(g), 298.15\,K]$ values range from $-74.4$ to $-74.88$ $kJ\,mol^{-1}$. The evaluation of Gurvich *et al.* [1991GVA] contains good discussion of the data, although the actual date of the evaluation is uncertain (the value selected therein is the same as in the previous edition, [1979G]). Gurvich *et al.* [1991GVA] based their value on an average of the combustion calorimetric measurements of Rossini and co-workers [1931Ra], [1931Rb], [1945PR] and Pittam and Pilcher [1972PP]. After review, we have accepted their evaluation, $\Delta_f H^o[CH_4(g), 298.15\,K] = -(74.6 \pm 0.3)\,kJ\,mol^{-1}$.

### 3.2. Chloromethane

*Enthalpy of Vaporization:* Chloromethane is a gas at 298.15 K and standard pressure (100 kPa). Yates [1926Y] has measured the enthalpy of vaporization between 285 and 299 K and his fit to the data results in $\Delta_{vap}H(298.15\,K) = (19.95 \pm 0.3)\,kJ\,mol^{-1}$, where the uncertainty is that estimated by us from the scatter in his data. Messerly and Aston [1940MA] measured the vapor pressure of $CH_3Cl$ between 191 and 248.9 K and, at the boiling point of 248.94 K, derived $\Delta_{vap}H(248.9\,K) = (21.54 \pm 0.07)\,kJ\,mol^{-1}$. The heat capacity of vaporization can be derived as $\Delta_{vap}C_p(CH_3Cl) = -37.0\,J\,mol^{-1}\,K^{-1}$, from the entropy data of Messerly and Aston [1940MA] or as $\Delta_{vap}C_p(CH_3Cl) = -42.2\,J\,mol^{-1}\,K^{-1}$ from the difference of the reported heat capacities of the gas [1991GVA] and liquid [1940AG]. Using the average value $\Delta_{vap}C_p(CH_3Cl) = -39.8\,J\,mol^{-1}\,K^{-1}$, we derive $\Delta_{vap}H(298.15\,K) = (19.58 \pm 0.3)\,kJ\,mol^{-1}$. Near the boiling point, Shorthose [1924S] reported $\Delta_{vap}H(249.4\,K) = 21.6\,kJ\,mol^{-1}$, which, with $\Delta_{vap}C_p$ as above, becomes $\Delta_{vap}H(298.15\,K) = 19.66\,kJ\,mol^{-1}$. The results of all the above studies are in good agreement and we recommend $\Delta_{vap}H(298.15\,K) = (19.7 \pm 0.3)\,kJ\,mol^{-1}$. Using Eq. (1) and second virial coefficients taken from the DIPPR Tables [2001DIP] (datasheet revision date August, 1997), the correction to $\Delta_{vap}H(298.15\,K)$ due to nonideality of the gas is calculated as 0.82 $kJ\,mol^{-1}$. This leads to $\Delta_{vap}H^o[CH_3Cl,\ 298.15\,K] = (20.5 \pm 0.3)\,kJ\,mol^{-1}$.

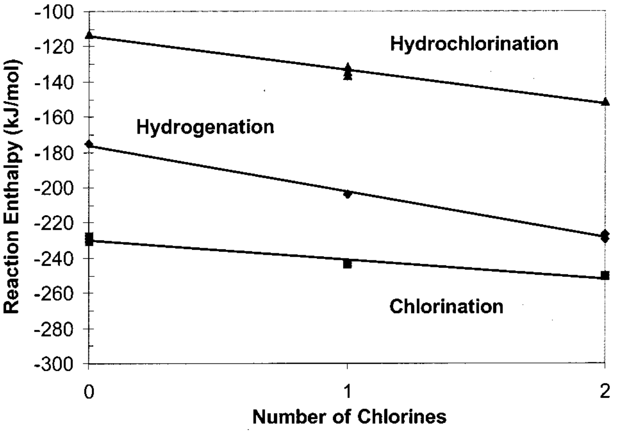

FIG. 5. Plot of the enthalpies of chlorination, hydrogenation, and hydrochlorination for the chloroethynes. Least squares analyses are: $\Delta_r H(\text{chlorination})/kJ\,mol^{-1} = -11.0N - 229.9$; $\Delta_r H(\text{hydrogenation})/kJ\,mol^{-1} = -26.2N - 176.0$; $\Delta_r H(\text{hydrochlorination})/kJ\,mol^{-1} = -19.2N - 114.3$, where $N$ is the number of chlorines in the ethyne. Data are derived from our recommended values.

*Enthalpy of Formation. Recommendation.* Data are summarized in Table 3. The enthalpy of formation of chloromethane determined by Fletcher and Pilcher [1971FP] from flame calorimetry is somewhat more positive (3–4 $kJ\,mol^{-1}$) than that derived from the hydrogenation studies of Lacher and co-workers [1965FLP], [1956LEB]. It has been suggested [1983KP], [1991GVA] that the hydrogenation catalyst employed by Lacher may not be sufficiently inert and that this could have perturbed the results. Whatever the reason, we note that for other chlorinated compounds where the enthalpies of formation are not in dispute, the hydrogenation re-

TABLE 3. Enthalpies of formation of chloromethane derived from reported experimental data

| $\Delta_f H^o$(g), 298.15 K (kJ mol$^{-1}$) | Reported uncertainty (kJ mol$^{-1}$) | Temp. (K) | Method(s) | Reference | Comments |
|---|---|---|---|---|---|
| Experimental | | | | | |
| −81.9 | 0.6 | 298 | Combustion calorimetry of gas | [1971FP] | 1, Flame calorimetry. |
| −85.4 | 0.6$^a$ | 298 | Enthalpy of hydrogenation<br>$CH_3Cl(g)+H_2(g)\rightarrow CH_4(g)+HCl(g)$ | [1965FLP] | 2, Data reanalyzed by [1970CP]. |
| −86.1 | 0.6$^a$ | 298 | Enthalpy of hydrogenation<br>$CH_3Cl(g)+H_2(g)\rightarrow CH_4(g)+HCl(g)$ | [1956LEB] | 3, Data reanalyzed by [1970CP]. |
| Reviews and Evaluations | | | | | |
| −83.68 | 2.1 | 298 | | [1998C] | 1972 evaluation. |
| −81.87 | 0.6 | 298 | | [1991GVA] | Evaluation date uncertain; same value as previous edition [1979G]. |
| −81.9 | 0.5 | 298 | | [1986PNK] | |
| −81.96 | N.R.$^b$ | 298 | | [1981C] | |
| −81.96 | 0.67 | 298 | | [1974RCW] | |
| −86.0 | 0.4 | 298 | | [1970CP] | |
| −86.3 | N.R.$^b$ | 298 | | [1969SWS] | |

[a] Precision only, does not include systematic errors or uncertainty in auxiliary thermodynamic quantities.
[b] Not reported.

**Comments:**

1. Flame calorimetry of gas. $\Delta_c H^o_{298} = -(764.0 \pm 0.5)$ kJ mol$^{-1}$, refers to reaction $CH_3Cl(g)+1.5O_2(g)\rightarrow CO_2(g)+H_2O(l)+HCl(aq{:}600)$. The following auxiliary values were used: $\Delta_f H^o[CO_2(g), 298.15\text{ K}] = -(393.51 \pm 0.13)$ kJ mol$^{-1}$, $\Delta_f H^o[H_2O(l), 298.15\text{ K}] = -(285.830 \pm 0.040)$ kJ mol$^{-1}$, and $\Delta_f H^o[HCl(aq{:}600), 298.15\text{ K}] = -(166.540 \pm 0.10)$ kJ mol$^{-1}$. This yields $\Delta_f H^o[CH_3Cl(g), 298.15\text{ K}] = -(81.88 \pm 0.5)$ kJ mol$^{-1}$.
2. $\Delta_r H(298.15\text{ K}) = -(81.5 \pm 0.4)$ kJ mol$^{-1}$. Value in Table calculated using $\Delta_f H^o[CH_4(g), 298.15\text{ K}] = -(74.60 \pm 0.3)$ kJ mol$^{-1}$ [1991GVA], $\Delta_f H^o[HCl(g), 298.15\text{ K}] = -(92.31 \pm 0.10)$ kJ mol$^{-1}$ [1989CWM].
3. $\Delta_r H(298.15\text{ K}) = -(80.8 \pm 0.4)$ kJ mol$^{-1}$. Auxiliary quantities as in Comment 2.

sults are often at odds with other experimental data. In addition to chloromethane, Fletcher and Pilcher [1971FP] determined enthalpies of formation of chloroethane and 1-chloropropane in the same study. In those cases there are equilibrium hydrochlorination studies which corroborate their results. This leads us to believe their results are correct. Because of this we have selected the flame value, $\Delta_f H^o[CH_3Cl(g),\ 298.15\text{ K}] = -(81.9 \pm 1.5)\text{ kJ mol}^{-1}$, rather than taking a weighted average of the results. We have, however, increased the uncertainty to reflect the disagreement and the general level of accuracy expected for the chlorinated compounds. The value for the hypothetical liquid under standard conditions is derived as $\Delta_f H^o[CH_3Cl(l),\ 298.15\text{ K}] = -(102.4 \pm 1.5)\text{ kJ mol}^{-1}$.

### 3.3. Dichloromethane

*Enthalpy of Vaporization:* Cox and Pilcher [1970CP] extrapolated the calorimetric measurements of Mathews [1926M] and derived $\Delta_{vap}H(298.15\text{ K}) = (28.45 \pm 0.42)\text{ kJ mol}^{-1}$, while Stull *et al.* [1969SWS] determined $\Delta_{vap}H^o(298.15\text{ K}) = 28.74\text{ kJ mol}^{-1}$ from this same data. More recently Majer *et al.* [1980MSS] found $\Delta_{vap}H(298.15\text{ K}) = (28.85 \pm 0.07)\text{ kJ mol}^{-1}$ using an isothermal adiabatic calorimeter. This latter value is adopted. A correction of 0.18 kJ mol$^{-1}$ due to nonideality of the gas was taken from the work of Majer and Svoboda [1985MS] (our calculation gives 0.19 kJ mol$^{-1}$) and $\Delta_{vap}H^o(298.15\text{ K}) = (29.03 \pm 0.08)\text{ kJ mol}^{-1}$ is derived. The heat capacity of vaporization is derived as $\Delta_{vap}C_p = -52.0\text{ J mol}^{-1}\text{ K}^{-1}$ from the temperature dependence of the $\Delta_{vap}H$ data of [1980MSS].

*Enthalpy of Formation. Recommendation*. Data are summarized in Table 4. The enthalpy of formation of dichloromethane determined by Hu and Sinke [1969HS] using a rotating-bomb combustion calorimeter is in very good agreement with the hydrogenation work of Lacher *et al.* [1967LAP]. This is somewhat surprising since for many of the chlorinated compounds studied by Lacher and coworkers, the hydrogenation results are at odds with other experimental data. The early combustion value of Eftring obtained using a static bomb calorimeter is much less precise but is only slightly more positive than the more recent values. This is somewhat surprising, given that in almost all cases the enthalpies of formation determined by Eftring [1938E] are too positive in comparison with more modern techniques (see Sec. 2.2 and Fig. 3). However, in their paper, Hu and Sinke reported the enthalpies of formation of several chlorinated compounds in addition to dichloromethane. Many of these other values have been borne out by subsequent work. This, together with concerns about the reliability of the other methods, leads us to accept their value rather than taking a weighted average of all the data. We have, however, increased the uncertainty to what we feel is a more realistic value given the general accuracy observed for other

TABLE 4. Enthalpies of formation of dichloromethane derived from reported experimental data

| $\Delta_f H^o$(g), 298.15 K (kJ mol$^{-1}$) | Reported uncertainty (kJ mol$^{-1}$) | Temp. (K) | Method(s) | Reference | Comments |
|---|---|---|---|---|---|
| Experimental | | | | | |
| −95.1 | 0.8 | 298 | Combustion calorimetry of liquid | [1969HS] | 1, Rotating bomb. |
| −95.8 | 1.3 | 298 | Enthalpy of hydrogenation $CH_2Cl_2$ (g)+$H_2$ (g)→$CH_4$ (g)+2HCl (g) | [1967LAP] | 2, Data reanalyzed by [1970CP]. |
| −91.8 | 8.4 | 298 | Combustion calorimetry of liquid | [1938E]<br>[1953SBK]<br>[1970CP] | 3, Static bomb. Data corrected by [1953SBK]. Reanalyzed and auxiliary quantities updated by [1970CP]. |
| Reviews and Evaluations | | | | | |
| −95.5 | 1.3 | 298 | | [1998C] | 1968 evaluation. |
| −95.0 | 0.3 | 298 | | [1991GVA] | Evaluation date uncertain; same value as previous edition [1979G]. |
| −95.6 | 1.2 | 298 | | [1986PNK] | |
| −95.4 | N.R.[a] | 298 | | [1981C] | |
| −95.40 | 0.84 | 298 | | [1974RCW] | |
| −96.1 | 1.2 | 298 | | [1970CP] | |
| −95.4 | N.R.[a] | 298 | | [1969SWS] | |

[a] Not reported.

**Comments:**

1. $\Delta_c H^o_{298} = -(602.5 \pm 0.8)$ kJ mol$^{-1}$, which refers to reaction $CH_2Cl_2$ (l)+$O_2$ (g)→$CO_2$ (g)+2HCl (aq:600). Results obtained with rotating bomb calorimeter. The following auxiliary values were used: $\Delta_f H^o[CO_2\ (g),\ 298.15\ K] = -(393.51 \pm 0.13)$ kJ mol$^{-1}$, and $\Delta_f H^o$[HCl(aq:600), 298.15 K]$= -(166.540 \pm 0.10)$ kJ mol$^{-1}$. Data yield $\Delta_f H^o[CH_2Cl_2\ (l),\ 298.15\ K] = -(124.09 \pm 0.8)$ kJ mol$^{-1}$.
2. $\Delta_r H(298.15\ K) = -(163.4 \pm 1.3)$ kJ mol$^{-1}$, as per reanalysis of Cox and Pilcher [1970CP]. Value in Table calculated using $\Delta_f H^o[CH_4\ (g),\ 298.15\ K] = -(74.60 \pm 0.3)$ kJ mol$^{-1}$ [1991GVA], $\Delta_f H^o$[HCl (g), 298.15 K]$= -(92.31 \pm 0.10)$ kJ mol$^{-1}$ [1989CWM].
3. $\Delta_c H^o_{298} = -(605.8 \pm 8.4)$ kJ mol$^{-1}$, which refers to reaction $CH_2Cl_2$ (l)+$O_2$ (g)→$CO_2$ (g)+2HCl (aq:600). Results obtained with static bomb calorimeter. Auxiliary quantities as in Comment 1. Data yield $\Delta_f H^o[CH_2Cl_2\ (l),\ 298.15\ K] = -(120.8 \pm 0.8)$ kJ mol$^{-1}$.

chlorinated compounds with this technique. Thus we recommend $\Delta_f H^o[CH_2Cl_2(l),\ 298.15\ K] = -(124.1 \pm 2.5)$ kJ mol$^{-1}$, and, in conjunction with the enthalpy of vaporization, $\Delta_f H^o[CH_2Cl_2(g),\ 298.15\ K] = -(95.1 \pm 2.5)$ kJ mol$^{-1}$.

### 3.4. Trichloromethane

*Enthalpy of Vaporization:* The calorimetric measurements of Fletcher and Tyrer [1913FT] between 294 and 328 K result in $\Delta_{vap}H(298.15\ K) = 31.27$ kJ mol$^{-1}$. Mathews [1926M] reported $\Delta_{vap}H(334.4\ K) = 29.37$ kJ mol$^{-1}$, while the calorimetric measurements of Majer *et al.* [1980MSS] between 298 and 358 K result in $\Delta_{vap}H(298.15\ K) = 31.14 \pm 0.08$ kJ mol$^{-1}$. The temperature dependence of the $\Delta_{vap}H$ data of [1980MSS] can be used to derive $\Delta_{vap}C_p = -53.1$ J mol$^{-1}$ K$^{-1}$. Using this value, the data of Mathews [1926M] extrapolate to $\Delta_{vap}H(298.15\ K) = 31.30$ kJ mol$^{-1}$. All the data are in very good agreement, but the measurements of Majer *et al.* [1980MSS] are weighted most heavily. We recommend $\Delta_{vap}H(298.15\ K) = 31.20 \pm 0.08$ kJ mol$^{-1}$. A correction of 0.12 kJ mol$^{-1}$ due to nonideality of the gas was taken from the work of Majer and Svoboda [1985MS] (our calculation is the same) and $\Delta_{vap}H^o(298.15\ K) = 31.32 \pm 0.08$ kJ mol$^{-1}$ is derived.

*Enthalpy of Formation.* Data are summarized in Table 5. Eftring [1938E] originally determined the enthalpy of combustion of trichloromethane. The results were corrected by Smith *et al.* [1953SBK] and reevaluated by Cox and Pilcher [1970CP]. The data have subsequently been compiled by Pedley *et al.* [1986PNK] and lead to $\Delta_f H^o[CHCl_3(l),\ 298.15\ K] = -(133.3 \pm 8.4)$ kJ mol$^{-1}$. This is in excellent agreement with the 1969 combustion calorimetry value of Hu and Sinke [1969HS], $\Delta_f H^o[CHCl_3(l),\ 298.15\ K] = -(134.1 \pm 0.9)$ kJ mol$^{-1}$. This is somewhat surprising, given the general trends observed in Fig. 3. The enthalpy of chlorination of $CHCl_3$, reaction (2), has been measured by

$$CHCl_3(l) + Cl_2 \rightarrow CCl_4(l) + HCl(g). \tag{2}$$

Kirkbride [1956K] but the results of two experiments differ by 8.6 kJ mol$^{-1}$ and the statistical uncertainty is 19.3 kJ mol$^{-1}$ at the 90% level of confidence (see Comment 2 in Table 5). These data result in $\Delta_f H^o[CHCl_3(l),\ 298.15\ K] = \Delta_f H^o[CCl_4(l),\ 298.15\ K] + 0.7$ kJ mol$^{-1}$, and $\Delta_f H^o[CHCl_3(l),\ 298.15\ K] = -(127.4 \pm 19.5)$ kJ mol$^{-1}$.

A value relative to tetrachloromethane can also be derived from the combined data on bromination equilibria (3) and (4):

$$CHCl_3(g) + Br_2(g) \rightleftarrows CBrCl_3(g) + HBr(g) \tag{3}$$

$$CCl_4(g) + Br_2(g) \rightleftarrows CBrCl_3(g) + BrCl(g). \tag{4}$$

TABLE 5. Enthalpies of formation of trichloromethane derived from reported experimental data

| $\Delta_f H^o$(g), 298.15 K (kJ mol$^{-1}$) | Reported uncertainty (kJ mol$^{-1}$) | Temp. (K) | Method(s) | Reference | Comments |
|---|---|---|---|---|---|
| Experimental | | | | | |
| −102.9 | 0.8 | 298 | Combustion calorimetry of liquid | [1969HS] | 1 |
| −96.2 | N.R.[a]<br>(19.3) | 298 | Reaction enthalpy<br>$CHCl_3$ (l)+$Cl_2$→$CCl_4$ (l)+HCl (g) | [1956K] | 2, Present analysis uses updated $\Delta_f H^o[CCl_4\,(l)]$. |
| −105.0 | 1.4 | 559 | Equilibrium<br>$CHCl_3$ (g)+$Br_2$ (g)⇄$CBrCl_3$ (g)+HBr (g) | [1973MGB] | 3, 4, Third Law analysis, reevaluated in this work in conjunction with data of [1951SD]. |
| — | — | 420−455 | Equilibrium<br>$CCl_4$ (g)+$Br_2$ (g)⇄$CBrCl_3$ (g)+BrCl (g) | [1951SD] | 3, 4, Third Law analysis, reevaluated in this work. |
| −102.1 | 8.4 | 298 | Combustion calorimetry of liquid | [1938E]<br>[1953SBK]<br>[1970CP] | 5, Static Bomb. Data corrected by Smith *et al.* in 1953. Reanalyzed and auxiliary quantities updated by [1970CP]. |
| Reviews and Evaluations | | | | | |
| −103.18 | 1.3 | 298 | | [1998C] | 1968 evaluation. |
| −102.7 | 1.1 | 298 | | [1991GVA] | Evaluation date uncertain; same value as previous edition [1979G]. |
| −103.6 | 1.3 | 298 | | [1986PNK] | |
| −102.93 | N.R.[b] | 298 | | [1981C] | |
| −102.93 | 0.84 | 298 | | [1974CW] | |
| −102.9 | 8.8 | 298 | | [1970CP] | |
| −101.3 | N.R.[b] | 298 | | [1969SWS] | |

[a] Not reported, the parenthetical value is that derived from our statistical analysis at the 90% level of confidence and refers to the measured reaction enthalpy only.

[b] Not reported.

**Comments:**

1. $\Delta_c H^o_{298} = -(473.2\pm0.8)$ kJ mol$^{-1}$, refers to reaction $CHCl_3$ (l)+$H_2O$ (l)+0.5 $O_2$→$CO_2$ (g)+3HCl (aq:600), and yields $\Delta_f H^o[CHCl_3\,(l), 298.15\,K] = -(134.10\pm0.8)$ kJ mol$^{-1}$. Results obtained with rotating bomb calorimeter. The following auxiliary values were used: $\Delta_f H^o[CO_2\,(g), 298.15\,K] = -(393.51\pm0.13)$ kJ mol$^{-1}$, $\Delta_f H^o[H_2O\,(l), 298.15\,K] = -(285.830\pm0.040)$ kJ mol$^{-1}$, and $\Delta_f H^o[HCl(aq:600), 298.15\,K] = -(166.540\pm0.10)$ kJ mol$^{-1}$.
2. The two measurements of the reaction enthalpy were $\Delta_r H(298.15\,K) = -88.7$ kJ mol$^{-1}$ and $\Delta_r H(298.15\,K) = -97.3$ kJ mol$^{-1}$. At the 90% level of confidence we derive $\Delta_r H(298.15\,K) = -(93.0\pm19.3)$ kJ mol$^{-1}$. The agreement with other values in the Table is significantly better than the large uncertainty, but it suggests that this result should not be weighted very heavily. With $\Delta_f H^o[CCl_4\,(l), 298.15\,K] = -(128.1\pm2.5)$ kJ mol$^{-1}$ (see Sec. 3.5), and $\Delta_f H^o[HCl\,(g), 298.15\,K] = -(92.31\pm0.10)$ kJ mol$^{-1}$ [1989CWM] we find $\Delta_f H^o[CHCl_3\,(l), 298.15\,K] = -(127.41\pm19.5)$ kJ mol$^{-1}$.
3. $K(559\,K) = (0.0046\pm0.001)$ yields $\Delta_r G(559\,K) = 25.02(+3.2/-1.9)$ kJ mol$^{-1}$. This becomes $\Delta_r H(559\,K) = (35.1\pm1.3)$ kJ mol$^{-1}$ and $\Delta_r H(298.15\,K) = (35.23\pm1.3)$ kJ mol$^{-1}$ (see Discussion). The quoted value is obtained in conjunction with the data of [1951SD] on the equilibrium $CCl_4$ (g)+$Br_2$ (g) ⇄$CBrCl_3$ (g)+BrCl (g) (see Discussion and Comment 4), together with $\Delta_f H^o[CCl_4\,(g), 298.15\,K] = -(95.6\pm2.5)$ kJ mol$^{-1}$ (see Sec. 3.5), and $\Delta_f H^o[HBr\,(g), 298.15\,K] = -3(6.29\pm0.16)$ kJ mol$^{-1}$ [1989CWM], $\Delta_f H^o[BrCl\,(g), 298.15\,K] = -14.64$ kJ mol$^{-1}$ [1998C].
4. $K(442\,K) = (1.94\pm0.19)$ yields $\Delta_r G(442\,K) = (2.44\pm0.4)$ kJ mol$^{-1}$. This becomes $\Delta_r H(442\,K) = -(4.73\pm0.5)$ kJ mol$^{-1}$ and $\Delta_r H(298.15\,K) = -(6.34\pm0.5)$ kJ mol$^{-1}$ (see Discussion). The quoted value is obtained in conjunction with the data of [1951SD] on the equilibrium $CCl_4$ (g)+$Br_2$ (g)⇄$CBrCl_3$ (g)+BrCl (g) (see Discussion and Comment 3).
5. $\Delta_c H(298.15\,K) = -(474.0\pm8.4)$ kJ mol$^{-1}$. The original results of Eftring were corrected by Smith *et al.* [1953SBK] and reevaluated by Cox and Pilcher [1970CP]. The data have subsequently been compiled by Pedley *et al.* [1986PNK]. See Comment 1 for auxiliary thermodynamic values.

Sullivan and Davidson [1951SD] have studied the kinetics and equilibrium of Reaction (3) between 420 and 455 K by following the bromine concentration, while Reaction (4) has been studied by optical and gas chromatographic techniques by Mendenhall *et al.* [1973MGB] at 559 K. As pointed out by Mendenhall *et al.*, when the data on $K_3$ and $K_4$ are combined, the enthalpy of formation of $CBrCl_3$ (which is otherwise uncertain) cancels out and we obtain $\Delta_f H^o[CHCl_3(g)] - \Delta_f H^o[CCl_4(g),\ 298.15\,K] = \Delta_r H_2(298.15\,K) - \Delta_r H_3(298.15\,K) \quad - \Delta_f H^o[HBr(g),\ 298.15\,K] + \Delta_f H^o[BrCl(g),\ 298.15\,K]$. We have updated the original Third Law analysis of Mendenhall *et al.* using newer information on the properties of various compounds. We have taken thermodynamic data for $Br_2$, BrCl, and HBr from the NIST-JANAF Thermochemical Tables, [1998C], except for $\Delta_f H^o[HBr(g),\ 298.15\,K] = -(36.29\pm0.16)$ kJ mol$^{-1}$, which is from the 1989 CODATA evaluation [1989CWM]. The properties of $CHCl_3$, $CCl_4$, and $CBrCl_3$, were taken from the TRC Tables [1981C] or from Gurvich *et al.* [1991GVA]. Using $K_3(442\,K) = (1.94\pm0.19)$, we find $\Delta_r H_3(298.15\,K) = -(6.34\pm0.5)$ kJ mol$^{-1}$ from both the TRC and Gurvich data. For reaction (3), $K_4(559\,K) = (0.0046\pm0.001)$, [1973MGB], where the uncertainty is approximately $2\sigma$. This leads to $\Delta_r H_4(298.15\,K) = (34.86\pm1.3)$ kJ mol$^{-1}$ and $\Delta_r H_4(298.15\,K) = (35.56\pm1.3)$kJ mol$^{-1}$ from the data of TRC and Gurvich, respectively. These are only slightly different from the values of $\Delta_r H_3(298.15\,K) = -(5.90$

$\pm 0.4)$ kJ mol$^{-1}$ and $\Delta_r H_4(298.15\ \mathrm{K}) = (37.0 \pm 1.3)$ kJ mol$^{-1}$ originally derived by Mendenhall *et al.* Averaging the updated values, we find $\Delta_f H^o[\mathrm{CHCl_3(g)},\ 298.15\ \mathrm{K}] - \Delta_f H^o[\mathrm{CCl_4(g)},\ 298.15\ \mathrm{K}] = -(9.39 \pm 1.4)$ kJ mol$^{-1}$. This is in good agreement with the difference of $-(7.3 \pm 1.6)$ kJ mol$^{-1}$ derived from the combustion calorimetry data of Hu and Sinke [1969HS], but in poor agreement with the chlorination result of Kirkbride [1956K]. However, as noted above, the Kirkbride data have a very large statistical uncertainty and should not be weighted heavily.

*Recommendation*. The best data appear to be the combustion result of Hu and Sinke [1969HS] and the relative value from the bromination equilibria. The bromination equilibria suggest the difference in the enthalpies of formation of $\mathrm{CHCl_3}$ and $\mathrm{CCl_4}$ should be slightly larger than that given by the combustion calorimetry results of Hu and Sinke [1969HS]. However, since there is no reason to favor the calorimetry data on one or the other of these compounds, we have adopted the absolute values of Hu and Sinke [1969HS] for both compounds, although we have increased the uncertainties to reflect the slight disagreement.

### 3.5. Tetrachloromethane

*Enthalpy of Vaporization:* The enthalpy of vaporization has been measured several times and the results are in good agreement. Reported values are $\Delta_{\mathrm{vap}} H(298.15\ \mathrm{K}) = (32.43 \pm 0.08)$ kJ mol$^{-1}$, [1959HKM], $\Delta_{\mathrm{vap}} H(298.15\ \mathrm{K}) = (32.43 \pm 0.06)$ kJ mol$^{-1}$ [1966W], $\Delta_{\mathrm{vap}} H(298.15\ \mathrm{K}) = (32.54 \pm 0.1)$ kJ mol$^{-1}$ [1973K], and $\Delta_{\mathrm{vap}} H(298.15\ \mathrm{K}) = (32.40 \pm 0.08)$ kJ mol$^{-1}$ [1980MSS]. The selected value is $\Delta_{\mathrm{vap}} H(298.15\ \mathrm{K}) = 32.44 \pm 0.06$ kJ mol$^{-1}$. A correction of 0.11 kJ mol$^{-1}$ due to nonideality of the gas was taken from the work of Majer and Svoboda [1985MS] (our calculation gives 0.08 kJ mol$^{-1}$) and $\Delta_{\mathrm{vap}} H^o(298.15\ \mathrm{K}) = (32.55 \pm 0.07)$ kJ mol$^{-1}$ is derived. The heat capacity of vaporization is derived as $\Delta_{\mathrm{vap}} C_p = -50.3$ J mol$^{-1}$ K$^{-1}$ from the temperature dependence of the $\Delta_{\mathrm{vap}} H$ data of [1980MSS].

*Enthalpy of Formation*. Data are summarized in Table 6. Eftring determined the enthalpy of combustion of tetrachloromethane [1938E]. The results were corrected by Smith *et al.* [1953SBK] and later reevaluated by Cox and Pilcher [1970CP]. The data have subsequently been compiled by Pedley *et al.* [1986PNK], and lead to $\Delta_f H^o[\mathrm{CCl_4(l)},\ 298.15\ \mathrm{K}] = -(122.3 \pm 8.4)$ kJ mol$^{-1}$. This is significantly more positive than the 1969 combustion calorimetry value of Hu and Sinke [1969HS], $\Delta_f H^o[\mathrm{CCl_4(l)},\ 298.15\ \mathrm{K}] = -(128.11 \pm 0.6)$ kJ mol$^{-1}$. This is not surprising, given that for most other chlorinated compounds the values of Eftring appear to be systematically too positive (Fig. 3). The enthalpy of substitutive chlorination of $\mathrm{CHCl_3}$,

$$\mathrm{CHCl_3(l) + Cl_2 \rightarrow CCl_4(l) + HCl(g)} \qquad (5)$$

has been measured by Kirkbride [1956K], but the results of two experiments differ by 8.6 kJ mol$^{-1}$ and the statistical uncertainty is 19.3 kJ mol$^{-1}$ at the 90% level of confidence. These data lead to $\Delta_f H^o[\mathrm{CCl_4(l)},\ 298.15\ \mathrm{K}] = \Delta_f H^o[\mathrm{CHCl_3(l)},\ 298.15\ \mathrm{K}] - 0.7$ kJ mol$^{-1}$, or, in conjunction with our value for $\mathrm{CHCl_3}$, $\Delta_f H^o[\mathrm{CCl_4(l)},\ 298.15\ \mathrm{K}] = -(134.8 \pm 19.5)$ kJ mol$^{-1}$.

A value relative to tetrachloromethane can also be derived from the combined results on the bromination equilibria $\mathrm{CHCl_3(g) + Br_2(g) \rightleftarrows CBrCl_3(g) + HBr(g)}$ and $\mathrm{CCl_4(g) + Br_2(g) \rightleftarrows CBrCl_3(g) + BrCl(g)}$. The former reaction has been studied by Sullivan and Davidson [1951SD] between 420 and 445 K, while the latter equilibrium was measured by Mendenhall *et al.* [1973MGB] at 559 K. These data are discussed in the evaluation for trichloromethane and lead to $\Delta_f H^o[\mathrm{CHCl_3(g)},\ 298.15\ \mathrm{K}] - \Delta_f H^o[\mathrm{CCl_4(g)},\ 298.15\ \mathrm{K}] = -(9.39 \pm 1.4)$ kJ mol$^{-1}$. This is in reasonable agreement with the difference of $-(7.3 \pm 1.6)$ kJ mol$^{-1}$ derived from the combustion calorimetry data of Hu and Sinke. It is, however, in poor agreement with the chlorination result of Kirkbride, although this latter result has a large statistical uncertainty and we do not consider it to be very reliable. Several older determinations $\Delta_f H^o[\mathrm{CCl_4}]$ were discussed in the 1968 evaluation in the NIST-JANAF Thermochemical Tables [1998C], but will not be re-examined as they do not appear to be of good reliability.

*Recommendation*. We believe the best data are the combustion result of Hu and Sinke [1969HS] and the relative value from the bromination equilibria. Although these latter data suggest the difference in the relative enthalpies of formation of $\mathrm{CHCl_3}$ and $\mathrm{CCl_4}$ should be slightly larger than determined by combustion calorimetry, there are no definitive reasons to favor the calorimetry data on one or the other of these compounds. We have therefore adopted the absolute values of Hu and Sinke for both compounds, and recommend $\Delta_f H^o[\mathrm{CCl_4(g)},\ 298.15\ \mathrm{K}] = -(95.6 \pm 2.5)$ kJ mol$^{-1}$. We have, however, increased the uncertainty to reflect the slight disagreement.

## 4. Evaluated Enthalpies of Formation and Vaporization of the (Chloro)ethynes

### 4.1. Ethyne

*Enthalpy of Formation. Recommendation*. Recommended values of the enthalpy of formation of ethyne from several commonly cited sources are listed in Table 1. There are no recent experimental determinations of its value and the previous evaluations are in good agreement. The $\Delta_f H^o[\mathrm{C_2H_2(g)},\ 298.15\ \mathrm{K}]$ values of Table 1 range from 226.7 to 228.2 kJ mol$^{-1}$. The evaluation of Gurvich *et al.* [1991GVA] contains good discussion of the data, although the actual date of the evaluation is uncertain (the selected value is the same as in the previous edition, [1979G]). Their recommended value is based on calorimetric measurements of the enthalpy of the hydrogenation reaction $\mathrm{C_2H_2 + 2H_2 \leftrightarrows C_2H_6}$ by Conn *et al.* [1939CKS], together with the Gurvich *et al.* [1991GVA] selected value of $\Delta_f H^o[\mathrm{C_2H_6(g)},\ 298.15\ \mathrm{K}]$ (see Sec. 6.1). After review, we have accepted their evaluation, $\Delta_f H^o[\mathrm{C_2H_2(g)},\ 298.15\ \mathrm{K}] = (227.4 \pm 0.8)$ kJ mol$^{-1}$.

TABLE 6. Enthalpies of formation of tetrachloromethane derived from reported experimental data

| $\Delta_f H^o(g)$, 298.15 K (kJ mol$^{-1}$) | Reported uncertainty (kJ mol$^{-1}$) | Temp. (K) | Method(s) | Reference | Comments |
|---|---|---|---|---|---|
| Experimental | | | | | |
| −95.6 | 0.6 | 298 | Combustion calorimetry of liquid | [1969HS] | 1 |
| −102.2 | N.R.[a]<br>(19.3) | 298 | Enthalpy of substitutive chlorination<br>$CHCl_3$ (l)+$Cl_2$→$CCl_4$ (l)+HCl (g) | [1956K] | 2, Present analysis uses updated $\Delta_f H^o[CHCl_3 (l)]$. |
| −93.5 | 1.4 | 559 | Equilibrium<br>$CHCl_3$ (g)+$Br_2$ (g)$\rightleftarrows$$CBrCl_3$ (g)+HBr (g) | [1973MGB] | 3, Third Law analysis, reevaluated in conjunction with data of [1951SD]. |
| — | — | 420–455 | Equilibrium<br>$CCl_4$ (g)+$Br_2$ (g)$\rightleftarrows$$CBrCl_3$ (g)+BrCl (g) | [1951SD] | 4, Third Law analysis, reevaluated in this work. See above. |
| −89.8 | N.R.[b]<br>(8.4) | 298 | Combustion calorimetry of liquid | [1938E]<br>[1953SBK]<br>[1970CP] | 5, Static Bomb. Data corrected by [1953SBK]. Reanalyzed and auxiliary quantities updated by [1970CP]. |
| −107.3 | 1.5 | 298 | Reaction Enthalpy<br>$CCl_4$ (l)+$2H_2$→C(s)+4HCl (g) | [1926BGb]<br>[1998C] | 6, As cited and reanalyzed in 1968 JANAF evaluation [1998C]. |
| Reviews and Evaluations | | | | | |
| −95.98 | 2.1 | 298 | | [1998C] | 1968 evaluation. |
| −95.60 | 1.0 | 298 | | [1991GVA] | Evaluation date uncertain; same value as previous edition [1979G]. |
| −95.60 | 1.0 | 298 | | [1986PNK] | |
| −95.81 | N.R.[a] | 298 | | [1981C] | |
| −98.81 | 0.59 | 298 | | [1974RCW] | |
| −105.4 | 6.3 | 298 | | [1970CP] | |
| −100.4 | N.R.[a] | 298 | | [1969SWS] | |

[a] Not reported.

[b] Not reported. The parenthetical value is that derived from our statistical analysis at the 90% level of confidence and refers to the measured reaction enthalpy only.

**Comments:**

1. $\Delta_c H^o_{298} = -(359.9 \pm 0.6)$ kJ mol$^{-1}$, refers to reaction $CCl_4$ (l)+$2H_2O$ (l)→$CO_2$ (g)+4HCl (aq:600). Results obtained with rotating bomb calorimeter. Auxiliary quantities: $\Delta_f H^o[CO_2\ (g), 298.15\ K] = -(393.51 \pm 0.13)$ kJ mol$^{-1}$, $\Delta_f H^o[H_2O\ (l), 298.15\ K] = -(285.830 \pm 0.040)$ kJ mol$^{-1}$, $\Delta_f H^o[HCl(aq{:}600), 298.15\ K] = -(166.540 \pm 0.10)$ kJ mol$^{-1}$. Data yield $\Delta_f H^o[CCl_4\ (l), 298.15\ K] = -(128.11 \pm 0.6)$ kJ mol$^{-1}$.
2. The two measurements of the reaction enthalpy were $\Delta_r H(298.15\ K) = -88.7$ kJ mol$^{-1}$ and $\Delta_r H(298.15\ K) = -97.3$ kJ mol$^{-1}$. At the 90% level of confidence we derive $\Delta_r H(298.15\ K) = -(93.0 \pm 19.3)$ kJ mol$^{-1}$. The agreement with other values in the Table is significantly better than the large uncertainty, but it suggests that this result should not be weighted very heavily. With $\Delta_f H^o[CHCl_3(l),\ 298.15\ K] = -(134.1 \pm 2.5)$ kJ mol$^{-1}$ (see Sec. 3.4), and $\Delta_f H^o[HCl(g),\ 298.15\ K] = -(92.31 \pm 0.10)$ kJ mol$^{-1}$ [1989CWM] we find $\Delta_f H^o[CCl_4(l),\ 298.15\ K] = -(134.79 \pm 19.5)$ kJ mol$^{-1}$.
3. $K(559\ K) = (0.0046 \pm 0.001)$ yields $\Delta_r G(559\ K) = (25.02 \pm 1.26)$ kJ mol$^{-1}$. This becomes $\Delta_r H(559\ K) = (35.1 \pm 1.4)$ kJ mol$^{-1}$ and $\Delta_r H(298.15\ K) = (35.23 \pm 1.6)$ kJ mol$^{-1}$ (see Sec. 3.4). The quoted value is obtained in conjunction with the data of [1951SD] on the equilibrium $CCl_4(g)+Br_2(g) \rightleftarrows CBrCl_3(g)+BrCl(g)$ (see Comment 4), together with $\Delta_f H^o[CHCl_3(g),\ 298.15\ K] = -(102.6 \pm 2.5)$ kJ mol$^{-1}$ (see Sec. 3.4), and $\Delta_f H^o[HBr(g),\ 298.15\ K] = -(36.29 \pm 0.16)$ kJ mol$^{-1}$ [1989CWM], $\Delta_f H^o[BrCl(g),\ 298.15\ K] = -14.64$ kJ mol$^{-1}$ [1998C]. The data lead to $\Delta_f H^o[CHCl_3(g),\ 298.15\ K] - \Delta_f H^o[CCl_4(g),\ 298.15\ K] = -(9.39 \pm 1.4)$ kJ mol$^{-1}$.
4. $K(552\ K) = (1.94 \pm 0.19)$ yields $\Delta_r G(442\ K) = (2.44 \pm 0.4)$ kJ mol$^{-1}$. This becomes $\Delta_r H(442\ K) = -(4.73 \pm 0.5)$ kJ mol$^{-1}$ and $\Delta_r H(298.15\ K) = -(6.34 \pm 0.5)$ kJ mol$^{-1}$ (see Sec. 3.4). The quoted value is obtained in conjunction with the data of [1951SD] on the equilibrium $CCl_4(g)+Br_2(g) \rightleftarrows CBrCl_3(g)+BrCl(g)$ (see Comment 3).
5. $\Delta_c H^o_{298} = -(365.7 \pm 8.4)$ kJ mol$^{-1}$. The original results of Eftring [1938E] were corrected by Smith *et al.* [1953SBK] and reevaluated by Cox and Pilcher [1970CP]. The data have subsequently been complied by Pedley *et al.* [1986PNK]. See Comment 1 for auxiliary thermodynamic values. The data lead to $\Delta_f H^o[CCl_4(l),\ 298.15\ K] = -(122.3 \pm 12.5)$ kJ mol$^{-1}$. For most chlorinated compounds we believe the values of Eftring to be systematically too positive.
6. $\Delta_r H(298.15\ K) = -(261.8 \pm 2.5)$ J mol$^{-1}$. As discussed in the 1968 JANAF evaluation for $CCl_4$ [1998C], the value may need a positive correction of between 8 and 17 kJ mol$^{-1}$ because the carbon formed may not all be in its reference state. This would bring the result more in line with the recommended value.

## 4.2. Chloroethyne

*Enthalpy of Vaporization*. Chloroethyne is a gas at standard temperature and pressure. The vapor pressure of chloroethyne has been measured by Bashford *et al.* [1938BEB] between 205.2 and 237.2 K. The normal boiling point was given by these authors as $T_{bp} = (243.55 \pm 0.1)$K. They reported $\Delta_{vap}H(243.6\ K) = 22.5$ kJ mol$^{-1}$, although details of the calculations were not given. Using the Clapyron equation and a fit to vapor pressure data in the upper half of their temperature range (only part of the data were used since, as expected, slight curvature in the plot is evident) we derive the slightly different value $\Delta_{vap}H(231.2\ K) = 21.4$ kJ mol$^{-1}$. This was extrapolated to $\Delta_{vap}H(298.15\ K) = 18.9$ kJ mol$^{-1}$, using an estimated value $\Delta_{vap}C_p(C_2HCl) = -(37 \pm 8)$ J mol$^{-1}$ K$^{-1}$. We have also estimated the enthalpy of vaporization based on a correlation of $\Delta_{vap}H(298.15\ K)$ with the normal boiling point for all other chlorinated compounds in this review (*vide infra*, see Fig. 9 of Sec. 6.9). This method gives $\Delta_{\mathrm{vap}}H(298.15\,\mathrm{K})=(17.8\pm 1.5)\,\mathrm{kJ\,mol^{-1}}$, where the uncertainty is based on the fit to the known values. Finally, for chlorinated ethenes and ethanes with experimentally known enthalpies of vaporization, we have found that $\Delta_{\mathrm{vap}}H/T_{\mathrm{b}}=(88.0\pm 3.0)\,\mathrm{J\,mol^{-1}\,K^{-1}}$, in the range of typical statements of Trouton's Rule [1978A]. If this is assumed to hold for $C_2HCl$, we derive $\Delta_{\mathrm{vap}}H(243.6\,\mathrm{K})=(21.4\pm 0.7)\,\mathrm{kJ\,mol^{-1}}$ and $\Delta_{\mathrm{vap}}H(298.15\,\mathrm{K})=(19.4\pm 1.0)\,\mathrm{kJ\,mol^{-1}}$. The estimated values are in good agreement with that derived from the data of Bashford *et al.* We favor the experimentally derived value and recommend $\Delta_{\mathrm{vap}}H(298.15\,\mathrm{K})=(18.9\pm 1.0)\,\mathrm{kJ\,mol^{-1}}$. The correction for nonideality is estimated based on the correlation with boiling point given in Fig. 1 and is 0.99 $\mathrm{kJ\,mol^{-1}}$. This leads to $\Delta_{\mathrm{vap}}H^{\mathrm{o}}(298.15\,\mathrm{K})=(19.9\pm 1.0)\,\mathrm{kJ\,mol^{-1}}$.

*Enthalpy of Formation*. Data are summarized in Table 7. No experimental information on the enthalpy of formation of chloroethyne appear to exist. Qualitatively, haloethynes are known to be unstable [1967STS] and chloroethyne ignites and may explode upon contact with air [1938BEB]. Enthalpy of formation values have previously been estimated by assuming equal enthalpies of chlorination for ethyne and chloroethyne [1998C], or assuming equality of average bond energies in $C_2H_2$, $C_2HCl$, and $C_2Cl_2$ ([1991GVA], where the values for $C_2Cl_2$ were themselves estimates, see Sec. 4.2). As detailed in Table 7, we have derived values using enthalpies of chlorination, hydrochlorination, and hydrogenation, while using updated thermodynamic values. The $\Delta_{\mathrm{f}}H^{\mathrm{o}}(298.15\,\mathrm{K})$ values so derived range from 197 kJ to 212 $\mathrm{kJ\,mol^{-1}}$. For the chloro*ethenes*, enthalpies of chlorination and hydrochlorination vary considerably, while enthalpies of hydrogenation are remarkably constant (see Fig. 4). On this basis, the empirical estimate based on the enthalpy of hydrogenation might seem to be the best choice. However, it is not obvious that the correlation should hold equally well for the ethenes and ethynes. Indeed, to the extent that steric and electronic factors are responsible, it would seem likely that these would vary with changes in the hybridization in the molecule. Thus one might expect high level calculations to be more reliable.

Calculated values using AM1 and PM3 [1998ZBL], and BAC-MP4 [1993M] are available. The values from AM1 and PM3 are close to the value based on the enthalpy of hydrogenation. The agreement is apparently coincidental, since AM1 and PM3 predictions for related species were often in marginal agreement with known values. Zhu *et al.* [1998ZBL] have also calculated the value $\Delta_{\mathrm{f}}H^{\mathrm{o}}[\mathrm{HC{\equiv}CCl(g)},\ 298.15\,\mathrm{K}]=215\,\mathrm{kJ\,mol^{-1}}$ using a modified group additivity scheme. This method apparently uses the 1968 estimates of $HC{\equiv}CCl$ and $C_2Cl_2$ found in the NIST-JANAF Thermochemical Tables (see Table 7) as reference values, however, and is therefore only a fit to those estimates.

In an attempt to decide between the available values, we have carried out a series of *ab initio* calculations, using MP2, MP4, QCI, and DFT methods. The isodesmic reaction $C_2H_2+C_2H_3Cl\rightarrow C_2HCl+C_2H_4$ was then used to obtain $\Delta_{\mathrm{f}}H^{\mathrm{o}}[\mathrm{HC{\equiv}CCl(g)},\ 298.15\,\mathrm{K}]$. As shown in Table 7, these methods lead to $\Delta_{\mathrm{f}}H^{\mathrm{o}}(298.15\,\mathrm{K})$ values 25 kJ–30 $\mathrm{kJ\,mol^{-1}}$ more positive than the empirical estimate based on the enthalpy of hydrogenation. The calculated value was not strongly dependent on the size of the basis sets or type of methodology used. Parthiban *et al.* [2001PML] have recently obtained a similar value from atomization energies obtained using the W1 and W2 methodologies.

*Recommendation*. The large difference between the empirical and calculated enthalpies of formation is somewhat disturbing. It is possible that the molecule could have some low-lying electronic states and this could affect the calculations. In this respect, a calculation involving a multiconfiguration methodology such as CASSPT2 would be desirable. Nonetheless the excellent agreement between the parameterized DFT calculations and standard *ab initio* methodologies involving approximate wave functions is suggestive that there are no major errors. Further, the empirical methods are quite tenuous and cannot be checked against any experimental value for a chloroalkyne. The larger enthalpy of formation predicted by the calculations also seems completely consistent with the high reactivity [1967STS] of chloroethyne. We recommend $\Delta_{\mathrm{f}}H^{\mathrm{o}}[\mathrm{HC{\equiv}CCl(g)},\ 298.15\,\mathrm{K}]=(226.4\pm 10)\ \mathrm{kJ\,mol^{-1}}$, based on the values derived from isodesmic reactions (see Table 7). This is significantly higher than most previous estimates but we feel is better supported by the available data. The stated uncertainty is $2\sigma$ and is estimated based on the spread in our calculated values over the range of theories used. It includes uncertainty in the zero point energy. There remains some possibility that low-lying electronic states or other factors could have perturbed the calculations. An experimental check would therefore be desirable.

### 4.3. Dichloroethyne

*Enthalpy of Vaporization*. No experimental data appear to exist and we are unaware of any other attempt to estimate this quantity. We have estimated the value based on a correlation of $\Delta_{\mathrm{vap}}H(298.15\,\mathrm{K})$ with the normal boiling point, $T_{\mathrm{b}}$, for all other chlorinated compounds in this review (*vide infra*, see Fig. 9 of Section 6.9). With $T_{\mathrm{b}}=306\,\mathrm{K}$ [1967STS], [1930SKH], we derive $\Delta_{\mathrm{vap}}H(298.15\,\mathrm{K})=(27.2\pm 1.5)\ \mathrm{kJ\,mol^{-1}}$, where the uncertainty is based on the fit to known values. As an alternative methodology, our comparisons show that for chlorinated ethenes and ethanes with experimentally known enthalpies of vaporization, $\Delta_{\mathrm{vap}}H/T_{\mathrm{b}}=(88.0\pm 3.0)\ \mathrm{J\,mol^{-1}\,K^{-1}}$, in the range of typical statements of Trouton's Rule [1978A]. If this is assumed to hold for $C_2Cl_2$, we derive $\Delta_{\mathrm{vap}}H(306\,\mathrm{K})=(26.9\pm 0.9)\ \mathrm{kJ\,mol^{-1}}$ and $\Delta_{\mathrm{vap}}H(298.15\,\mathrm{K})=(27.2\pm 0.9)\ \mathrm{kJ\,mol^{-1}}$. Since our correlation is based on alkanes and alkenes we have increased the uncertainty and recommend $\Delta_{\mathrm{vap}}H(298.15\,\mathrm{K})=(27.2\pm 1.2)\ \mathrm{kJ\,mol^{-1}}$. The correction for nonideality is estimated based on the correlation with the normal boiling point given in Fig. 1 and is 0.24 $\mathrm{kJ\,mol^{-1}}$ and we obtain $\Delta_{\mathrm{vap}}H^{\mathrm{o}}(298.15\,\mathrm{K})=(27.4\pm 1.2)\ \mathrm{kJ\,mol^{-1}}$.

TABLE 7. Suggested enthalpies of formation of chloroethyne

| $\Delta_f H^o(g)$, 298.15 K (kJ mol$^{-1}$) | Reported uncertainty (kJ mol$^{-1}$) | Temp. (K) | Method(s) | Reference | Comments |
|---|---|---|---|---|---|
| Values from Calculations | | | | | |
| 225.9 | 10[a] | 298 | QCISD(T)/6-311+G(3df,p) | [2001BAM] | 1, Derived from isodesmic reaction. |
| 227.1 | 10[a] | 298 | QCISD(T)/6-311+G(2df,p) | [2001BAM] | 1, Derived from isodesmic reaction. |
| 226.4 | 10[a] | 298 | B3LYP/aug-cc-pVTZ | [2001BAM] | 1, Derived from isodesmic reaction. |
| 228.9 | 10[a] | 298 | B3LYP/aug-cc-pVDZ | [2001BAM] | 1, Derived from isodesmic reaction. |
| 224.7 | 10[a] | 298 | MP2/6-311+G(3df,2p) | [2001BAM] | 1, Derived from isodesmic reaction. |
| 229.4 | N.R.[b] | 298 | W2 | [2001PML] | Derived from the atomization energy. |
| 199.9 | N.R.[b] | 298 | AM1 | [1998ZBL] | |
| 194.8 | N.R.[b] | 298 | PM3 | [1998ZBL] | |
| 230.5 | N.R.[b] | 298 | BAC-MP4 | [1993M] | |
| Reviews and Evaluations | | | | | |
| 212 | [c] | 298 | Estimated from $\Delta_r H$(chlorination). | This work | 2 |
| 204 | [c] | 298 | Estimated from $\Delta_r H$(hydrochlorination). | This work | 3 |
| 197 | [c] | 298 | Estimated from $\Delta_r H$(hydrogenation). | This work | 4 |
| 213.8 | 42 | 298 | Estimated from $\Delta_r H$(chlorination). | [1998C] | 5, 1968 evaluation. |
| 212 | 30 | 298 | Estimated from $\Delta_r H$(chlorination). | [1991GVA] | 6, Evaluation date uncertain; same value as previous edition [1979G]. |

[a] No estimate was made for the individual calculations. Based on the global consistency of our calculations, the overall uncertainty was estimated as ±14 kJ mol$^{-1}$ (see text).

[b] Not reported.

[c] Not estimated. The basis for this estimate is considered unreliable (see text).

**Comments:**

1. Derived from the enthalpy change calculated for the isodesmic reaction $C_2H_2+C_2H_3Cl \rightarrow C_2H_4+C_2HCl$. Zero point energies have neen added and the values adjusted to 298.15 K. Auxiliary thermodynamic quantities: $\Delta_f H^o[C_2H_2(g),\ 298.15\ K]=(227.4\pm 0.8)$ kJ mol$^{-1}$, $\Delta_f H^o[C_2H_3Cl(g),\ 298.15\ K]=(22.0\pm 3.0)$ kJ mol$^{-1}$, and $\Delta_f H^o[C_2H_4(g),\ 298.15\ K]=-(52.4\pm 0.5)$ kJ mol$^{-1}$, (see Secs. 4.1, 5.1, and 5.2).
2. Estimate assumes enthalpy increments for reactions $C_2H_2(g)+Cl_2(g)\rightarrow E/Z\text{-}CHCl{=}CHCl(g)$ and HC CCl(g)$+Cl_2(g)\rightarrow C_2HCl_3(g)$ are the same. This assumption is tenuous (see Fig. 4) and our *ab initio* calculations suggest it to be incorrect (see text). Calculated value uses $\Delta_r H(298.15\ K)$ $\Delta_r H(298.15\ K)=-229.2$ kJ mol$^{-1}$. Auxiliary thermodynamic quantities: $\Delta_f H^o[C_2H_2(g),\ 298.15\ K]=(227.4\pm 0.8)$ kJ mol$^{-1}$, $\Delta_f H^o[E\text{-}C_2H_2Cl_2(g),\ 298.15\ K]=-(0.5\pm 2.0)$ kJ mol$^{-1}$, $\Delta_f H^o[Z\text{-}C_2H_2Cl_2(g),\ 298.15\ K]=-(3.0\pm 2.0)$ kJ mol$^{-1}$, and $\Delta_f H^o[C_2HCl_3(g),\ 298.15\ K]=-(17.5\pm 3.0)$ kJ mol$^{-1}$, (see Secs. 4.1, 5.4, 5.5, and 5.6).
3. Estimate assumes $\Delta_r H(298.15\ K)$ for the reaction $C_2H_2(g)+HCl(g)\rightarrow C_2H_3Cl(g)$ is the same as for $HC{\equiv}CCl(g)+HCl(g)\rightarrow C_2H_2Cl_2$. This assumption is tenuous (see Fig. 4) and our *ab initio* calculations suggest it to be incorrect (see text). Calculated value uses $\Delta_r H(298.15\ K)=-(113.1\pm 30)$ kJ mol$^{-1}$. $\Delta_f H^o[HCl(g),\ 298.15\ K]=(92.31\pm 0.10)$ kJ mol$^{-1}$ with other auxiliary thermodynamic quantities as in Comment 1.
4. Estimate assumes enthalpy increment for reaction $C_2H_2(g)+H_2(g)\rightarrow C_2H_4(g)$ is the same as for $HC{\equiv}CCl(g)+H_2(g)\rightarrow C_2H_3Cl(g)$. This assumption is tenuous (see Fig. 4) and our *ab initio* calculations suggest it to be incorrect (see text). Calculated value uses $\Delta_r H(298.15\ K)=-175.0$ kJ mol$^{-1}$. $\Delta_f H^o[C_2H_3Cl(g),\ 298.15\ K]=(22.0\pm 3.0)$ kJ mol$^{-1}$ (see Sec. 5.2) with other auxiliary thermodynamic quantities as in Comment 1.
5. Estimate uses assumption of Comment 2, but used older thermodynamic data. Reported value derived with $\Delta_r H(298.15\ K)=(221.8\pm 42)$ kJ mol$^{-1}$.
6. Estimated by assuming equality of average bond energies in $C_2H_2$, $C_2HCl$, and $C_2Cl_2$.

*Enthalpy of Formation*. Data are summarized in Table 8. As with chloroethyne, no experimental determination of the enthalpy of formation of dichloroethyne appears to exist. Dichloroethyne is unstable, igniting upon contact with air and exploding on heating [1967STS], [1930SKH]. Enthalpy of formation values have previously been estimated by assuming equal enthalpies of chlorination for ethyne and dichloroethyne [1998C], [1991GVA]. Table 8 details empirical values that can be derived using enthalpies of chlorination, hydrochlorination, and hydrogenation, while using updated thermodynamic values. The $\Delta_f H^o(298.15\ K)$ values so derived range from 173 to 208 kJ mol$^{-1}$. As we argued in the evaluation for chloroethyne, on the surface the best of these empirical values would seem to be that derived based on the enthalpy of hydrogenation, since this quantity varies little in the chloro*ethene* series (see Fig. 4). We would contend, however, that steric and electronic factors are expected to be important and quite different in chloroethanes, chloroethenes, and chloroethynes, and that such correlations are therefore problematic. As with chloroethyne, calculated values (Table 8) are very different from the empirical estimates, with *ab initio* results indicating an enthalpy of formation some 50 kJ mol$^{-1}$ more positive than the value based on the enthalpy of hydrogenation. The calculated value was not strongly dependent on the size of the basis sets or type of methodology used.

*Recommendation*. The difference between the ‘‘best’’ empirical and calculated enthalpies of formation is 50 kJ mol$^{-1}$, approximately twice as large as that found for chloroethyne. We again favor the calculated values, largely because the

TABLE 8. Suggested enthalpies of formation of dichloroethyne

| $\Delta_f H^o$(g), 298.15 K (kJ mol$^{-1}$) | Reported uncertainty (kJ mol$^{-1}$) | Temp. (K) | Methods | Reference | Comments |
|---|---|---|---|---|---|
| Values from Calculations | | | | | |
| 225.8 | 14[a] | 298 | QCISD(T)/6-311+G(3df,p) | [2001BAM] | 1, Derived from isodesmic reaction. |
| 227.8 | 14[a] | 298 | QCISD(T)/6-311+G(2df,p) | [2001BAM] | 1, Derived from isodesmic reaction. |
| 226.6 | 14[a] | 298 | B3LYP/aug-cc-pVTZ | [2001BAM] | 1, Derived from isodesmic reaction. |
| 230.0 | 14[a] | 298 | B3LYP/aug-cc-pVDZ | [2001BAM] | 1, Derived from isodesmic reaction. |
| 224.3 | 14[a] | 298 | MP2/6-311+G(3df,2p) | [2001BAM] | 1, Derived from isodesmic reaction. |
| 235.2 | N.R.[b] | 298 | W2 | [2001PML] | Derived from the atomization energy. |
| 174.0 | N.R.[b] | 298 | AM1 | [1998ZBL] | Calculated value. |
| 175.8 | N.R.[b] | 298 | PM3 | [1998ZBL] | Calculated value. |
| 235.1 | N.R.[b] | 298 | BAC-MP4 | [1993M] | Calculated value. |
| Reviews and Evaluations | | | | | |
| 205 | [c] | 298 | Estimated from $\Delta_r H$(chlorination). | This work | 2 |
| 187 | [c] | 298 | Estimated from $\Delta_r H$(hydrochlorination). | This work | 3 |
| 173 | [c] | 298 | Estimated from $\Delta_r H$(hydrogenation). | This work | 4 |
| 209.6 | 42 | 298 | Estimated from $\Delta_r H$(chlorination). | [1998C] | 5, 1968 evaluation. |
| 200 | 40 | 298 | Estimated from $\Delta_r H$(chlorination). | [1991GVA] | 6, Evaluation date uncertain; same value as previous edition [1979G]. |

[a] No estimate was made for the individual calculations. Based on the global consistency of our calculations, the overal uncertainty was estimated as ±14 kJ mol$^{-1}$ (see text).

[b] Not reported.

[c] Not estimated. The basis for this estimate is considered unreliable (see text).

**Comments:**

1. Derived from the enthalpy change calculated for the isodesmic reaction $C_2H_2 + Z$-1,2-$C_2H_2Cl_2 \rightarrow C_2H_4 + C_2Cl_2$. Zero point energies have been added and the values adjusted to 298.15 K. Auxiliary thermodynamic quantities: $\Delta_f H^o[C_2H_2(g), 298.15\ K] = (227.4 \pm 0.8)$ kJ mol$^{-1}$, $\Delta_f H^o[Z\text{-}C_2H_2Cl_2(g), 298.15\ K] = -(3.0 \pm 2.0)$ kJ mol$^{-1}$, and $\Delta_f H^o[C_2H_4(g), 298.15\ K] = -(52.4 \pm 0.5)$ kJ mol$^{-1}$ (see Secs. 4.1, 5.1, and 5.4).
2. Estimate assumes enthalpy increments for reaction $C_2H_2(g) + Cl_2(g) \rightarrow E/Z\text{-CHCl}{=}\text{CHCl}(g)$ is the same as for $C_2Cl_2(g) + Cl_2(g) \rightarrow C_2Cl_4(g)$. This assumption is tenuous (see Fig. 4) and our *ab initio* calculations suggest it to be incorrect (see text). Calculated value uses $\Delta_f H(298.15\ K) = -(229.2 \pm 50)$ kJ mol$^{-1}$. Auxiliary thermodynamic quantities: $\Delta_f H^o[C_2H_2(g), 298.15\ K] = (227.4 \pm 0.8)$ kJ mol$^{-1}$, $\Delta_f H^o[E\text{-}C_2H_2Cl_2(g), 298.15\ K] = -(0.5$ ΔfHo[E-C2H2Cl2(g), 298.15 K]$=-(0.5 \pm 2.0)$ kJ mol$^{-1}$, $\Delta_f H^o[Z\text{-}C_2H_2Cl_2(g), 298.15\ K] = -(3.0 \pm 2.0)$ kJ mol$^{-1}$, and $\Delta_r H^o[C_2Cl_4(g), 298.15\ K] = -(24.2 \pm 4.0)$ kJ mol$^{-1}$, (see Secs. 4.1, 5.4, 5.5, and 5.7).
3. Estimate assumes enthalpy increment for reaction $C_2H_2(g) + HCl(g) \rightarrow C_2H_3Cl(g)$ is the same as for $C_2Cl_2(g) + HCl(g) \rightarrow C_2HCl_3(g)$. This assumption is tenuous (see Fig. 4) and our *ab initio* calculations suggest it to be incorrect (see text). Calculated value uses $\Delta_r H(298.15\ K) = -112.1$ kJ mol$^{-1}$. Auxiliary thermodynamic quantities: $\Delta_f H^o[C_2HCl_3(g), 298.15\ K] = -(17.5 \pm 3.0)$ kJ mol$^{-1}$, $\Delta_f H^o[HCl(g), 298.15\ K] = -(92.31 \pm 0.10)$ kJ mol$^{-1}$ (see Secs. 5.6, 1.4, and Comment 1).
4. Estimate assumes enthalpy increment for reaction $C_2H_2(g) + H_2(g) \rightarrow C_2H_4(g)$ is the same as for $C_2Cl_2(g) + H_2(g) \rightarrow$ 1,2-$C_2H_2Cl_2(g)$. This assumption is tenuous (see Fig. 4) and our *ab initio* calculations suggest it to be incorrect (see text). Calculated value uses $\Delta_r H(298.15\ K) = -175.0$ kJ mol$^{-1}$. See Comment 1 for auxiliary thermodynamic quantities.
5. Estimate uses assumption of Comment 2, but used older thermodynamic data. Reported value derived with $\Delta_r H(298.15\ K) = -(221.8 \pm 42)$ kJ mol$^{-1}$.
6. Estimated mainly based on enthalpy of chlorination as in Comment 2, but details not reported.

empirical method is tenuous and cannot be validated against an experimental value for any chloroalkyne. The calculations suggest that the molecule is destabilized by significant loss of electron density in the carbon–carbon bond (relative to that in acetylene). This seems to be consistent with the very high reactivity [1967STS] of $C_2Cl_2$. Since there is a small possibility that low-lying electronic states could affect the calculations, it would be desirable to carry out further checks using a multi-configuration methodology such as CASSPT2. Nonetheless the excellent agreement between the parameterized DFT calculations and standard *ab initio* methodologies involving approximate wave functions is suggestive that there are no major errors. We recommend $\Delta_f H^o[C_2Cl_2(g), 298.15\ K] = (226.6 \pm 14)$ kJ mol$^{-1}$, based on the values derived from isodesmic reactions (see Table 8). This is significantly higher than many previous estimates but we feel is better supported by the available data. The stated uncertainty is $2\sigma$ and is estimated based on the spread in our calculated values over the range of theories used. It includes uncertainty in the zero point energy.

## 5. Evaluated Enthalpies of Formation and Vaporization of the (Chloro)ethenes

### 5.1. Ethene

*Enthalpy of Formation. Recommendation*. Several previous evaluations of the enthalpy of formation of ethene are listed in Table 1. The range of $\Delta_f H^o[C_2H_4(g),\ 298.15\,K]$ values from these sources is 52.1–52.5 $kJ\,mol^{-1}$. There are no recent experimental determinations of its value and no serious controversy regarding the correct value. The evaluation of Gurvich *et al.* [1991GVA] contains good discussion of the data, although the actual date of the evaluation is uncertain (the selected value is the same as in the previous Russian edition of this work, [1979G]). Gurvich *et al.* based their value on the combined treatment of combustion calorimetric measurements of the enthalpies of formation $C_2H_4$ [1937RK] and $C_2H_6$ [1934R], [1972PP], together with calorimetric [1935KRR] and equilibrium [1942K] measurements of the enthalpy of the hydrogenation reaction $C_2H_4+H_2\rightarrow C_2H_6$. After review, we have accepted their evaluation, $\Delta_f H^o[C_2H_4(g),\ 298.15\,K]=(52.4\pm0.5)\ kJ\,mol^{-1}$.

## 5.2. Chloroethene

*Enthalpy of Vaporization*. Chloroethene is a gas at standard temperature and pressure. Dana *et al.* [1927DBJ] measured the vapor pressure of purified chloroethene (stated purity ⩾99.9%) between 244.4 and 333.5 K. They used both the Clapyron equation and the law of corresponding states to fit the data. These fits yield $\Delta_{vap}H(298.15\,K)=20.1\,kJ\,mol^{-1}$ and $\Delta_{vap}H(298.15\,K)=20.8\,kJ\,mol^{-1}$, respectively. As checks, for the other compounds in this review we were able to correlate $\Delta_{vap}H(298.15\,K)$ with the normal boiling point (*vide infra*, see Fig. 9 of Sec. 6.9) and also found $\Delta_{vap}H/T_b=(88.0\pm3.0)\ J\,mol^{-1}\,K^{-1}$. These respective estimations lead to $\Delta_{vap}H(298.15\,K)=(20.2\pm1.5)\ kJ\,mol^{-1}$ and $(21.3\pm1.0)\ kJ\,mol^{-1}$, in good agreement. The experimental values are favored and we recommend $\Delta_{vap}H(298.15\,K)=(20.4\pm1.0)\ kJ\,mol^{-1}$, where the uncertainty is estimated. The heat capacity of vaporization was derived as $\Delta_{vap}C_p=-35.8\,J\,mol^{-1}\,K^{-1}$ from the difference of the reported heat capacities of the gas [1991GVA] and liquid [1967LRB]. Using Eq. (1) and second virial coefficients taken from the DIPPR database [2001DIP] (datasheet revision data August, 1994), the correction for nonideality of the gas is calculated as 0.40 $kJ\,mol^{-1}$. However, as shown in Fig. 1, this value does not appear to be consistent with the other data in the series, although we were unable to ascertain the reason for the problem. In any case, the empirical fit given in Fig. 1 is used to derive $(H^o-H)_{298}=0.70\,kJ\,mol^{-1}$ and $\Delta_{vap}H^o(298.15\,K)=(21.1\pm1.0)\ kJ\,mol^{-1}$ is calculated.

*Enthalpy of Formation*. Data are summarized in Table 9. The enthalpy of formation of liquid or gaseous chloroethene has not been determined by combustion calorimetry. However, the value for the amorphous polymer of chloroethene obtained from static bomb calorimetry, $\Delta_f H^o[C_2H_3Cl(poly,s)]=-(94.1\pm1.3)\ kJ\,mol^{-1}$ [1958SS], may be combined with the calorimetrically determined enthalpy of polymerization of the liquid, $\Delta_{poly}H^o_{298}=-(95.8\pm1.3)\ kJ\,mol^{-1}$ ([1964J], see Comment 6 of Table 9) and $\Delta_{vap}H^o[C_2H_3Cl,\ 298.15\,K]=(21.1\pm1.0)\ kJ\,mol^{-1}$ to derive $\Delta_f H^o[C_2H_3Cl(g),\ 298.15\,K]=-(22.8\pm2.1)\ kJ\,mol^{-1}$. The quoted uncertainty refers to the combined precisions of the various measurements. Given the general historical accuracy of static bomb calorimetry on chlorinated compounds, and the fact that the enthalpy of polymerization value for the liquid was not rigorously corrected to 298.15 K, we think a more realistic uncertainty value is $\pm6\ kJ\,mol^{-1}$.

Very different values are derived from the enthalpies of hydrogenation of chloroethene [1956LEB] and hydrochlorination of ethyne [1962LGP] measured calorimetrically by Lacher and co-workers. These works yield $\Delta_f H^o[C_2H_3Cl(g),\ 298.15\,K]=-(37.6\pm1.7)\ kJ\,mol^{-1}$ and $\Delta_f H^o[C_2H_3Cl(g),\ 298.15\,K]=-(34.6\pm1.5)\ kJ\,mol^{-1}$, respectively (see Comments 4 and 5). From equilibrium studies of the chloropropenes, Alfassi *et al.* [1973AGB] derived a value for the Benson-style $C_d-(Cl)(H)$ group [1976B] and suggested that the above hydrogenation studies must be incorrect. The original Second Law analysis of Alfassi *et al.* has since been updated [1997CT] using a Third Law analysis and newer values for the enthalpy of formation of 3-chloropropene. The updated analysis (see Comment 9 of Table 9) of the Alfassi *et al.* data results in the group $C_d-(Cl)(H)=-5.48\,kJ\,mol^{-1}$ and $\Delta_f H^o[C_2H_3Cl(g),\ 298.15\,K]=20.75\,kJ\,mol^{-1}$. While this is not a direct experimental determination, experimental data on the chloroalkanes show that group additivity provides excellent results for *mono* chlorinated alkanes. We would be very surprised if it failed badly for mono chlorinated alkenes. We would estimate the accuracy of this procedure to be $\pm4.0\ kJ\,mol^{-1}$. In a related group additivity procedure, if one examines the experimental data on a series of monosubstituted ethenes and benzenes, one finds that the enthalpy increment is approximately constant [1986ML], [1986L], [1987GBT]. This has most recently been examined by Luo and Holmes [1992LH], who suggested $\Delta_f H^o[C_2H_3X(g),\ 298.15\,K]=\Delta_f H^o[C_6H_5X(g),\ 298.15\,K]-(29.7\pm6.3)\ kJ\,mol^{-1}$. Using $\Delta_f H^o[C_6H_5Cl(g),\ 298.15\,K]=(52.0\pm1.3)\ kJ\,mol^{-1}$ [1994P], one derives $\Delta_f H^o[C_2H_3Cl(g),\ 298.15\,K]=(22.3\pm6.4)\ kJ\,mol^{-1}$. This methodology is somewhat less direct than the above discussed approach of Alfassi *et al.*, but nonetheless provides independent confirmation of the quantity.

The enthalpy of formation of chloroethene should also be consistent with the gas and liquid phase measurements of Levanova *et al.* [1976LTV] on the hydrochlorination equilibria $CH_2{=}CHCl+HCl\rightleftarrows CH_3CHCl_2$. These data are listed in Table 1 and discussed in our evaluation of 1,1-dichloroethane (Sec. 6.3). Although we think this data can better be used to derive an accurate value of $\Delta_f H^o[1,1\text{-}C_2H_4Cl_2]$, the spread in results for 1,1-dichloroethane is narrow enough that these data are only compatible with the lower range of values for chloroethene. Finally, high level *ab initio* calculations by Colegrove and Thompson [1997CT] utilizing a variety of isodesmic reactions also support the low value (see Table 9, Comment 8).

*Recommendation*. The results of Lacher and co-workers on the hydrochlorination of ethyne [1962LGP] and hydrogenation of chloroethene [1956LEB] entail an enthalpy of for-

TABLE 9. Enthalpies of formation of chloroethene derived from reported data

| $\Delta_f H^o$(g), 298.15 K (kJ mol$^{-1}$) | Reported uncertainty kJ mol$^{-1}$ | Temp. (K) | Method(s) | Ref/Year | Comments |
|---|---|---|---|---|---|
| Experimental | | | | | |
| 21.0 | 0.7[a]<br>(4.0) | 403–438 | Equilibrium of hydrochlorination<br>$1,1\text{-}C_2H_2Cl_2(g) \rightleftarrows CH_2{=}CHCl(g) + HCl(g)$ | [1976LTV] | 1, Second Law analysis, updated using our value for $\Delta_f H^o[1,1\text{-}C_2H_4Cl_2(g)]$. |
| 22.0 | 0.7[a]<br>(4.0) | 403–438 | Equilibrium of hydrochlorination<br>$1,1\text{-}C_2H_2Cl_2(g) \rightleftarrows CH_2{=}CHCl(g) + HCl(g)$ | [1976LTV] | 2, Third Law analysis, updated using our value for $\Delta_f H^o[1,1\text{-}C_2H_4Cl_2(g)]$. |
| 22.7 | 0.7[a]<br>(4.0) | 293–323 | Equilibrium of hydrochlorination<br>$CH_2{=}CHCl(g) + HCl(g) \rightleftarrows CH_3CHCl_2(l)$ | [1976LTV] | 3, Second Law analysis, updated using our value for $\Delta_f H^o[1,1\text{-}C_2H_4Cl_2(g)]$. |
| 34.6 | 1.5[b] | 373 | Enthalpy of hydrochlorination<br>$C_2H_2(g) + HCl(g) \rightarrow CH_2{=}CHCl(g)$ | [1962LGP] | 4, Data reanalyzed at NIST; updated using our value for $\Delta_f H^o[C_2H_2(g)]$. |
| 37.6 | 1.7[b] | 521 | Enthalpy of polymerization<br>$CH_2{=}CHCl(g) + 2H_2(g) \rightarrow C_2H_6(g) + HCl(g)$ | [1956LEB] | 5, Data reanalyzed at NIST; updated using our value for $\Delta_f H^o[C_2H_6(g)]$. |
| — | 0.7 | 347.7 | Enthalpy of polymerization<br>$CH_2{=}CHCl(l) \rightarrow C_2H_3Cl$ (poly,s) | [1964J] | 6, These data used in conjunction with that of [1958SS], below. |
| 22.8 | 2.2[c]<br>(6.0) | 298 | Combustion calorimetry of solid polymer | [1958SS] | 7, Static Bomb, data used in conjunction with that of [1964J], above. |
| Estimates and Calculations | | | | | |
| 20.9 | 4.2 | 298 | *Ab initio* calculations | [1997CT] | 8 |
| 22.3 | 6.4 | 298 | Group additivity; Estimated value for $C_d$-(Cl)(H) | [1992LH] | 9 |
| 20.8 | N.R.[d] (4.0) | 298 | Group additivity; Value for $C_d$-(Cl)(H) group derived from $\Delta_f H^o[E\text{-}1\text{-chloropropene}]$ | [1973AGB]<br>[1997CT] | 10 |
| Reviews and Evaluations | | | | | |
| 23.0 | 2.1 | 298 | | [1991GVA] | Evaluation date uncertain; same value as previous edition [1979G]. |
| 37.2 | 1.2 | 298 | | [1986PNK] | |
| 23.0 | 2.1 | 298 | | [1983KP] | |
| 28.5 | N.R.[d] | 298 | | [1982R] | |
| 36.0 | 1.3 | 298 | | [1970CP] | |
| 35.1 | N.R.[d] | 298 | | [1969SWS] | |

[a] Reported uncertainty refers only to the precision of the measured reaction enthalpy. The parenthetical value is our estimate of the overall uncertainty of this technique derived by comparison of the results of similar studies of related chemical systems.

[b] Reported uncertainty refers only to the precision of the measured reaction enthapy and auxiliary thermodynamic quantities, but does not include systematic uncertainties.

[c] Reported uncertainty refers to the combined precisions of the measured reaction enthalpies. The parenthetical value is what we consider to be a more realistic combined uncertainty.

[d] Not reported.

**Comments:**

1. From the Second Law analysis of Levanova *et al.*, $\Delta_r H(403\ K) = (61.70 \pm 1.0)$ kJ mol$^{-1}$. This was adjusted to $\Delta_r H(298.15\ K) = (61.23 \pm 1.3)$ kJ mol$^{-1}$ using the heat capacity data from the TRC Tables [1981C], [1985R]. With $\Delta_f H^o[1,1\text{-}C_2H_4Cl_2(g),\ 298.15\ K] = -132.5$ kJ mol$^{-1}$ and $\Delta_f H^o[HCl(g),\ 298.15\ K] = -(92.31 \pm 0.10)$ kJ mol$^{-1}$ (see Secs. 6.3 and 1.4), one finds $\Delta_f H^o[C_2H_3Cl(g),\ 298.15\ K] = 21.0$ kJ mol$^{-1}$. This was a primary (though not sole) result used to derive $\Delta_f H^o[1,1\text{-}C_2H_4Cl_2(g),\ 298.15\ K]$. Thus, although self-consistent, these data cannot provide a completely independent confirmation of the selected value.

2. Taking entropies and heat capacities from the TRC Tables [1981C], [1985R], our Third Law analysis results in $\Delta_r H(298.15\ K) = 62.2$ kJ mol$^{-1}$. With auxiliary quantities as in Comment 1 we calculate $\Delta_f H^o[C_2H_3Cl(g),\ 298.15\ K] = 22.0$ kJ mol$^{-1}$. This was a primary (though not sole) result used to derive $\Delta_f H^o[1,1\text{-}C_2H_4Cl_2(g),\ 298.15\ K]$. Thus, although self-consistent, these data cannot provide a completely independent confirmation of the selected value.

3. From the Second Law analysis of Levanova *et al.*, $\Delta_r H(308\ K) = (93.24 \pm 0.7)$ kJ mol$^{-1}$. Taking gas phase heat capacity data from the TRC Tables [1981C], [1985R], and using $\Delta_{vap} C_p(1,1\text{-}C_2H_4Cl_2) = -50.2$ J mol$^{-1}$K$^{-1}$ [1956LP], $\Delta_{vap} H^o(1,1\text{-}C_2H_4Cl_2,\ 298.15\ K) = (30.83 \pm 0.1)$ kJ mol$^{-1}$, this becomes $\Delta_r H(298.15\ K) = (93.74 \pm 1.0)$ kJ mol$^{-1}$. This leads to $\Delta_f H^o[C_2H_3Cl(g),\ 298.15\ K] = 22.7$ kJ mol$^{-1}$. This was a primary (though not sole) result used to derive $\Delta_f H^o[1,1\text{-}C_2H_4Cl_2(g),\ 298.15\ K]$. Thus, although self-consistent, these data cannot provide a completely independent confirmation of the selected value.

4. $\Delta_r H(373\ K) = -(101.99 \pm 1.0)$ kJ mol$^{-1}$ was adjusted to $\Delta_r H(298.15\ K) = -(100.54 \pm 1.3)$ kJ mol$^{-1}$ using the heat capacity data from the TRC Tables [1981C]. In conjunction with $\Delta_f H^o[C_2H_2(g),\ 298.15\ K] = -(227.4 \pm 0.8)$ kJ mol$^{-1}$ and $\Delta_f H^o[HCl(g),\ 298.15\ K] = -(92.31 \pm 0.10)$ kJ mol$^{-1}$ (see Secs. 4.1 and 1.4), we derive $\Delta_f H^o[C_2H_3Cl(g),\ 298.15\ K] = -(34.55 \pm 1.5)$ kJ mol$^{-1}$.

5. $\Delta_r H(521\ K) = -(220.12 \pm 1.1)$ kJ mol$^{-1}$ was adjusted to $\Delta_r H(298.15\ K) = -(213.89 \pm 1.6)$ kJ mol$^{-1}$ using the heat capacity data from the TRC Tables [1981C]. In conjunction with $\Delta_f H^o[C_2H_6(g),298.15\ K] = -(84.0 \pm 0.4)$ kJ mol$^{-1}$ and $\Delta_f H^o[HCl(g),298.15\ K] = -(92.31 \pm 0.10)$ kJ mol$^{-1}$ (see Secs. 6.1 and 1.4), we derive $\Delta_f H^o[C_2H_3Cl(g),298.15\ K] = (37.58 \pm 1.7)$ kJ mol$^{-1}$.

6. $\Delta_r H(347.65K) = -(95.81 \pm 1.3)$ kJ mol$^{-1}$ for the polymerization $C_2H_3Cl(l) \rightarrow C_2H_3Cl$ (poly, s) was determined in an isothermal distillation calorimeter. In the absence of heat capacity data for the polymer and liquid, this value was assumed to be approximately equal to $\Delta_{poly} H[C_2H_3Cl(l),\ 298.15\ K]$.

7. Static bomb calorimetry. $\Delta_c H[(poly,s),\ 298.15\ K] = -(1145.3 \pm 1.3)$ kJ mol$^{-1}$, refers to reaction $C_2H_3Cl\ (poly,s) + 2.5O_2(g) \rightarrow 2CO_2(g) + H_2O(l) + HCl$ (aq:600). The following auxiliary thermodynamic values were used: $\Delta_f H^o[CO_2(g),\ 298.15\ K] = -(393.51 \pm 0.13)$ kJ mol$^{-1}$, $\Delta_f H^o[H_2O(l),298.15K] = K] = -(285.830 \pm 0.040)$ kJ mol$^{-1}$, and $\Delta_f H^o[HCl\ (aq:600),\ 298.15\ K] = -(166.540 \pm 0.10)$ kJ mol$^{-1}$. This leads to $\Delta_f H^o[C_2H_3Cl\ (poly,s)] = -(94.09 = -(94.09 \pm 1.3)$ kJ mol$^{-1}$. In conjunction with the enthalpy of polymerization (Comment 6) and $\Delta_{vap} H^o[C_2H_3Cl,\ 298.15\ K] = (21.1 \pm 1.0)$ kJ mol$^{-1}$ (see below) we derive $\Delta_f H^o[C_2H_3Cl(g),\ 298.15\ K] = (22.8 \pm 2.2)$ kJ mol$^{-1}$.

8. Energies for several C1, C2, and C3 chlorocarbons were derived at several levels of theory up to and including G2 calculations. Isodesmic reactions were used to derive the best calculated enthalpies of formation and values for benchmark compounds were used to confirm the results.

9. The enthalpy increment $\Delta_f H^o[C_2H_3X(g),\ 298.15\ K] = \Delta_f H^o[C_6H_5X(g),\ 298.15\ K] - (29.7 \pm 6.3)\ kJ\ mol^{-1}$ was derived from the data on or a variety of substituted enthenes and benzenes. Using $\Delta_f H^o[C_6H_5Cl(g),\ 298.15\ K] = (52.0 \pm 1.3)\ kJ\ mol^{-1}$ [1994P], one derives $\Delta_f H^o[C_2H_3Cl(g),\ 298.15\ K] = (22.3 \pm 6.4)\ kJ\ mol^{-1}$. Luo and Holmes originally used $\Delta_f H^o[C_6H_5Cl(g),\ 298.15\ K] = 54.4\ kJ\ mol^{-1}$ [1985PS], which results $\Delta_f H^o[C_2H_3Cl(g),\ 298.15\ K] = 24.7\ kJ\ mol^{-1}$.

10. Based on measured equilibrium constants for $E$-1-chloropropene⇋3-chloropropene (A) and $Z$-1-chloropropene⇋3-chloropropene (B). Original Second Law analysis has been updated with a Third Law analysis to give $\Delta_A H(298.15\ K) = 8.08\ kJ\ mol^{-1}$, and $\Delta_B H(298.15\ K) = 10.13\ kJ\ mol^{-1}$ [1997CT]. Absolute values were derived using $\Delta_f H^o$[3-chloropropene(g), 298.15 K] $= -(3.3 \pm 2.1)\ kJ\ mol^{-1}$ [1997CT], resulting in the group value $C_d$-(Cl)(H) $= 5.48\ kJ\ mol^{-1}$. This leads to the group additivity estimate $\Delta_f H^o[C_2H_3Cl(g),\ 298.15\ K] = 20.75\ kJ\ mol^{-1}$.

mation of chloroethene that is 10–15 $kJ\ mol^{-1}$ higher than five other independent methods of deriving this value. The Lacher *et al.* studies [1956LEB], [1962LGP] have accordingly not been considered in making our final selection. The calorimetry work on the polymer [1958SS], [1963J], the equilibrium dehydrochlorination of 1,1-dichloroethane [1976LTV], two independent group additivity methods [1973AGB], [1992LH], and *ab initio* calculations [1997CT] all suggest very similar values. All of these data were considered and lead us to recommend $\Delta_f H^o[C_2H_3Cl(g),\ 298.15\ K] = (22.0 \pm 3.0)\ kJ\ mol^{-1}$. The value for the hypothetical liquid under standard conditions is derived as $\Delta_f H^o[C_2H_3Cl(l),\ 298.15\ K] = (0.9 \pm 3.2)\ kJ\ mol^{-1}$.

### 5.3. 1,1-Dichloroethene

*Enthalpy of Vaporization*. The enthalpy of vaporization at 298.15 K has been derived by Hildenbrand *et al.* [1959HKM] from vapor pressure measurements as $\Delta_{vap}H(298.15\ K) = (26.48 \pm 0.09)\ kJ\ mol^{-1}$. A correction of 0.26 $kJ\ mol^{-1}$ due to nonideality of the gas was taken from the work of Majer and Svoboda [1985MS] (our calculation gives 0.28 $kJ\ mol^{-1}$) and $\Delta_{vap}H^o(298.15\ K) = (26.74 \pm 0.09)\ kJ\ mol^{-1}$ is derived. The heat capacity of vaporization was derived as $\Delta_{vap}C_p = -44.2\ J\ mol^{-1}\ K^{-1}$ from the difference of the reported heat capacities of the gas [1991GVA] and liquid [1959HKM].

*Enthalpy of Formation*. Data are summarized in Table 10. The enthalpy of formation of 1,1-dichloroethene is one of the better determined of the chloroethenes. Two high quality combustion calorimetry studies are available, the first by Sinke and Stull [1958SS] used a static bomb calorimeter and the second by Månsson *et al.* [1971MRS] used a rotating bomb calorimeter. The results, $\Delta_f H^o[CH_2{=}CCl_2(l),\ 298.15\ K] = -(23.8 \pm 1.3)\ kJ\ mol^{-1}$ and $\Delta_f H^o[CH_2{=}CCl_2(l),\ 298.15\ K] = -(24.1 \pm 1.4)\ kJ\ mol^{-1}$, respectively, are in excellent agreement.

The gas phase hydrochlorination equilibrium

$$CH_2{=}CCl_2(g) + HCl(g) \rightleftarrows CH_3CCl_3(g) \qquad (6)$$

was studied by Hu *et al.* [1972HSM] and their Third Law analysis results in $\Delta_r H(298.15\ K) = -(54.64 \pm 0.84)\ kJ\ mol^{-1}$. This measurement is particularly important as it sets the relative enthalpies of formation of the alkene and alkane quite precisely. The enthalpy of formation of 1,1,1-trichloroethane has been determined several times and we have confidence in its value of $\Delta_f H^o[CH_3CCl_3(g),\ 298.15\ K] = -(144.6 \pm 2.0)\ kJ\ mol^{-1}$ (see Sec. 6.5), which leads to $\Delta_f H^o[CH_2{=}CCl_2(g),\ 298.15\ K] = (2.4 \pm 2.2)\ kJ\ mol^{-1}$. This is in excellent agreement with the combustion values (see Table 10).

Finally, Levanova *et al.* [1975LTVa], [1975LTVb] have studied the hydrochlorination equilibrium in chlorobenzene between 293 and 353 K.

$$CH_2{=}CCl_2(soln) + HCl(g) \rightleftarrows CH_3CCl_3\ (soln). \qquad (7)$$

They report $\log_{10} K = (2900/T) - 7.69$. This Second Law analysis corresponds to $\Delta_r H(323\ K) = -(55.5 \pm 2)\ kJ\ mol^{-1}$. Using $C_p[CH_2{=}CCl_2(l)] = 111.29\ J\ mol^{-1}\ K^{-1}$ [1993DH], and $C_p[CH_3CCl_3(l)] = 144.39\ J\ mol^{-1}\ K^{-1}$ [1993DH], and $C_p[HCl(g)] = 29.14\ J\ mol^{-1}\ K^{-1}$, we calculate $\Delta_r C_p = 3.96\ J\ mol^{-1}\ K^{-1}$, and $\Delta_r H(298.15\ K) = -(55.4 \pm 2)\ kJ\ mol^{-1}$. Together with $\Delta_f H^o[CH_3CCl_3(l),\ 298.15\ K] = -(177.1 \pm 3)\ kJ\ mol^{-1}$ (see Sec. 6.5), we obtain $\Delta_f H^o[CH_2{=}CCl_2(l),\ 298.15\ K] = -29.4\ kJ\ mol^{-1}$. A Third Law analysis was also performed from the calculated value of the equilibrium constant at 298.15 K. With $S[CH_2{=}CCl_2(l),\ 298.15\ K] = 201.54\ J\ mol^{-1}\ K^{-1}$ [1993DH], and $S[CH_3CCl_3(l),\ 298.15\ K] = 226.69\ J\ mol^{-1}\ K^{-1}$ [1993DH], we find $\Delta_r H(298.15\ K) = -59.7\ kJ\ mol^{-1}$, which leads to $\Delta_f H^o[CH_2{=}CCl_2(l),\ 298.15\ K] = -25.1\ kJ\ mol^{-1}$. The Second and Third Law analyses are in only fair agreement with each other. In part this may be because the excess thermodynamic properties of solvation have been neglected. This may also explain the slight disagreement with the combustion result and gas phase equilibrium data. Nonetheless all the data are in reasonable agreement.

*Recommendation*. All of the data are considered in our final selection, but the combustion calorimetry results of Månsson *et al.* [1971MRS] using a rotating bomb and the gas phase hydrochlorination equilibrium data [1972HSM] are weighted most heavily. The former study also reported the enthalpy of formation of 1,1,1-trichloroethane. In that case the results were in reasonable agreement with other work, although the overall uncertainty appears to be somewhat larger than the statistical precision (see Sec. 6.5). In consideration of this and the other data, we have slightly increased the uncertainty limits for 1,1-dichloroethene and recommend $\Delta_f H^o[CH_2{=}CCl_2(l),\ 298.15\ K] = -(24.3 \pm 2.0)\ kJ\ mol^{-1}$. Combined with $\Delta_{vap}H^o(298.15\ K) = (26.74 \pm 0.09)\ kJ\ mol^{-1}$, the value for the ideal gas is derived as $\Delta_f H^o[CH_2{=}CCl_2(g),\ 298.15\ K] = (2.4 \pm 2.0)\ kJ\ mol^{-1}$.

TABLE 10. Enthalpies of formation of 1,1-dichloroethane derived from reported experimental data

| $\Delta_f H^o$ (g), 298.15 K (kJ mol$^{-1}$) | Reported uncertainty kJ mol$^{-1}$ | Temp. (K) | Method(s) | Ref/Year | Comments |
|---|---|---|---|---|---|
| Experimental | | | | | |
| −2.7 | 2.1$^a$ | 293–353 | Equilibrium of hydrochlorination $CH_2{=}CCl_2(soln)+HCl(g) \rightleftarrows CH_3CCl_3(soln)$ | [1975LTVa]<br>[1975LTVb] | 1, Second Law analysis, $\Delta_f H^o[CH_3CCl_3]$ used in calculation. |
| 1.5 | 2.1$^a$ | 293–353 | Equilibrium of hydrochlorination $CH_2{=}CCl_2(soln)+HCl(g) \rightleftarrows CH_3CCl_3(soln)$ | [1975LTVa]<br>[1975LTVb] | 2, Third Law analysis, $\Delta_f H^o[CH_3CCl_3]$ used in calculation. |
| 2.3 | 8 | 348–399 | Equilibrium of hydrochlorination $CH_2{=}CCl_2(g)+HCl(g) \rightleftarrows CH_3CCl_3(g)$ | [1972HSM] | 3, Third Law analysis, $\Delta_f H^o[CH_3CCl_3]$ used in calculation. |
| 2.6 | 1.4 | 298 | Combustion calorimetry of liquid | [1971MRS] | 4, Rotating Bomb. |
| 2.9 | 1.3 | 298 | Combustion calorimetry of liquid | [1958SS]<br>[1970CP] | 5, Static Bomb. Data reanalyzed and auxiliary quantities updated by [1970CP]. |
| Reviews and Evaluations | | | | | |
| 2.3 | 1.4 | 298 | | [1991GVA] | Evaluation date uncertain; same value as previous edition [1979G]. |
| 2.8 | 1.3 | 298 | | [1986PNK] | |
| 2.3 | 1.4 | 298 | | [1983KP] | |
| 2.38 | N.R.$^b$ | 298 | | [1982R] | |
| 2.55 | 1.5 | 298 | | [1970CP] | |
| 1.3 | N.R.$^b$ | 298 | | [1969SWS] | |

[a] Reported uncertainty refers only to the measured reaction enthalpy and does not include uncertainty in auxiliary thermodynamic quantities.
[b] Not reported.

**Comments:**

1. Reaction carried out in chlorobenzene. The Second Law analysis gives $\Delta_r H(298.15\ \mathrm{K}) = -(55.4 \pm 2.1)\ \mathrm{kJ\ mol^{-1}}$ (see Discussion). Together with $\Delta_f H^o[CH_3CCl_3(l),\ 298.15\ \mathrm{K}] = -(177.2 \pm 2.0)\ \mathrm{kJ\ mol^{-1}}$ (see Sec. 6.5), we obtain $\Delta_f H^o[CH_2{=}CCl_2(l),\ 298.15\ \mathrm{K}] = -(29.4 \pm 2.9)\ \mathrm{kJ\ mol^{-1}}$. Excess thermodynamic properties of solvation were neglected in the analysis.
2. Reaction carried out in chlorobenzene. The Third Law analysis gives $\Delta_r H(298.15\ \mathrm{K}) = -59.7\ \mathrm{kJ\ mol^{-1}}$ (see Discussion). Together with $\Delta_f H^o[CH_3CCl_3(l),\ 298.15\ \mathrm{K}] = -(177.1 \pm 3.0)\ \mathrm{kJ\ mol^{-1}}$ (see Sec. 6.5), we obtain to $\Delta_f H^o[CH_2{=}CCl_2(l),\ 298.15\ \mathrm{K}] = -25.1\ \mathrm{kJ\ mol^{-1}}$. Excess thermodynamic properties of solvation were neglected in the analysis.
3. Third Law analysis of equilibrium $CH_2{=}CCl_2(g)+HCl(g) \rightleftarrows CH_3CCl_3(g)$ yields $\Delta_r H(298.15\ \mathrm{K}) = -(54.6 \pm 8)\ \mathrm{kJ\ mol^{-1}}$. The quoted value is obtained using $\Delta_f H^o[1,1,1\text{-}C_2H_3Cl_3(g),\ 298.15\ \mathrm{K}] = -(144.6 \pm 2.0)\ \mathrm{kJ\ mol^{-1}}$ (see Sec. 6.5), and $\Delta_f H^o[HCl(g),\ 298.15\ \mathrm{K}] = -(92.31 \pm 0.10)\ \mathrm{kJ\ mol^{-1}}$.
4. Rotating bomb calorimetry. $\Delta_c H(298.15\ \mathrm{K})(l),\ 298.15\ \mathrm{K} = -(1096.0 \pm 1.4)\ \mathrm{kJ\ mol^{-1}}$, refers to reaction $1,1\text{-}C_2H_2Cl_2(l)+2O_2(g) \rightarrow 2CO_2(g)+2HCl$ (aq:600). The following auxiliary values were used. $\Delta_f H^o[CO_2(g),\ 298.15\ \mathrm{K}] = -(393.51 \pm 0.13)\ \mathrm{kJ\ mol^{-1}}$ and $\Delta_f H^o[HCl(aq{:}600),\ 298.15\ \mathrm{K}] = -(166.540 \pm 0.10)\ \mathrm{kJ\ mol^{-1}}$. This leads to $\Delta_f H^o[CH_2{=}CCl_2(l),\ 28.15\ \mathrm{K}] = -(24.10 \pm 1.4)\ \mathrm{kJ\ mol^{-1}}$.
5. Static bomb calorimetry. $\Delta_c H[(l),\ 298.15\ \mathrm{K}] = -(1096.3 \pm 1.3)\ \mathrm{kJ\ mol^{-1}}$. Stated value is from reevaluation compiled by Pedley *et al.* in 1986 using updated auxiliary thermodynamic quantities. Auxiliary data as in Comment 4. Data lead to $\Delta_f H^o[CH_2{=}CCl_2(l),\ 298.15\ \mathrm{K}] = -(23.8 \pm 1.3)\ \mathrm{kJ\ mol^{-1}}$.

## 5.4. *E*-1,2-Dichloroethene

*Enthalpy of Vaporization*. Cox and Pilcher [1970CP] derived $\Delta_{vap}H(298.15\ \mathrm{K}) = (29.3 \pm 1.3)\ \mathrm{kJ\ mol^{-1}}$ from vapor pressures measured over the temperature range 235–358 K by Ketelaar *et al.* [1947KVZ], slightly different from the value of $\Delta_{vap}H(298.15\ \mathrm{K}) = 28.95\ \mathrm{kJ\ mol^{-1}}$ calculated from this same data by Stull *et al.* [1969SWS]. Simple interpolation between the values derived by Ketelaar *et al.* at 273.15 and 320.82 K yields $\Delta_{vap}H(298.15\ \mathrm{K}) = 29.44\ \mathrm{kJ\ mol^{-1}}$. For other compounds in this review we were able to correlate $\Delta_{vap}H(298.15\ \mathrm{K})$ with the normal boiling point (*vide infra*, see Fig. 9 of Sec. 6.9) and also found $\Delta_{vap}H/T_b = (88.0 \pm 3.0)\ \mathrm{J\ mol^{-1}\ K^{-1}}$. These respective estimation methodologies lead to $\Delta_{vap}H(298.15\ \mathrm{K}) = (29.4 \pm 1.5)\ \mathrm{kJ\ mol^{-1}}$ and $(29.2 \pm 1.0)\ \mathrm{kJ\ mol^{-1}}$, in excellent agreement with experiment. We recommend $\Delta_{vap}H(298.15\ \mathrm{K}) = (29.3 \pm 1.0)\ \mathrm{kJ\ mol^{-1}}$. The correction to $\Delta_{vap}H(298.15\ \mathrm{K})$ due to nonideality of the gas is calculated as $0.20\ \mathrm{kJ\ mol^{-1}}$, using Eq. (1) and second virial coefficients taken from the DIPPR Tables [2001 DIP] (datasheet revision data August, 1994). This leads to $\Delta_{vap}H^o[E\text{-}1,2\text{-}C_2H_2Cl_2,\ 298.15\ \mathrm{K}] = (29.5 \pm 1.0)\ \mathrm{kJ\ mol^{-1}}$. The heat capacity of vaporization was derived as $\Delta_{vap}C_p = -47.7\ \mathrm{J\ mol^{-1}\ K^{-1}}$ from the difference of the reported heat capacities of the gas [1991GVA] and liquid [1934M].

*Enthalpy of Formation*. Data are summarized in Table 11. The only combustion calorimetry value for the enthalpy of formation of *E*-1,2-dichloroethene is that of Eftring [1938E]. The results were corrected by Smith *et al.* [1953SBK] and reevaluated by Cox and Pilcher [1970CP]. The data have subsequently been compiled by Pedley *et al.* [1986PNK] and lead to $\Delta_f H^o[Z\text{-CHCl}{=}\text{CHCl}(l),\ 298.15\ \mathrm{K}] = -(24.3 \pm 8.4)\ \mathrm{kJ\ mol^{-1}}$. However, in cases where there are data from newer combustion studies, the enthalpies of formation de-

TABLE 11. Enthalpies of formation of *E*-1,2-dichloroethene derived from reported experimental data

| $\Delta_f H^o$ (g), 298.15 K (kJ mol$^{-1}$) | Reported uncertainty kJ mol$^{-1}$ | Temp. (K) | Method(s) | Ref/Year | Comments |
|---|---|---|---|---|---|
| Experimental | | | | | |
| −0.3 | N.R.<br>(0.5)[a] | 447–673 | Equilibrium<br>$CH_2{=}CCl_2$ (g)$\rightleftarrows$*E*-CHCl=CHCl (g) | [1974RLD] | 1, Reported data reanalyzed at NIST using Second Law, $\Delta_f H^o[CH_2{=}CCl_2]$ used in calculation. |
| −0.5 | N.R.<br>(0.4)[b] | 447–673 | Equilibrium<br>$CH_2{=}CCl_2$ (g)$\rightleftarrows$*E*-CHCl=CHCl (g) | [1974RLD] | 2, Reported data reanalyzed at NIST using Third Law, $\Delta_f H^o[CH_2{=}CCl_2]$ used in calculation. |
| 5.0 | 8.4 | 298 | Combustion calorimetry of liquid | [1938E]<br>[1953SBK]<br>[1970CP] | 3, Static Bomb. Data corrected by Smith *et al.* in 1953. Reanalyzed and auxiliary quantities updated by [1970CP]. |
| Reviews and Evaluations | | | | | |
| 6.1 | 1.4 | 298 | | [1991GVA] | Evaluation date uncertain; same value as previous edition [1979G]. |
| 5.0 | 8.5 | 298 | | [1986PNK] | |
| 6.1 | 1.0 | 298 | | [1983KP] | |
| −0.4 | N.R.[c] | 298 | | [1982R] | |
| 5.0 | 8.8 | 298 | | [1970CP] | |
| 4.2 | N.R.[c] | 298 | | [1969SWS] | |

[a] Not reported, the parenthetical value is that estimated in this work and refers only to the measured reaction enthalpy.
[b] Not reported, the parenthetical value is that estimated in this work.
[c] Not reported.

**Comments:**

1. Isomerized in a flow reactor in the presence of catalysts ($NiCl_2$ on activated carbon or $BiCl_3$ on activated carbon). Data reanalyzed at NIST (see Discussion). $\Delta_r H(560\ K) = -(3.29 \pm 0.3)$ kJ mol$^{-1}$. Using heat capacities from Gurvich, $\Delta_r H(298.15\ K) = -(3.06 \pm 0.4)$ kJ mol$^{-1}$. The heat capacities of Rodgers [1982R] give a very similar result. Reported value calculated using $\Delta_f H^o[CH_2{=}CCl_2\ (g), 298.15\ K] = (2.42.0)$ kJ mol$^{-1}$.
2. Isomerized in a flow reactor in the presence of catalysts $NiCl_2$ on activated carbon or $BiCl_3$ on activated carbon. Reanalyzed at NIST (see Discussion). $\Delta_r H(560\ K) = -(3.09 \pm 0.2)$ kJ mol$^{-1}$. Using heat capacities from Gurvich *et al.* [1991GVA], $\Delta_r H(298.15\ K) = -(2.86 \pm 0.3)$ kJ mol$^{-1}$. The heat capacities of Rodgers [1982R] give a very similar result. Calculated using $\Delta_f H^o[CH_2{=}CCl_2\ (g), 298.15\ K] = (2.4 \pm 2.0)$ kJ mol$^{-1}$.
3. The original results of Eftring [1938E] were corrected by Smith *et al.* [1953SBK] and reevaluated by Cox and Pilcher [1970CP]. The data have subsequently been compiled by Pedley *et al.* [1986PNK]. Purity of the sample is uncertain. $\Delta_c H[(l), 298.15\ K] = -(1095.8 \pm 8.4)$ kJ mol$^{-1}$, refers to reaction *E*-1,2-$C_2H_2Cl_2$ (l)+$2O_2$ (g)→$2CO_2$ (g)+2HCl (aq:600). The following auxiliary values were used: $\Delta_f H^o[CO_2\ (g), 298.15\ K] = -(393.51 \pm\ 0.13)$ kJ mol$^{-1}$ and $\Delta_f H^o[HCl\ (aq{:}600), 298.15\ K] = -(166.540 \pm 0.10)$ kJ mol$^{-1}$. The data result in $\Delta_f H^o[CH_2{=}CCl_2\ (l), 298.15\ K] = -(24.30 \pm 8.4)$ kJ mol$^{-1}$.

rived from the data of Eftring [1938E] appear to be systematically too positive. This observation suggests that these data should be treated cautiously.

The best data from which to obtain a reliable value for $\Delta_f H$(*E*-CHCl=CHCl) are from the study of Rozhnov *et al.* [1974RLD], who have measured the equilibrium between the three dichloroethene isomers in the gas phase between 447 and 673 K.

$$CH_2{=}CCl_2(g) \rightleftarrows E\text{-}CHCl{=}CHCl(g). \tag{8}$$

The compounds were isomerized in a flow reactor in the presence of catalysts ($NiCl_2$ on activated carbon or $BiCl_3$ on activated carbon). We have plotted their data (Fig. 6) and find $\log K_8 = (172 \pm 25)/T + (4.71 \pm 4.71) \times 10^{-2}$, where the uncertainties are $2\sigma$. This corresponds to $\Delta_8 H(560\ K) = -(3.29 \pm 0.48)$ kJ mol$^{-1}$. Using the gas phase heat capacities from Gurvich *et al.* [1991GVA], this becomes $\Delta_8 H(298.15\ K) = -(3.06 \pm 0.48)$ kJ mol$^{-1}$. A Third Law analysis was also performed. Using entropies and heat capacities from Gurvich *et al.* [1991GVA], we find $\Delta_8 H(560\ K) = -(3.09 \pm 0.4)$ kJ mol$^{-1}$, $\Delta_8 H(298.15\ K) = -(2.86 \pm 0.4)$ kJ mol$^{-1}$. The uncertainties are estimated $2\sigma$ values and include both the uncertainty in the equilibrium constant and uncertainty in the thermodynamic properties. The Second and Third Law analyses are in excellent agreement, although the latter is preferred since the molecular properties of the dichloroethenes are well known. In conjunction with $\Delta_f H^o[CH_2{=}CCl_2(g), 298.15\ K] = (2.4 \pm 2.0)$ kJ mol$^{-1}$, we obtain $\Delta_f H^o[E\text{-}CHCl{=}CHCl(g), 298.15\ K] = -(0.46 \pm 2.0)$ kJ mol$^{-1}$. Very similar numbers are obtained if the entropies and heat capacities are taken from Rodgers [1982R] instead of Gurvich *et al.* [1991GVA].

As a consistency check we have compared the data of Rozhnov *et al.* [1974RLD] on the *Z*/*E* equilibrium (Reaction 9) with other literature data. The data are

$$Z\text{-}CHCl{=}CHCl(g) \rightleftarrows E\text{-}CHCl{=}CHCl(g) \tag{9}$$

shown in Fig. 7. The data taken prior to 1970 were derived from measurements of the dielectric constant while the later measurements are based on gas chromatographic analyses. The data are all in good agreement, although there is some-

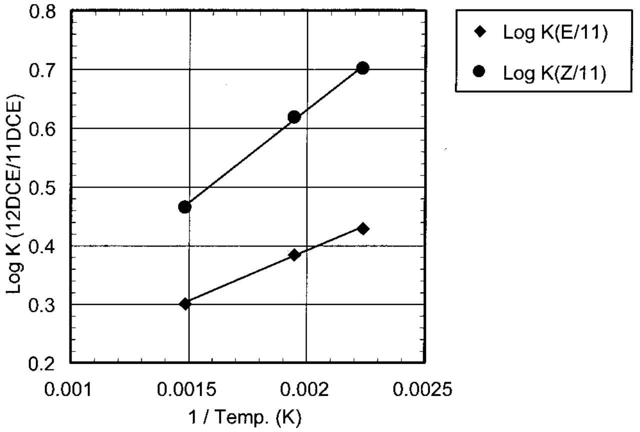

FIG. 6. Plot of the equilibrium constants of Rozhnov *et al.* [1974RLD] for the reactions $CH_2{=}CCl_2(g) \rightleftarrows Z\text{-}CHCl{=}CHCl(g)$ and $CH_2{=}CCl_2(g) \rightleftarrows E\text{-}CHCl{=}CHCl(g)$. The least squares fits are $\log K(Z\text{-12DCE/11-DCE}) = (316 \pm 42)/T + (-2.90 \pm 79.6) \times 10^{-3}$ and $\log K(E\text{-12DCE/11-DCE}) = (172 \pm 25)/T + (4.71 \pm 4.71) \times 10^{-2}$. Uncertainties are $2\sigma$.

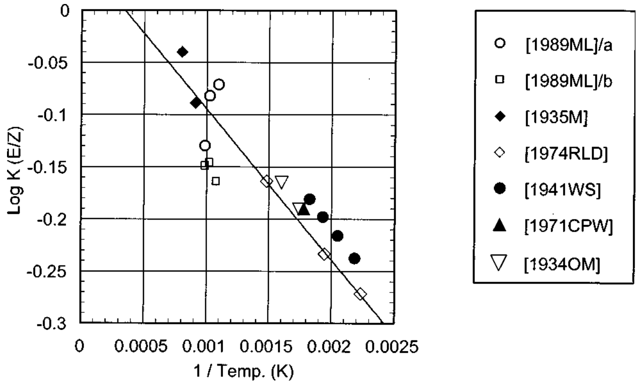

FIG. 7. Literature data on the gas-phase equilibrium $Z\text{-}CHCl{=}CHCl \rightleftarrows E\text{-}CHCl{=}CHCl$. The data of Manion and Louw [1989ML] are from a kinetic study not specifically designed to obtain information on the position of the $E/Z$ equilibrium. The line corresponds to $\log K(E/Z) = (5.00 \pm 3.2) \times 10^{-2} - (145 \pm 17)/T$ and is that derived from the data of Rozhnov *et al.* [1974RLD] The uncertainties are $2\sigma$. As shown, the reaction enthalpy (slope) is consistent with the other data. Key: [1989ML]/a: from kinetic study of $C_2HCl_3$ hydrogenolysis; [1989ML]/b; from kinetic study of $E$-CHCl═CHCl hydrogenolysis; others as in reference list.

spread in the high temperature data. It should be noted, however, that one of the high temperature studies [1989ML] was a kinetic study not specifically designed to obtain information on the position of the $Z/E$ equilibrium. The study of Rozhnov *et al.* [1974RLD] is the only one to also report on the equilibrium with 1,1-dichloroethene. Since that information is critical to establishing the absolute enthalpy of formation values, and all the data are in reasonable agreement, we have based our selected values on their data. The Second Law analysis performed at NIST on their data yields $\Delta_9 H(560\,\mathrm{K}) = (2.77 \pm 0.32)\,\mathrm{kJ\,mol^{-1}}$, while a Third Law analysis using entropy values from Gurvich *et al.* [1991GVA] results in $\Delta_9 H(560\,\mathrm{K}) = (2.80 \pm 0.3)\,\mathrm{kJ\,mol^{-1}}$, in near-perfect agreement. Extrapolated to 298.15 K, again using the data of Gurvich *et al.*, [1991GVA] the Third Law analysis yields $\Delta_9 H(298.15\,\mathrm{K}) = (2.57 \pm 0.3)\,\mathrm{kJ\,mol^{-1}}$.

Since all relative enthalpies of formation of the dichloroethenes were obtained from the same equilibrium data, this value is in perfect agreement with that derived from equilibrium Eq. (8) and our preferred value of $\Delta_f H^o[Z\text{-}CHCl{=}CHCl(g),\ 298.15\,\mathrm{K}]$. For comparison, the largest values of $K_8$(T) are those of Wood and Stevenson [1941WS] (Fig. 7). Their data result in $\Delta_9 H(298.15\,\mathrm{K}) = 2.22\,\mathrm{kJ\,mol^{-1}}$ (Third Law), and $\Delta_9 H(298.15\,\mathrm{K}) = 2.80\,\mathrm{kJ\,mol^{-1}}$ (Second Law). The average is in excellent agreement with the value derived from the data of Rozhnov *et al.* [1974RLD] and suggests that the relative energies of the two isomers are very well defined. We recommend $\Delta_f H^o[Z\text{-}CHCl{=}CHCl(g),\ 298.15\,\mathrm{K}] = \Delta_f H^o[E\text{-}CHCl{=}CHCl(g),\ 298.15\,\mathrm{K}] - (2.57 \pm 0.3)\,\mathrm{kJ\,mol^{-1}}$.

*Recommendation*. The equilibrium results [1974RLD] should be reliable and the value $\Delta_f H^o[E\text{-}CHCl{=}CHCl(g),\ 298.15\,\mathrm{K}] = -(0.5 \pm 2.0)\,\mathrm{kJ\,mol^{-1}}$ derived from the Third Law analysis is selected. The combustion value of Eftring [1938E] appears to be too positive, as is the case for several other chlorine compounds for which independent data are available. Notice that the equilibrium data define the *relative* enthalpies of formation of the three dichloroethenes very precisely, within about 0.4 $\mathrm{kJ\,mol^{-1}}$. The absolute numbers are somewhat less well determined.

### 5.5. *Z*-1,2-Dichloroethene

*Enthalpy of Vaporization*. The vapor pressure measurements of Ketelaar *et al.* [1947KVZ] between 240 and 372 K were used by Stull *et al.* [1969SWS] to derive $\Delta_{vap} H(298.15\,\mathrm{K}) = 31.1\,\mathrm{kJ\,mol^{-1}}$. Cox and Pilcher [1970CP] derived $\Delta_{vap} H(298.15\,\mathrm{K}) = (31.0 \pm 1.3)\,\mathrm{kJ\,mol^{-1}}$ from these same measurements. Simple interpolation between the values derived by Ketelaar *et al.* [1947KVZ] at 273.15 and 333.78 K yields $\Delta_{vap} H(298.15\,\mathrm{K}) = 31.0\,\mathrm{kJ\,mol^{-1}}$. As checks, for the other compounds in this review we were able to correlate $\Delta_{vap} H(298.15\,\mathrm{K})$ with the normal boiling point (*vide infra*, see Fig. 9 of Sec. 6.9) and also found $\Delta_{vap} H/T_b = (88.0 \pm 3.0)\,\mathrm{J\,mol^{-1}\,K^{-1}}$, in the range of typical statements of Trouton's Rule [1978A]. These estimations lead to $\Delta_{vap} H(298.15\,\mathrm{K}) = (31.2 \pm 1.5)\,\mathrm{kJ\,mol^{-1}}$ and $(30.9 \pm 1.0)\,\mathrm{kJ\,mol^{-1}}$, respectively. The value $\Delta_{vap} H(298.15\,\mathrm{K}) = (31.0 \pm 1.0)\,\mathrm{kJ\,mol^{-1}}$ is recommended. Using Eq. (1) and second virial coefficients taken from the DIPPR Tables [2001DIP] (datasheet revision date August, 1994), the correction to $\Delta_{vap} H(298.15\,\mathrm{K})$ due to nonideality of the gas is calculated as 0.13 $\mathrm{kJ\,mol^{-1}}$, which leads to $\Delta_{vap} H^o[Z\text{-}1,2\text{-}C_2H_2Cl_2] = (31.1 \pm 1.0)\,\mathrm{kJ\,mol^{-1}}$. The heat capacity of vaporization was derived as $\Delta_{vap} C_p = -45.0\,\mathrm{J\,mol^{-1}\,K^{-1}}$ from the difference of the reported heat capacities of the gas [1991GVA] and liquid [1934M].

*Enthalpy of Formation*. Data are summarized in Table 12. The only combustion calorimetry value for the enthalpy of formation of $Z$-1,2-dichloroethene is that of Eftring [1938E], who used a static bomb calorimeter and the "quartz spiral" method. The original results of Eftring were corrected by Smith *et al.* [1953SBK] and reevaluated by Cox and Pilcher [1970CP]. The data have subsequently been compiled by Pedley *et al.* [1986PNK] and lead to $\Delta_f H^o[Z\text{-CHCl}{=}\text{CHCl(l)}, 298.15\,\text{K}] = -(26.4 \pm 8.4)\,\text{kJ mol}^{-1}$ and $\Delta_f H^o[Z\text{-CHCl}{=}\text{CHCl(g)}, 298.15\,\text{K}] = (4.7 \pm 8.5)\,\text{kJ mol}^{-1}$. However, in cases where there are data from newer combustion studies, the enthalpies of formation derived from the data of Eftring appear to be systematically too positive (see Fig. 3). This observation suggests that these data should be treated cautiously.

The enthalpy of formation of $Z$-CHCl═CHCl is linked to that of 1,1,2,2-tetrachloroethane through the enthalpy of reaction (10), which was determined by Kirkbride [1956K] as $\Delta_{10}H(298.15\,\text{K}) = -(169.0 \pm 8.4)\,\text{kJ mol}^{-1}$, where the uncertainty is that estimated by Cox and Pilcher [1970CP]

$$Z\text{-CHCL}{=}\text{CHCl(l)} + \text{Cl}_2\text{(g)} \rightarrow 1{,}2{,}2\text{-C}_2\text{H}_2\text{Cl}_4\text{(l)}. \qquad (10)$$

Taking $\Delta_f H^o[1{,}1{,}2{,}2\text{-C}_2\text{H}_2\text{Cl}_4\text{(l)}, 298.15\,\text{K}] = -(202.4 \pm 2.9)\,\text{kJ mol}^{-1}$ (see Sec. 6.8), we calculate $\Delta_f H^o[Z\text{-CHCl}{=}\text{CHCl(l)}, 298.15\,\text{K}] = -(33.4 \pm 8.9)\,\text{kJ mol}^{-1}$ and $\Delta_f H^o[Z\text{-CHCl}{=}\text{CHCl(g)}, 298.15\,\text{K}] = -(2.4 \pm 9.0)\,\text{kJ mol}^{-1}$. Although the uncertainty in this result appears high, it is mostly due to the uncertainty in the enthalpy of chlorination estimated by Cox and Pilcher. It is not clear how they assigned the uncertainty and it is interesting that the data appear to be of much better accuracy when compared with our independent estimate of $\Delta_f H^o[Z\text{-CHCl}{=}\text{CHCl(g)}, 298.15\,\text{K}]$ (see below).

Another link is to the enthalpy of formation of 1,1,2-trichloroethane through equilibrium (11), which was studied by Levanova *et al.* [1975LTVa], [1975LTVb]

$$Z\text{-CHCl}{=}\text{CHCl(soln)} + \text{HCl(g)} \rightleftarrows 1{,}1{,}2\text{-}C_2\text{H}_3\text{Cl}_3\text{(soln)}. \qquad (11)$$

The equilibrium was established in tetrachloroethane solvent (isomer not specified) between 343 and 363 K with the catalysts $\text{AlCl}_3$ and $\text{FeCl}_3$. Experiments were also carried out with the $E$ isomer, but in that case the results were considered unreliable due to the presence of side reactions. For reaction (11) Levanova *et al.* [1975LTVa], [1975LTVb] derived $\log K_{11} = 3190/T - 7.4$, which corresponds to $\Delta_r H(353\,\text{K}) = -(61.1 \pm 2.1)\,\text{kJ mol}^{-1}$, where the uncertainty is that reported by Levanova *et al.* and is taken as $2\sigma$. To correct these values to 298.15 K, the heat capacity of gas phase 1,1,2-$\text{C}_2\text{H}_3\text{Cl}_3$ [1918C] was modified using $\Delta_{\text{vap}}C_p = -60.3\,\text{J mol}^{-1}\,\text{K}^{-1}$, derived from the temperature dependence of $\Delta_{\text{vap}}H$ measured by Majer *et al.* [1980MSS]. The gas phase $C_p$ data [1928R] on $Z$-CHCl═CHCl was corrected using $\Delta_{\text{vap}}C_p = -48.8\,\text{J mol}^{-1}\,\text{K}^{-1}$, derived from the data listed in reference [1982WEP]. These minor corrections yield $\Delta_{11}H(298.15\,\text{K}) = -(61.2 \pm 2.1)\,\text{kcal mol}^{-1}$. Enthalpies of specific interaction with the solvent are expected to be small, e.g., for $Z$-1,2-$\text{C}_2\text{H}_2\text{Cl}_2$ in chlorobenzene, $\Delta_{\text{interaction}}H = -0.3\,\text{kJ mol}^{-1}$ [1991BSI]. If these are neglected, and using $\Delta_f H^o[1{,}1{,}2\text{-C}_2\text{H}_3\text{Cl}_3\text{(l)}, 298.15\,\text{K}] = -(187.3 \pm 4.0)\,\text{kJ mol}^{-1}$ (see discussion for this compound), we calculate $\Delta_f H^o[Z\text{-CHCl}{=}\text{CHCl(l)}, 298.15\,\text{K}] = -(34.8 \pm 4.5)\,\text{kJ mol}^{-1}$ and $\Delta_f H^o[Z\text{-CHCl}{=}\text{CHCl(g)}, 298.15\,\text{K}] = -(2.8 \pm 4.7)\,\text{kJ mol}^{-1}$.

Because of the short temperature range of the experiments, we have also performed a Third Law analysis on the data. For 1,1,2-$\text{C}_2\text{H}_3\text{Cl}_3$, $\Delta_{\text{vap}}S(386.6\,\text{K}) = 89.81\,\text{J mol}^{-1}\,\text{K}^{-1}$ was calculated from the enthalpy of vaporization at the boiling point reported by Majer *et al.* [1980MSS]. Using $\Delta_{\text{vap}}C_p$ as above, $\Delta_{\text{vap}}S(298.15\,\text{K})[1{,}1{,}2\text{-C}_2\text{H}_3\text{Cl}_3] = 105.5\,\text{J mol}^{-1}\,\text{K}^{-1}$ was calculated. This is in good agreement with the value 104.6 $\text{J mol}^{-1}\,\text{K}^{-1}$ derived from the gas and liquid phase entropy data of reference [1982WEP]. The value $\Delta_{\text{vap}}S(298.15\,\text{K})[Z\text{-CHCl}{=}\text{CHCl}] = 91.2\,\text{J mol}^{-1}\,\text{K}^{-1}$ was derived from the entropy data of reference [1982WEP]. The Third Law analysis yields $\Delta_r H(298.15\,\text{K}) = -66.6\,\text{kJ mol}^{-1}$ and $\Delta_f H^o[Z\text{-CHCl}{=}\text{CHCl(g)}, 298.15\,\text{K}] = 2.6\,\text{kJ mol}^{-1}$. The agreement between the Second and Third Law analysis is only fair, which may be due to the estimations involved, the short temperature range of the experiments, the presence of side reactions, and the excess thermodynamic properties of solvation.

Finally, Rozhnov *et al.* [1974RLD] have studied the equilibrium between the three dichloroethene isomers in the gas phase between 447 and 673 K

$$\text{CH}_2{=}\text{CCl}_2\text{(g)} \leftrightharpoons E/Z\text{-CHCl}{=}\text{CHCl(g)}. \qquad (12)$$

The compounds were isomerized in a flow reactor in the presence of catalysts $\text{NiCl}_2$ on activated carbon or $\text{BiCl}_3$ on activated carbon. We have plotted their data (Fig. 6) and find $\log K_{12} = (316 \pm 42)/\text{T} + (-2.90 \pm 79.6) \times 10^{-3}$, where the uncertainties are $2\sigma$. This corresponds to $\Delta_{12}H(560\,\text{K}) = -(6.05 \pm 0.80)\,\text{kJ mol}^{-1}$. Using gas phase heat capacities from Gurvich *et al.* [1991GVA], this becomes $\Delta_{12}H(298.15\,\text{K}) = -(5.60 \pm 0.80)\,\text{kJ mol}^{-1}$. A Third Law analysis was also performed. Using entropies and heat capacities from Gurvich *et al.* [1991GVA], we find $\Delta_{12}H(560\,\text{K}) = -(5.88 \pm 0.4)\,\text{kJ mol}^{-1}$ and $\Delta_{12}H(298.15\,\text{K}) = -(5.43 \pm 0.4)\,\text{kJ mol}^{-1}$. The uncertainties are estimated $2\sigma$ values and include both the uncertainty in the equilibrium constant and uncertainty in the thermodynamic properties. The Second and Third Law analyses are in excellent agreement. The latter is preferred since the molecular properties of the dichloroethenes are well established and have no uncertainties relating to low frequency internal rotational modes. In conjunction with $\Delta_f H^o[\text{CH}_2{=}\text{CCl}_2\text{(g)}, 298.15\,\text{K}] = (2.4 \pm 2.0)\,\text{kJ mol}^{-1}$, we obtain $\Delta_f H^o[Z\text{-CHCl}{=}\text{CHCl(g)}, 298.15\,\text{K}] = -(3.03 \pm 2.0)\,\text{kJ mol}^{-1}$. A very similar result is obtained if the entropies and heat capacities of Rodgers [1982R] are used instead of those of Gurvich.

*Recommendation*. The values of Rozhnov *et al.* [1974RLD] on the $E/Z$ equilibrium (Fig. 7, discussed in the evaluation for the $E$ isomer, Sec. 5.4) are in excellent agreement with several other studies. This gives us confidence that their data are of good accuracy and the value derivable from that work, $\Delta_f H^o[Z\text{-CHCl}{=}\text{CHCl(g)}, 298.15\,\text{K}] = -(3.0 \pm 2.0)\,\text{kJ mol}^{-1}$, is selected. The combustion value of Eftring

TABLE 12. Enthalpies of formation of *Z*-1,2-dichloroethene derived from reported experimental data

| $\Delta_f H^o$ (g), 298.15 K (kJ mol$^{-1}$) | Reported uncertainty kJ mol$^{-1}$ | Temp. (K) | Methos(s) | Ref/Year | Comments |
|---|---|---|---|---|---|
| Experimental | | | | | |
| −3.6 | 2.1[a] | 293–353 | Equilibrium of hydrochlorination<br>$Z$-$C_2H_2Cl_2$ (sol)+HCl (g)$\rightarrow$1,1,2-$C_2H_3Cl_3$ (sol) | [1975LTVa,b] | 1, Second Law analysis, $\Delta_f H^o$[1,1,2-$C_2H_3Cl_3$] used in calculation. |
| 1.7 | 2.1[a] | 293–353 | Equilibrium of hydrochlorination<br>$Z$-$C_2H_2Cl_2$ (sol)+HCl (g)$\rightarrow$1,1,2-$C_2H_3Cl_3$ (sol) | [1975LTVa,b] | 2, Third Law analysis, $\Delta_f H^o$[1,1,2-$C_2H_3Cl_3$] used in calculation. |
| −3.2 | N.R.<br>(0.5)[b] | 447–673 | Equilibrium<br>$CH_2{=}CCl_2$ (g)$\rightleftarrows Z$-CHCl$=$CHCl (g) | [1974RLD] | 3, Reported data reanalyzed at NIST using Second Law, $\Delta_f H^o$[$CH_2{=}CCl_2$] used in calculation. |
| −3.0 | N.R.<br>(0.4)[b] | 447–673 | Equilibrium<br>$CH_2{=}CCl_2$ (g)$\rightleftarrows Z$-CHCl$=$CHCl (g) | [1974RLD] | 4, Reported data reanalyzed at NIST using Third Law, $\Delta_f H^o$[$CH_2{=}CCl_2$] used in calculation. |
| −2.4 | N.R.<br>(8.4)[c] | 298 | Enthalpy of chlorination<br>$Z$-1,2-$C_2H_2Cl_2$ (l)+$Cl_2$ (g)$\rightarrow$1,1,2,2-$C_2H_2Cl_4$ (l) | [1956K] | 5, Reanalyzed by [1970CP]. We have used a newer value of $\Delta_f H^o$[1,1,2,2-$C_2H_2Cl_2$ (l)] in the calculation. |
| 4.6 | 8.4 | 298 | Combustion calorimetry of liquid | [1938E]<br>[1953SBK]<br>[1970CP] | 6, Static Bomb. Data corrected by Smith *et al.* in 1953. Reanalyzed and auxiliary quantities updated by [1970CP]. |
| Reviews and Evaluations | | | | | |
| 4.1 | 1.4 | 298 | | [1991GVA] | Evaluation date uncertain; same value as previous edition [1979G]. |
| 4.6 | 8.5 | 298 | | [1986PNK] | |
| 4.1 | 1.1 | 298 | | [1983KP] | |
| −2.8 | N.R.[d] | 298 | | [1982R] | |
| 4.2 | 8.8 | 298 | | [1970CP] | |
| 1.3 | N.R.[d] | 298 | | [1969SWS] | |

[a] Reported uncertainty refers only to the measured reaction enthalpy and does not include uncertainty in auxiliary thermodynamic quantities.

[b] Not reported, the parenthetical value is that estimated in this work and refers only to the measured reaction enthalpy.

[c] Not reported, the parenthetical value is that estimated by Cox and Pilcher [1970CP].

[d] Not reported.

**Comments:**

1. Reaction carried out in tetrachloroethane. $\Delta_r H(353\ \mathrm{K}) = -61.1$ kJ mol$^{-1}$ and $\Delta_r H(398.15\ \mathrm{K}) = -61.2$ kJ mol$^{-1}$ and (see Discussion). Together with $\Delta_f H^o$[1,1,2-$C_2H_3Cl_3$ (l), 298.15 K]$=-(188.3\pm 4.0)$ kJ mol$^{-1}$ (see Sec. 6.6), we obtain calculate $\Delta_f H^o$[$Z$-CHCl$=$CHCl (l), 298.15 K]$=-34.7$ kJ mol$^{-1}$. Excess thermodynamic properties of solvation were neglected in the analysis.
2. Reaction carried out in tetrachloroethane. $\Delta_r H(353\ \mathrm{K}) = -66.5$ kJ mol$^{-1}$ and $\Delta_r H(298.15\ \mathrm{K}) = -66.6$ kJ mol$^{-1}$ and (see Discussion). Together with $\Delta_f H^o$[1,1,2-$C_2H_3Cl_3$ (l), 298.15 K]$=-(188.3\pm 4.0)$ mol$^{-1}$ (see Sec. 6.6), we obtain calculate $\Delta_f H^o$[$Z$-CHCl$=$CHCl (l), 298.15 K]$=-29.4$ kJ mol$^{-1}$. Excess thermodynamic properties of solvation were neglected in the analysis.
3. Reanalyzed at NIST (see Discussion). $\Delta_r H(560\ \mathrm{K}) = -(6.05\pm 0.4)$ kJ mol$^{-1}$. Using heat capacities from Gurvich, $\Delta_r H(298.15\ \mathrm{K}) = -(5.60\pm 0.5)$ kJ mol$^{-1}$. The heat capacities of Rodgers give a very similar result. Reported value calculated using $\Delta_r H^o$[$CH_2{=}CCl_2$ (g), 298.15 K]$=(2.4\pm 2.0)$ kJ mol$^{-1}$.
4. Reanalyzed at NIST (see Discussion). $\Delta_r H(560\ \mathrm{K}) = -(5.88\pm 0.4)$ kJ mol$^{-1}$. Using heat capacities from Gurvich *et al.* [1991GVA], $\Delta_r H(298.15\ \mathrm{K}) = (-5.40\pm 0.4)$ kJ mol$^{-1}$. The heat capacities of Rodgers [1982R] give a very similar result. Calculated using $\Delta_f H^o$[$CH_2{=}CCl_2$ (g), 298.15 K]$=(2.4\pm 2.0)$ kJ mol$^{-1}$.
5. $\Delta_r H(298.15\ \mathrm{K}) = -(169.0\pm 8.4)$ kJ mol$^{-1}$. The quoted value is obtained using $\Delta_f H^o$[1,1,2,2-$C_2H_2Cl_4$ (l), 298.15 K]$=-(202.4\pm 2.9)$ kJ mol$^{-1}$.
6. The original results of Eftring [1938E] were corrected by Smith *et al.* [1953SBK] and reevaluated by Cox and Pilcher [1970CP]. The data have subsequently been compiled by Pedley *et al.* [1986PNK]. The purity of the sample is uncertain. Corrected results are $\Delta_c H$[(l), 298.15 K]$=-(1093.7\pm 8.4)$ kJ mol$^{-1}$, refers to reaction $E$-1,2-$C_2H_2Cl_2$ (l)+2$O_2$ (g)$\rightarrow$2$CO_2$ (g)+2HCl (aq:600). The following auxiliary values were used: $\Delta_f H^o$[$CO_2$ (g), 298.15 K]$=-(393.51\pm 0.13)$ kJ mol$^{-1}$ and $\Delta_f H^o$[HCl (aq:600), 298.15 K]$=-(166.540\pm 0.10)$ kJ mol$^{-1}$. The data result in $\Delta_f H^o$[$CH_2{=}CCl_2$ (l), 298.15 K]$=-(26.40\pm 8.4)$ kJ mol$^{-1}$.

[1938E] appears to be much too positive, as is the case for several other chlorine compounds for which independent data are available (see Fig. 3). Notice that the equilibrium data define the *relative* enthalpies of formation of the three dichloroethenes very precisely, within about 0.4 kJ mol$^{-1}$. The absolute numbers are somewhat less well determined. Note that the least stable dichloroethene isomer is that with all chlorines on a single carbon.

## 5.6. Trichloroethene

*Enthalpy of Vaporization*. The enthalpy of vaporization at 298.15 K has been determined by Mathews [1926M] as $\Delta_{vap}H(298.15\ \mathrm{K}) = (34.7\pm 0.4)$ kJ mol$^{-1}$ from measurements made near the boiling point. More recently, Majer *et al.* [1980MSS] calorimetrically measured the enthalpy of vaporization between 298.15 and 353 K and found

$\Delta_{\mathrm{vap}}H(298.15\ \mathrm{K})=(34.49\pm0.09)$. The value $\Delta_{\mathrm{vap}}H(298.15\ \mathrm{K})=(34.49\pm0.09)\ \mathrm{kJ\ mol^{-1}}$ is selected. Using Eq. (1) and other data from the DIPPR database [2001DIP] (datasheet revision date August, 1989), the correction due to non-ideality of the gas is calculated as 0.18 $\mathrm{kJ\ mol^{-1}}$, slightly different from the value of 0.08 $\mathrm{kJ\ mol^{-1}}$ calculated by Majer and Svoboda [1985MS]. Based on Fig. 1, the latter value appears to be correct and $\Delta_{\mathrm{vap}}H^{\mathrm{o}}(298.15\ \mathrm{K})=(34.57\pm0.09)\ \mathrm{kJ\ mol^{-1}}$ is derived. The heat capacity of vaporization is derived as $\Delta_{\mathrm{vap}}C_{\mathrm{p}}=-50.3\ \mathrm{J\ mol^{-1}\ K^{-1}}$ from the temperature dependence of the vaporization data of [1980MSS].

*Enthalpy of Formation*. Data are summarized in Table 13. The enthalpy of formation has been measured by combustion calorimetry by two groups. The results of Eftring [1938E] were corrected by Smith *et al.* [1953SBK] and have been used as the basis of several previous critical evaluations. These data have been reevaluated by Cox and Pilcher [1970CP] and subsequently compiled and updated by Pedley *et al.* [1986PNK], who used a newer value for the enthalpy of dilution of HCl. These data yield $\Delta_{\mathrm{f}}H^{\mathrm{o}}[\mathrm{C_2HCl_3(l)},\ 298.15\ \mathrm{K}]=-40.2\ \mathrm{kJ\ mol^{-1}}$. The more recent results of Papina and Kolesov [1985PK] using a rotating bomb calorimeter yield the significantly lower value $\Delta_{\mathrm{f}}H^{\mathrm{o}}[\mathrm{C_2HCl_3(l)},\ 298.15\ \mathrm{K}]=-(53.11\pm2.9)\ \mathrm{kJ\ mol^{-1}}$. The enthalpy of formation of $\mathrm{C_2HCl_3}$ is also linked to that of pentachloroethane through the enthalpy of chlorination measured by Kirkbride [1956K]. However, since $\Delta_{\mathrm{f}}H(\mathrm{C_2HCl_5})$ is not well established by an independent methodology (see discussion for that compound), the experiments of Kirkbride establish only a relative and not absolute value.

More helpful are the data of Levanova *et al.* [1976LBR], who measured the hydrochlorination equilibrium in an organic solvent (not further specified) and reported $\log K=7.54-2372/T$ between 313 and 353 K

$$\mathrm{CH_2ClCCl_3(soln)}\rightleftarrows\mathrm{C_2HCl_3(soln)}+\mathrm{HCl(g)}. \qquad (13)$$

Since the value of $\Delta_{\mathrm{f}}H(\mathrm{CH_2ClCCl_3})$ is one of the better established of the highly chlorinated compounds, these data should help us choose between the combustion calorimetry data. From their Second Law analysis of Levanova *et al.* [1976LBR] report $\Delta_{\mathrm{r}}H(333\ \mathrm{K})=(45.4\pm0.4)\ \mathrm{kJ\ mol^{-1}}$. To adjust this to 298.15 K, the gas phase $C_p$ values [1981C], [1982R] were converted to the liquid phase by subtraction of $\Delta_{\mathrm{vap}}C_{\mathrm{p}}$. For trichloroethene $\Delta_{\mathrm{vap}}C_{\mathrm{p}}=-50.3\ \mathrm{J\ mol^{-1}\ K^{-1}}$ was derived from the temperature dependent enthalpies of vaporization measured calorimetrically by Majer *et al.* [1980MSS] between 298 and 353 K. For 1,1,1,2-$\mathrm{C_2H_2Cl_4}$, $\Delta_{\mathrm{vap}}C_{\mathrm{p}}=-65.8\ \mathrm{J\ mol^{-1}\ K^{-1}}$ was derived from the correlations discussed in the evaluation of pentachloroethane, Sec. 6.9. These small corrections yield $\Delta_{\mathrm{r}}H(298.15\ \mathrm{K})=(45.8\pm0.4)\ \mathrm{kJ\ mol^{-1}}$. Using $\Delta_{\mathrm{f}}H^{\mathrm{o}}[1,1,1,2\text{-}\mathrm{C_2H_2Cl_4(l)},\ 298.15\ \mathrm{K}]=-(193.45\pm2.3)\ \mathrm{kJ\ mol^{-1}}$, which should be a reliable value (see Sec. 6.7), and $\Delta_{\mathrm{f}}H^{\mathrm{o}}[\mathrm{HCl(g)},\ 298.15\ \mathrm{K}]=-(92.31\pm0.10)\ \mathrm{kJ\ mol^{-1}}$, gives $\Delta_{\mathrm{f}}H^{\mathrm{o}}[\mathrm{C_2HCl_3(l)},\ 298.15\ \mathrm{K}]=-(55.3\pm2.3)\ \mathrm{kJ\ mol^{-1}}$. A Third Law analysis was also performed. The gas phase data [1982R] on trichloroethene were adjusted to the liquid phase using data derived from the study of Majer *et al.* [1980MSS], and that for 1,1,1,2-$\mathrm{C_2H_2Cl_4}$ from the correlations discussed in the section on pentachloroethane. This analysis yields $\Delta_{\mathrm{r}}H(298.15\ \mathrm{K})=(51.7\pm0.4)\ \mathrm{kJ\ mol^{-1}}$ and $\Delta_{\mathrm{f}}H^{\mathrm{o}}[\mathrm{C_2HCl_3(l)},\ 298.15\ \mathrm{K}]=-(49.4\pm2.3)\ \mathrm{kJ\ mol^{-1}}$. Note that the Second and Third Law analyses are in only fair agreement and that the reaction enthalpies from the two analyses do not agree within the uncertainty limits indicated by Levanova *et al.* [1976LBR]. The difference presumably results from the summed uncertainties in the estimated properties, the excess thermodynamic properties associated with solvation, and the uncertainty in the Second Law analysis due to the short experimental temperature range. Our evaluations of data from this type of experiment would suggest that more realistic uncertainty limits for the reaction enthalpy are $\pm4\ \mathrm{kJ\ mol^{-1}}$. Despite this, the equilibrium hydrochlorination results clearly support the more negative of the combustion values.

*Recommendation*. The rotating bomb combustion calorimetry result of Papina and Kolesov [1985PK] should be superior to the static combustion experiments of Eftring [1938E], especially considering the trends observed in Fig. 3. It is also supported by the equilibrium hydrochlorination data of Levanova *et al.* [1976LBR]. Finally, selection of the more negative value brings all of the experimental enthalpy of reaction data linking trichloroethene, tetrachloroethene, pentachloroethane, and hexachloroethane (see Secs. 5.7, 6.9, and 6.10) into approximate agreement. This is not the case if the combustion data of Eftring are accepted. Our final selected values are $\Delta_{\mathrm{f}}H^{\mathrm{o}}[\mathrm{C_2HCl_3(l)},\ 298.15\ \mathrm{K}]=-(52.1\pm3.0)\ \mathrm{kJ\ mol^{-1}}$ and $\Delta_{\mathrm{f}}H^{\mathrm{o}}[\mathrm{C_2HCl_3(g)},\ 298.15\ \mathrm{K}]=-(17.5\pm3.0)\ \mathrm{kJ\ mol^{-1}}$. These are based primarily on the combustion result of Papina and Kolesov [1985PK], although the value was made slightly more positive ($1\ \mathrm{kJ\ mol^{-1}}$) to give a better global fit with all results interlinking $\mathrm{C_2HCl_3}$, $\mathrm{C_2HCl_5}$, $\mathrm{C_2Cl_4}$, and $\mathrm{C_2Cl_6}$.

## 5.7. Tetrachloroethene

*Enthalpy of Vaporization*. Majer *et al.* [1980MSS] calorimetrically measured the enthalpy of vaporization between 298 and 358 K and found $\Delta_{\mathrm{vap}}H(298.15\ \mathrm{K})=(39.70\pm0.09)\ \mathrm{kJ\ mol^{-1}}$. A much earlier determination is that of Mathews [1926M], who determined the value near the boiling point as $\Delta_{\mathrm{vap}}H(393.8\ \mathrm{K})=(34.72\pm0.04)\ \mathrm{kJ\ mol^{-1}}$. Cox and Pilcher [1970CP] extrapolated this data and obtained $\Delta_{\mathrm{vap}}H(298.15\ \mathrm{K})=(39.7\pm0.8)\ \mathrm{kJ\ mol^{-1}}$, similar to the value of $\Delta_{\mathrm{vap}}H^{\mathrm{o}}(298.15\ \mathrm{K})=(40.0\pm0.4)\ \mathrm{kJ\ mol^{-1}}$ obtained by Gurvich *et al.* [1991GVA] from this same data. No details were given of the extrapolation procedures. More reliably, we can use the temperature dependent $\Delta_{\mathrm{vap}}H$ data of Majer *et al.* [1980MSS] to obtain $\Delta_{\mathrm{vap}}C_{\mathrm{p}}(\mathrm{C_2Cl_4})=-(51.8\pm0.5)\ \mathrm{J\ mol^{-1}\ K^{-1}}$. Using this value, the extrapolated data of Mathews yield $\Delta_{\mathrm{vap}}H(298.15\ \mathrm{K})=(39.67\pm0.06)\ \mathrm{kJ\ mol^{-1}}$, in excellent agreement with the measurement of Majer *et al.* The value $\Delta_{\mathrm{vap}}H(298.15\ \mathrm{K})=(39.68$

TABLE 13. Enthalpies of formation of trichloroethene derived from reported experimental data

| $\Delta_f H^o$ (g), 298.15 K (kJ mol$^{-1}$) | Reported uncertainty kJ mol$^{-1}$ | Temp. (K) | Method(s) | Ref/Year | Comments |
|---|---|---|---|---|---|
| Experimental | | | | | |
| −18.5 | 2.9 | 298 | Combustion calorimetry of liquid | [1985PK] | 1, Reported value updated using newer enthalpy of vaporization. |
| −20.7 | 0.4[a]<br>(4.0) | 313–353 | Equilibrium of hydrochlorination<br>$CH_2ClCCl_3$ (soln)$\rightleftarrows C_2HCl_3$ (soln)$+$HCl (g) | [1976LBR] | 2, Second Law analysis, $\Delta_f H^o[CH_2ClCCl_3]$ used in calculation. |
| −14.8 | 0.4[a]<br>(4.0) | 313–353 | Equilibrium of hydrochlorination<br>$CH_2ClCCl_3$ (soln)$\rightleftarrows C_2HCl_3$ (soln)$+$HCl (g) | [1976LBR] | 3, Third Law analysis, $\Delta_f H^o[CH_2ClCCl_3]$ used in calculation. |
| −17.5 | N.R.[b]<br>(5.0) | 298 | Enthalpy of chlorination<br>$C_2HCl_3$ (l)$+Cl_2$ (g)$\rightarrow C_2HCl_5$ (l) | [1956K] | 4, This was a primary result used to derive $\Delta_f H^o[C_2HCl_5$ (l)$]$. |
| 9.7 | 8.4 | 298 | Combustion calorimetry of liquid | [1938E]<br>[1953SBR]<br>[1986PNK] | 5, Data corrected by Smith *et al.* in 1953; data reanalyzed and auxiliary quantities updated by [1986PNK]. |
| Reviews and Evaluations | | | | | |
| 19.1 | 3.1 | 298 | | [1991GVA] | Evaluation data uncertain; different value from previous edition, [1979G]. |
| 9.0 | 8.8 | 298 | | [1986PNK] | |
| −4.1 | 1.2 | 298 | | [1983KP] | |
| −9.6 | N.R.[c] | 298 | | [1982R] | |
| −8.4 | 6.7 | 298 | | [1970CP] | |
| −5.9 | N.R.[c] | 298 | | [1969SWS] | |

[a] Reported uncertainty refers only to the measured reaction enthalpy. The parenthetical value is that estimated by us by comparison with similar experiments.

[b] Not reported. The parenthetical value refers to the reaction enthalpy and is $2\sigma$ as calculated by us from the reported data.

[c] Not reported.

**Comments:**

1. Rotating bomb calorimetry. High purity sample (99.97 mol %). $\Delta_c H[(\mathrm{l}), 298.15\,\mathrm{K}] = -(947.7 \pm 2.9)$ kJ mol$^{-1}$, refers to reaction $C_2HCl_3$ (l)$+H_2O$ (l) $+$ $1.5O_2$ (g)$\rightarrow 2CO_2$ (g)$+3$HCl (aq:600). The following auxiliary values were used: $\Delta_f H^o[CO_2\,(\mathrm{g}), 298.15\,\mathrm{K}] = -(393.51 \pm 0.13)$ kJ mol$^{-1}$, $\Delta_f H^o[H_2O\,(\mathrm{l}), 298.15\,\mathrm{K}] = -(285.830 \pm 0.040)$ kJ mol$^{-1}$, and $\Delta_f H^o[\mathrm{HCl\,(aq:600)}, 298.15\,\mathrm{K}] = -(166.540 \pm 0.10)$ kJ mol$^{-1}$. These data result $\Delta_f H^o[C_2HCl_3\,(\mathrm{l}), 298.15\,\mathrm{K}] = -(53.11 \pm 2.9)$ kJ mol$^{-1}$. Papina and Kolesov used $\Delta_{vap} H^o(298.15\,\mathrm{K}) = (33.97 \pm 0.13)$ from [1979G] to obtain the gas phase value, while we prefer $\Delta_{vap} H^o(298.15\,\mathrm{K}) = (34.57 \pm 0.09)$ kJ mol$^{-1}$.
2. Second Law analysis of equilibrium $CH_2ClCCl_3$ (soln)$\rightleftarrows C_2HCl_3$ (soln)$+$HCl (g) yields $\Delta_r H(333\,\mathrm{K}) = (45.4 \pm 0.4)$ kJ mol$^{-1}$; This becomes $\Delta_r H(298.15\,\mathrm{K}) = (45.8 \pm 0.5)$ kJ mol$^{-1}$ (see Discussion). The quoted value is obtained using $\Delta_f H^o[CH_2ClCCl_3\,(\mathrm{l}), 298.15\,\mathrm{K}] = -(193.45 \pm 2.3)$ kJ mol$^{-1}$ (see Sec. 6.7), and $\Delta_f H^o[\mathrm{HCl\,(g)}, 298.15\,\mathrm{K}] = -(92.31 \pm 0.10)$ kJ mol$^{-1}$. Excess thermodynamic properties of solvation have been neglected.
3. Third Law analysis of equilibrium $CH_2ClCCl_3$ (soln)$\rightleftarrows C_2HCl_3$ (soln)$+$HCl (g) yields $\Delta_r H(298.15\,\mathrm{K}) = 51.7$ kJ mol$^{-1}$ (see Discussion). The quoted value is obtained using $\Delta_f H^o[CH_2ClCCl_3\,(\mathrm{l}), 298.15\,\mathrm{K}] = -(193.45 \pm 2.3)$ kJ mol$^{-1}$ (see Sec. 6.7), and $\Delta_f H^o[\mathrm{HCl\,(g)}, 298.15\,\mathrm{K}] = -(92.31 \pm 0.10)$ kJ mol$^{-1}$. Excess thermodynamic properties of solvation have been neglected.
4. $\Delta_r H(298.15\,\mathrm{K}) = -151.2$ kJ mol$^{-1}$. This was a primary (though not only) result used to derive $\Delta_f H^o[C_2HCl_5\,(\mathrm{l}), 298.15\,\mathrm{K}]$, the value of which is not well established. Thus, although self-consistent, these data cannot provide a completely independent confirmation of the selected value. In conjunction with $\Delta_f H^o[C_2HCl_5\,(\mathrm{l}), 298.15\,\mathrm{K}] = -(203.3 \pm 4.0)$ kJ mol$^{-1}$ (see Sec. 6.9), we derive $\Delta_f H^o[C_2HCl_3\,(\mathrm{l}), 298.15\,\mathrm{K}] = -(52.1 \pm 2.9)$ kJ mol$^{-1}$.
5. Experiments by Eftring in 1938 as listed and corrected by Smith *et al.* in 1953. $\Delta_c H(298.15\,\mathrm{K}) = -(956.5 \pm 8.4)$ kJ mol$^{-1}$. Purity of substrate tested is uncertain. Auxiliary quantities as in Comment 1. These data result in $\Delta_f H^o[C_2HCl_3\,(\mathrm{l}), 298.15\,\mathrm{K}] = -(44.31 \pm 8.4)$ kJ mol$^{-1}$.

$\pm 0.05)$ kJ mol$^{-1}$ is selected. A correction of 0.04 kJ mol$^{-1}$ at 298.15 K due to nonideality of the gas was taken from Majer and Svoboda [1985MS] (our calculation gives 0.045 kJ mol$^{-1}$) and $\Delta_{vap} H^o(298.15\,\mathrm{K}) = (39.72 \pm 0.05)$ kJ mol$^{-1}$ is derived.

*Enthalpy of Formation*. Data are summarized in Table 14.

*Combustion Results*. The only measurement of the enthalpy of combustion is by Eftring [1938E]. The results of Eftring were corrected by Smith *et al.* [1953SBK] and have been used as the basis of several previous critical evaluations. These data have been reevaluated by Cox and Pilcher [1970CP] and subsequently compiled and updated by Pedley *et al.* [1986PNK], who used a newer value for the enthalpy of dilution of HCl. These data yield $\Delta_f H^o[C_2Cl_4(\mathrm{l}),\ 298.15\,\mathrm{K}] = -(50.6 \pm 8.4)$ kJ mol$^{-1}$. We do not believe this value to be reliable, since for the other compounds where there is newer data, the enthalpies of formation derived from the combustion studies of Eftring appear to be too positive (see Fig. 2). In general, the difficulties appear worse for the more highly chlorinated species.

Alternative values may be derived through various reactions that link $\Delta_f H(C_2Cl_4)$ with enthalpies of formation of other chlorinated species. Several studies have related $\Delta_f H(C_2Cl_4)$ and $\Delta_f H(C_2Cl_6)$ through the enthalpy of chlorination. Unfortunately $\Delta_f H(C_2Cl_6)$ is not well known, so these works establish only a relative value. For an absolute value there are essentially two currently available sets of data with which to work. First, through studies of the hydrochlorination reaction, we are able to relate $\Delta_f H(C_2Cl_4)$ and $\Delta_f H(C_2HCl_5)$. Since $\Delta_f H(C_2HCl_5)$ is linked to $\Delta_f H(C_2HCl_3)$, which has a reliable value, we are able to derive an absolute value for $\Delta_f H(C_2Cl_4)$. More directly, the recent study of Huybrechts *et al.* [1996HNMa] on the gas phase pyrolysis of $CCl_4$ establishes values for the high temperature equilibria involving $CCl_4$, $C_2Cl_4$, $C_2Cl_6$, and $Cl_2$. In this case we can use the well-known properties of tetrachloromethane to establish $\Delta_f H(C_2Cl_4)$.

*Hydrochlorination*. The solution phase hydrochlorination equilibrium, reaction (14), has been studied by Levanova *et al.* [1979LBR]

$$C_2HCl_5(soln) \rightleftarrows C_2Cl_4(soln) + HCl(g). \tag{14}$$

They found $\log K_{14} = 7.42 - 2360/T$ between 363 and 383 K. Their Second Law analysis yields $\Delta_r H(373\,\mathrm{K}) = (45.1 \pm 4.2)\,\mathrm{kJ\,mol^{-1}}$, where the uncertainty is $2\sigma$ and is that estimated by us by comparison with similar experiments. To correct this to 298.15 K, the gas phase heat capacity data of [1994FKM] were adjusted using $\Delta_{vap}C_p(C_2Cl_4) = -51.8\,\mathrm{J\,mol^{-1}\,K^{-1}}$, derived from the data of Majer *et al.* [1980MSS], and $\Delta_{vap}C_p(C_2HCl_5) = -67.7\,\mathrm{J\,mol^{-1}\,K^{-1}}$, (see Sec. 6.9). These data yield $\Delta_r H(298.15\,\mathrm{K}) = (46.2 \pm 4.2)\,\mathrm{kJ\,mol^{-1}}$. A Third Law analysis using $\Delta_{vap}S(C_2Cl_4,\ 298.15\,\mathrm{K}) = 102.3\,\mathrm{J\,mol^{-1}\,K^{-1}}$, derived from the data of Majer *et al.* [1980MSS], and $\Delta_{vap}S(C_2HCl_5,\ 298.15\,\mathrm{K}) = 115.0\,\mathrm{J\,mol^{-1}\,K^{-1}}$, derived as discussed in Sec. 6.9, yields $\Delta_r H(298.15\,\mathrm{K}) = (51.5 \pm 4.2)\,\mathrm{kJ\,mol^{-1}}$, where the uncertainty is $2\sigma$ and is that estimated by us by comparison with similar experiments. In general the Third Law analysis would be expected to be more accurate given the short temperature range of the experiments. However, given the uncertainties associated with the estimated data and the fact that we have ignored the excess thermodynamic properties of solvation, we choose to average the results. Combined with the selected value of $\Delta_f H^o[C_2HCl_5(l),\ 298.15\,\mathrm{K}] = -(203.3 \pm 4.0)\,\mathrm{kJ\,mol^{-1}}$, we calculate $\Delta_f H^o[C_2Cl_4(l),\ 298.15\,\mathrm{K}] = -62.2\,\mathrm{kJ\,mol^{-1}}$. Using $\Delta_{vap}H^o(298.15\,\mathrm{K}) = (34.72 \pm 0.09)\,\mathrm{kJ\,mol^{-1}}$, we derive $\Delta_f H^o[C_2Cl_4(g),\ 298.15\,\mathrm{K}] = -22.5\,\mathrm{kJ\,mol^{-1}}$.

*Tetrachloromethane Pyrolysis*. Pyrolysis of tetrachloromethane has recently been studied in detail by Huybrechts *et al.* [1996HNMa], [1996HNMb] and leads to a mixture of $CCl_4$, $C_2Cl_4$, $C_2Cl_6$, and $Cl_2$. They followed the reaction in a static system at 696.6 K for a period of about 1 week and their data show that the above components approach equilibrium after about 3 days. Huybrechts *et al.* determined the organic components by GC analyses and the end $Cl_2$ fraction by condensing out the organics at 189 K and ascribing the remaining pressure in the vessel to $Cl_2$. These data should be reliable. They report the equilibrium pressures at 696.6 K as $p(C_2Cl_6) = 3.8 \times 10^{-4}$ atm (38.5 Pa), $p(C_2Cl_4) = 7.22 \times 10^{-3}$ atm (731.6 Pa), $p(CCl_4) = 9.55 \times 10^{-2}$ atm (9677 Pa), and $p(Cl_2) = 1.48 \times 10^{-2}$ atm (1500 Pa).

These data can be used to calculate the equilibrium constants for reactions (15) and (16):

$$2CCl_4(g) \rightleftarrows C_2Cl_4(g) + 2Cl_2(g) \tag{15}$$

$$C_2Cl_6(g) \rightleftarrows C_2Cl_4(g) + Cl_2(g). \tag{16}$$

The data correspond to $K_{15}(696.6\,\mathrm{K}) = 17.6\,\mathrm{Pa}$ and $K_{16}(696.6\,\mathrm{K}) = 28.5\,\mathrm{kPa}$. Huybrechts *et al.* made no estimates of the uncertainty in their data. For reaction (15), where all components were present in large amounts, we have generously estimated the $2\sigma$ uncertainty in $K_{14}$ to be ±50%. For reaction (16), $C_2Cl_6$ was present in very small amounts and there was more scatter in the concentration of this component (see Fig. 12 of [1996HNMa]). We estimate the $2\sigma$ uncertainty in $K_{16}$ to be a factor of 2. From a Third Law analysis, using entropies and heat capacities from the TRC Tables [1981C], [1985R], we calculate $\Delta_{15}H(696.6\,\mathrm{K}) = (161.7 \pm 2.4)\,\mathrm{kJ\,mol^{-1}}$ and $\Delta_{15}H(298.15\,\mathrm{K}) = (165.1 \pm 2.4)\,\mathrm{kJ\,mol^{-1}}$. Using $\Delta_f H^o[CCl_4(g),\ 298.15\,\mathrm{K}] = -(95.6 \pm 2.5)\,\mathrm{kJ\,mol^{-1}}$ (see Sec. 3.5), this leads to $\Delta_f H^o[C_2Cl_4(g),\ 298.15\,\mathrm{K}] = -(25.9 \pm 3.5)\,\mathrm{kJ\,mol^{-1}}$. Alternatively, if entropies and heat capacities are taken from Gurvich *et al.* [1991GVA], we derive $\Delta_f H^o[C_2Cl_4(g),\ 298.15\,\mathrm{K}] = -(24.7 \pm 3.5)\,\mathrm{kJ\,mol^{-1}}$. These values are in very poor agreement with the combustion value, but in good agreement with that derived from the liquid phase hydrochlorination equilibrium.

*Hexachloroethane Pyrolysis*. Pyrolysis of hexachloroethane leads to the rapid establishment of equilibrium (15), and is discussed in detail in the evaluation for hexachloroethane, Sec. 6.10. Values from three independent studies are available and lead to values of $\Delta_{16}H(298.15\,\mathrm{K})$ equal to $(124.9 \pm 2.3)\,\mathrm{kJ\,mol^{-1}}$, $(126.6 \pm 2.6)\,\mathrm{kJ\,mol^{-1}}$, and $-139.5\,\mathrm{kJ\,mol^{-1}}$ (see Sec. 6.10 and Comments 5, 6, 7, and 10 of Table 14). The first two of these values are in reasonable agreement with the tetrachloromethane pyrolysis data of Huybrechts *et al.* [1996HNMa], [1996HNMb], while the third is a clear outlier and assumed to be incorrect. The absence of independent reliable data on $\Delta_f H^o[C_2Cl_6(g),\ 298.15\,\mathrm{K}]$ means that the data on equilibrium (16) cannot be used to set an absolute value for $C_2Cl_4$. Nonetheless, the data on hexachloroethane pyrolysis appear to validate the tetrachloromethane pyrolysis results of Huybrechts *et al.*, which allow us to derive an absolute value relative to the well-known value of $\Delta_f H^o[CCl_4(g),\ 298.15\,\mathrm{K}]$.

*Recommendation*. The most reliable value is that derivable from the data of Huybrechts *et al.* [1996HNMa], [1996HNMb] data on equilibrium (15). The average value derivable from this result and the available entropy and heat capacity data [1981C], [1985R], [1991GVA] $\Delta_f H^o[C_2Cl_4(g),\ 298.15\,\mathrm{K}] = -(25.3 \pm 3.5)\,\mathrm{kJ\,mol^{-1}}$. To achieve a slightly better global fit to the sets of data interrelating $C_2Cl_4$, $C_2Cl_6$, $C_2HCl_5$, and $C_2HCl_3$, we have selected a final recommended value of $\Delta_f H^o[C_2Cl_4(g),\ 298.15\,\mathrm{K}] = -(24.2 \pm 4.0)\,\mathrm{kJ\,mol^{-1}}$. This value is about 12 $\mathrm{kJ\,mol^{-1}}$ more negative than previous evaluations, all of which appear to be heavily based on the combustion data of Eftring [1938E]. However, for the Eftring result to be correct, $K_{15}$ determined by Huybrechts *et al.* [1996HNMa] would have to

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TABLE 14. Enthalpies of formation of tetrachloroethene derived from reported experimental data

| $\Delta_f H^o$ (g), 298.15 K (kJ mol$^{-1}$) | Reported uncertainty kJ mol$^{-1}$ | Temp. (K) | Method(s) | Ref/Year | Comments |
|---|---|---|---|---|---|
| Experimental | | | | | |
| −25.9 | N.R.<br>(2.5)$^a$ | 696.6 | Equilibrium of reaction<br>$2CCl_4$ (g)$\rightleftarrows C_2Cl_4$ (g)$+2Cl_2$ (g) | [1996HNMa] | 1, Pyrolysis of $CCl_4$. Third Law analysis, $\Delta_f H^o[CCl_4$ (g)] used in calculation. |
| −27.8 | N.R.<br>(4.0)$^b$ | 696.6 | Equilibrium of reaction<br>$C_2Cl_6$ (g)$\rightleftarrows C_2Cl_4$ (g)$+Cl_2$ (g) | [1996HNMa] | 2, Pyrolysis of $CCl_4$. Third Law analysis, $\Delta_f H^o[C_2Cl_6$ (g)] used in calculation. |
| −25.1 | N.R.<br>(4.2)$^c$ | 313–353 | Equilibrium of hydrochlorination<br>$C_2HCl_5$ (soln)$\rightleftarrows C_2Cl_4$ (soln)$+$HCl (g) | [1979LBR] | 3, Second Law, $\Delta_f H^o[C_2HCl_5$ (l)] used in calculation. |
| −19.8 | N.R.<br>(4.2)$^c$ | 313–353 | Equilibrium of hydrochlorination<br>$C_2HCl_5$ (soln)$\rightleftarrows C_2Cl_4$ (soln)$+$HCl (g) | [1979LBR] | 4, Third Law analysis, $\Delta_f H^o[C_2HCl_5$ (l)] used in calculation. |
| −8.7 | N.R.$^d$ | 773–873 | Equilibrium of reaction<br>$C_2Cl_6$ (g)$\rightleftarrows C_2Cl_4$ (g)$+Cl_2$ (g) | [1979BLR] | 5, Pyrolysis of $C_2Cl_6$. Third Law analysis, $\Delta_f H^o[C_2Cl_6$ (g)] used in calculation. |
| −11.7 | N.R.$^d$ | 773–873 | Equilibrium of reaction<br>$C_2Cl_6$ (g)$\rightleftarrows C_2Cl_4$ (g)$+Cl_2$ (g) | [1979BLR] | 6, Pyrolysis of $C_2Cl_6$. 2nd law analysis, $\Delta_f H^o[C_2Cl_6$ (g)] used in calculation. |
| −21.6 | N.R.<br>(2.6)$^a$ | 776 | Equilibrium of reaction<br>$C_2Cl_6$ (g)$\rightleftarrows C_2Cl_4$ (g)$+Cl_2$ (g) | [1963PBM]<br>[1962PMN] | 7, Pyrolysis of $C_2Cl_6$. Third Law analysis, $\Delta_f H^o[C_2Cl_6$ (g)] used in calculation. |
| −24.3 | N.R.<br>(4.2)$^e$ | 298 | Enthalpy of dehydrochlorination<br>$2C_2HCl_5$ (l)$+CaO_2H_2$ (c)$\rightarrow$<br>$2C_2Cl_4$ (l)$+CaCl_2$(aq:400)$+2H_2O$ (l) | [1956K] | 8, Data reanalyzed by [1970CP], $\Delta_f H^o[C_2HCl_5$ (l)] used in calculation. |
| −22.2 | N.R.<br>(6.0)$^c$ | 298 | Enthalpy of chlorination<br>$C_2Cl_4$ (l)$+Cl_2$ (g)$\rightarrow C_2Cl_6$ (s) | [1956K] | 9, $\Delta_f H^o[C_2Cl_6$ (s)] used in calculation. |
| −23.3 | N.R.<br>(2.3)$^a$ | 671 | Equilibrium of reaction<br>$C_2Cl_6$ (g)$\rightleftarrows C_2Cl_4$ (g)$+Cl_2$ (g) | [1950DI]<br>[1980WB] | 10, $C_2Cl_6$ Pyrolysis. Third Law analysis, $\Delta_f H^o[C_2Cl_6$ (g)] used in calculation. |
| −10.9 | 8.4 | 298 | Combustion calorimetry of liquid | [1938E]<br>[1953SBK]<br>[1970CP] | 11, Data corrected by Smith *et al.* in 1953; data reanalyzed and auxiliary quantities updated by [1970CP]. |
| Reviews and Evaluations | | | | | |
| −11.0 | 2.1 | 298 | | [1991GVA] | Evaluation date uncertain; same value as previous edition [1979G]. |
| −10.9 | 8.3 | 298 | | [1986PNK] | |
| −11.0 | 2.1 | 298 | | [1983KP] | |
| −12.1 | N.R.$^d$ | 298 | | [1985R] | |
| −11.3 | 8.4 | 298 | | [1970CP] | |
| −14.2 | N.R.$^d$ | 298 | | [1969SWS] | |

[a] Not reported. The parenthetical value is the uncertainty in $\Delta_r H$ derived assuming a 50% uncertainty in the equilibrium constant.

[b] Not reported. The parenthetical value is the uncertainty in $\Delta_r H$ derived assuming a factor of 2 uncertainty in the equilibrium constant.

[c] Not reported. The parenthetical value is that estimated by us by comparison with similar experiments.

[d] Not reported.

[e] Not reported. The parenthetical value refers to the reaction enthalpy and is $2\sigma$ as calculated by us from the reported data.

**Comments:**

1. Third Law analysis using entropies and heat capacities from [1981C], [1985R] yields $\Delta_r H(696.6\,\mathrm{K}) = -161.9\,\mathrm{kJ\,mol^{-1}}$ and $\Delta_r H(298.15\,\mathrm{K}) = -165.3\,\mathrm{kJ\,mol^{-1}}$. Using $\Delta_f H^o[CCl_4\,(g), 298.15\,\mathrm{K}] = -95.6 \pm 2.5\,\mathrm{kJ\,mol^{-1}}$ (see Sec. 3.5) we derive $\Delta_f H^o[C_2Cl_4\,(g), 298.15\,\mathrm{K}] = 25.9\,\mathrm{kJ\,mol^{-1}}$. If entropies and heat capacities are taken from [1991GVA], this becomes $\Delta_f H^o[C_2Cl_4\,(g), 298.15\,\mathrm{K}] = -24.7\,\mathrm{kJ\,mol^{-1}}$.

2. This was a primary (though not only) result used to derive $\Delta_f H^o[C_2Cl_6\,(g), 298.15\,\mathrm{K}]$, the value of which is otherwise not well established. Thus, although self-consistent, these data cannot provide a completely independent confirmation of the selected value. $K(696.6) = 28.5$ kPa. We estimate the $2\sigma$ uncertainty in $K$ to be a factor of 2. From a Third Law analysis, taking entropies and heat capacities from the TRC Tables [1981C], [1985R], we obtain $\Delta_r H(696.6\,\mathrm{K}) = -(115.6 \pm 4.0)\,\mathrm{kJ\,mol^{-1}}$ and $\Delta_r H(298.15\,\mathrm{K}) = -(120.4 \pm 4.0)\,\mathrm{kJ\,mol^{-1}}$. Stated value is obtained using $\Delta_f H^o[C_2Cl_6\,(g), 298.15\,\mathrm{K}] = -148.2\,\mathrm{kJ\,mol^{-1}}$ (see Sec. 6.10).

3. Second Law analysis yields $\Delta_f H^o[C_2Cl_4\,(l), 298.15\,\mathrm{K}]\ \Delta_f H^o[C_2HCl_5\,(l), 298.15\,\mathrm{K}] + 138.5\,\mathrm{kJ\,mol^{-1}}$. Analysis ignores excess thermodynamic properties of solvation. Using $\Delta_f H^o[C_2HCl_5\,(l), 298.15\,\mathrm{K}] = -(203.3 \pm 4.0)\,\mathrm{kJ\,mol^{-1}}$ (see Sec. 6.9), $\Delta_f H^o[C_2Cl_4\,(l), 298.15\,\mathrm{K}] = -64.8\,\mathrm{kJ\,mol^{-1}}$ and $\Delta_f H^o[C_2Cl_4\,(g), 298.15\,\mathrm{K}] = -25.1\,\mathrm{kJ\,mol^{-1}}$.

4. Third Law analysis yields $\Delta_f H^o[C_2Cl_4\,(l), 298.15\,\mathrm{K}] = \Delta_f H^o[C_2HCl_5\,(l), 298.15\,\mathrm{K}] + 143.8\,\mathrm{kJ\,mol^{-1}}$. Analysis ignores excess thermodynamic properties of solvation. Using $\Delta_f H^o[C_2HCl_5\,(l), 298.15\,\mathrm{K}] = -(203.3 \pm 4.0)\,\mathrm{kJ\,mol^{-1}}$ (see Sec. 6.9), $\Delta_f H^o[C_2Cl_4\,(l), 298.15\,\mathrm{K}] = -59.5\,\mathrm{kJ\,mol^{-1}}$ and $\Delta_f H^o[C_2Cl_4\,(g), 298.15\,\mathrm{K}] = -19.8\,\mathrm{kJ\,mol^{-1}}$.

5. For $C_2Cl_6\,(g) \rightleftarrows C_2Cl_4\,(g) + Cl_2\,(g)$, measured equilibrium constants are $K(773\,\mathrm{K}) = 0.102$ atm (10.34 kPa), $K(823\,\mathrm{K}) = 0.345$ atm (34.94 kPa), $K(873\,\mathrm{K}) = 0.947\ 1.042$ atm (105.5 kPa). Using entropies and heat capacities from [1981C], [1985R] these yield $\Delta_f H(773\,\mathrm{K}) = 134.6\,\mathrm{kJ\,mol^{-1}}$, $\Delta_r H(823\,\mathrm{K}) = 133.3\,\mathrm{kJ\,mol^{-1}}$, and $\Delta_r H(873\,\mathrm{K}) = 132.6\,\mathrm{kJ\,mol^{-1}}$. Averaging the data, $\Delta_r H(298.15\,\mathrm{K}) = 139.5\,\mathrm{kJ\,mol^{-1}}$ is obtained. Stated value is obtained using $\Delta_f H^o[C_2Cl_6\,(g), 298.15\,\mathrm{K}] = -148.2\,\mathrm{kJ\,mol^{-1}}$ (see Sec. 6.10). These data are in poor agreement with the three other measurements of the equilibrium constant for this reaction.

6. Second Law analysis (773–873 K) of $C_2Cl_4$ (g)+$Cl_2$ (g)$\rightleftarrows$$C_2Cl_6$ (g) yields $\Delta_rH(823\,K)=-130.5\,kJ\,mol^{-1}$. $\Delta_rH(298.15\,K)=-136.5\,kJ\,mol^{-1}$ is obtained using entropies and heat capacities from [1981C], [1985R]. Stated value is obtained using $\Delta_fH^o[C_2Cl_6\,(g), 298.15\,K]=-148.2\,kJ\,mol^{-1}$ (see Sec.6.10). Result is in good agreement with Third Law analysis (Comment 5), but in poor agreement with the three other measurements of the equilibrium constant for this reaction.

7. This was a primary (though not only) result used to derive $\Delta_fH^o[C_2Cl_6\,(g), 298.15\,K]$, the value of which is otherwise not well established. Thus, although self-consistent, these data cannot provide a completely independent confirmation of the selected value. $K(776\,K)=0.80$ atm (81.1 kPa). We estimate the $2\sigma$ uncertainty in $K$ to be ±50%. From a Third Law analysis, taking entropies and heat capacities from the TRC Tables [1981C], [1985R], we obtain $\Delta_rH(776\,K)=(120.7\pm2.6)\,kJ\,mol^{-1}$ and $\Delta_rH(298.15\,K)=(126.6\pm2.6)\,kJ\,mol^{-1}$. Stated value is obtained using $\Delta_fH^o[C_2Cl_6\,(g), 298.15\,K]=-148.2\,kJ\,mol^{-1}$ (see Sec. 6.10).

8. $\Delta_rH(298.15\,K)=-(181.6\pm4.2)\,kJ\,mol^{-1}$. This was a primary (though not only) result used to derive $\Delta_fH^o[C_2HCl_5\,(l), 298.15\,K]$. Thus, although self-consistent, these data cannot provide a completely independent confirmation of the selected value. Data reanalyzed Cox and Pilcher [1970CP] and lead to $\Delta_fH^o[C_2HCl_5\,(l), 298.15\,K]=\Delta_fH^o[C_2Cl_4\,(l), 298.15\,K]-139.3\,kJ\,mol^{-1}$. With $\Delta_fH^o[C_2HCl_5\,(l), 298.15\,K]=-(203.3\pm4.0)\,kJ\,mol^{-1}$ (see Sec. 6.10), we obtain $\Delta_fH^o[vC_2Cl_4\,(l), 298.15\,K]=-(64.0\pm5.8)\,kJ\,mol^{-1}$.

9. Results of four experiments for $C_2Cl_4$ (l)+$Cl_2$ (g)→$C_2Cl_6$ (sol) give $\Delta_rH(298.15\,K)=-(135.6\pm3.9)\,kJ\,mol^{-1}$ (Kirkbride [1956K] rounds the average value to two digits and reports $\Delta_rH(298.15\,K)=-32\,kcal\,mol^{-1}$, although each experiment is reported to a precision of 0.1 kcal $mol^{-1}$ and the actual average is −32.4 kcal $mol^{-1}$). Kirkbride [1956K] determined the approximate enthalpies of solution of $C_2Cl_6$ in $C_2Cl_4$ to be 19.7 $kJ\,mol^{-1}$, so for $C_2Cl_4$ (l)+$Cl_2$ (g)→$C_2Cl_6$ (s) we derive $\Delta_rH(298.15\,K)=-(155.3\pm6)\,kJ\,mol^{-1}$, where the uncertainty is estimated. In conjunction with $\Delta_fH^o[C_2Cl_6\,(s), 298.15\,K]=-(217.2\pm7.6)\,kJ\,mol^{-1}$ (see Sec. 6.10), we obtain $\Delta_fH^o[C_2Cl_4\,(l), 298.15\,K]=-(61.9\pm9.7)\,kJ\,mol^{-1}$.

10. This was a primary (though not only) result used to derive $\Delta_fH^o[C_2Cl_6\,(g), 298.15\,K]$, the value of which is otherwise not well established. Thus, although self-consistent, these data cannot provide a completely independent confirmation of the selected value. $K(671\,K)=5.83$ kPa, derived as discussed in Sec. 6.10 A Third Law analysis using entropies and heat capacities from [1981C], [1985R] yields $\Delta_rH(671\,K)=(120.4\pm2.3)\,kJ\,mol^{-1}$ and $\Delta_rH(298.15\,K)=(124.9\pm2.3)\,kJ\,mol^{-1}$. Stated value is obtained using $\Delta_fH^o[C_2Cl_6\,(g), 298.15\,K]=-148.2\,kJ\,mol^{-1}$ (Sec. 6.10).

11. Static bomb calorimetry. Experiments by Eftring in 1938 as corrected by Smith *et al.* in 1953 and updated by Cox and Pilcher [1970CP]. Sample purity uncertain. $\Delta_cH(298.15\,K)=-(830.9\pm8.4)\,kJ\,mol^{-1}$, refers to reaction $C_2Cl_4$ (l)+$2H_2O$ (l)+$O_2$ (g)→$2CO_2$ (g)+4HCl (aq:600). The following auxiliary values were used: $\Delta_fH^o[CO_2\,(g), 298.15\,K]=-(393.51\pm0.13)\,kJ\,mol^{-1}$, $\Delta_fH^o[H_2O\,(l), 298.15\,K]=-(285.830\pm0.040)\,kJ\,mol^{-1}$, and $\Delta_fH^o[HCl\,(aq{:}600), 298.15\,K]=-(166.540\pm0.10)\,kJ\,mol^{-1}$. These data result in $\Delta_fH^o[C_2Cl_4\,(l), 298.15\,K]=-(50.62\pm8.4)\,kJ\,mol^{-1}$.

be wrong by more than an order of magnitude. This is exceedingly unlikely. Finally, the results of high level *ab initio* calculations carried out at NIST [2001BAM], up to and including composite QCISD(T)/6-311+G(3df,2p) calculations, result in values of $\Delta_fH^o[C_2Cl_4(g), 298.15\,K]$ in the range of −22–−26 $kJ\,mol^{-1}$, in very good agreement with that suggested here.

## 6. Evaluated Enthalpies of Formation and Vaporization of the (Chloro)ethanes

### 6.1. Ethane

*Enthalpy of Formation. Recommendation*. Recommended values of the enthalpy of formation of ethane from several commonly cited sources are listed in Table 1. There are no recent experimental determinations of its value and the previous evaluations are in good agreement. The $\Delta_fH^o[C_2H_g(g), 298.15\,K]$ values of Table 1 range from −83.8 to −84.68 $kJ\,mol^{-1}$. The evaluation of Gurvich *et al.* [1991GVA] contains good discussion of the data, although the actual date of the evaluation is uncertain (the value is the same as in the previous edition, [1979G]). Gurvich *et al.* based their value on the combined treatment of combustion calorimetric measurements of the enthalpies of formation $C_2H_4$ [1937RK] and $C_2H_6$ [1934R], [1972PP], together with calorimetric [1935KRR] and equilibrium [1942K] measurements of the enthalpy of the hydrogenation reaction $C_2H_4+H_2\rightarrow C_2H_6$. After review, we have accepted their evaluation, $\Delta_fH^o[C_2H_6(g), 298.15\,K]=(84.0\pm0.4)\,kJ\,mol^{-1}$.

### 6.2. Chloroethane

*Enthalpy of Vaporization*. Chloroethane is a gas at 298.15 K and standard pressure (100 kPa). Gordon and Giauque [1948GG] determined the enthalpy of vaporization at the boiling point, $\Delta_{vap}H(285.4\,K)=(24.65\pm0.1)\,kJ\,mol^{-1}$, where the uncertainty is $2\sigma$ and is that estimated by us based on the scatter in his data and comparison with similar experiments. This was adjusted to 298.15 K using $\Delta_{vap}C_p(C_2H_5Cl)=-43.4\,J\,mol^{-1}\,K^{-1}$, derivable from the difference between the heat capacities of the gas [1981C] and liquid [1948GG], [1948K], [1940R], and leads to $\Delta_{vap}H(298.15\,K)=(24.10\pm0.1)\,kJ\,mol^{-1}$. Yates [1926Y] measured the enthalpy of vaporization between 285.3 and 300.6 K and his data yield $\Delta_{vap}H(298.15\,K)=(24.78\pm0.1)\,kJ\,mol^{-1}$, where the uncertainty is the precision only and does not take into account possible systematic uncertainties. We note that over the short temperature range of his experiments, a plot of his $\Delta_{vap}H$ data versus $T$ results in $\Delta_{vap}C_p(C_2H_5Cl)=-17.4\,J\,mol^{-1}\,K^{-1}$, which is much too small. Older values cited by Yates are $\Delta_{vap}H(294\,K)=24.2\,kJ\,mol^{-1}$ [1923JS] and $\Delta_{vap}H(294\,K)=24.5\,kJ\,mol^{-1}$ [1871R]. These become $\Delta_{vap}H(298.15\,K)=24.0\,kJ\,mol^{-1}$ and $\Delta_{vap}H(298.15\,K)=24.3\,kJ\,mol^{-1}$, respectively. All of the data are in good agreement, but the results of Gordon and Giauque [1948GG] are weighted most heavily. We recommend $\Delta_{vap}H(298.15\,K)=(24.2\pm0.3)\,kJ\,mol^{-1}$. Using Eq. (1) and data from the DIPPR database [2001DIP] (datasheet revision date August, 1994), the correction for nonideality of the gas is calculated as 0.42 $kJ\,mol^{-1}$, which leads to $\Delta_{vap}H^o(298.15\,K)=(24.6\pm0.3)\,kJ\,mol^{-1}$.

TABLE 15. Enthalpies of formation of chloroethane derived from reported experimental data

| $\Delta_f H^o$ (g), 298.15 K (kJ mol$^{-1}$) | Reported uncertainty kJ mol$^{-1}$ | Temp. (K) | Method(s) | Ref/Year | Comments |
|---|---|---|---|---|---|
| Experimental | | | | | |
| −112.1 | 0.7 | 298 | Combustion calorimetry of gas | [1971FP] | 1, Flame Calorimeter. |
| −106.9 | 0.4$^a$ | 521 | Enthalpy of hydrogenation<br>$C_2H_5Cl$ (g)$+H_2$ (g)$\rightleftarrows C_2H_6$ (g)$+$HCl (g) | [1956LEB] | 2, Data reanalyzed by [1970CP] and [1974CRW]. |
| −111.9 | N.R.$^b$<br>(3.0) | 448–528 | Reaction equilibrium<br>$C_2H_4$ (g)$+$HCl (g)$\rightleftarrows C_2H_5Cl$ (g) | [1955H] | 3, Second Law analysis. |
| −112.4 | N.R.$^b$<br>(2.5) | 448–528 | Reaction equilibrium<br>$C_2H_4$ (g)$+$HCl (g)$\rightleftarrows C_2H_5Cl$ (g) | [1955H] | 4, Third Law analysis. |
| −115.8 | N.R.$^b$<br>(4.0) | 722–764 | Reaction equilibrium<br>$C_2H_4$ (g)$+$HCl (g)$\rightleftarrows C_2H_5Cl$ (g) | [1953LLO] | 5, Second Law analysis. |
| −109.4 | N.R.$^b$<br>(2.5) | 722–764 | Reaction equilibrium<br>$C_2H_4$ (g)$+$HCl (g)$\rightleftarrows C_2H_5Cl$ (g) | [1953LLO] | 6, Third Law analysis. |
| −97.5 | 10.5 | 293 | Combustion calorimetry of gas | [1951CF] | 7, Flame Calorimeter. Data reanalyzed by [1970CP] and [1974CRW]. |
| Reviews and Evaluations | | | | | |
| −112.1 | 1.1 | 298 | | [1986PNK] | |
| −112.2 | 0.7 | 298 | | [1983KP] | |
| −112.3 | N.R.$^b$ | 298 | | [1981C] | |
| −112.3 | 0.8 | 298 | | [1974CRW] | |
| −109.2 | 1.3 | 298 | | [1970CP] | |
| −111.6 | N.R.$^b$ | 298 | | [1969SWS] | |

[a] Precision only, does not include systematic errors or uncertainty in auxiliary thermodynamic quantities.

[b] Not reported, the parenthetical values are estimated.

**Comments:**

1. Flame calorimetry of gas. $\Delta_c H^o_{298} = -(1413.1 \pm 0.6)$ kJ mol$^{-1}$, refers to reaction $C_2H_5Cl$ (g)$+3O_2$ (g)$\rightarrow 2CO_2$ (g)$+2H_2O$ (l)$+$HCl (aq;600). The following auxiliary values were used: $\Delta_f H^o[CO_2$ (g), 298.15 K$] = -(393.51 \pm 0.13)$ kJ mol$^{-1}$, $\Delta_f H^o[H_2O$ (l)$] = -(285.830 \pm 0.040)$ kJ mol$^{-1}$, and $\Delta_f H^o$[HCl (aq:600), 298.15 K$] = -(166.540 \pm 0.10)$ kJ mol$^{-1}$. These data yield $\Delta_f H^o[CH_3Cl$ (g), 298.15 K$] = -(112.12 \pm 0.7)$ kJ mol$^{-1}$.
2. $\Delta_r H(521\ K) = -(71.80 \pm 0.25)$ kJ mol$^{-1}$ was adjusted to $\Delta_r H(298.15\ K) = -(69.29 \pm 0.42)$ kJ mol$^{-1}$ as per Chao *et al.* [1974CRW]. Value in Table calculated using $\Delta_f H^o[C_2H_6$ (g), 298.15 K$] = -(83.85 \pm 0.29)$ kJ mol$^{-1}\Delta_f H^o$[HCl (g), 298.15 K$] = -(92.31 \pm 0.10)$ kJ mol$^{-1}$.
3. Reported equilibrium constant $\log K/\mathrm{Pa} = 3812/T - 1.879$ (original value $\log K/\mathrm{atm} = 3812/T - 6.885$) was adjusted to $\Delta_r H(298.15\ K) = -(72.0 \pm 3.0)$ kJ mol$^{-1}$ using heat capacity data from [1994FKM].
4. Reported equilibrium constant $\log K/\mathrm{Pa} = 3812/T - 1.879$ (original value $\log K/\mathrm{atm} = 3812/T - 6.885$) was adjusted to $\Delta_r H(298.15\ K) = -(72.5 \pm 2.1)$ kJ mol$^{-1}$ using entropy and heat capacity data from [1994FKM].
5. Reported equilibrium constant $\log K/\mathrm{Pa} = 3993/T - 2.352$ (original value $\log K/\mathrm{atm} = 3993/T - 6.885$) was adjusted to $\Delta_r H(298.15\ K) = -(75.9 \pm 4.0)$ kJ mol$^{-1}$ using heat capacity data from [1994FKM].
6. Reported equilibrium constant $\log K/\mathrm{Pa} = 3993/T - 2.352$ (original value $\log K/\mathrm{atm} = 3993/T - 7.358$) was adjusted to $\Delta_r H(298.15\ K) = -(69.5 \pm 2.1)$ kJ mol$^{-1}$ using entropy and heat capacity data from [1994FKM].
7. Flame calorimetry of gas. Gas contained 90% $H_2$ to ensure complete conversion of chlorine to HCl.

*Enthalpy of Formation. Recommendation*. Data are summarized in Table 15. The enthalpy of formation of chloroethane appears to be well determined. The equilibrium constants for the hydrochlorination of ethene to chloroethane have been measured by Lane *et al.* [1953LLO] between 722 and 754 K and Howlett [1955H] between 448 and 528 K. The results are in excellent agreement with each other and the combustion calorimetry study of Fletcher and Pilcher [1971FP] (see Table 15). The earlier combustion result of Casey and Fordham [1951CF], which had a large uncertainty, and the enthalpy of hydrogenation reported by Lacher *et al.* [1956LEB] do not agree well with the other studies. After review, we have given preference to the flame calorimetry value of Fletcher and Pilcher [1971FP] and selected $\Delta_f H^o[C_2H_5Cl(g),\ 298.15\ K] = -(112.1 \pm 0.7)$ kJ mol$^{-1}$. Very similar values have been adopted by other reviewers.

### 6.3. 1,1-Dichloroethane

*Enthalpy of Vaporization*. The enthalpy of vaporization was measured calorimetrically by Li and Pitzer [1956LP] as $\Delta_{vap} H(293\ K) = (31.00 \pm 0.06)$ kJ mol$^{-1}$. Using $\Delta_{vap} C_p(1{,}1\text{-}C_2H_4Cl_2) = -50.2$ J mol$^{-1}$ K$^{-1}$ [1956LP], this becomes $\Delta_{vap} H(298.15\ K) = (30.74 \pm 0.06)$ kJ mol$^{-1}$. From vapor pressure measurements Li and Pitzer [1956LP] independently derived $\Delta_{vap} H(293\ K) = 30.97$ kJ mol$^{-1}$ ($\Delta_{vap} H(298.15\ K) = 30.71$ kJ mol$^{-1}$). These values are in excellent agreement with the calorimetric value of Laynez and Wadso [1972LW], $\Delta_{vap} H(298.15\ K) = (30.62 \pm 0.14)$ kJ mol$^{-1}$. These data lead us to recommend $\Delta_{vap} H(298.15\ K) = (30.68 \pm 0.08)$ kJ mol$^{-1}$. A correction of 0.15 kJ mol$^{-1}$ due to nonideality of the gas was taken from the work of Majer and Svoboda [1985MS] (our calculation gives 0.12 kJ mol$^{-1}$) and we adopt $\Delta_{\rm vap}H^{\rm o}(298.15\,{\rm K}) = (30.83 \pm 0.08)$ kJ mol$^{-1}$.

*Enthalpy of Formation*. Data are summarized in Table 16. The enthalpy of formation of 1,1-dichloroethane is not firmly established. The only combustion measurement is from the static combustion study of Eftring [1938E] as corrected by Smith *et al.* [1953SBK], subsequently updated by Cox and Pilcher [1970CP] and compiled by Pedley *et al.* [1986PNK]. These data yield $\Delta_{\rm f}H^{\rm o}[1,1\text{-}C_2H_4Cl_2(l),\ 298.15\,{\rm K}] = -(159.5 \pm 8.4)$ kJ mol$^{-1}$ (see Table 16 and Comment 4), or, in conjunction with the enthalpy of vaporization, $\Delta_{\rm f}H^{\rm o}[1,1\text{-}C_2H_4Cl_2(g),\ 298.15\,{\rm K}] = -(128.3 \pm 8.4)$ kJ mol$^{-1}$. In general the results of Eftring [1938E] on chlorinated compounds yield enthalpies formation that are too positive when compared with later work. The hydrogenation data of Lacher *et al.* [1967LAP] (Table 16 and Comment 5) result in $\Delta_{\rm f}H^{\rm o}[1,1\text{-}C_2H_4Cl_2(g), 298.15\,{\rm K}] = -(129.3 \pm 6.0)$ kJ mol$^{-1}$, where the uncertainty is that estimated by us based on comparison with related studies on other chlorinated species. The $AlCl_3$-catalyzed equilibrium $1,1\text{-}C_2H_4Cl_2 \rightleftarrows 1,2\text{-}C_2H_4Cl_2$ has been investigated by Rozhnov [1968R] (Table 16 and Comment 4), but this work leads to a much more positive value than the other studies and, as discussed in our evaluation of $1,2\text{-}C_2H_4Cl_2$ (Sec. 6.4), these results are considered erroneous. The best experimental data appear to be from the hydrochlorination reaction equilibrium that has been investigated in both the gas and liquid phases by Levanova *et al.* [1976LTVa], [1976LTVb]. The Second and Third Law Analyses (Table 16 and Comments 1 to 3) of these data are in good agreement and lead to an enthalpy of formation somewhat more negative than the other studies.

*Recommendation*. We do not consider either the combustion calorimetry data of Eftring [1938E] or the hydrogenation data of Lacher *et al.* [1967LAP] to be particularly reliable. In our evaluation of 1,2-dichloroethane (Sec. 6.4) we have argued that the equilibrium data of Rozhnov [1968R] must be incorrect. The best experimental data appear to be the equilibrium hydrochlorination results of Levanova *et al.* [1976LTVa], [1976LTVb] which allow one to derive an enthalpy value relative to that of chloroethene, which we feel has a fairly well established value despite the contradictory nature of some of the data (see Sec. 5.2). Our calculations further suggest that the enthalpy of formation of 1,1-dichloroethane must be quite close to that of 1,2-dichloroethane (*vide infra*, see Table 18 and Section 6.4), for which $\Delta_{\rm f}H^{\rm o}[1,2\text{-}C_2H_4Cl_2(g),\ 298.15\,{\rm K}] = -(132.0 \pm 3.5)$ kJ mol$^{-1}$. Consideration of the above leads us to recommended $\Delta_{\rm f}H^{\rm o}[1,1\text{-}C_2H_4Cl_2(g),\ 298.15\,{\rm K}] = -(132.5 \pm 3.5)$ kJ mol$^{-1}$. Note that it remains unclear which of the dichloroethanes is the more stable.

### 6.4. 1,2-Dichloroethane

*Enthalpy of Vaporization*. The enthalpy of vaporization was measured calorimetrically by Mathews [1926M] as $\Delta_{\rm vap}H(355.4\,{\rm K}) = (32.02 \pm 0.1)$ kJ mol$^{-1}$, where the uncertainty is that estimated by us by comparison with similar experiments (originally reported precision was ±0.012 kJ mol$^{-1}$). Sinke and Stull [1958SS] report an otherwise unpublished measurement by McDonald [1958M] of $\Delta_{\rm vap}H(298.15\,{\rm K}) = (35.44 \pm 0.84)$ kJ mol$^{-1}$. More recent calorimetric measurements are those Wadso [1968W] who reported $\Delta_{\rm vap}H(298.15\,{\rm K}) = (35.15 \pm 0.1)$ kJ mol$^{-1}$ and those of Majer *et al.* [1980MSS], who measured the enthalpy of vaporization between 298 and 358 K and report $\Delta_{\rm vap}H(298.15\,{\rm K}) = (35.17 \pm 0.09)$ kJ mol$^{-1}$. Using the temperature dependent data of Majer *et al.*, we derive $\Delta_{\rm vap}C_p(1,2\text{-}C_2H_4Cl_2) = -54.3$ J mol$^{-1}$ K$^{-1}$ (see Fig. 8 and Sec. 6.9). This value can be used to adjust the measurement of Mathews [1926M] to 298.15 K and results in $\Delta_{\rm vap}H(298.15\,{\rm K}) = (35.13 \pm 0.2)$ kJ mol$^{-1}$. The three measurements by Mathews [1926M], Wadso [1968W], and Majer *et al.* [1980MSS] are in excellent agreement and more precise than those of McDonald [1958M]. These data lead us to recommend $\Delta_{\rm vap}H(298.15\,{\rm K}) = (35.15 \pm 0.05)$ kJ mol$^{-1}$. A correction of 0.06 kJ mol$^{-1}$ due to nonideality of the gas was taken from the work of Majer and Svoboda [1985MS] (our calculation gives 0.07 kJ mol$^{-1}$) and we adopt $\Delta_{\rm vap}H^{\rm o}(298.15\,{\rm K}) = (35.21 \pm 0.05)$ kJ mol$^{-1}$.

*Enthalpy of Formation*. Data are summarized in Table 17. Despite several determinations by several techniques, the enthalpy of formation of 1,2-dichloroethane is not firmly established. Three combustion studies of the liquid are available. The early static combustion study of Eftring [1938E] was corrected by Smith *et al.* [1953SBK], subsequently updated by Cox and Pilcher [1970CP] and the data later compiled by Pedley *et al.* [1986PNK]. These data yield $\Delta_{\rm f}H^{\rm o}[1,2\text{-}C_2H_4Cl_2(l),\ 298.15\,{\rm K}] = -(159.5 \pm 8.4)$ kJ mol$^{-1}$. Using static bomb calorimetry, Sinke and Stull [1958SS] obtained a significantly more negative result, $\Delta_{\rm f}H^{\rm o}[1,2\text{-}C_2H_4Cl_2(l),\ 298.15\,{\rm K}] = -(164.4 \pm 1.7)$ kJ mol$^{-1}$. A still more negative value, $\Delta_{\rm f}H^{\rm o}[1,2\text{-}C_2H_4Cl_2(l),\ 298.15\,{\rm K}] = -(169.5 \pm 1.1)$ kJ mol$^{-1}$, was obtained by Hu and Sinke [1969HS] using rotating bomb calorimetry. In general the early results of Eftring [1938E] have not proved reliable and one expects the rotating bomb calorimetry of Hu and Sinke [1969HS] to be more dependable than the static bomb methodology employed by Sinke and Stull [1958SS].

Several noncombustion values are also available. The enthalpy of chlorination of ethene measured calorimetrically by Conn *et al.* [1938CKS] leads to $\Delta_{\rm f}H^{\rm o}[1,2\text{-}C_2H_4Cl_2(g)] = -(130.4 \pm 0.8)$ kJ mol$^{-1}$ (see Table 17 and Comment 6). The liquid phase enthalpy of substitutive chlorination of $1,2\text{-}C_2H_4Cl_2$ reported by Kirkbride [1956K] (see Table 1 and Comment 4) leads to $\Delta_{\rm f}H^{\rm o}[1,2\text{-}C_2H_4Cl_2(g)] = -(129.1 \pm 6.0)$ kJ mol$^{-1}$, where the uncertainty includes both that of the reaction enthalpy measurement and auxiliary thermodynamic quantities. The enthalpy of hydrogenation measured by Lacher *et al.* [1967LAP] leads to $\Delta_{\rm f}H^{\rm o}[1,2\text{-}C_2H_4Cl_2(g)] = -(125.6 \pm 0.8)$ kJ mol$^{-1}$.

Finally, Rozhnov [1968R] reports measurements of the equilibrium isomerization of the dichloroethanes in both the

TABLE 16. Enthalpies of formation of 1,1-dichloroethane derived from reported experimental data

| $\Delta_r H^o$ (g), 298.15 K (kJ mol$^{-1}$) | Reported uncertainty kJ mol$^{-1}$ | Temp. (K) | Method(s) | Ref/Year | Comments |
|---|---|---|---|---|---|
| Experimental | | | | | |
| −131.5 | 0.7[a]<br>(3.6) | 403–438 | Equilibrium of hydrochlorination<br>1,1-$C_2H_4Cl_2$ (g)$\rightleftarrows C_2H_3Cl$ (g)+HCl (g) | [1976LTV] | 1, Second Law analysis, updated using our value for $\Delta_f H^o$[1,1-$C_2H_4Cl_2$ (g)]. |
| −132.5 | 0.7[a]<br>(3.6) | 403–438 | Equilibrium of hydrochlorination<br>1,1-$C_2H_4Cl_2$ (g)$\rightleftarrows C_2H_3Cl$ (g)+HCl (g) | [1976LTV] | 2, Third Law analysis, updated using our value for $\Delta_f H^o$[1,1-$C_2H_4Cl_2$ (g)]. |
| −133.2 | 0.7[a]<br>(3.6) | 293–323 | Equilibrium of hydrochlorination<br>$CH_2{=}CHCl$ (g)+HCl (g)$\rightleftarrows CH_3CHCl_2$ (l) | [1976LTV] | 3, Second Law analysis, updated using our value for $\Delta_f H^o$[1,1-$C_2H_4Cl_2$ (g)]. |
| −122.3 | 1.4[a] | 385 | Equilibrium<br>1,1-$C_2H_4Cl_2 \rightleftarrows$ 1,2-$C_2H_4Cl_2$ | [1968R] | 4, Second Law analysis; calculation uses our value of $\Delta_f H^o$[1,2-$C_2H_4Cl_2$]. |
| −129.3 | 0.5[a] | 523 | Enthalpy of hydrogenation<br>1,1-$C_2H_4Cl_2$ (g)+2$H_2$ (g)$\rightarrow C_2H_6$ (g)+2HCl (g) | [1967LAP] | 5, Reanalyzed at NIST; updated using our value for $\Delta_f H^o$[$C_2H_6$ (g)]. |
| −128.3 | 8.4 | 298 | Combustion calorimetry of liquid | [1938E]<br>[1953SBK]<br>[1970CP] | 6, Static Bomb. Data corrected by Smith *et al.* in 1953. Reanalyzed and auxiliary quantities updated by [1970CP]. |
| Reviews and Evaluations | | | | | |
| −127.7 | 1.4 | 298 | | [1986PNK] | |
| −130.6 | 3.0 | 298 | | [1983KP] | |
| −130.1 | N.R.[b] | 298 | | [1981C] | |
| −130.1 | 0.8 | 298 | | [1974CRW] | |
| −128.2 | 1.3 | 298 | | [1970CP] | |
| −129.9 | N.R.[b] | 298 | | [1969SSW] | |

[a] Precision only, does not include systematic errors or uncertainty in auxiliary thermodynamic quantities. The parenthetical value is our estimate of the overall uncertainty in the derived enthalpy of formation.

[b] Not reported, the parenthetical values are those estimated by Cox and Pilcher.

**Comments:**

1. From the Second Law analysis of Levanova *et al.*, $\Delta_r H(403\ \mathrm{K}) = (61.70 \pm 0.7)\ \mathrm{kJ\ mol^{-1}}$. This was adjusted to $\Delta_r H(298.15\ \mathrm{K}) = (61.23 \pm 1.0)\ \mathrm{kJ\ mol^{-1}}$ using the heat capacity data from the TRC Tables [1981C], [1985R]. With $\Delta_f H^o[C_2H_3Cl\ (g), 298.15\ \mathrm{K}] = (22.0 \pm 3.0)\ \mathrm{kJ\ mol^{-1}}$ and $\Delta_f H^o[HCl\ (g), 298.15\mathrm{K}] = -(92.31 \pm 0.10)\ \mathrm{kJ\ mol^{-1}}$ (see Secs. 5.2 and 1.4), we derive $\Delta_f H^o[1,1\text{-}C_2H_4Cl_2\ (g), 298.15\ \mathrm{K}] = -(131.5 \pm 3.6)\ \mathrm{kJ\ mol^{-1}}$, where the uncertainty is the expanded $2\sigma$ value estimated by us.
2. Taking entropies and heat capacities from the TRC Tables [1981C], [1985R], our Third Law analysis results in $\Delta_r H(298.15\ \mathrm{K}) = (62.2 \pm 0.8)\ \mathrm{kJ\ mol^{-1}}$.With auxiliary quantities as in Comment 1 we calculate $\Delta_f H^o[1,1\text{-}C_2H_4Cl_2\ (g), 298.15\ \mathrm{K}] = -(132.5 \pm 3.6)\ \mathrm{kJ\ mol^{-1}}$.
3. From the Second Law analysis of Levanova *et al.*, $\Delta_r H(308\ \mathrm{K}) = (93.24 \pm 0.7)\ \mathrm{kJ\ mol^{-1}}$. Taking gas phase heat capacity data from the TRC Tables [1981C], [1985R], and using $\Delta_{vap} C_p(1,1\text{-}C_2H_4Cl_2) = -50.2\ \mathrm{J\ mol^{-1} K^{-1}}$ [1956LP], $\Delta_{vap} H^o(1,1\text{-}C_2H_4Cl_2, 298.15\ \mathrm{K}) = (30.83 \pm 0.1)\ \mathrm{kJ\ mol^{-1}}$, this becomes $\Delta_r H(298.15\ \mathrm{K}) = (93.74 \pm 1.0)\ \mathrm{kJ\ mol^{-1}}$. This leads $\Delta_f H^o[1,1\text{-}C_2H_4Cl_2\ (g), 298.15\ \mathrm{K}] = -(133.2 \pm 3.6)\ \mathrm{kJ\ mol^{-1}}$.
4. From the Second Law analysis of Rozhnov, $\Delta_r H(385\ \mathrm{K}) = -(9.63 \pm 0.6)\ \mathrm{kJ\ mol^{-1}}$ for 1,1-$C_2H_4Cl_2$ (g)$\rightleftarrows$1,2-$C_2H_4Cl_2$ (g). Taking heat capacity data from Chao [1981C], $\Delta_r H(298.15\ \mathrm{K}) = -(9.68 \pm 0.6)\ \mathrm{kJ\ mol^{-1}}$. In conjunction with $\Delta_f H^o[1,2\text{-}C_2H_4Cl_2\ (g)] = -(132.0 \pm 3.5)\ \mathrm{kJ\ mol^{-1}}$ (see Sec. 6.4), we derive $\Delta_f H^o[1,1\text{-}C_2H_4Cl_2\ (g)] = -(123.3 \pm 4.0)\ \mathrm{kJ\ mol^{-1}}$. This work is not considered reliable, however (see Sec. 6.4).
5. $\Delta_r H(523\ \mathrm{K}) = -(144.99 \pm 0.52)\ \mathrm{kJ\ mol^{-1}}$ was adjusted to $\Delta_r H(298.15\ \mathrm{K}) = -(139.30 \pm 1.0)\ \mathrm{kJ\ mol^{-1}}$ using the heat capacity data from the TRC Tables [1981C]. In conjunction with $\Delta_f H^o[C_2H_6\ (g), 298.15\ \mathrm{K}] = -(84.0 \pm 0.4)\ \mathrm{kJ\ mol^{-1}}$ and $\Delta_f H^o[HCl\ (g), 298.15\ \mathrm{K}] = -(92.31 \pm 0.10)\ \mathrm{kJ\ mol^{-1}}$, we derive $\Delta_f H^o[1,1\text{-}C_2H_4Cl_2\ (g), 298.15\ \mathrm{K}] = -(129.32 \pm 1.0)\ \mathrm{kJ\ mol^{-1}}$.
6. The original results of Eftring [1938E] were corrected by Smith *et al.* [1953SBK] and reevaluated by Cox and Pilcher [1970CP]. The data have subsequently been compiled by Pedley *et al.* [1986PNK]. $\Delta_c H^o_{298} = -(1246.8 \pm 8.4)\ \mathrm{kJ\ mol^{-1}}$, refers to reaction 1,1-$C_2H_4Cl_2$ (l) $+2.5O_2\ (g) \rightarrow 2CO_2\ (g) + H_2O\ (l) + 2HCl$ (aq:600). The following auxiliary values were used: $\Delta_f H^o[CO_2\ (g), 298.15\ \mathrm{K}] = -(393.51 \pm 0.13)\ \mathrm{kJ\ mol^{-1}}$, $\Delta_f H^o[H_2O\ (l), 298.15\ \mathrm{K}] = -(285.830 \pm 0.040)\ \mathrm{kJ\ mol^{-1}}$, and $\Delta_f H^o[HCl\ (aq{:}600), 298.15\ \mathrm{K}] = -(166.540 \pm 0.10)\ \mathrm{kJ\ mol^{-1}}$. These data yield $\Delta_f H^o[1,1\text{-}C_2H_4Cl_2\ (l), 298.15\ \mathrm{K}] = -(159.13 \pm 8.4)\ \mathrm{kJ\ mol^{-1}}$.

gas and liquid phase. The equilibrium, established using $AlCl_3$ as a catalyst, was approached from both sides of the equilibrium point and was studied in both the gas and liquid phase. The liquid phase equilibrium constants were converted to gas phase values and $\log K_p = 0.323 + 503/T$ was determined over the temperature range of 331–440 K. From the Second Law analysis, $\Delta_r H[(g), 385\ \mathrm{K}] = -9.6\ \mathrm{kJ\ mol^{-1}}$ is derived. As a check, we performed Third Law analyses on the original data. From the reported liquid phase data, $K$ (liquid) = 153 and 97.0 at 330.5 and 371.2 K, respectively, we obtained an average $\Delta_r H[(l), 298.15\ \mathrm{K}] = -14.8\ \mathrm{kJ\ mol^{-1}}$. Third Law analyses of the reported gas phase results, $K[(g), 423.2\ \mathrm{K}] = 32.0$ and $K[(g), 440.2\ \mathrm{K}] = 26.8$ yield an average value $\Delta_r H[(g), 298.15\ \mathrm{K}] = -10.5\ \mathrm{kJ\ mol^{-1}}$. The Third Law analyses of the gas and liquid phase results differ by about the difference in the enthalpies of vaporization of the two compounds and are consistent with the Second Law analysis of Rozhnov [1968R]. His data lead to $\Delta_f H^o[1,2\text{-}C_2H_4Cl_2(g), 298.15\ \mathrm{K}] - \Delta_f H^o[1,1\text{-}C_2H_4Cl_2(g)] = -(9.65 \pm 1.4)\ \mathrm{kJ\ mol^{-1}}$ (see Table 17 and Comment 2). Unfortunately this result appears

TABLE 17. Enthalpies of formation of 1,2-dichloroethane derived from reported experimental data

| $\Delta_f H^o$ (g), 298.15 K (kJ mol$^{-1}$) | Reported uncertainty kJ mol$^{-1}$ | Temp. (K) | Method(s) | Ref/Year | Comments |
|---|---|---|---|---|---|
| Experimental | | | | | |
| −134.3 | 1.1 | 298 | Combustion calorimetry of liquid | [1969HS] | 1, Rotating bomb. |
| −142.7 | 1.4[a] | 385 | Equilibrium $1,1\text{-}C_2H_4Cl_2 \rightleftarrows 1,2\text{-}C_2H_4Cl_2$ | [1968R] | 2, Second Law analysis; calculation uses our value of $\Delta_f H^o[1,1\text{-}C_2H_4Cl_2]$. |
| −125.6 | 0.5[a] | 523 | Enthalpy of hydrogenation $1,2\text{-}C_2H_4Cl_2\ (g)+2H_2\ (g)\rightarrow C_2H_6\ (g)+2HCl\ (g)$ | [1967LAP] | 3, Data reanalyzed by [1970CP]; updated using our value for $\Delta_f H^o[C_2H_6\ (g)]$. |
| −129.2 | 1.7 | 298 | Combustion calorimetry of liquid | [1958SS] | 4, Static bomb. |
| −129.1 | 4.5[b] | 298 | Enthalpy of substitutive chlorination $1,2\text{-}C_2H_4Cl_2\ (l)+Cl_2\ (g)\rightarrow 1,1,2\text{-}C_2H_2H_4Cl_2\ (l)+HCl$ | [1956K] | 5, Reanalyzed at NIST; updated using our value for $\Delta_f H^o[1,1,2\text{-}C_2H_4Cl_2\ (l)]$. |
| −124.3 | 8.4 | 298 | Combustion calorimetry of liquid | [1938E]<br>[1953SBK]<br>[1970CP] | 6, Static Bomb. Data corrected by Smith *et al.* in 1953. Reanalyzed and auxiliary quantities updated by [1970CP]. |
| −130.4 | 0.8[a] | 355 | Enthalpy of chlorination $C_2H_4\ (g)+Cl_2\ (g)\rightarrow 1,2\text{-}C_2H_4Cl_2\ (g)$ | [1938CKS] | 7, Reanalyzed at NIST; updated using our value for $\Delta_f H^o[C_2H_4\ (g)]$. |
| Calculations | | | | | |
| −131.1 | 4.0 | 298 | Composite QCISD(T)/6−311+G(df,2p) *ab initio* calculations. | [2001BAM] | |
| Reviews and Evaluations | | | | | |
| −126.4 | 2.3 | 298 | | [1986PNK] | |
| −134.1 | 1.2 | 298 | | [1983KP] | |
| −126.8 | N.R.[c] | 298 | | [1981C] | |
| −128.4 | 1.7 | 298 | | [1970CP] | |
| −129.9 | N.R.[b] | 298 | | [1969SWS] | |

[a] Precision only, does not include systematic errors or uncertainty in auxiliary thermodynamic quantities.

[b] Precision of measured reaction enthalpy at the 95% level based on our statistical analysis.

[c] Not reported, the parenthetical values are those estimated by Cox and Pilcher.

**Comments:**

1. $\Delta_c H^o_{298} = -(1236.4\pm1.1)$ kJ mol$^{-1}$, refers to reaction $1,2\text{-}C_2H_4Cl_2(l)+2.5O_2(g)\rightarrow 2CO_2(g)+H_2O(l)+2HCl$ (aq:600). The following auxiliary values were used: $\Delta_f H^o[CO_2(g),\ 298.15\ K] = -(393.51\pm0.13)$ kJ mol$^{-1}$, $\Delta_f H^o[H_2O(l),\ 298.15\ K] = -(285.830\pm0.40)$ kJ mol$^{-1}$, and $\Delta_f H^o[HCl\ (aq{:}600),\ 298.15\ K] = -(166.540\pm0.10)$ kJ mol$^{-1}$. These data yield $\Delta_f H^o[1,2\text{-}C_2H_4Cl_2\ (l),\ 298.15\ K] = -(169.53\pm1.1)$ kJ mol$^{-1}$.
2. From the Second Law analysis of Rozhnov, $\Delta_r H(385\ K) = -(9.63\pm0.6)$ kJ mol$^{-1}$ for $1,1\text{-}C_2H_4Cl_2(g)\rightleftarrows 1,2\text{-}C_2H_4Cl_2(g)$. Taking heat capacity data from Chao [1981C], $\Delta_r H(298.15\ K) = -(9.68\pm0.6)$ kJ mol$^{-1}$. In conjuction with $\Delta_f H^o[1,1\text{-}C_2H_4Cl_2(g)] = -(133.0\pm4.0)$ kJ mol$^{-1}$ (see Sec. 6.3), we derive $\Delta_f H^o[1,2\text{-}C_2H_4Cl_2(g)] = -(142.7\pm4.0)$ kJ mol$^{-1}$. This work is not considered reliable, however (see Discussion).
3. $\Delta_r H(523\ K) = -(147.77\pm0.48)$ kJ mol$^{-1}$ was adjusted to $\Delta_r H(298.15\ K) = -(141.8\pm1.0)$ kJ mol$^{-1}$ using the heat capacity data from the TRCTables [1981C]. In conjunction with $\Delta_f H^o[C_2H_6(g),\ 298.15\ K] = -(84.0\pm0.4)$ kJ mol$^{-1}$ and $\Delta_f H^o[HCl(g),\ 298.15\ K] = -(92.31\pm0.10)$ kJ mol$^{-1}$, we derive $\Delta_f H^o[1,2\text{-}C_2H_4Cl_2(g),\ 298.15\ K] = -(126.86\pm1.0)$ kJ mol$^{-1}$.
4. Sample purity ⩾99.9%. $\Delta_c H^o_{298} = -(1241.5\pm1.7)$ kJ mol$^{-1}$, refers to reaction $1,2\text{-}C_2H_4Cl_2(l)+2.5O_2(g)\rightarrow 2CO_2(g)+H_2O(l)+2HCl$ (aq:600). Data yields $\Delta_f H^o[1,2\text{-}C_2H_4Cl_2,(l),\ 298.15\ K] = -(164.43\pm1.7)$ kJ mol$^{-1}$. See Comment 1 for auxiliary thermodynamic values.
5. Two measurements of the enthalpies of reaction yield $\Delta_r H(298.15\ K) = -(116.3\pm4.5)$ kJ mol$^{-1}$, where the uncertainty limits represent 95% confidence levels based on a statistical analysis of the precision only. Corrections relating to dissolution of HCl and evaporation of reactant were applied by Kirkbride. Combined with $\Delta_f H^o[1,1,2\text{-}C_2H_3Cl_3(l),\ 298.15\ K] = -(188.3\pm4.0)$ kJ mol$^{-1}$, $\Delta_f H^o[HCl(g)] = -(92.31\pm0.10)$ kJ mol$^{-1}$ we calculate $\Delta_f H^o[1,2\text{-}C_2H_4Cl_2(l),\ 298.15\ K] = -(164.3\pm6.0)$ kJ mol$^{-1}$.
6. The original results of Eftring [1938E] were corrected by Smith *et al.* [1953SBK] and reevaluated by Cox and Pilcher [1970CP]. The data have subsequently been compiled by Pedley *et al.* [1986PNK]. $\Delta_c H^o_{298} = -(1246.4\pm8.4)$ kJ mol$^{-1}$, refers to reaction $1,2\text{-}C_2H_4Cl_2(l)+2.5O_2(g)\rightarrow 2CO_2(g)+H_2O(l)+2HCl$ (aq:600). These data yield $\Delta_f H^o[1,2\text{-}C_2H_4Cl_2,(l),\ 298.15\ K] = -(159.53\pm8.4)$ kJ mol$^{-1}$. See Comment 1 for auxiliary thermodynamic values.
7. $\Delta_r H(355\ K) = -(182.64\pm0.6)$ kJ mol$^{-1}$ for reaction $C_2H_4(g)+Cl_2(g)\rightarrow 1,2\text{-}C_2H_4Cl_2(g)$ was derived from calorimetric measurements. This was adjusted to $\Delta_r H(298.15\ K) = -(182.78\pm0.6)$ kJ mol$^{-1}$ using the heat capacity data from the TRC Tables [1981C]. Combined with our recommended value $\Delta_f H^o[C_2H_4(g),\ 298.15\ K] = (52.4\pm0.5)$ kJ mol$^{-1}$ (see Sec. 5.1), we derive $\Delta_f H^o[1,2\text{-}C_2H_4Cl_2(g),\ 298.15\ K] = -(130.4\pm0.8)$ kJ mol$^{-1}$.

to be at odds with other data. Note for instance that Lacher *et al.* [1967LAP] measure very similar enthalpies of hydrogenation for the dichloroethanes and the data of Lacher indicates the 1,1 isomer to be the more stable of the dichloroethanes. The combustion results of Eftring [1938E] also suggest the 1,1-isomer is the more stable.

As a check of the relative stability of the dichloroethanes, we have carried out a series of *ab initio* calculations [2001BAM] on the isomeric chlorinated C2 compounds. The results are shown in Table 18. For the dichloroethenes, trichloroethanes, and tetrachloroethanes, theory and experiment are in very good agreement, with a largest deviation of 2.1 kJ mol$^{-1}$. For the dichloroethanes, all levels of our calculations predict the 1,1- and 1,2 isomers to have very similar enthalpies of formation. The highest level calculations predict the 1,1-isomer to be more stable than the 1,2- by 2.1

TABLE 18. Comparison of calculated and experimental results on the relative stabilities of chlorinated C2 isomers

| | Relative enthalpies of formation at 298.15 K (kJ mol$^{-1}$)[a] | | | |
|---|---|---|---|---|
| | Experimental | Calculated[b] | Calculated−experimental | Data of Rozhnov[c] on dichloroethanes |
| Dichloroethanes | | | | |
| 1,1-$C_2H_4Cl_2$ | (0)[d] | 0 | 0 | 9.7 |
| 1,2-$C_2H_4Cl_2$ | (0.5)[d] | 2.1±1.2 | 1.6 | 0 |
| Dichloroethenes | | | | |
| $CH_2{=}CCl_2$ | 5.4 | 3.2±0.8 | −2.1 | — |
| *E*-CHCl=CHCl | 2.5 | 2.4±1.3 | −0.1 | — |
| *Z*-CHCl=CHCl | 0 | 0 | 0 | — |
| Trichloroethanes | | | | |
| 1,1,1-$C_2H_3Cl_3$ | 3.4 | 4.6±2.1 | +1.2 | — |
| 1,1,2-$C_2H_3Cl_3$ | 0 | 0 | 0 | — |
| Tetrachloroethanes | | | | |
| 1,1,1,2-$C_2H_2Cl_4$ | 4.4 | 2.9±1.4 | −1.5 | — |
| 1,1,2,2-$C_2H_2Cl_4$ | 0 | 0 | 0 | — |

[a] The most stable isomer (based on experiment) is set to 0 in all cases.

[b] Highest level result from a series of *ab initio* calculations up to and including QCISD(T)/6-311++G(3df,3pd). The quoted calculated value is the most reliable calculation, while the quoted uncertainty is a bounds that spans all of the calculated values. Zero point energies have been added and the results adjusted to 298.15 K.

[c] [1968R].

[d] As derived from the final recommended values.

kJ mol$^{-1}$. Based on our calculations the results of Rozhnov [1968R] cannot be even approximately correct and we have not used these data to make our recommendations.

*Recommendation*. The best experimental data appear to be the rotating bomb combustion measurements of Hu and Sinke [1969HS]. Slightly less reliable are the early ethene chlorination measurements by Conn *et al.* [1938CKS], and the static bomb calorimetry results of Sinke and Stull [1958SS]. The measurement of the enthalpy of substitutive chlorination of 1,2-$C_2H_4Cl_2$ by Kirkbride [1956K] has a larger uncertainty. The enthalpy of hydrogenation studies of Lacher [1967LAP] and the early static combustion work of Eftring [1938E] generally seem to result in values that are systematically too positive. However these two studies examined both the dichloroethane isomers and, to the extent that the postulated systematic errors are similar in each study, the results suggest that the isomers have similar enthalpies of formation with the 1,1-isomer slightly more stable than 1,2-dichloroethane. This is in agreement with our high level calculations. We believe that the calculations are of sufficiently proven accuracy that the equilibrium results of Rozhnov [1968R] must be erroneous. Our best calculated absolute value [2001BAM] for 1,2-dichloroethane is $\Delta_f H^o[1,2\text{-}C_2H_4Cl_2(g)] = -(131.1\pm4.0)$ kJ mol$^{-1}$, where the uncertainty is estimated based on our ability to predict the enthalpies of formation of the other chloroethanes. Consideration of all the above data leads us to recommend $\Delta_f H^o[1,2\text{-}C_2H_4Cl_2(g)] = -(132.0\pm3.5)$ kJ mol$^{-1}$. Note there is still no clear answer as to which dichloroethane isomer is the more stable.

## 6.5. 1,1,1-Trichloroethane

*Enthalpy of Vaporization*. The enthalpy of vaporization at 298.15 K has been measured by three groups as 32.44 kJ mol$^{-1}$ [1972HSM], $(32.47\pm0.07)$ kJ mol$^{-1}$ [1972LW], and $(32.53\pm0.08)$ kJ mol$^{-1}$ [1980MSS]. The value $\Delta_{vap}H(298.15\,K) = (32.47\pm0.07)$ kJ mol$^{-1}$ is selected. The correction due to nonideality of the gas was calculated both by us and Majer and Svoboda [1985MS] as 0.12 kJ mol$^{-1}$. The value $\Delta_{vap}H^o(298.15\,K) = (32.59\pm0.07)$ kJ mol$^{-1}$ is derived. The heat capacity of vaporization is derived as $\Delta_{vap}C_p = -55.1$ J mol$^{-1}$ K$^{-1}$ from the temperature dependence of the $\Delta_{vap}H$ data of [1980MSS] (see Fig. 8 and Sec. 6.9).

*Enthalpy of Formation. Recommendation*. Of the chlorinated ethanes, 1,1,1-trichloroethane has one of the better known enthalpies of formation. Two high quality combustion studies [1971MRS], [1972HSM] using rotating bomb calorimetry and high purity samples are available. The data are in reasonable agreement, although they do not agree within the authors stated uncertainty limits. This is perhaps indicative of the general difficulties inherent in such experiments with chlorinated compounds. Hu, Sinke, and Mintz [1972HSM] showed the earlier study of Hu and Sinke [1969HS] to be in error and speculated that this was due to an impure sample. The latter study yields an enthalpy of formation 8 kJ mol$^{-1}$ more negative, which gives some indication of the importance of sample purity. In general this has implications for much of the early work on chlorinated compounds, where there is little or no information on the purity of the samples used. The gas phase study of equilibrium hydrochlorination

TABLE 19. Enthalpies of formation of 1,1,1-trichloroethane derived from reported experimental data

| $\Delta_f H^o$(g), 298.15 K (kJ mol$^{-1}$) | Reported uncertainty kJ mol$^{-1}$ | Temp. (K) | Method(s) | Ref/Year | Comments |
|---|---|---|---|---|---|
| Experimental | | | | | |
| −146.1 | 1.1 | 298 | Combustion calorimetry of liquid | [1972HSM] | 1, Rotating bomb calorimetry. |
| −144.6 | 0.84[a]<br>(2.2) | 348–399 | Equilibrium of hydrochlorination<br>$CH_2{=\!=}CCl_2(g)+HCl(g)\rightleftarrows CH_3CCl_3(g)$ | [1972HSM] | 2, Third Law analysis, $\Delta_f H^o[CH_2{=\!=}CCl_2]$ used in calculation. |
| −142.0 | 1.4 | 298 | Combustion calorimetry of liquid | [1971MRS] | 3, Rotating bomb calorimetry. |
| −138.2 | 1.0 | 298 | Combustion calorimetry of liquid | [1969HS] | 4, Later shown [1971MRS], [1972HSM] to be in error because sample was impure. |
| −141.0 | 2.4[b]<br>(4.2) | 293–353 | Equilibrium of hydrochlorination<br>$CH_2{=\!=}CCl_2(soln)+HCl(g)\rightleftarrows CH_3CCl_3(soln)$ | [1975LTVa,b] | 5, Second Law analysis, $\Delta_f H^o[CH_2{=\!=}CCl_2]$ used in calculation. |
| Reviews and Evaluations | | | | | |
| −144.4 | 1.7 | 298 | | [1986PNK] | |
| −144.6 | 0.8 | 298 | | [1983KP] | |
| −142.3 | N.R.[c] | 298 | | [1981C] | |
| −142.3 | 1.4 | 298 | | [1974C] | |

[a] Precision of enthalpy change only; the parenthetical value is our estimate of the overall uncertainty in the derived $\Delta_f H^o[298.15\ K]$.

[b] Precision only, does not include systematic errors or uncertainty in auxiliary thermodynamic quantities; the parenthetical value is the overall uncertainty estimated by us by comparison of similar experiments.

[c] Not reported.

**Comments:**

1. Rotating bomb calorimetry. High purity sample (99.96 mol%). $\Delta_c H[(l),\ 298.15\ K] = -(1108.0\pm0.8)\ kJ\ mol^{-1}$, refers to reaction $1,1,1\text{-}C_2H_3Cl_3(l) + 2O_2(g) \rightarrow 3CO_2(g) + 3HCl\ (aq{:}600)$. The following auxiliary values were used: $\Delta_f H^o[CO_2(g),\ 298.15\ K] = -(393.51\pm0.13)\ kJ\ mol^{-1}$, and $\Delta_f H^o[HCl\ (aq{:}600),\ 298.15\ K] = -(166.540\pm0.10)\ kJ\ mol^{-1}$. The data result in $\Delta_f H^o[1,1,1\text{-}C_2H_3Cl_3(l),\ 298.15\ K] = -(178.64\pm0.8)\ kJ\ mol^{-1}$.
2. Third Law analysis of equilibrium $CH_2{=\!=}CCl_2(g)+HCl(g)\rightleftarrows CH_3CCl_3(g)$ yields $\Delta_r H(298.15\ K) = -(54.64\pm0.84)\ kJ\ mol^{-1}$. With $\Delta_f H^o[CH_2{=\!=}CCl_2(g),\ 298.15\ K] = (2.4\pm2.0)\ kJ\ mol^{-1}$ (see Sec. 5.3), and $\Delta_f H^o[HCl(g),\ 298.15\ K] = -(92.31\pm0.10)\ kJ\ mol^{-1}$, we find $\Delta_f H^o[1,1,1\text{-}C_2H_3Cl_3(g), 298.15\ K] = -(144.55\pm2.2)\ kJ\ mol^{-1}$.
3. Rotating bomb calorimetry. High purity sample (99.99 mol%). $\Delta_c H[(l),\ 298.15\ K] = -(1112.0\pm1.3)\ kJ\ mol^{-1}$. Auxiliary data as in Comment 1. The data result in $\Delta_f H^o[1,1,1\text{-}C_2H_3Cl_3(l),\ 298.15\ K] = -(174.54\pm1.3)\ kJ\ mol^{-1}$.
4. Later shown [1971MRS], [1972HSM] to be in error because sample was impure. $\Delta_c H[(l), 298.15\ K] = -(1115.9\pm1.0)\ kJ\ mol^{-1}$. Auxiliary data as in Comment 1. The data result in $\Delta_f H^o[1,1,1\text{-}C_2H_3Cl_3(l)] = -(170.74\pm1.0)\ kJ\ mol^{-1}$.
5. Reaction carried out in chlorobenzene. $\Delta_r H(323\ K) = -(56.9\pm2.0)\ kJ\ mol^{-1}$, from which $\Delta_f H^\circ[CH_3CCl_3\ (g),\ 298.15\ K] = 141.0\ kJ\ mol^{-1}$ is derived. Excess thermodynamic properties of solvation were neglected in the analysis.

of 1,1-dichloroethene [1972HSM] appears to have been carefully done and sets the relative enthalpies of formation of 1,1-dichloroethene and 1,1,1-trichloroethane to within about 0.8 kJ mol$^{-1}$. This result lies approximately midway between the two rotating bomb combustion studies and suggests that all species involved have been reasonably well characterized. The liquid phase study of the hydrochlorination equilibrium by Levanova *et al.* [1975LTVa], [1975LTVb] leads to a somewhat more positive enthalpy value, but it is not considered as reliable because of the neglect of excess thermodynamic properties of solvation in the analysis. We have taken a weighted average of the gas phase equilibrium data [1972HSM] and the two rotating bomb combustion studies [1971MRS], [1972HSM], and recommend $\Delta_f H^o[1,1,1\text{-}C_2H_3Cl_3(g),\ 298.15\ K] = -(144.6\pm2.0)\ kJ\ mol^{-1}$.

## 6.6. 1,1,2-Trichloroethane

*Enthalpy of Vaporization*. Williamson and Harrison [1957WH] obtained $\Delta_{vap}H(298.15\ K) = 40.0\ kJ\ mol^{-1}$ from extrapolation of the enthalpy of vaporization measured between 330 and 358 K, while Majer *et al.* [1980MSS] calorimetrically measured $\Delta_{vap}H$ between 298 and 358 K and reported $\Delta_{vap}H(298.15\ K) = (40.24\pm0.10)\ kJ\ mol^{-1}$. Laynez and Wadso [1972LW] found $\Delta_{vap}H(298.15\ K) = (40.28\pm0.06)\ kJ\ mol^{-1}$. The data are in good agreement and $\Delta_{vap}H(298.15\ K) = (40.26\pm0.07)\ kJ\ mol^{-1}$ is selected. Our calculated correction due to nonideality of the gas is 0.04 kJ mol$^{-1}$, the same value derived by Majer and Svoboda [1985MS]. This yields $\Delta_{vap}H^o(298.15\ K) = (40.30\pm0.07)\ kJ\ mol^{-1}$. The heat capacity of vaporization is derived as $\Delta_{vap}C_p = -60.3\ J\ mol^{-1}\ K^{-1}$ from the temperature dependence of the $\Delta_{vap}H$ data of [1980MSS].

*Enthalpy of Formation*. Data are summarized in Table 20. Papina and Kolesov [1987PK] have measured the enthalpy of combustion in a rotating bomb calorimeter, obtaining $\Delta_c H(298.15\ K)[1,1,2\text{-}C_2H_3Cl_3(l),\ 298.15\ K] = -(1098.1\pm4.4)\ kJ\ mol^{-1}$, which yields $\Delta_f H^o[1,1,2\text{-}C_2H_3Cl_3(l),\ 298.15\ K] = -(188.54\pm4.4)\ kJ\ mol^{-1}$ and $\Delta_f H^o[1,1,2\text{-}C_2H_3Cl_3(g),\ 298.15\ K] = -(148.2\pm4.4)\ kJ\ mol^{-1}$. Stull *et al.* [1969SWS] report an otherwise unpublished combustion calorimetry study by Sinke [1969S] that leads to $\Delta_f H^o[1,1,2\text{-}C_2H_3Cl_3(l),\ 298.15\ K]$

TABLE 20. Enthalpies of formation of 1,1,2-trichloroethane derived from reported experimental data

| $\Delta_f H^\bullet$ (g), 298.15 K (kJ mol$^{-1}$) | Reported uncertainty kJ mol$^{-1}$ | Temp. (K) | Method(s) | Ref/Year | Comments |
|---|---|---|---|---|---|
| Experimental | | | | | |
| −148.2 | 4.4 | 298 | Combustion calorimetry of liquid | [1987PK] | 1 |
| −147.2 | N.R.[a] | 348–399 | Equilibrium of hydrochlorination | [1975LTVa,b] | 2, Second Law analysis. |
| | (4.2) | | $Z$-$C_2H_2Cl_2$ (soln)+HCl (g)$\rightleftarrows$$CH_2ClCHCl_2$ (soln) | | $\Delta_f H^\circ$[$Z$-CHCl═CHCl] used in calculation. |
| −152.6 | N.R.[a] | 348–399 | Equilibrium of hydrochlorination | [1975LTVa,b] | 3, Third Law analysis, |
| | (4.2) | | $Z$-$C_2H_2Cl_2$ (soln)+HCl (g)$\rightleftarrows$$CH_2ClCHCl_2$ (soln) | | $\Delta_f H^\circ$[$Z$-CHCl═CHCl] used in analysis. |
| −145.6 | N.R.[a] | 373–473 | Equilibrium | [1975LTVa,b] | 4, Second Law analysis. |
| | (4.2) | | 1,1,2,-$C_2H_3Cl_3$ (l)$\rightleftarrows$1,1,1-$C_2H_3Cl_3$ (l) | | $\Delta_f H^\circ$[$CH_3CCl_3$] used in analysis. |
| −149.9 | N.R.[a] | 373–473 | Equilibrium | [1975LTVa,b] | 5, Third Law analysis, $\Delta_f H^\circ$[$CH_3CCl_3$] |
| | (4.2) | | 1,1,2,-$C_2H_3Cl_3$ (l)$\rightleftarrows$1,1,1-$C_2H_3Cl_3$ (l) | | used in analysis. |
| −138.3 | N.R.[b] | 298 | Combustion calorimetry of liquid | [1969SWS] | 6, Unpublished work cited in [1969SWS]. |
| −150.9 | 4.5[b] | 298 | Enthalpy of substitutive chlorination | [1956K] | 7, $\Delta_f H^\circ$[1,2,-$C_2H_4Cl_2$ (l)] used in |
| | | | 1,2,-$C_2H_4Cl_2$(l)+$Cl_2$(g)→1,1,2-$C_2H_3Cl_3$ (l)+HCl | [1970CP] | calculation. |
| Reviews and Evaluations | | | | | |
| −151.2 | 2.9 | 298 | | [1986PNK] | |
| −144.7 | 1.9 | 298 | | [1983KP] | |
| −145.6 | N.R.[b] | 298 | | [1981C] | |
| −148.5 | 0.8 | 298 | | [1970CP] | |
| −138.5 | N.R.[b] | 298 | | [1969SWS] | |

[a] Not reported; the parenthetical value is the $2\sigma$ uncertainty estimated by us.

[b] Not reported.

[c] Precision of measured reaction enthalpy at the 95% level based our statistical analysis. Does not include systematic errors or uncertainty in auxiliary thermodynamic quantities.

**Comments:**

1. Rotating bomb calorimetry. High purity sample (99.975 mol%). $\Delta_c H(298.15\ \mathrm{K}) = -1098.1 \pm 4.4\ \mathrm{kJ\ mol^{-1}}$, refers to reaction [1,1,2-$C_2H_3Cl_3$ (l)]+2$O_2$ (g)→2$CO_2$ (g)+3HCl (aq:600). The following auxiliary values were used: $\Delta_f H^\bullet$[$CO_2$ (g), 298.15 K]$= -(393.51 \pm 0.13)\ \mathrm{kJ\ mol^{-1}}$ and $\Delta_f H^\bullet$[HCl (aq:600), 298.15 K]$= -(166.540 \pm 0.10)\ \mathrm{kJ\ mol^{-1}}$. These data lead to $\Delta_f H^\circ$[$CH_2$═$CCl_2$ (l), 298.15 K]$= -(188.54 \pm 4.4)\ \mathrm{kJ\ mol^{-1}}$.

2. Second Law analysis $\Delta_r H(353\ \mathrm{K}) = -61.2\ \mathrm{kJ\ mol^{-1}}$ was adjusted to $\Delta_r H(298.15\ \mathrm{K}) = -61.2\ \mathrm{kJ\ mol^{-1}}$ (see Discussion): Combined with $\Delta_f H^\circ$[$Z$-CHCl═CHCl(l)]$= -(34.0 \pm 2.0)\ \mathrm{kJ\ mol^{-1}}$, and $\Delta_f H^\circ$[HCl (g), 298.15 K]$= -(92.31 \pm 0.10)\ \mathrm{kJ\ mol^{-1}}$ we calculate $\Delta_f H^\circ$[1,1,2-$C_2H_3Cl_3$(l), 298.15 K]$= -187.5\ \mathrm{kJ\ mol^{-1}}$. This analysis neglects excess thermodynamic properties of solvation.

3. Third Law analysis is as follows. $\Delta_{vap} S$(1,1,2-$C_2H_3Cl_3$, 353 K)$= 90.28\ \mathrm{J\ mol^{-1}\ K^{-1}}$ and $\Delta_{vap} C_p$(1,1,2-$C_2H_3Cl_3$)$= -60.33\ \mathrm{J\ mol^{-1}\ K^{-1}}$ were derived as in Comment 5. The value at the boiling point $\Delta_{vap} S$[$Z$-CHCl═CHCl, 333 K]$= 91.2\ \mathrm{J\ mol^{-1}\ K^{-1}}$ was derived using our enthalpy of vaporization and $\Delta_{vap} C_p = -48.0\ \mathrm{J\ mol^{-1}\ K^{-1}}$, from the data listed in references [1982WEP], [1985R]. This becomes $\Delta_{vap} S$[$Z$-CHCl═CHCl, 353 K]$= 85.27\ \mathrm{J\ mol^{-1}\ K^{-1}}$ and results in $\Delta_r H$(liquid, 353 K)$= -65.54\ \mathrm{kJ\ mol^{-1}}$ and $\Delta_r H$(gas, 353 K)$= -65.39\ \mathrm{kJ\ mol^{-1}}$. Using heat capacity data from [1981C] and [1985R] leads to $\Delta_r H$(gas, 298.15 K)$= -66.15\ \mathrm{kJ\ mol^{-1}}$. With $\Delta_f H^\circ$[$Z$-CHCl═CHCl (g), 298.15 K]$= -(3.0 \pm 2.0)\ \mathrm{kJ\ mol^{-1}}$ and $\Delta_f H^\circ$[HCl (g), 298.15 K]$= -(92.31 \pm 0.10)\ \mathrm{kJ\ mol^{-1}}$, we calculate $\Delta_f H^\circ$[1,1,2-$C_2H_3Cl_3$ (g), 298.15 K]$= -192.9\ \mathrm{kJ\ mol^{-1}}$. This analysis neglects excess thermodynamic properties of solvation.

4. The Second Law analysis gives $\Delta_r H$(liquid, 423 K)$= (8.7 \pm 1.7)\ \mathrm{kJ\ mol^{-1}}$. This was converted to the gas phase value $\Delta_r H$(gas,423)$= (1.64 \pm 1.7)\ \mathrm{kJ\ mol^{-1}}$ using $\Delta_{vap} H$[$CH_3CCl_3$,423 K]$= 25.71\ \mathrm{kJ\ mol^{-1}}$ and $\Delta_{vap} H$[1,1,2-$C_2H_3Cl_3$, 423 K]$32.77\ \mathrm{kJ\ mol^{-1}}$, which are derived from temperature dependent enthalpies of vaporization of [1980MSS]. $\Delta_r H$(gas, 423)$= (1.64 \pm 1.7)\ \mathrm{kJ\ mol^{-1}}$ was then adjusted to $\Delta_r H$(gas, 298)$= (1.02 \pm 2.0)\ \mathrm{kJ\ mol^{-1}}$ using the ideal gas heat capacity data of Chao [1981C]. Combined with $\Delta_f H^\circ$[$CH_3CCl_3$ (g), 298.15 K]$= -(144.6 \pm 2.0)\ \mathrm{kJ\ mol^{-1}}$, we calculate $\Delta_f H^\circ$[1,1,2-$C_2H_3Cl_3$ (g), 298.15 K]$= -(145.6 \pm 4.2)\ \mathrm{kJ\ mol^{-1}}$, where the overall uncertainty has been estimated. This analysis neglects excess thermodynamic properties of solvation.

5. Third Law analysis is as follows. The data of Majer *et al.* [1980MSS] and the boiling point relation $\Delta_{vap} S_{bp} = \Delta_{vap} H_{bp}/T$ were used to derive the following: $\Delta_{vap}$(1,1,1-$C_2H_3Cl_3$, 347.1 K)$= 86.02\ \mathrm{J\ mol^{-1}\ K^{-1}}$, $\Delta_{vap} S$(1,1,2-$C_2H_3Cl_3$, 386.6 K)$= 90.28\ \mathrm{J\ mol^{-1}\ K^{-1}}$, $\Delta_{vap} C_p$(1,1,1-$C_2H_3Cl_3$)$= -55.06\ \mathrm{J\ mol^{-1}\ K^{-1}}$, $\Delta_{vap} C_p$ (1,1,2-$C_2H_3Cl_3$)$= -60.33\ \mathrm{mol^{-1}\ K^{-1}}$, $\Delta_{vap} S$(1,1,1-$C_2H_3Cl_3$, 423 K)$= 75.11\ \mathrm{J\ mol^{-1}\ K^{-1}}$, and $\Delta_{vap} S$(1,1,2-$C_2H_3Cl_3$, 298.15 K)$= 84.83\ \mathrm{J\ mol^{-1}\ K^{-1}}$. Combined with the gas phase entropy data of Chao [1981C] we derive $\Delta_r S$(liquid, 423 K)$= 1.53\ \mathrm{J\ mol^{-1}\ K^{-1}}$ and $\Delta_r H$(liquid, 423 K)$= 12.85\ \mathrm{kJ\ mol^{-1}}$. This was adjusted to $\Delta_r H$(gas, 298.15 K)$= 5.17\ \mathrm{kJ\ mol^{-1}}$ as in Comment 4. Combined with $\Delta_f H^o$[$CH_3CCl_3$ (g), 298.15 K]$= -(144.6 \pm 2.0)\ \mathrm{kJ\ mol^{-1}}$, we calculate $\Delta_f H^o$[1,1,2-$C_2H_3Cl_3$ (g), 298.15 K]$= -(149.77 \pm 4.2)\ \mathrm{kJ\ mol^{-1}}$, where the overall uncertainty has been estimated. This analysis neglects excess thermodynamic properties of solvation.

6. Unpublished combustion calorimetry work of Sinke [1969S] cited in [1969SWS]. No details are available.

7. Two measurements of the enthalpies of reaction yield $\Delta_r H(298.15\ \mathrm{K}) = -(116.3 \pm 4.5)\ \mathrm{kJ\ mol^{-1}}$, where the uncertainty limits represent 95% confidence levels based on a statistical analysis of the precision only. Corrections relating to dissolution of HCl and evaporation of reactant were applied by Kirkbride. Combined with $\Delta_f H^o$[1,2-$C_2H_4Cl_2$ (l), 298.15 K]$= -(167.2 \pm 3.5)\ \mathrm{kJ\ mol^{-1}}$, $\Delta_f H^o$[HCl (g), 298.15 K]$= -(92.31 \pm 0.10)\ \mathrm{kJ\ mol^{-1}}$ we calculate $\Delta_f H^o$[1,1,2-$C_2H_3Cl_3$ (l), 298.15 K]$= -(191.1 \pm 5.7)\ \mathrm{kJ\ mol^{-1}}$.

$=-178.6\,\mathrm{kJ\,mol^{-1}}$. The enthalpy of chlorination of 1,2-dichloroethane from Kirkbride [1956K] results in $\Delta_f H^o[1,1,2\text{-}C_2H_3Cl_3(l),\ 298.15\,K]=-191.1\,\mathrm{kJ\,mol^{-1}}$. The enthalpy of formation of 1,1,2-$C_2H_3Cl_3$ can also be related to that of *Z*-1,2-$C_2H_2Cl_2$ through the hydrochlorination equilibrium, which was studied by Levanova *et al.* [1975LTVa], [1975LTVb]

$$Z\text{-CHCl}{=\!=}\text{CHCl(sol)}+\text{HCl(g)}\rightleftarrows 1,1,2\text{-}C_2H_3Cl_3\text{(sol)}. \tag{17}$$

The equilibrium was established in tetrachloroethane solvent (isomer not specified) with the catalysts $AlCl_3$ and $FeCl_3$. Experiments were also carried out with the *E* isomer, but the authors felt those results were unreliable due to the presence of side reactions. For the *Z* isomer Levanova *et al.* [1975LTVa], [1975LTVb] report $\log K_p(343\text{–}363\,K)=3190/T-7.4$. Second and Third Law analyses of these data (see Comments 2 and 3 of Table 20) yield $\Delta_f H^o[1,1,2\text{-}C_2H_3Cl_3(g),298.15\,K]=-(147.2\pm4.2)\,\mathrm{kJ\,mol^{-1}}$ and $\Delta_f H^o[1,1,2\text{-}C_2H_3Cl_3(g),298.15\,K]=-(152.6\pm4.2)\,\mathrm{kJ\,mol^{-1}}$, respectively. The uncertainties have been estimated by us by comparison with the results of similar experiments. The agreement between the Second and Third Law analyses is reasonably good. Differences may be due to the estimations involved, the short temperature range of the experiments, and neglect of excess thermodynamic properties of solvation.

Also useful are the data on the trichloroethane isomerization reaction which has been studied by Levanova *et al.* [1975LTVa], [1975LTVb]

$$1,1,2\text{-}C_2H_3Cl_3(l)\rightleftarrows 1,1,1\text{-}C_2H_3Cl_3(l). \tag{18}$$

They found $\log K=-0.48-437/T$ between 373 and 473 K. As detailed in Comments 4 and 5, the Second and Third Law analyses of this data result in $\Delta_f H^o[1,1,2\text{-}C_2H_3Cl_3(g),298.15\,K]=-(145.6\pm4.2)\,\mathrm{kJ\,mol^{-1}}$ and $\Delta_f H^o[1,1,2\text{-}C_2H_3Cl_3(g),298.15\,K]=-(149.6\pm4.2)\,\mathrm{kJ\,mol^{-1}}$, respectively. The uncertainties have been estimated by us by comparison with the results of similar experiments. The agreement between the Second and Third Law analyses is reasonably good. The estimations involved, the short temperature range of the experiments, and neglect of excess thermodynamic properties of solvation may be responsible for differences between the Second and Third Law analyses.

*Recommendation*. The otherwise unpublished combustion value of Sinke [1969S] cited by Stull *et al.* [1969SWS] is significantly more positive than the other values and this result is rejected. All other data are considered. With regard to the equilibrium data [1975LTVa], [1975LTVb], one would normally prefer the Third Law analyses to those of the Second Law. However, because of the estimations and simplifications employed in the Third Law analyses we have weighted them equally. The rotating-bomb combustion calorimetry result of Papina and Kolesov [1987PK] is considered the most reliable measurement. The final recommended values are based primarily on this work and are $\Delta_f H^o[1,1,2\text{-}C_2H_3Cl_3(l),\ 298.15\,K]=-(188.3\pm4.0)\,\mathrm{kJ\,mol^{-1}}$, and $\Delta_f H^o[1,1,2\text{-}C_2H_3Cl_3(g),\ 298.15\,K]=-(148.0\pm4.0)\,\mathrm{kJ\,mol^{-1}}$. Notice that the isomer with the more distributed chlorines is the more stable of the trichloroethanes. This is in agreement with our high level calculations [2001BAM] (see Table 18).

## 6.7. 1,1,1,2-Tetrachloroethane

*Enthalpy of Vaporization*. No calorimetric measurements of the enthalpy of vaporization appear to exist. Gundry and Head [1978GH] list the value $\Delta_{vap}H(298.15\,K)=(41.1\pm0.2)\,\mathrm{kJ\,mol^{-1}}$, derived from an unspecified fit to vapor pressure data. We note, however, that the correlation between $\Delta_{vap}H(298.15\,K)$ and boiling points discussed in Sec. 6.9 would give a value of 42.6 $\mathrm{kJ\,mol^{-1}}$. Levanova *et al.* [1976LBR] estimated $\Delta_{vap}H(298.15\,K)=42.2\,\mathrm{kJ\,mol^{-1}}$ based on Benson's boiling point correlation [1969B]. In the absence of a calorimetric measurement, we have adopted the recommendation of Gundry and Head [1978GH], although we feel the uncertainty limits are unrealistically small. The correction due to nonideality of the gas at 298.15 K is calculated to be 0.03 $\mathrm{kJ\,mol^{-1}}$ and we adopt $\Delta_{vap}H^o(298.15\,K)=(41.1\pm0.5)\,\mathrm{kJ\,mol^{-1}}$.

*Enthalpy of Formation*. Data are summarized in Table 21. The rotating-bomb combustion calorimetry result of Gundry and Head [1978GH] is $\Delta_f H^o[1,1,1,2\text{-}C_2H_2Cl_4(l),\ 298.15\,K]=-(193.35\pm1.35)\,\mathrm{kJ\,mol^{-1}}$ and should be a reliable value. As a check, we can compare the data of Levanova *et al.* [1976LBR], who measured equilibrium dehydrochlorination [Eq. (19)] in an unspecified organic solvent and reported $\log K_p(19)=7.54-2372/T$ between 313 and 353 K

$$CH_2ClCCl_3\text{(soln)}\rightleftarrows C_2HCl_3\text{(soln)}+\text{HCl(g)}. \tag{19}$$

From the Second Law analysis of Levanova, $\Delta_r H(333\,K)=45.4\,\mathrm{kJ\,mol^{-1}}$. To adjust this to 298.15 K, the gas phase $C_p$ values [1981C], [1982R] were converted to the liquid phase by subtraction of $\Delta_{vap}C_p$. For trichloroethene $\Delta_{vap}C_p=-50.3\,\mathrm{J\,mol^{-1}\,K^{-1}}$ was derived from the temperature dependent enthalpies of vaporization measured calorimetrically by Majer *et al.* [1980MSS] between 298 and 353 K. For 1,1,1,2-$C_2H_2Cl_4$, $\Delta_{vap}C_p=-65.8\,\mathrm{J\,mol^{-1}\,K^{-1}}$ was derived from the correlations discussed in the section on pentachloroethane. These small corrections yield $\Delta_r H(298.15\,K)=45.8\,\mathrm{kJ\,mol^{-1}}$. Using $\Delta_f H^o[C_2HCl_3(l),\ 298.15\,K]=-(52.1\pm3.0)\,\mathrm{kJ\,mol^{-1}}$, which should be a reliable value (see discussion for that compound), and $\Delta_f H^o[\mathrm{HCl}(g),\ 298.15\,K]=-(92.31\pm0.10)\,\mathrm{kJ\,mol^{-1}}$, gives $\Delta_f H^o[1,1,1,2\text{-}C_2H_2Cl_4(l),\ 298.15\,K]=-190.2\,\mathrm{kJ\,mol^{-1}}$. A Third Law analysis was also performed. The gas phase data [1982R] on trichloroethene were adjusted to the liquid phase using data derived from the study of Majer *et al.* [1980MSS], and that for 1,1,1,2-$C_2H_2Cl_4$ from the correlations discussed in the section on pentachloroethane. This analysis yields $\Delta_r H(298.15\,K)=51.7\,\mathrm{kJ\,mol^{-1}}$ and $\Delta_f H^o[1,1,1,2\text{-}C_2H_2Cl_4(l),\ 298.15\,K]=-196.1\,\mathrm{kJ\,mol^{-1}}$. The Second and Third Law analyses are in only fair agree-

TABLE 21. Enthalpies of formation of 1,1,1,2-tetrachloroethane derived from reported experimental data

| $\Delta_f H^o$ (g), 298.15 K (kJ mol$^{-1}$) | Reported uncertainty kJ mol$^{-1}$ | Temp. (K) | Method(s) | Reference | Comments |
|---|---|---|---|---|---|
| Experimental | | | | | |
| −152.3 | 1.4[a] (2.3) | 298 | Combustion calorimetry of liquid | [1978GH] | 1 |
| −149.1 | 0.4[a]<br>(4.2) | 313–353 | Equilibrium of dehydrochlorination $CH_2ClCCl_3$ (soln)$\rightleftarrows C_2HCl_3$ (soln)$+$HCl (g) | [1976LBR] | 2, Second Law analysis. Present analysis uses updated $\Delta_f H^o[C_2HCl_3$ (l)]. |
| −155.0 | 0.4[a]<br>(4.2) | 313–353 | Equilibrium of dehydrochlorination $CH_2ClCCl_3$ (soln)$\rightleftarrows C_2HCl_3$ (soln)$+$HCl (g) | [1976LBR] | 3, Third Law analysis. Present analysis uses updated $\Delta_f H^o[C_2HCl_3$ (l)]. |
| −152.4 | 2.1[b] | 453–493 | Equilibrium 1,1,2,2,-$C_2H_2Cl_4$ (soln)$\rightleftarrows$1,1,1,2-$C_2H_2Cl_4$ (soln) | [1980B]<br>[1983KP] | 4, Second Law analysis. This was a primary data used to derive the enthalpy value for the 1,1,2,2- isomer, so the result is not independent. |
| Reviews and Evaluations | | | | | |
| −152.3 | 1.4 | 298 | | [1983KP] | |
| −149.4 | N.R.[c] | 298 | | [1981C] | |
| −149.4 | 4.2 | 298 | | [1974CRa] | Group additivity estimate. |

[a] Reported uncertainty refers only to the precision of the measured reaction enthalpy. The parenthetical value is the standard uncertainty ($2\sigma$) estimated by us by comparison with the results of similar experiments.

[b] Reported uncertainty refers only to the precision of the measured reaction enthalpy.

[c] Not reported.

**Comments:**

1. Results obtained with a tantalum-lined rotating bomb calorimeter. Sample purity 99.95 mass %. $\Delta_c H$[(l), 298.15 K]$=-(973.90\pm 1.28)$ kJ mol$^{-1}$, refers to reaction 1,1,1,2-$C_2H_2Cl_4$ (l)$+H_2O$ (l)$+1.5O_2$ (g)$\rightarrow 2CO_2$ (g)$+$4HCl(aq:600). The following auxiliary values were used: $\Delta_f H^o[CO_2$ (g), 298.15 K]$=-(393.51\pm 0.13)$ kJ mol$^{-1}$, $\Delta_f H^o[H_2O$ (l), 298.15 K]$=-(285.830\pm 0.040)$ kJ mol$^{-1}$, and $\Delta_f H^o$[HCl (aq:600), 298.15 K]$=-(166.540\pm 0.10)$ kJ mol$^{-1}$. The data result in $\Delta_f H^o$[1,1,1,2-$C_2H_2Cl_4$ (l), 298.15 K]$=-(193.45\pm 1.35)$ kJ mol$^{-1}$.
2. Second Law analysis of equilibrium $CH_2ClCCl_3$ (soln)$\rightleftarrows C_2HCl_3$ (soln)$+$HCl (g) yields $\Delta_r H(333\text{ K})=(45.4\pm 0.4)$ kJ mol$^{-1}$. At 298.15 K this becomes $\Delta_r H(298.15\text{ K})=(45.8\pm 0.5)$ kJ mol$^{-1}$ (see Discussion). The quoted value is obtained using $\Delta_f H^o[C_2HCl_3$ (l), 298.15 K]$=-(52.1\pm 3.0)$ kJ mol$^{-1}$ (see Sec. 5.6), and $\Delta_f H^o$[HCl (g), 298.15 K]$=-(92.31\pm 0.10)$ kJ mol$^{-1}$. Excess thermodynamic properties of solvation have been neglected.
3. Third Law analysis of equilibrium $CH_2ClCCl_3$ (soln)$\rightleftarrows C_2HCl_3$ (soln)$+$HCl (g) yields $\Delta_r H(298.15\text{ K})=51.7$ kJ mol$^{-1}$ (see Discussion). The quoted values is obtained using $\Delta_f H^o[C_2HCl_3$ (l), 298.15 K]$=-(52.1\pm 3.0)$ kJ mol$^{-1}$ (see Sec. 5.6), and $\Delta_f H^o$[HCl (g), 298.15 K]$=-(92.31\pm 0.10)$ kJ mol$^{-1}$. Excess thermodynamic properties of solvation have been neglected.
4. This was a primary (though not only) result used to derive $\Delta_f H^o$[1,1,2,2-$C_2H_2Cl_4$ (l), 298.15 K], so the agreement is not an independent confirmation of the other values. The Second Law analysis yields $\Delta_r H(473\text{ K})=10.0\pm 2.1$ kJ mol$^{-1}$, which was adjusted to $\Delta_r H(298.15\text{ K})=8.9$ kJ mol$^{-1}$ (see Sec. 6.8). No Third Law analysis was performed, as values of the equilibrium constant have not been published in the accessible literature.

ment. This presumably results from the summed uncertainties of the estimated properties, the excess thermodynamic properties associated with solvation, and the uncertainty in the Second Law analysis due to the short experimental temperature range. Despite this, the data straddle the combustion calorimetry result and appear to confirm its value. The limited information available on the result of Bushneva [1980B] on the liquid-phase equilibrium 1,1,2,2-$C_2H_2Cl_4\rightleftarrows$1,1,2,2-$C_2H_2Cl_4$ is discussed in Sec. 6.8 and results in a value consistent with that of the combustion study [1978GH]. However, since the data of Bushneva were a primary (though not sole) result used to derive $\Delta_f H^o$[1,1,2,2-$C_2H_2Cl_4$(l), 298.15 K], this is not a completely independent confirmation.

*Recommendation*. The recommended value is that from the combustion calorimetry study of Gundry and Head [1978GH], although we have increased the uncertainty limits to reflect our experience with the absolute accuracy of such experiments with highly chlorinated compounds. We thus adopt $\Delta_f H^o$[1,1,1,2-$C_2H_2Cl_4$(l), 298.15 K]$=-193.4\pm 2.3$ kJ mol$^{-1}$, from which $\Delta_f H^o$[1,1,1,2-$C_2H_2Cl_4$(g), 298.15 K]$=-152.3\pm 2.4$ kJ mol$^{-1}$ is calculated. Notice that this compound is less stable than 1,1,2,2-tetrachloroethane $\Delta_f H^o$[1,1,2,2-$C_2H_2Cl_4$(g), 298.15 K]$=-156.7\pm 3.5$ kJ mol$^{-1}$). For highly chlorinated species, the isomer with the more distributed chlorines appears to be the more stable. This can be rationalized on both steric and electrostatic grounds.

## 6.8. 1,1,2,2-Tetrachloroethane

*Enthalpy of Vaporization*. The enthalpy of vaporization at 298.15 K has been derived by Cox and Pilcher [1970CP] from the data of Mathews [1926M] as $(45.2\pm 1.3)$ kJ mol$^{-1}$. Newer values are $(45.78\pm 0.16)$ kJ mol$^{-1}$ [1972LW], and $(45.69\pm 0.11)$ kJ mol$^{-1}$ [1980MSS]. Taking a weighted average of the latter two results, we obtain $\Delta_{vap}H(298.15\text{ K})=(45.72\pm 0.09)$ kJ mol$^{-1}$. A correction of 0.01 kJ mol$^{-1}$ due to non-ideality of the gas was taken from the work of Majer and Svoboda [1985MS] (our calculation gives 0.02 kJ mol$^{-1}$) and $\Delta_{vap}H^o(298.15\text{ K})=(45.73\pm 0.09)$ kJ mol$^{-1}$ is derived. The heat capacity of vaporiza-

TABLE 22. Enthalpies of formation of 1,1,2,2,-tetrachloroethane derived from reported experimental data

| $\Delta_f H^o$ (g), 298.15 K (kJ mol$^{-1}$) | Reported uncertainty kJ mol$^{-1}$ | Temp. (K) | Method(s) | Ref/Year | Comments |
|---|---|---|---|---|---|
| Experimental | | | | | |
| −156.7 | $2.1^{a}$<br>(4.2) | 453−493 | Equilibrium<br>1,1,2,2-$C_2H_2Cl_4$ (soln)$\rightleftarrows$1,1,1,2-$C_2H_2Cl_4$ (soln) | [1980B]<br>[1983KP] | 1, Second Law analysis. Present analysis uses updated $\Delta_f H^o$[1,1,1,2-$C_2H_2Cl_4$]. |
| −158.7 | N.R.<br>$(8.4)^{b}$ | 298 | Enthalpy of dehydrochlorination<br>2[1,1,2,2-$C_2H_2Cl_2$(l)]+$CaO_2H_2$(c)$\rightarrow$<br>2$C_2HCl_3$(l)+$CaCl_2$(aq:400)+2$H_2O$(l) | [1956K] | 2, Reanalyzed and auxiliary quantities updated by [1970CP]. Present analysis uses updated $\Delta_f H^o$[$C_2HCl_3$ (l)]. |
| −157.3 | N.R.<br>$(8.4)^{b}$ | 298 | Enthalpy of chlorination<br>$Z$-1,2-$C_2H_2Cl_2$(l)+$Cl_2$(g)$\rightarrow$$C_2H_2Cl_4$(l) | [1956K] | 3, Reanalyzed by [1970CP]. Updated $\Delta_f H^o$[$Z$-1,2-$C_2H_2Cl_2$(l)] used in present calculation. |
| −148.8 | 8.4 | 298 | Combustion calorimetry of liquid | [1938E]<br>[1953SBK]<br>[1970CP] | 4, Static Bomb. Data corrected by Smith *et al.* in 1953. Reanalyzed and auxiliary quantities updated by [1970CP]. |
| Reviews and Evaluations | | | | | |
| −152.3 | 1.4 | 298 | | [1983KP] | |
| −149.4 | N.R.$^{c}$ | 298 | | [1981C] | |
| −149.4 | 4.2 | 298 | | [1974CRW] | Group additivity estimate |
| −150.2 | 6.3 | 298 | | [1970CP] | |

[a] Reported uncertainty refers only to the precision of the measured reaction enthalpy and does not include uncertainty in auxiliary thermodynamic quantities. The parenthetical value is that estimated by us by comparison of the reliability of similar experiments.

[b] Not reported, the parenthetical value is that estimated by Cox and Pilcher [1970CP].

[c] Not reported.

**Comments:**

1. Second Law analysis yields $\Delta_r H(473\ \mathrm{K}) = (10.0 \pm 2.1)$ kJ mol$^{-1}$. This becomes $\Delta_r H(298.15\ \mathrm{K}) = (8.9 \pm 2.5)$ kJ mol$^{-1}$ (see Discussion). The quoted value is obtained using $\Delta_f H^o$[1,1,2,2-$C_2H_2Cl_4$ (l), 298.15 K]$= -(193.4 \pm 2.3)$ kJ mol$^{-1}$ (see Sec. 6.8). Excess thermodynamic properties of solvation have been neglected.
2. $\Delta_r H(298.15\ \mathrm{K}) = -(155.6 \pm 8.4)$ kJ mol$^{-1}$. The results were reevaluated by Cox and Pilcher [1970CP]. Their analysis leads to $\Delta_f H^o$[1,1,2,2-$C_2H_2Cl_4$ (l), 298.15 K]$=\Delta_f H^o$[$C_2HCl_3$ (l), 298.15 K]$-152.3$ kJ mol$^{-1}$. The stated value was derived using $\Delta_f H^o$[$C_2HCl_3$ (l), 298.15 K]$= -(52.1 \pm 3.0)$ kJ mol$^{-1}$ (see Sec. 5.6).
3. $\Delta_r H(298.15\ \mathrm{K}) = -(169.1 \pm 8.4)$ kJ mol$^{-1}$. The quoted value is obtained using $\Delta_f H^o$[$Z$-CHCl$=$CHCl (l), 298.15 K]$= -(34.0 \pm 2.5)$ kJ mol$^{-1}$.
4. Sample purity uncertain. $\Delta_c H$[(l), 298.15 K]$= -(972.80 \pm 8.4)$ kJ mol$^{-1}$, refers to reaction 1,1,2,2-$C_2H_2Cl_4$ (l)+$H_2O$ (l)+1.5$O_2$ (g)$\rightarrow$2$CO_2$ (g) +4HCl(aq:600). The original results of Eftring [1938E] were corrected by Smith *et al.* [1953SBK] and reevaluated by Cox and Pilcher [1970CP]. The data have subsequently been compiled by Pedley *et al.* [1986PNK]. The following auxiliary values were used: $\Delta_f H^o$[$CO_2$ (g), 298.15 K] $= -(393.51 \pm 0.13)$kJ mol$^{-1}$, $\Delta_f H^o$[$H_2O$ (l), 298.15 K]$= -(285.830 \pm 0.040)$ kJ mol$^{-1}$, and $\Delta_f H^o$[HCl (aq:600), 298.15 K]$= -(166.540 \pm 0.10)$ kJ mol$^{-1}$. The data result in $\Delta_f H^o$[1,1,2,2-$C_2H_2Cl_4$ (l), 298.15 K]$= -(194.55 \pm 8.4)$ kJ mol$^{-1}$.

tion is derived as $\Delta_{\mathrm{vap}} C_p = -62.7$ J mol$^{-1}$ K$^{-1}$ from the temperature dependence of the $\Delta_{\mathrm{vap}} H$ data of [1980MSS].

*Enthalpy of Formation*. Data are summarized in Table 22. The enthalpy of combustion has been measured by Eftring [1938E] using a static bomb calorimeter and the ‘‘quartz spiral’’ method. These results were corrected by Smith *et al.* [1953SBK], subsequently updated by Cox and Pilcher [1970CP] and the data later compiled by Pedley *et al.* [1986PNK], who used a newer value for the enthalpy of dilution of HCl. The combustion result yields $\Delta_f H^o$[1,1,2,2-$C_2H_2Cl_4$(l), 298.15 K] $= -(194.55 \pm 8.4)$ kJ mol$^{-1}$, but is suspect because the early combustion data on chlorinated compounds often yield enthalpies of formation that appear systematically too positive when compared with newer data (see Fig. 2). The enthalpy of formation of 1,1,2,2-$C_2H_2Cl_4$ is also linked to that of $Z$-CHCL$=$CHCl through the enthalpy of chlorination

$$Z\text{-CHCl}{=}\text{CHCl(l)} + \text{Cl}_2\text{(g)} \rightarrow \text{C}_2\text{H}_2\text{Cl}_4\text{(l)} \qquad (20)$$

measured by Kirkbride [1956K], who reported $\Delta_r H(298.15\ \mathrm{K}) = -169.0$ kJ mol$^{-1}$. Cox and Pilcher [1970CP] have estimated the uncertainty of the result to be about 8.4 kJ mol$^{-1}$, although we are uncertain how they arrived at that number. Using $\Delta_r H(298.15\ \mathrm{K}) = -(169.0 \pm 8.4)$ kJ mol$^{-1}$, and our updated enthalpy value $\Delta_f H^o$[$Z$-CHCl$=$CHCl(l),298.15 K] $= -(34.0 \pm 2.0)$ kJ mol$^{-1}$ (see Sec. 5.5) we obtain $\Delta_f H^o$[1,1,2,2-$C_2H_2Cl_4$(l), 298.15 K]$= -(203.0 \pm 8.8)$ kJ mol$^{-1}$. Kirkbride [1956K] also reports an otherwise unpublished measurement by Parker and Dickinson [1956PD] of the enthalpy of dehydrochlorination of 1,1,2,2-tetrachloroethane:

$$2[1,1,2,2\text{-C}_2\text{H}_2\text{Cl}_2\text{(l)}] + \text{CaO}_2\text{H}_2\text{(c)}$$
$$\rightarrow 2\text{C}_2\text{HCl}_3\text{(l)} + \text{CaCl}_2\text{(aq:400)} + 2\text{H}_2\text{O(l)}. \qquad (21)$$

Cox and Pilcher [1970CP] have reevaluated the data using updated values for some auxiliary thermodynamic quantities.

They report $\Delta_r H(298.15\,\mathrm{K}) = -(155.6 \pm 8.4)\,\mathrm{kJ\,mol^{-1}}$, where the uncertainty is that estimated by Cox and Pilcher. This leads to $\Delta_f H^o[1,1,2,2\text{-}C_2H_2Cl_4(l),\ 298.15\,\mathrm{K}] = \Delta_f H^o[C_2HCl_3(l),\ 298.15\,\mathrm{K}] - 152.3\,\mathrm{kJ\,mol^{-1}}$. Using our updated enthalpy $\Delta_f H^o[C_2HCl_3(l),\ 298.15\,\mathrm{K}] = -(52.1 \pm 3.0)\,\mathrm{kJ\,mol^{-1}}$, which we believe to be reliable (Sec. 5.2), we obtain $\Delta_f H^o[1,1,2,2\text{-}C_2H_2Cl_4(l),\ 298.15\,\mathrm{K}] = -(204.3 \pm 8.9)\,\mathrm{kJ\,mol^{-1}}$.

Kolesov and Papina [1983KP] have reported a study [1980B] of the isomerization of tetrachloroethanes between 453 and 493 K

$$1,1,2,2\text{-}C_2H_2Cl_4(l) \rightleftarrows 1,1,1,2\text{-}C_2H_2Cl_4(l). \tag{22}$$

Since the value $\Delta_f H^o[1,1,1,2\text{-}C_2H_2Cl_4(l),\ 298.15\,\mathrm{K}] = -(193.4 \pm 2.5)\,\mathrm{kJ\,mol^{-1}}$ has been determined by modern rotating bomb calorimetry study and appears to be well established (see Sec. 6.7), these data are particularly interesting. Unfortunately, this work does not appear to have been published in the primary literature and no details are available. Kolesov and Papina quote $\Delta_r H(473\,\mathrm{K}) = 10.0 \pm 2.1\,\mathrm{kJ\,mol^{-1}}$ from a Second Law analysis of the data. We have extrapolated this to 298.15 K using the gas phase heat capacities of Chao [1981C], [1974CRW], adjusting them based on $\Delta_{vap}C_p(1,1,2,2\text{-}C_2H_2Cl_4) = -62.7\,\mathrm{J\,mol^{-1}\,K^{-1}}$, derived from the enthalpy of vaporization data of [1980MSS], and $\Delta_{vap}C_p(1,1,2,2\text{-}C_2H_2Cl_4) = -65.8\,\mathrm{J\,mol^{-1}\,K^{-1}}$ from the tables of Domalski and Hearing [1993DH]. This yields $\Delta_r H(298.15\,\mathrm{K}) = 8.9 \pm 2.5\,\mathrm{kJ\,mol^{-1}}$, which leads to $\Delta_f H^o[1,1,2,2\text{-}C_2H_2Cl_4(l),\ 298.15\,\mathrm{K}] = -202.4 \pm 2.9\,\mathrm{kJ\,mol^{-1}}$. This is significantly more negative than the combustion result of Eftring [1938E], but is in excellent agreement with values obtained from dehydrochlorination of $1,1,2,2\text{-}C_2H_2Cl_4$ and chlorination of Z-CHCl═CHCl. It is interesting that, although Cox and Pilcher [1970CP] have estimated the uncertainties of the latter two results to be about 8.4 $\mathrm{kJ\,mol^{-1}}$, the data appear to be of much better accuracy when newer values of the enthalpies of formation of the chloroethenes are used.

Finally, we have examined the relative stability of the tetrachloroethane isomers using a series of *ab initio* calculations [2001BAM], up to and including level of composite QCISD(T)/6-311++G(3df,3pd) calculations. These results show $1,1,2,2\text{-}C_2H_2Cl_4$ to be the most stable isomer and are in good agreement with the above data.

*Recommendation*. All the above information were considered but little weight was given to the early combustion result. We recommend $\Delta_f H^o[1,1,2,2\text{-}C_2H_2Cl_4(l),\ 298.15\,\mathrm{K}] = -202.4 \pm 3.5\,\mathrm{kJ\,mol^{-1}}$. Although all three of the primary measurements used in selecting our recommended value are in excellent agreement, we lack details of two of these experiments. The overall uncertainty we have estimated is therefore still relatively high. In conjunction with the enthalpy of vaporization, $\Delta_f H^o[1,1,2,2\text{-}C_2H_2Cl_4(g),\ 298.15\,\mathrm{K}] = -156.7 \pm 3.5\,\mathrm{kJ\,mol^{-1}}$ is obtained.

## 6.9. Pentachloroethane

*Enthalpy of Vaporization*. No direct measurements of the enthalpy of vaporization appear to exist and values of $\Delta_{vap}H(298.15\,\mathrm{K})$ ranging from 45.6 to 52.1 $\mathrm{kJ\,mol^{-1}}$ have been proposed. Chao *et al.* [1974CRW] recommend $\Delta_{vap}H(298.15\,\mathrm{K}) = 45.6\,\mathrm{kJ\,mol^{-1}}$, a value stated to stem from a calorimetric measurement made by Eftring. However, an examination of the thesis of Eftring [1938E] shows the above value to have been derived from the vapor pressure data of Nelson [1930N] using the Clapyron equation. Chao *et al.* also fit the vapor pressure data of Nelson using an Antoine equation, deriving $\Delta_{vap}H(433\,\mathrm{K}) = 37.8\,\mathrm{kJ\,mol^{-1}}$, and $\Delta_{vap}H(298.15\,\mathrm{K}) = 48.5\,\mathrm{kJ\,mol^{-1}}$. Papina and Kolesov [1985PK] used $\Delta_{vap}H(433\,\mathrm{K}) = 40.2 \pm 2.1\,\mathrm{kJ\,mol^{-1}}$ from [1971G], which derived this value from a fit to the data of Nelson, although the fitting procedure was not described. The $\Delta_{vap}H$ value at the boiling point was adjusted by Papina and Kolesov to $\Delta_{vap}H(298.15\,\mathrm{K}) = 52.1\,\mathrm{kJ\,mol^{-1}}$ based on heat capacity data from Kobe and Harrison [1957KH] for the gas and Kurbatov [1948K] for the liquid. Stull *et al.* [1969SWS] have suggested that the heat capacity data of Kurbatov for the liquid are far too high, but no other data are available. Stull *et al.* recommended $\Delta_{vap}H(433\,\mathrm{K}) = 40.6\,\mathrm{kJ\,mol^{-1}}$, again derived from the vapor pressure data of Nelson [1930N]. To correct this to 298.15 K, they used an estimated $\Delta_{vap}C_p = -50.2\,\mathrm{J\,mol^{-1}\,K^{-1}}$ to obtain $\Delta_{vap}H(C_2HCl_5,\ 298.15\,\mathrm{K}) = 47.3\,\mathrm{kJ\,mol^{-1}}$. This compares with the average value of $\Delta_{vap}C_p = -88.1\,\mathrm{J\,mol^{-1}\,K^{-1}}$ used by Papina and Kolesov [1985PK]. As a check, we have derived $\Delta_{vap}C_p$ values for a series of chloroethanes from the temperature dependent enthalpies of vaporization measured calorimetrically by Majer *et al.* [1980MSS]. The slope of a plot of $\Delta_{vap}H$ vs $T$ (Fig. 8) yields $\Delta_{vap}C_p$. The heat capacity of vaporization values are nearly independent of temperature over the studied range, 298–358 K, and are −54.3, −60.3, −55.1, and −62.7 $\mathrm{J\,mol^{-1}\,K^{-1}}$ for $1,2\text{-}C_2H_2Cl_2$, $1,1,2\text{-}C_2H_3Cl_3$, $1,1,1\text{-}C_2H_3Cl_3$, and $1,1,2,2\text{-}C_2H_2Cl_4$, respectively. For $1,1\text{-}C_2H_4Cl_2$, the heat capacity of vaporization was derived as $\Delta_{vap}C_p = -50.0\,\mathrm{J\,mol^{-1}\,K^{-1}}$ from the difference of the reported heat capacities of the gas [1994FKM] and liquid [1956LP]. Using Benson-style groups [1976B], [1993CB] a simple group additivity fit to these data would predict $\Delta_{vap}C_p(C_2HCl_5) = -67.7\,\mathrm{J\,mol^{-1}\,K^{-1}}$. This suggests that the value used by Papina and Kolesov ($\Delta_{vap}C_p = -88.1\,\mathrm{J\,mol^{-1}\,K^{-1}}$) is too large, and supports the contention of Stull *et al.* that the heat capacity data of Kurbatov [1948K] for the liquid are unreliable. As an independent procedure for obtaining $\Delta_{vap}H(298.15\,\mathrm{K})$, we have correlated this property with the normal boiling point for the above chloroethanes. As shown in Fig. 9, the expression $\Delta_{vap}H(298.15\,\mathrm{K})/\mathrm{kJ\,mol^{-1}} = 0.1593(T_b) - 21.60$ fits all the calorimetrically determined data within 1 $\mathrm{kJ\,mol^{-1}}$, and gives $\Delta_{vap}H/(C_2HCl_5,\ 298.15\,\mathrm{K}) = 47.4\,\mathrm{kJ\,mol^{-1}}$. The estimated expanded uncertainty $(2\sigma)$ is 1.5 $\mathrm{kJ\,mol^{-1}}$. A similar relationship yields $\Delta_{vap}H(C_2HCl_5,\ 433\,\mathrm{K}) = 38.3\,\mathrm{kJ\,mol^{-1}}$, from which we can deduce $\Delta_{vap}C_p(C_2HCl_5)$

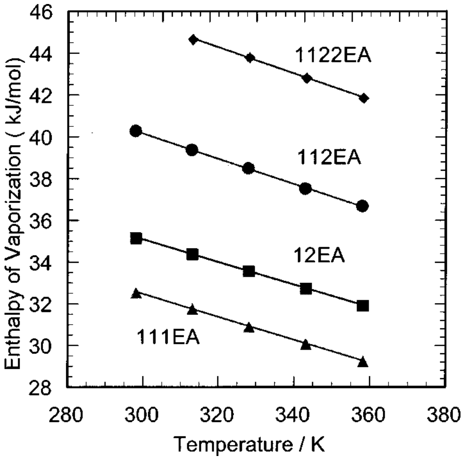

FIG. 8. Plot of the enthalpy of vaporization vs temperature for a series of chloroethanes. The data are from [1980MSS]. The slope gives the average $\Delta_{vap}C_p$. Symbols: 12EA=1,2-dichloro-ethane, 111EA =1,1,1-trichloro-ethane, 112EA=1,1,2-trichloroethane, 1122EA =1,1,2,2-tetrachloroethane. The derived $-\Delta_{vap}C_p$ values are 54.3 J mol$^{-1}$ K$^{-1}$, 60.3 J mol$^{-1}$ K$^{-1}$, 55.1 J mol$^{-1}$ K$^{-1}$, and 62.7 J mol$^{-1}$ K$^{-1}$ for 12EA, 112EA, 111EA, and 1122, respectively. Line fits are: $\Delta_{vap}H(12EA) = -0.0543T + 51.3$; $\Delta_{vap}H(112EA) = -0.0603T + 58.2$; $\Delta_{vap}H(111EA) = -0.0551T + 48.9$; $\Delta_{vap}H(1122EA) = -0.0627T + 64.3$.

$= -67.4$ J mol$^{-1}$ K$^{-1}$, in excellent agreement with the group additivity value. The combination of our $\Delta C_p$ value together with the various derived literature values of $\Delta_{vap}H(433\ K)$ yields $\Delta_{vap}H(C_2HCl_5,\ 298.15\ K)$ values between 46.9 and 49.5 kJ mol$^{-1}$. These are in very good agreement with the value derived in Fig. 9. We recommend yields $\Delta_{vap}H(C_2HCl_5,\ 298.15\ K) = (47.4 \pm 1.5)$ kJ mol$^{-1}$. The correction due to non-ideality of the gas is calculated by us as 0.017 kJ mol$^{-1}$ and we adopt $\Delta_{vap}H(298.15\ K) \approx \Delta_{vap}H^o(298.15\ K) = (47.4 \pm 1.5)$ kJ mol$^{-1}$.

*Enthalpy of Formation.* Data are summarized in Table 23. Eftring [1938E] originally determined the enthalpy of combustion of pentachloroethane. These data were corrected by Smith *et al.* [1953SBK], reevaluated by Cox and Pilcher [1970CP], and compiled and updated by Pedley *et al.* [1986PNK], who used a newer value for the enthalpy of dilution of HCl. The data result in $\Delta_f H^o[C_2HCl_5(l),\ 298.15\ K] = -(185.8 \pm 8.4)$ kJ mol$^{-1}$. After corrections, Kolesov and Papina [1983KP] derived $\Delta_f H^o[C_2HCl_5(l),\ 298.15\ K] = -183.5$ kJ mol$^{-1}$ from this same data, although our calculation from their listed enthalpies of combustion, $\Delta_c H(298.15\ K) = -858.9$ kJ mol$^{-1}$, gives a value of $\Delta_f H^o[C_2HCl_5(l),\ 298.15\ K] = -189.2$ kJ mol$^{-1}$. In any case the precision of the experiments is low and the reliability questionable, given that Eftring's values for most chlorinated compounds are systematically too positive when compared with newer determinations (Fig. 2).

The enthalpy of formation of pentachloroethane is also linked to those of $C_2Cl_4$ and $C_2HCl_3$. The link to trichloroethene is through the enthalpy of chlorination measured by Kirkbride [1956K]

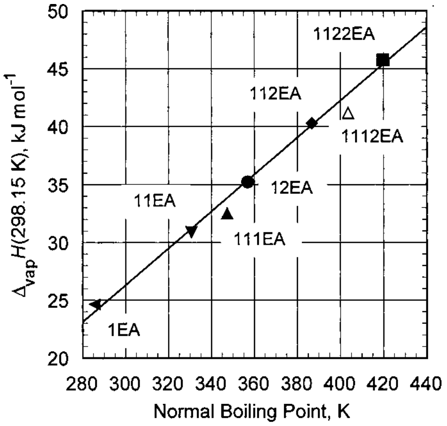

FIG. 9. Correlation between the enthalpy of vaporization at 298.15 K and the normal boiling point for a series of chloroethanes. Symbols: 1EA=chloroethane, 12EA=1,2-dichloroethane, 11EA=1,1-dichloroethane, 111EA=1,1,1-trichloroethane, 112EA =1,1,2-trichloroethane, 1122EA=1,1,2,2-tetrachloroethane, 1112EA =1,1,1,2-tetrachloroethane. Note that the $\Delta_{vap}H$ value for 1,1,1,2-tetrachloroethane is estimated from the vapor pressure, while the others are calorimetric values. Boiling point data are taken from Horvath [1993H]. The expression $\Delta_{vap}H(298.15\ K)/kJ\ mol^{-1} = 0.1593(T_b) - 21.60$ fits all the calorimetrically determined data within 1 kJ mol$^{-1}$, and for pentachloroethane (b.p. 433.1 K) gives yields $\Delta_{vap}H(C_2HCl_5,\ 298.15\ K) = 47.4$ kJ mol$^{-1}$. If experimental data on the chloromethanes and chloroethenes are included, the expression becomes $\Delta_{vap}H(298.15\ K)kJ\ mol^{-1} = 0.1497(T_b) - 18.64$ and gives yields $\Delta_{vap}H(C_2HCl_5,\ 298.15\ K) = 46.2$ kJ mol$^{-1}$. For pentachloroethane, we prefer the expression derived using data on the chloroethanes only, while estimates for the chloroethynes use the latter parameters.

$$C_2HCl_3(l) + Cl_2(g) \rightleftarrows C_2HCl_5(l). \tag{23}$$

From three experiments, his data yield $\Delta_r H(298.15\ K) = -(151.2 \pm 5.0)$ kJ mol$^{-1}$, where the listed uncertainty is twice the standard uncertainty ($2\sigma$) and refers to precision only. Using $\Delta_f H^o[C_2HCl_3(l),298.15\ K] = -(52.1 \pm 3.0)$ kJ mol$^{-1}$ (see Sec. 5.6), we $\Delta_f H^o[C_2HCl_5(l),298.15\ K] = -(203.3 \pm 5.8)$ kJ mol$^{-1}$.

Kirkbride [1956K] also reports an otherwise unpublished measurement by Parker and Dickinson [1956PD] of the enthalpy of dehydrochlorination of pentachloroethane:

$$2C_2HCl_5(l) + CaO_2H_2(c) \rightarrow 2C_2Cl_4(l) + CaCl_2(aq{:}400) + 2H_2O(l). \tag{24}$$

The reported enthalpy of reaction is $\Delta_r H(298.15\ K) = -(181.6 \pm 8.4)$ kJ mol$^{-1}$ where the uncertainty is that estimated by Cox and Pilcher [1970CP] and is approximately $2\sigma$. Following their analysis, we find $\Delta_f H^o[C_2HCl_5(l),\ 298.15\ K] = \Delta_f H^o[C_2Cl_4(l),\ 298.15\ K] - 139.3$ kJ mol$^{-1}$. Using $\Delta_f H^o[C_2Cl_4(l),\ 298.15\ K] = -(63.9 \pm 4.0)$ kJ mol$^{-1}$ (see Sec. 5.7) we find $\Delta_f H^o[C_2HCl_5(l),\ 298.15\ K] = -(203.2 \pm 9.3)$ kJ mol$^{-1}$.

The dehydrochlorination equilibrium has been studied by Levanova *et al.* [1979LBR]

$$C_2HCl_5(soln) \rightleftarrows C_2Cl_4(soln) + HCl(g). \tag{25}$$

They found $\log K = 7.42 - 2360/T$ between 363 and 383 K. Their Second Law analysis yields $\Delta_r H(373\ K)$

TABLE 23. Enthalpies of formation of pentachloroethane derived from reported experimental data

| $\Delta_f H^o$ (g), 298.15 K (kJ mol$^{-1}$) | Reported uncertainty kJ mol$^{-1}$ | Temp. (K) | Method(s) | Ref/Year | Comments |
|---|---|---|---|---|---|
| Experimental | | | | | |
| −155.0 | N.R.<br>(4.2)[a] | 313–353 | Equilibrium of reaction<br>$C_2HCl_5$ (soln)$\rightleftarrows C_2Cl_4$ (soln)+HCl (g) | [1979LBR] | 1, Second Law analysis. Present analysis uses updated $\Delta_f H^o[C_2Cl_4(l)]$. |
| −160.0 | N.R.<br>(4.2)[a] | 313–353 | Equilibrium of reaction<br>$C_2HCl_5$ (soln)$\rightleftarrows C_2Cl_4$ (soln)+HCl (g) | [1979LBR] | 2, Third Law analysis. Present analysis uses updated $\Delta_f H^o[C_2Cl_4$ (l)]. |
| −138.4 | N.R.<br>(8.4)[b] | 298 | Combustion calorimetry of liquid | [1938E]<br>[1953SBK]<br>[1970CP] | 3, Data corrected by Smith *et al.* in 1953; data reanalyzed and auxiliary quantities updated by [1970CP]. |
| −155.9 | N.R.<br>(5.0)[c] | 298 | Enthalpy of chlorination<br>$C_2HCl_3$ (l)+$Cl_2$ (g)→$C_2HCl_5$ (l) | [1956K] | 4, Data reanalyzed by [1970CP], updated $\Delta_f H^o[C_2HCl_3$ (l)] used in present analysis. |
| −155.8 | N.R.<br>(4.2)[b] | 298 | Enthalpy of dehydrochlorination<br>2$C_2HCl_5$ (l)+$CaO_2H_2$(c)→2$C_2Cl_4$ (l)<br>+$CaCl_2$(aq:400)+2$H_2O$ (l) | [1956K] | 5, Data renalyzed by [1970CP], updated $\Delta_f H^o[C_2Cl_4$ (l)] used in present analysis. |
| Reviews and Evaluations | | | | | |
| −142.0 | 9.0 | 298 | | [1986PNK] | |
| −155.4 | N.R.[d] | 298 | | [1983KP] | 6, Modified group additivity calculation. |
| −145.6 | N.R.[d] | 298 | | [1981C] | |
| −145.6 | 4.2 | 298 | | [1974CRW] | |
| −142.7 | 10.5 | 298 | | [1970CP] | |
| −142.3 | N.R.[d] | 298 | | [1969SWS] | |

[a] Not reported, the parenthetical value is the estimated by us by comparison with similar experiments.
[b] Not reported, the parenthetical value is that estimated by Cox and Pilcher [1970CP] (approximately $2\sigma$).
[c] Not reported, the parenthetical value is $2\sigma$ as calculated by us from the reported data.
[d] Not reported.

**Comments:**

1. Second Law analysis yields $\Delta_f H^o[C_2HCl_5$ (l), 298.15 K] $\Delta_f H^o[C_2Cl_4$ (l), 298.15 K]−138.5 kJ mol$^{-1}$. Analysis ignores excess thermodynamic properties of solvation. With $\Delta_f H^o[C_2Cl_4$ (l), 298.15 K]=−(63.9±4.0) kJ mol$^{-1}$ (see Sec. 5.7), we derive $\Delta_f H^o[C_2HCl_5$ (l), 298.15 K]=−202.4 kJ mol$^{-1}$.
2. Third Law analysis yields $\Delta_f H^o[C_2HCl_5$ (l), 298.15 K]=$\Delta_f H^o[C_2Cl_4$ (l), 298.15 K]−143.8 kJ mol$^{-1}$. Analysis ignores excess thermodynamic properties of solvation. With $\Delta_f H^o[C_2Cl_4$ (l), 298.15 K]=−(63.9±4.0) kJ mol$^{-1}$ (see Sec. 5.7), we derive $\Delta_f H^o[C_2HCl_5$ (l), 298.15 K]=−207.7 kJ mol$^{-1}$.
3. $\Delta_c H^o_{298}$=−(862.3±8.4) kJ mol$^{-1}$, refers to reaction $C_2HCl_5$ (l)+2$H_2O$ (l)+$O_2$ (g)→2$CO_2$ (g)+5HCl(aq.600). The original results of Eftring [1938E] were corrected by Smith *et al.* [1953SBK] and reevaluated by Cox and Pilcher [1970CP]. The data have subsequently been compiled by Pedley *et al.* [1986PNK]. The following auxiliary values were used: $\Delta_f H^o[CO_2$ (g), 298.15 K]=−(393.51±0.13) kJ mol$^{-1}$, $\Delta_f H^o[H_2O$ (l), 298.15 K] =−(285.830±0.040) kJ mol$^{-1}$, and $\Delta_f H^o$[HCl(aq:600), 298.15 K]=−(166.540±0.10) kJ mol$^{-1}$. Data lead to $\Delta_f H^o[C_2HCl_5$ (l), 298.15 K]=−(185.76 ±8.4) kJ mol$^{-1}$.
4. $\Delta_r H$(298.15 K)=−(151.2±5.0) kJ mol$^{-1}$. Enthalpy of formation listed in Table is based on $\Delta_f H^o[C_2HCl_3$ (l), 298.15 K]=−(52.1±3.0) kJ mol$^{-1}$ (see Sec. 5.7).
5. $\Delta_r H$(298.15 K)=−(181.6±4.2) kJ mol$^{-1}$. Data reanalyzed Cox and Pilcher [1970CP] and lead to $\Delta_f H^o[C_2HCl_5$ (l), 298.15 K]=$\Delta_f H^o[C_2Cl_4$ (l), 298.15K]−139.3 kJ mol$^{-1}$. With $\Delta_f H^o[C_2Cl_4$ (l), 298.15 K]=−(63.9±4.0) kJ mol$^{-1}$ (see Sec. 5.8), we derive $\Delta_f H^o[C_2HCl_5$ (l), 298.15 K]= −203.2 kJ mol$^{-1}$.
6. Because of uncertainties in the experimental data, Kolesov and Papina recommended a calculated value for this compound.

=45.1 kJ mol$^{-1}$. To correct this to 298.15 K, the gas phase heat capacity data [1982R], [1981C] were adjusted using $\Delta_{vap}C_p(C_2Cl_4)=-51.8$ J mol$^{-1}$ K$^{-1}$, derived from the data of Majer *et al.* [1980MSS], and $\Delta_{vap}C_p(C_2HCl_5)=-67.4$ J mol$^{-1}$ K$^{-1}$, derived as discussed above. These data yield $\Delta_r H$(298.15 K)=46.2 kJ mol$^{-1}$. A Third Law analysis using $\Delta_{vap}S(C_2Cl_4$, 298.15 K)=102.3 J mol$^{-1}$ K$^{-1}$, derived from the data of Majer *et al.* [1980MSS], and $\Delta_{vap}S(C_2HCl_5$, 298.15 K)=115.0 J mol$^{-1}$ K$^{-1}$, derived as discussed below, yields $\Delta_r H$(298.15 K)=51.5 kJ mol$^{-1}$. In general the Third Law analysis would be expected to be more accurate given the short temperature range of the experiments. However, given the uncertainties associated with the estimated data and the excess thermodynamic properties of solvation, we choose the average value $\Delta_r H$(298.15 K) =(48.9±4.0) kJ mol$^{-1}$, where the uncertainty is $2\sigma$ and is that estimated by us by comparison with similar experiments. Combined with the selected value of $\Delta_f H^o[C_2Cl_4$(l), 298.15 K]=−(63.9±4.0) kJ mol$^{-1}$, we calculate $\Delta_f H^o[C_2HCl_5$(l), 298.15 K]=−(205.1 ±5.7) kJ mol$^{-1}$.

*Recommendation*. The values of $\Delta_f H[C_2HCl_5]$. from the chlorination [1956K] and dehydrochlorination [1956PD], [1979LBR] studies are in very good agreement with each other, but in poor agreement with the combustion data [1938E]. We prefer the values derived relative to $C_2HCl_3$ [1956K] and $C_2Cl_4$ [1956PD], [1979LBR] and, based on these, recommended $\Delta_f H^o[C_2HCl_5$(l), 298.15 K]=−(203.2 ±4.0) kJ mol$^{-1}$. In conjunction with the enthalpy of vaporization we obtain $\Delta_f H^o[C_2HCl_5(g),\ 298.15\ K] = -(155.9 \pm 4.3)\ kJ\ mol^{-1}$.

### 6.10. Hexachloroethane

*Enthalpy of Sublimation*. Vapor pressures of solid hexachloroethane have been measured by several groups [1935L], [1941NS], [1947ID]. These data can be used to determine the enthalpy of sublimation, although the analysis is complicated by transitions of the crystal structure that occur over the temperature range of the experiments. Gurvich *et al.* [1991GVA] considered only the vapor pressure data of [1947ID] and obtained $\Delta_{sub1}H^o_{298}[C_2Cl_6(s,rhomb.)] = (60.7 \pm 4.2)\ kJ\ mol^{-1}$. Chao *et al.* [1974CRW] considered all three of the above references and pointed out some inconsistencies in the available data. They attempted to resolve these difficulties by fitting the vapor pressure data with the Antoine equation. They obtained values of $\Delta_{sub1}H^o_{298}$ ranging from 60.7 to 72.4 $kJ\ mol^{-1}$ and selected $\Delta_{sub1}H^o_{298}[C_2Cl_6(s),\ 298.15\ K] = (69.0 \pm 2.1)\ kJ\ mol^{-1}$ as the best available value. Their analysis will not be repeated here and the reader is referred to [1974CRW] for details. After review, we favor the analysis of Chao *et al.*, although we have increased the uncertainty limits and recommend $\Delta_{sub1}H^o_{298}[C_2Cl_6(s),\ 298.15\ K] = (69.0 \pm 4.0)\ kJ\ mol^{-1}$. For the purpose of obtaining $\Delta_f H^o[298.15\ K]$ for the ideal gas, the correctness of this value is not very important as a reliable enthalpy of formation of the solid is not available (see later discussion).

*Enthalpy of Vaporization*. For the chloroethanes with experimentally known enthalpies of vaporization, our comparisons show that $\Delta_{vap}H/T_b = (88.0 \pm 3.0)\ J\ mol^{-1}\ K^{-1}$, in the range of typical statements of Trouton's Rule [1978A]. On this basis, taking the normal boiling point $T_b = 457.8$ from Horvath [1993H], we find $\Delta_{vap}H(457.8\ K) = (40.3 \pm 2.2)\ kJ\ mol^{-1}$, where the uncertainty includes an estimated 5 K uncertainty in the normal boiling point, which is not firmly established. From a group additivity fit to experimental $\Delta_{vap}C_p$ data on the chloroethanes we find $\Delta_{vap}C_p(C_2Cl_6) = -(71.7 \pm 5)\ J\ mol^{-1}\ K^{-1}$, where the uncertainty has been estimated. For the hypothetical liquid at standard conditions we thus calculate $\Delta_{vap}H^o(298.15\ K) = (51.7 \pm 2.3)\ kJ\ mol^{-1}$ (our calculated correction for non-ideality is 0.01 $kJ\ mol^{-1}$). The two correlations of $\Delta_{vap}H^o(298.15\ K)$ with the boiling point given in Fig. 9 (Sec. 6.9) give $\Delta_{vap}H^o(298.15\ K)$ values of 51.3 and 49.9 $kJ\ mol^{-1}$. We recommend $\Delta_{vap}H^o(298.15\ K) = (51.0 \pm 2.3)\ kJ\ mol^{-1}$. As a rough check, we note that the sum of our $\Delta_{vap}H^o(298.15\ K)$ plus Kirkbride's [1956K] enthalpies of solution of $C_2Cl_6$ in $C_2Cl_4$ (19.7 $kJ\ mol^{-1}$), is close to the recommended enthalpy of sublimation.

*Enthalpy of Formation*. Data are summarized in Table 24. The only measurement of the enthalpy of combustion is by Eftring. The results of Eftring [1938E] were corrected by Smith *et al.* [1953SBK] and later by Cox and Pilcher [1970CP] and subsequently compiled and updated by Pedley *et al.* [1986PNK], who used newer values for some of the auxiliary thermodynamic quantities. These data yield $\Delta_f H^o[C_2Cl_6(s),\ 298.15\ K] = -(201.6 \pm 9.3)\ kJ\ mol^{-1}$. Using our recommended enthalpy of sublimation, $\Delta_{sub1}H^o_{298}[C_2Cl_6(s),\ 298.15\ K] = (69.0 \pm 4.0)\ kJ\ mol^{-1}$, we derive $\Delta_f H^o[C_2Cl_6(g),\ 298.15\ K] = -(132.6 \pm 9.8)\ kJ\ mol^{-1}$. This value may not be reliable, however, since for the other compounds where there is newer data, the enthalpies of formation derived from the combustion studies of Eftring appear to be too positive (see Fig. 2). In addition, there are uncertainties regarding the sample purity of the material used in the combustion experiments.

A relative value for the solid can be obtained from the liquid phase enthalpy of chlorination of tetrachloroethene measured by Kirkbride [1956K]. These data yield $\Delta_f H^o[C_2Cl_6(s),\ 298.15\ K] - \Delta_f H^o[C_2Cl_4(l),\ 298.15\ K] = -(155.3 \pm 6)\ kJ\ mol^{-1}$ (see Comment 6 of Table 24). Using our preferred value $\Delta_f H^o[C_2Cl_4(l),\ 298.15\ K] = -(63.9 \pm 4.0)\ kJ\ mol^{-1}$, we obtain $\Delta_f H^o[C_2Cl_6(s),\ 298.15\ K] = -(219.2 \pm 7.2)\ kJ\ mol^{-1}$ and $\Delta_f H^o[C_2Cl_6(g),\ 298.15\ K] = -(150.5 \pm 8.8)\ kJ\ mol^{-1}$. This number is 18 $kJ\ mol^{-1}$ lower than the combustion value.

Enthalpy of formation values for $C_2Cl_6$ in the gas phase can be obtained more directly from high temperature pyrolysis studies of $C_2Cl_6$ and $CCl_4$. These are discussed below.

Pyrolysis of tetrachloromethane has recently been studied by Huybrechts *et al.* [1996HNMa], [1996HNMb] and leads to an equilibrium mixture of $CCl_4$, $C_2Cl_4$, $C_2Cl_6$, and $Cl_2$. This study is discussed in detail in Sec. 5.7. Huybrechts *et al.* report the equilibrium vapor pressures at 696.6 K as $p(C_2Cl_6) = 3.8 \times 10^{-4}$ atm (38.5 Pa), $p(C_2Cl_4) = 7.22 \times 10^{-3}$ atm (731.6 Pa), $p(CCl_4) = 9.55 \times 10^{-2}$ atm (9677 Pa), and $p(Cl_2) = 1.48 \times 10^{-2}$ atm (1500 Pa). For the equilibrium

$$2CCl_4(g) \rightleftarrows C_2Cl_6(g) + Cl_2(g) \qquad (26)$$

these data correspond to $K_{26}(696.6\ K) = 61.7\ Pa$. We estimate the $2\sigma$ uncertainty in the equilibrium constant to be about a factor of 2, mainly due to the analysis of $C_2Cl_6$, which was present in small amounts (0.4% of $CCl_4$). From a Third Law analysis, using entropies and heat capacities from the TRC Tables [1981C], [1985R], we calculate $\Delta_{26}H(696.6\ K) = (46.3 \pm 4.0)\ kJ\ mol^{-1}$ and $\Delta_{26}H(298.15\ K) = (44.8 \pm 4.0)\ kJ\ mol^{-1}$. Using $\Delta_f H^o[CCl_4(g), 298.15\ K] = -(95.6 \pm 2.5)\ kJ\ mol^{-1}$ (see Sec. 3.5), this leads to $\Delta_f H^o[C_2Cl_6(g),\ 298.15\ K] = -(146.4 \pm 4.7)\ kJ\ mol^{-1}$. Alternatively, if entropies and heat capacities are taken from Gurvich *et al.* [1991GVA], we derive $\Delta_f H^o[C_2Cl_6(g),\ 298.15\ K] = -(145.6 \pm 4.7)\ kJ\ mol^{-1}$. These values are in very poor agreement with the combustion value, but in good agreement with that derived from liquid phase chlorination. The above value is linked to the enthalpy of formation of $CCl_4(g)$, which has a reliable value (see Sec. 3.5). The data of Huybrechts *et al.* [1996HNMa] can also be used to obtain information on equilibria (15) and (16):

$$2CCl_4(g) \rightleftarrows C_2Cl_4(g) + 2Cl_2(g) \qquad (15)$$

$$C_2Cl_6(g) \rightleftarrows C_2Cl_4(g) + Cl_2(g). \qquad (16)$$

TABLE 24. Enthalpies of formation of hexachloroethane derived from reported experimental data

| $\Delta_f H^o$ (g), 298.15 K (kJ mol$^{-1}$) | Reported uncertainty kJ mol$^{-1}$ | Temp. (K) | Method(s) | Ref/Year | Comments |
|---|---|---|---|---|---|
| Experimental | | | | | |
| −146.4 | N.R.<br>(4.0)[a] | 696.6 | Equilibrium of reaction $2CCl_4$ (g)$\rightleftarrows C_2Cl_6$ (g)$+Cl_2$ (g) | [1996HNMa] | 1, Pyrolysis of $CCl_4$. Third Law analysis, $\Delta_f H^o[CCl_4$ (g)] used in calculation. |
| −144.5 | N.R.<br>(4.0)[a] | 696.6 | Equilibrium of reaction $C_2Cl_6$ (g)$\rightleftarrows C_2Cl_4$ (g)$+Cl_2$ (g) | [1996HNMa] | 2, Pyrolysis of $CCl_4$. Third Law analysis, $\Delta_f H^o[C_2Cl_4$ (g)] used in calculation. |
| −163.3 | N.R.[b] | 773–873 | Equilibrium of reaction $C_2Cl_6$ (g)$\rightleftarrows C_2Cl_4$ (g)$+Cl_2$ (g) | [1979BLR] | 3, Pyrolysis of $C_2Cl_5$. Third Law analysis, $\Delta_f H^o[C_2Cl_4$ (g)] used in calculation. |
| −160.7 | N.R.[b] | 773–873 | Equilibrium of reaction $C_2Cl_6$ (g)$\rightleftarrows C_2Cl_4$ (g)$+Cl_2$ (g) | [1979BLR] | 4, Pyrolysis of $C_2Cl_6$. 2nd law analysis, $\Delta_f H^o[C_2Cl_4$ (g)] used in calculation. |
| −149.3 | N.R.<br>(2.6)[c] | 776 | Equilibrium of reaction $C_2Cl_6$ (g)$\rightleftarrows C_2Cl_4$ (g)$+Cl_2$ (g) | [1963PBM]<br>[1962PMN] | 5, Pyrolysis of $C_2Cl_6$. Third Law analysis, $\Delta_f H^o[C_2Cl_6$ (g)] used in calculation. |
| −150.5 | N.R.<br>(5.0)[d] | 298 | Enthalpy of Chlorination $C_2Cl_4$ (l)$+Cl_2$ (g)$\rightarrow C_2Cl_6$ (s) | [1956K] | 6, $\Delta_f H^o[C_2Cl_4$ (l)] used in calculation. |
| −149.1 | N.R.<br>(2.3)[c] | 671 | Equilibrium of reaction $C_2Cl_6$ (g)$\rightleftarrows C_2Cl_4$ (g)$+Cl_2$ (g) | [1950DI] | 7, Pyrolysis of $C_2Cl_6$. Third Law analysis, $\Delta_f H^o[C_2Cl_4$ (g)] used in calculation. |
| −132.6 | 8.4 | 298 | Combustion calorimetry of solid | [1938E]<br>[1953SBK]<br>[1970CP] | 8, Data corrected by Smith *et al.* in 1953; data reanalyzed and auxiliary quantities updated by [1970CP]. |
| Reviews and Evaluations | | | | | |
| −141.5 | 4.7 | 298 | | [1991GVA] | Evaluation date uncertain; same value as previous edition [1970CP]. |
| −143.6 | 9.1 | 298 | | [1986PNK] | |
| −149.5 | N.R.[e] | 298 | | [1983KP] | Value from group additivity. |
| −138.9 | N.R.[e] | 298 | | [1981C] | |
| −140.6 | 4.2 | 298 | | [1974CRW] | |
| −144.3 | 5.9 | 298 | | [1970CP] | |
| −141.4 | N.R.[e] | 298 | | [1969SWS] | |

[a] Not reported. The parenthetical value is the uncertainty in the reaction enthalpy estimated by us assuming a factor of two uncertainty in the equilibrium constant.

[b] Not reported.

[c] Not reported. The parenthetical value is the uncertainty in the reaction enthalpy estimated by us assuming a 50% uncertainty in the equilibrium constant.

[d] Not reported. The parenthetical value refers to the reaction enthalpy and is $2\sigma$ as calculated by us from the reported data.

[e] Not reported.

**Comments:**

1. Third Law analysis using entropies and heat capacities from [1981C], [1985R] yields $\Delta_r H(696.6\ \mathrm{K}) = -161.9$ kJ mol$^{-1}$ and $\Delta_r H(298.15\ \mathrm{K}) = -165.3$ kJ mol$^{-1}$. Using $\Delta_f H^o[CCl_4$ (g), 298.15 K$] = -95.6 \pm 2.5$ kJ mol$^{-1}$ (see Sec. 3.5) we derive $\Delta_f H^o[C_2Cl_4$ (g), 298.15 K$] = -26.0$ kJ mol$^{-1}$. If entropies and heat capacities are taken from [1991GVA], this becomes $\Delta_f H^o[C_2Cl_4$ (g), 298.15 K$] = -24.7$ kJ mol$^{-1}$.

2. Third Law analysis using entropies and heat capacities from [1981C], [1985R] yields $\Delta_r H(696.6\ \mathrm{K}) = -115.6$ kJ mol$^{-1}$ and $\Delta_r H(298.15\ \mathrm{K}) = -120.4$ kJ mol$^{-1}$. $\Delta_f H^o[CCl_4$ (g), 298.15 K$] = -95.6 \pm 2.5$ kJ mol$^{-1}$ (see Sec. 3.5) used in calculation.

3. For $C_2Cl_6$ (g)$\rightleftarrows C_2Cl_4$ (g)$+Cl_2$ (g), measured equilibrium constants are $K(773\ \mathrm{K}) = 0.102$ atm (10.34 kPa), $K(823\ \mathrm{K}) = 0.345$ atm (34.94 kPa), $K(873\ \mathrm{K}) = 1.042$ atm (105.5 kPa). Using entropies and heat capacities from [1981C], [1985R] these yield $\Delta_r H(773\ \mathrm{K}) = -134.6$ kJ mol$^{-1}$, $\Delta_r H(823\ \mathrm{K}) = -133.3$ kJ mol$^{-1}$, and $\Delta_r H(873\ \mathrm{K}) = -132.6$ kJ mol$^{-1}$. Averaging the data, $\Delta_r H(298.15\ \mathrm{K}) = -139.5$ kJ mol$^{-1}$ is obtained. These data are in poor agreement with the three other measurements of the equilibrium constant for this reaction.

4. Second Law analysis (773–873 K) of $C_2Cl_4$ (g)$+Cl_2$ (g)$\rightleftarrows C_2Cl_6$ (g) yields $\Delta_r H(823\ \mathrm{K}) = -130.5$ kJ mol$^{-1}$. $\Delta_r H(298.15\ \mathrm{K}) = -136.5$ kJ mol$^{-1}$ is obtained using entropies and heat capacities from [1981C], [1985R]. Result is in good agreement with Third Law analysis (Comment 5), but in poor agreement with the three other measurements of the equilibrium constant for this reaction.

5. $K(776\ \mathrm{K}) = 0.80$ atm (81.1 kPa). We estimate the $2\sigma$ uncertainty in $K$ to be ±50%. From a Third Law analysis, taking entropies and heat capacities from the TRC Tables [1981C], [1985R], we obtain $\Delta_r H(776\ \mathrm{K}) = (120.7 \pm 2.6)$ kJ mol$^{-1}$ and $\Delta_r H(298.15\ \mathrm{K}) = (126.6 \pm 2.6)$ kJ mol$^{-1}$. Stated value is obtained using $\Delta_f H^o[C_2Cl_4$ (g), 298.15 K$] = -(24.2 \pm 4.0)$ kJ mol$^{-1}$ (see Sec. 5.7).

6. Results of four experiments for $C_2Cl_4$ (l)$+Cl_2$ (g)$\rightarrow C_2Cl_6$ (s) give $\Delta_r H(298.15\ \mathrm{K}) = -(135.6 \pm 3.9)$ kJ mol$^{-1}$ (Kirkbride [1956K] rounds the average value to two significant figures and reports $\Delta_r H(298.15\ \mathrm{K}) = -32$ kcal mol$^{-1}$, although each experiment is reported to a precision of 0.1 kcal mol$^{-1}$ and the actual average is $-32.4$ kcal mol$^{-1}$). Kirkbride [1956K] determined the approximate enthalpies of solution of $C_2Cl_6$ in $C_2Cl_4$ to be 19.7 kJ mol$^{-1}$, so for the reaction $C_2Cl_4$ (l)$+Cl_2$ (g)$\rightarrow C_2Cl_6$ (s) we derive $\Delta_r H(298.15\ \mathrm{K}) = -(155.3 \pm 6.0)$ kJ mol$^{-1}$, where the uncertainty is estimated. In conjunction with $\Delta_f H^o[C_2Cl_4$ (l), 298.15 K$] = -(63.9 \pm 4.0)$ kJ mol$^{-1}$. We obtain $\Delta_f H^o[C_2Cl_6$ (s)$] = -(219.2 \pm 7.2)$ kJ mol$^{-1}$.

7. For $C_2Cl_6$ (g)$\rightleftarrows C_2Cl_4$ (g)$+Cl_2$ (g), at 671 K, the pressures $P_0(C_2Cl_6) = 87.5$ mm(11.67 kPa) and $P_{\mathrm{final}} = 1.5\ \mathrm{P}_0$ lead to $K_{16}(671\ \mathrm{K}) = 5.83$ kPa (see text). Taking entropies and heat capacities from the TRC Tables [1981], [1985R], we derive $\Delta_{16} H(671\ \mathrm{K}) = (120.4 \pm 2.3)$ kJ mol$^{-1}$ and $\Delta_{16} H(298.15\ \mathrm{K}) = (124.9 \pm 2.3)$ kJ mol$^{-1}$, where the uncertainties are based on an estimated 50% uncertainty in $K_{16}$.

8. Static bomb calorimetry. Experiments by Eftring [1938E] as corrected by Smith *et al.* [1953SBK] and Cox and Pilcher [1970CP]. Sample purity uncertain. $\Delta_c H(298.15\ \mathrm{K}) = -(727.2 \pm 8.4)$ kJ mol$^{-1}$, refers to reaction $C_2Cl_6$ (s)$+3H_2O$ (l)$+0.5O_2$ (g)$\rightarrow 2CO_2$ (g)$+6HCl$ (aq:600). The following auxiliary values were used: $\Delta_f H^o[CO_2$ (g), 298.15 K$] = -(393.51 \pm 0.13)$ kJ mol$^{-1}$, $\Delta_f H^o[H_2O$ (l), 298.15 K$] = -(285.830 \pm 0.040)$ kJ mol$^{-1}$, and $\Delta_f H^o[HCl$ (aq:600), 298.15 K$] = -(166.540 \pm 0.10)$ kJ mol$^{-1}$. These data result in $\Delta_f H^o[C_2Cl_6$ (s)$] = -(201.57 \pm 8.4)$ kJ mol$^{-1}$. Combined with $\Delta_{\mathrm{sub1}} H^o[C_2Cl_6$ (s), 298.15 K$] = (69.0 \pm 4.0)$ kJ mol$^{-1}$, we obtain $\Delta_f H^o[C_2Cl_6$ (g), 298.15 K$] = -(132.6 \pm 9.3)$ kJ mol$^{-1}$.

Equilibrium (15) is discussed in Sec. 5.7. For reaction (16), $K_{16}(696.6\,\mathrm{K})=28.5\,\mathrm{kPa}$. We estimate the $2\sigma$ uncertainty in the equilibrium constant to be about a factor of 2. Using entropies and heat capacities from the TRC Tables [1981C], [1985R], one calculates $\Delta_{16}H(696.6\,\mathrm{K})=(115.4\pm4.0)\,\mathrm{kJ\,mol^{-1}}$ and $\Delta_{16}H(298.15\,\mathrm{K})=(120.3\pm4.0)\,\mathrm{kJ\,mol^{-1}}$. If data are taken from Gurvich *et al.* [1991GVA] $\Delta_{16}H(298.15\,\mathrm{K})=(120.8\pm4.0)\,\mathrm{kJ\,mol^{-1}}$. As a check we can compare values of $\Delta_{16}H$ derived from studies of hexachloroethane pyrolysis.

Pyrolysis of hexachloroethane has been studied several times and detailed models of the reaction developed by Weissman and Benson [1980WB], and later by Huybrechts *et al.* [1996HNMa], [1996HNMb]. It is now accepted that pyrolysis of $C_2Cl_6$ leads to the rapid establishment of equilibrium (16), followed by the much slower progression of equilibrium (15) and various minor side channels. Puyo *et al.* [1962PMN] reported $K_{16}(776\,\mathrm{K})=0.80\,\mathrm{atm}$ (81.1 kPa). We estimate the $2\sigma$ uncertainty in $K_{16}$ to be ± 50%. From a Third Law analysis, taking entropies and heat capacities from [1981C], [1985R], we obtain $\Delta_{16}H(776\,\mathrm{K})=(120.7\pm2.6)\,\mathrm{kJ\,mol^{-1}}$ and $\Delta_{16}H(298.15\,\mathrm{K})=(126.6\pm2.6)\,\mathrm{kJ\,mol^{-1}}$.

Dainton and Ivin [1950DI] studied $C_2Cl_6$ pyrolysis between 573 and 693 K. They report that they attempted to measure $K_{16}$ at temperatures in the range of 573–623 K and were able to derive $\Delta_{16}H\approx125.5\,\mathrm{kJ\,mol^{-1}}$ (30 kcal $\mathrm{mol^{-1}}$). Details of these experiments were unfortunately not reported, and they do not specify if the stated enthalpy change refers to the temperature of their experiments or if it has been adjusted to 298.15 K. Although Dainton and Ivin were surprised by the low value, the data of Puyo *et al.* [1962PMN] and Huybrechts *et al.* [1996HNMa] are in good agreement. In their analysis of the results of Dainton and Ivin, Weissman and Benson [1980WB] assumed that the pressure change found at 671 K resulted mainly from reaction (16). The reaction model of Huybrechts *et al.* appears to support this assumption (see Fig. 6 of [1996HNMa]). With $P_0(C_2Cl_6)=87.5\,\mathrm{mm}$ (11.67 kPa) and $P_{\mathrm{final}}=1.5P_0$, these data lead to $K_{16}(671\,\mathrm{K})=5.83\,\mathrm{kPa}$. Taking entropies and heat capacities from the TRC Tables [1981C], [1985R], we derive $\Delta_{16}H(671\,\mathrm{K})=(120.4\pm2.3)\,\mathrm{kJ\,mol^{-1}}$ and $\Delta_{16}H(298.15\,\mathrm{K})=(124.9\pm2.3)\,\mathrm{kJ\,mol^{-1}}$, where the uncertainties are based on an estimated 50% uncertainty in $K_{16}$.

Finally, Bushneva *et al.* [1979BLR] studied pyrolysis of hexachloroethane and reported $K_{16}=0.102\,\mathrm{atm}$ (10.34 kPa), 0.345 atm (34.94 kPa), and 1.042 atm (105.5 kPa), at 773, 823, and 873 K, respectively. Their Second Law analysis gives $\Delta_{16}H(823\,\mathrm{K})=130.5\,\mathrm{kJ\,mol^{-1}}$, which becomes $\Delta_{16}H(298.15\,\mathrm{K})=136.5\,\mathrm{kJ\,mol^{-1}}$. Third Law analyses of their data result in $\Delta_{16}H(773\,\mathrm{K})=134.4\,\mathrm{kJ\,mol^{-1}}$, $\Delta_{16}H(823\,\mathrm{K})=133.1\,\mathrm{kJ\,mol^{-1}}$, and $\Delta_{16}H(823\,\mathrm{K})=132.4\,\mathrm{kJ\,mol^{-1}}$, which lead to values of $\Delta_{16}H(298.15\,\mathrm{K})$ in the range of 138.4–140.4 $\mathrm{kJ\,mol^{-1}}$. These data are in poor agreement with the other studies.

*Recommendation*. The best data from which to obtain a reliable value of $\Delta_fH^o[C_2Cl_6(g),\ 298.15\,\mathrm{K}]$ are the high temperature studies of the equilibria involved in $CCl_4$ and $C_2Cl_6$ pyrolysis. The pyrolysis data of Huybrechts *et al.* [1996HNMa], [1996HNMb], Puyo *et al.* [1962PMN], and Dainton and Ivin [1950DI] are in reasonable agreement, while the data of Bushneva *et al.* [1979BLR] lead to much larger values of $\Delta_{16}H$. This suggests there are problems with the latter study and those results were not used in making the final selection. The most direct value is obtainable from the study of Huybrechts *et al.* [1996HNMa], [1996HNMb] which relates $\Delta_fH^o[CCl_4(g),\ 298.15\,\mathrm{K}]$ and $\Delta_fH^o[C_2Cl_6(g),\ 298.15\,\mathrm{K}]$. However, the data in that study that relate $\Delta_fH^o[C_2Cl_4(g),\ 298.15\,\mathrm{K}]$ and $\Delta_fH^o[C_2Cl_6(g),\ 298.15\,\mathrm{K}]$ are slightly at odds with hexachloroethane pyrolysis studies of Puyo *et al.* [1962PMN] and Dainton and Ivin [1950DI]. This may be because $C_2Cl_6$ is a very minor product of tetrachloromethane pyrolysis and therefore its analysis is subject to greater uncertainty. By contrast, hexachloroethane pyrolysis results in large equilibrium amounts of $C_2Cl_4$ and $C_2Cl_6$ and these studies [1950DI], [1962PMN] should be more precise, despite the fact that the analytical techniques employed are now somewhat dated. The above three pyrolysis studies lead to $\Delta_{16}H(298.15\,\mathrm{K})=(120.3\pm4.0)\,\mathrm{kJ\,mol^{-1}}$ [1996HNMa], $\Delta_{16}H(298.15\,\mathrm{K})=(126.6\pm2.6)\,\mathrm{kJ\,mol^{-1}}$ [1962PMN], and $\Delta_{16}H(298.15\,\mathrm{K})=(124.9\pm2.3)\,\mathrm{kJ\,mol^{-1}}$ [1950DI]. We recommend $\Delta_fH^o[C_2Cl_4(g),\ 298.15\,\mathrm{K}]-\Delta_fH^o[C_2Cl_6(g),\ 298.15\,\mathrm{K}]=(124.0\pm4.0)\,\mathrm{kJ\,mol^{-1}}$, where the uncertainty is an estimated $2\sigma$ and corresponds to a 95% level of confidence. To derive an absolute value of $\Delta_fH^o[C_2Cl_6(g),\ 298.15\,\mathrm{K}]$ we use the recommended value $\Delta_fH^o[C_2Cl_4(g),\ 298.15\,\mathrm{K}]=-(24.2\pm4.0)\,\mathrm{kJ\,mol^{-1}}$. That value is based primarily on the chloromethane pyrolysis data of Huybrechts *et al.* [1996HNMa], [1996HNMb], together with dehydrochlorination studies that relate $\Delta_fH^o[C_2Cl_4]$ and $\Delta_fH^o[C_2Cl_5]$ (see Sec. 5.7). The final selected value is $\Delta_fH^o[C_2Cl_6(g),\ 298.15\,\mathrm{K}]=-(148.2\pm5.7)\,\mathrm{kJ\,mol^{-1}}$. This value is significantly lower than the combustion value. It is, however, in very good agreement with the enthalpy of chlorination data of Kirkbride [1956K], although we have not used those data directly because of the uncertainties surrounding the enthalpy of sublimation of the solid. Finally, the results of high level *ab initio* calculations carried out at NIST [2001BAM], up to and including composite QCISD(T)/6-311+G(3df,2p) calculations, suggest an enthalpy of formation value of $C_2Cl_6$ of $-150$–$-154\,\mathrm{kJ\,mol^{-1}}$, and thus also support the lower value.

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