



PII S0016-7037(99)00276-8

Halocarbons in the environment: Estimates of thermodynamic properties for aqueous chloroethylene species and their stabilities in natural settings

JOHNSON R. HAAS^{1,*} and EVERETT L. SHOCK²¹Department of Geography and Earth Sciences, University of North Carolina, Charlotte, NC 28223, USA²Department of Earth and Planetary Sciences, Washington University, St. Louis, MO 63130, USA

(Received October 15, 1998; accepted in revised form April 29, 1999)

Abstract—Standard partial molal thermodynamic parameters for the aqueous chlorinated-ethylene species, perchloroethylene (PCE), trichloroethylene (TCE), 1,1-dichloroethylene (1,1-DCE), *cis*-1,2-dichloroethylene (*cis*-1,2-DCE), *trans*-1,2-dichloroethylene (*trans*-1,2-DCE), and vinyl chloride (VC) have been estimated by using experimental gas-solubility data and correlation algorithms. The provided thermodynamic values may be used to calculate properties of reactions involving the aqueous chloroethylene species at a wide range of temperatures and pressures. Estimated values for the chloroethylenes were used, along with published values for minerals, gases, aqueous ions, and aqueous neutral organic species, to calculate the stability of chloroethylene species in equilibrium with the minerals magnetite, hematite, pyrite, and pyrrhotite in the subsurface. Estimated values for the aqueous chloroethylenes were also used to calculate reduction potentials for microbially-mediated reductive dechlorination half-reactions at elevated temperatures. Calculations indicate that all aqueous chloroethylene species are energetically favored to decompose to ethylene(aq) under a wide range of conditions in the subsurface, by both abiotic and biotic pathways. Anaerobic microbially mediated degradation is especially favored under conditions at least sufficiently reducing to promote sulfate-reduction, but not under conditions sufficient for microbial denitrification, pyrolusite reduction, or ferric-iron reduction. Copyright © 1999 Elsevier Science Ltd

1. INTRODUCTION

As illustrated recently by Harr (1996), the anthropogenic production, release, and dispersal of organochlorine compounds into natural settings at the earth's surface is a matter of widespread environmental and epidemiological concern. Chlorinated ethenes such as perchloroethylene, (PCE; $\text{Cl}_2\text{C}=\text{CCl}_2$), trichloroethylene, (TCE; $\text{ClHC}=\text{CCl}_2$), 1,1-dichloroethylene, (1,1-DCE; $\text{Cl}_2\text{C}=\text{CH}_2$), *cis*-1,2-dichloroethylene, (*cis*-1,2-DCE), *trans*-1,2-dichloroethylene, (*trans*-1,2-DCE; $\text{ClHC}=\text{CHCl}$), and vinyl chloride, (VC; $\text{ClHC}=\text{CH}_2$) are produced by substitution of one or more Cl atoms for an equal number of H atoms in the ethene (ethylene) structure. They collectively represent one of the most abundant forms of organochlorine contamination of surface and ground waters in the industrialized world. In 1995, industrial production of waste TCE and VC within the USA totaled at least 9.04×10^7 kg and 8.2×10^7 kg (*Toxics Release Inventory*, 1995), respectively. The maximum contaminant loads (MCLs) for TCE and VC in drinking water within the US, as mandated currently by the United States Environmental Protection Agency (USA EPA 1993), are 0.005 mg/L and 0.002 mg/L. If dispersed evenly throughout the entire volume of annually renewable fresh water in the USA (*World Resources Institute*, 1996), waste TCE and VC produced in 1995 would have been sufficient to contaminate 720% and 1640% of freshwater supplies, respectively. Organochlorine contamination is also problematic because these compounds tend to persist in the environment, where they remain available for bioaccumulation in organisms and their toxification.

A wide range of organochlorine compounds including chloroethylenes are produced naturally by microbial organisms and

some fungi (e.g., Gribble, 1994). Harper (1985) reports that global fungal production of chloromethane (CH_3Cl) gas may exceed 5×10^6 tons per year, compared with an estimated anthropogenic flux of 2.6×10^4 tons per year. Biotic and volcanogenic sources have been identified for natural production of PCE and TCE, although fluxes are unclear (Stoiber et al., 1971; Isidorov, 1990). Modern natural production of organochlorines, including chloroethenes but also a wide range of longer-chain chlorinated alkanes and other chlorinated aliphatic and aromatic species, demonstrates that these compounds are likely to have been produced by microbial and geochemical processes throughout geologic time. However, the absence of organochlorine deposits in the geologic record suggests that natural destruction of these compounds by microbial and geochemical processes is probably a highly efficient process.

Metabolic pathways and abiotic chemical processes that act to degrade organochlorine compounds under laboratory and natural conditions have been investigated extensively, but in general the link connecting these processes to the underlying thermodynamic principles that control them has not been substantively explored. Nonetheless, chemical reactions are fundamentally governed by their thermodynamic properties. Kinetic factors govern the alacrity with which energetically favored reactions proceed, but the energetic gradient itself is best described using an equilibrium thermodynamics framework. Investigations that address the problem of pollutant stability from a thermodynamic basis could greatly facilitate the search for more effective remediation technologies, advance understanding of the metabolic and biochemical diversity of microbial life, and promote a better grasp of the geologic fate of halocarbons in the deep subsurface.

In this article, we report estimates of standard partial molal thermodynamic properties of the aqueous chlorinated ethene

* Author to whom correspondence should be addressed (jrhaas@email.uncc.edu).

species, including PCE, TCE, 1,1-DCE, *cis*-1,2-DCE, *trans*-1,2-DCE, and VC. These values may be used to calculate thermodynamic properties for reactions involving the aqueous chloroethene species under a wide range of temperature and pressure conditions. Thermodynamic values for aqueous chloroethene species were calculated by regression of published experimental gas-solubility data, together with estimated parameters for the revised Helgeson–Kirkham–Flowers (HKF) equations of state (Shock et al., 1992) along with data and parameters for neutral organic species (Shock and Helgeson, 1990). We also present the results of calculations using our estimated thermodynamic properties and those of gases, minerals, and aqueous species from the literature to evaluate the energetic favorability of reductive dehalogenation reactions that eliminate aqueous chloroethene species under a wide range of temperature and pressure conditions and fluid compositions. These latter calculations are intended to demonstrate the versatility of this approach for evaluating potential reaction pathways that may serve to degrade chloroethenes under engineered conditions, abiotically in the deep geologic subsurface, and biotically by microbial life in surface and subsurface ecosystems.

2. ESTIMATION OF THERMODYNAMIC PROPERTIES FOR AQUEOUS CHLOROETHENE SPECIES

2.1. Summary of Available Experimental Data for Chloroethene Species and Methods used to Calculate Standard Partial Molal Free Energies of Formation from Experimental Values

Experimental measurements of the aqueous solubilities of chloroethylene gases as a function of temperature are available in the literature for PCE, TCE, all DCE isomers, and VC, and these values may be used to derive standard partial molal thermodynamic properties for the aqueous species, provided that corresponding properties of the gaseous species are also available.

Chloroethylene gas-solubility data are generally reported in the literature either as raw values describing concentrations of aqueous species in equilibrium with known partial pressures of the corresponding gas phase, or as Henry's law equilibrium constants derived from these experimental measurements. Henry's law relates the equilibrium concentration of an aqueous species (C_{aq}) to that of its corresponding gas phase (C_g) at any temperature, according to the equation:

$$H = \frac{C_{aq}}{C_g} \quad (1)$$

where H represents the Henry's law equilibrium constant (Stumm and Morgan, 1996) in units that vary depending on the treatment, i.e. C_{aq} symbolises aqueous concentration in terms of mole fraction, molality, molarity, or mol/m² and C_g means gas concentration. Values of H may be redefined in terms of equilibrium constants that are consistent with the standard state convention of a hypothetical aqueous solution of unit molality referenced to infinite dilution (Shock et al., 1989), consistent with conventions of the HKF equations of state (Helgeson et al., 1981; Tanger and Helgeson, 1988; Shock and Helgeson, 1988; 1990; Shock et al., 1989), by using the relation:

$$K_{sol} = \frac{f_i}{a_i} = \frac{\gamma_i P_i}{\gamma_{a_i} m_i}, \quad (2)$$

where K_{sol} represents the equilibrium constant at temperature, f_i represents the fugacity of the gaseous species i , a_i denotes activity of aqueous species i , P_i represents the equilibrium partial pressure of gas i , m_i stands for the concentration of aqueous i in molal units, and the terms γ_i and γ_{a_i} stand for the fugacity and activity coefficients of i . K_{sol} is dimensionless because the fugacity and activity coefficients have units of inverse concentration, cancelling with partial pressure and molality to yield dimensionless values for fugacity and activity. For our calculations, fugacity and activity coefficients of all chloroethene species were assumed to be unity.

The standard partial molal Gibbs free energy of reaction ($\Delta \bar{G}_r^\circ$) for a gas-solubility reaction is related to K_{sol} by the expression:

$$\Delta \bar{G}_r^\circ = -2.303RT \log K_{sol}, \quad (3)$$

where R stands for the gas constant and T represents temperature in K. The value of the standard partial molal Gibbs free energy of formation of the aqueous species ($\Delta \bar{G}_{r,aq}^\circ$) can be calculated using the standard partial molal Gibbs free energies of formation of the gas ($\Delta \bar{G}_{r,g}^\circ$) and of the gas-solubility reaction ($\Delta \bar{G}_r^\circ$) according to the relationship:

$$\Delta \bar{G}_{r,aq}^\circ = \Delta \bar{G}_r^\circ + \Delta \bar{G}_{r,g}^\circ. \quad (4)$$

Values of $\Delta \bar{G}_{r,aq}^\circ$ may therefore be calculated, provided that $\Delta \bar{G}_{r,g}^\circ$ and $\Delta \bar{G}_r^\circ$ are defined. Standard partial molal thermodynamic properties of chloroethene gases used in this study were those tabulated in the compilation of Stull et al. (1969). Values for $\Delta \bar{G}_r^\circ$ were calculated from published experimentally-determined values of H for each chloroethylene compound, or from published data that may be used to calculate H .

2.2. Vinyl chloride

Gas-solubility data for VC are provided by Hayduk and Laudie (1973) at temperatures ranging from 0 to 80°C. They were reported in terms of mole fraction aqueous VC in equilibrium with gaseous VC at one atmosphere partial pressure. These values were redefined in this study in terms of H by using Eqn. 1 and by converting mole fraction VC into molality, yielding values of K_{sol} as a function of temperature. Resulting H values were used to calculate $\Delta \bar{G}_r^\circ$ by using Eqn. 3 and, in conjunction with $\Delta \bar{G}_{r,g}^\circ$ and Eqn. 4, yield values of $\Delta \bar{G}_{r,aq}^\circ$ for VC_(aq).

2.3. Dichloroethylene Isomers

Tse et al. (1992) and Gossett (1987) report experimental Henry's law constants in units of m³-atm/mol for 1,1-DCE, *cis*-1,2-DCE, and *trans*-1,2-DCE at temperatures ranging from 20 to 40°C, along with appropriate values for equilibrium DCE vapor pressure during the experiments. The compilation of Horvath (1982) reports values that may be used to calculate H for 1,1-DCE at temperatures ranging from 0 to 80°C. Values of saturated 1,1-DCE vapor pressure as a function of temperature were not reported in Horvath (1982) but were calculated in this

study by using Antoine coefficients for 1,1-DCE gas (Stephenson and Malanowski, 1987). The Antoine equation:

$$\log P = A - \frac{B}{C + T} \quad (5)$$

may be used to calculate the saturated vapor-pressure of a gas over the corresponding pure liquid phase at a given temperature, where P represents the saturated vapor pressure of the gas in kilopascals (100 kPa = 1 bar), T represents temperature in K, and A , B , and C are empirical coefficients specific to each gas. Expression [5] yields values of P which may be used in conjunction with Eqn. [2] to determine K_{sol} as a function of temperature. Values of K_{sol} may then be redefined in terms of $\Delta\bar{G}_r^\circ$ by using Eqn. 3 and, in conjunction with $\Delta\bar{G}_{f,g}^\circ$ and Eqn. 4, yield values of $\Delta\bar{G}_{f,aq}^\circ$.

The temperature dependence of data reported in Horvath (1982) is not consistent with that displayed by the data of Tse et al. (1992) and Gossett (1987), whose results are themselves in general agreement. Thus, despite the more narrow temperature range of the data provided by Tse et al. (1992) and Gossett (1987), these values were adopted for this study. Values are reported in Horvath (1982) for *cis*-1,2-DCE and *trans*-1,2-DCE, but only at 10 to 25°C and 25°C, respectively.

2.4. Trichloroethylene

Heron et al. (1998) provide experimental values of H in units of L-atm/mol for TCE in the temperature range 0–80°C. These values are generally in agreement with analogous data reported by Tse et al. (1992) and Gossett (1987) in the temperature range 20–40°C, but are inconsistent at temperatures below ~40°C with the values reported in Horvath (1982) under TCE-saturated vapor pressures. At temperatures above ~40°C the values of Horvath (1982) and those of Heron et al. (1998) converge. This study adopts the values of Heron et al. (1998).

2.5. Perchloroethylene

Stephenson (1992) reports gas-solubility data for PCE in the temperature range 0–92°C under PCE-saturated vapor pressure conditions. Analogous values are reported by Horvath (1982) for PCE gas-solubility in the temperature range 0–80°C, and by Imhoff et al. (1997) in terms of PCE solubility in mg/L at temperatures of 5–40°C. The values of Imhoff et al. (1997) and Stephenson (1992) are in general agreement, but both are inconsistent with the values of Horvath (1982). In this study, we adopt the values of Stephenson (1992).

2.6. Regression of Experimental Gas-Solubility Data and Estimation of Standard Partial Molal Enthalpies and Entropies of Formation for Aqueous Chloroethylene Species

The standard partial molal Gibbs free energy, enthalpy, and entropy of a reaction may be related by the expression:

$$\Delta\bar{G}_r^\circ = \Delta\bar{H}_r^\circ - T\Delta\bar{S}_r^\circ \quad (6)$$

where $\Delta\bar{H}_r^\circ$ and $\Delta\bar{S}_r^\circ$ represent the standard partial molal enthalpy and entropy of the reaction, respectively. For small

intervals of T near the reference temperature of 298 K, $\Delta\bar{H}_r^\circ$ may be assumed to be constant as a function of temperature according to the Van't Hoff equation:

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta\bar{H}_r^\circ}{RT^2}, \quad (7)$$

which relates the equilibrium constant of a reaction at temperature in K to the standard partial molal enthalpy of that reaction. The implicit assumption in the Van't Hoff equation of constant enthalpy and thus zero heat capacity is not valid at temperatures that are significantly different from the reference temperature of 298 K. This tendency is demonstrated in Fig. 1, which illustrates experimental values of $\Delta\bar{G}_r^\circ$ for chloroethene gas-solubility reactions as a function of temperature (gray circles), determined by using the methods described in the previous section. Figure 1 shows that the trends of $\Delta\bar{G}_r^\circ$ as a function of temperature display apparently linear behavior over a fairly narrow range of temperature. However, within the interval where T and $\Delta\bar{G}_r^\circ$ are related by an approximately linear function, $\Delta\bar{H}_r^\circ$ may be approximated as a constant, and Eqn. 6 reduces to a linear equation in $\Delta\bar{G}_r^\circ$ and T , where $\Delta\bar{H}_r^\circ$ and $\Delta\bar{S}_r^\circ$ are represented by the intercept and negative of the slope of the regressed line.

Figure 1 shows least-squares linear regressions of $\Delta\bar{G}_r^\circ$ as a function of temperature (solid lines), calculated for each species using those subsets of the experimental data that could be approximated as linear in temperature. For 1,1-DCE, *cis*-1,2-DCE, and *trans*-1,2-DCE, this range includes all the available experimental data up to the maximum reported temperature of 313 K. For PCE and TCE, this range extended to ~300 K, and for VC this range extended to ~370 K. Values of $\Delta\bar{G}_r^\circ$, $\Delta\bar{H}_r^\circ$ and $\Delta\bar{S}_r^\circ$ calculated by using Eqn. 6 and the methods discussed in Section 2.1 are reported in Table 1.

Values for standard partial molal enthalpies of formation ($\Delta\bar{H}_{f,aq}^\circ$) for the aqueous chloroethylenes were calculated using values of standard partial molal enthalpies of formation ($\Delta\bar{H}_{f,g}^\circ$) for the corresponding gas species, and regressed values of $\Delta\bar{H}_r^\circ$ by using the relationship:

$$\Delta\bar{H}_{f,aq}^\circ = \Delta\bar{H}_r^\circ + \Delta\bar{H}_{f,g}^\circ, \quad (8)$$

which is analogous to Eqn. 4.

Entropies of formation were calculated by using the expression:

$$\Delta\bar{S}_r^\circ = \frac{\Delta\bar{H}_r^\circ - \Delta\bar{G}_r^\circ}{T}, \quad (9)$$

where $\Delta\bar{S}_r^\circ$ represents the standard partial molal entropy of formation of a chemical species from the elements. Third law entropy values may be calculated for a reaction forming a chemical species of interest from the elements if $\Delta\bar{S}_r^\circ$ is known, according to the expression:

$$\bar{S}_i^\circ = \Delta\bar{S}_r^\circ + \sum \bar{S}_{\text{elements}}^\circ, \quad (10)$$

where \bar{S}_i° and $\bar{S}_{\text{elements}}^\circ$ stand for the standard partial molal third-law entropies of the chemical species of interest and the stoichiometric sum of the third law entropies of elements (in their standard reference states) forming the species. Values of

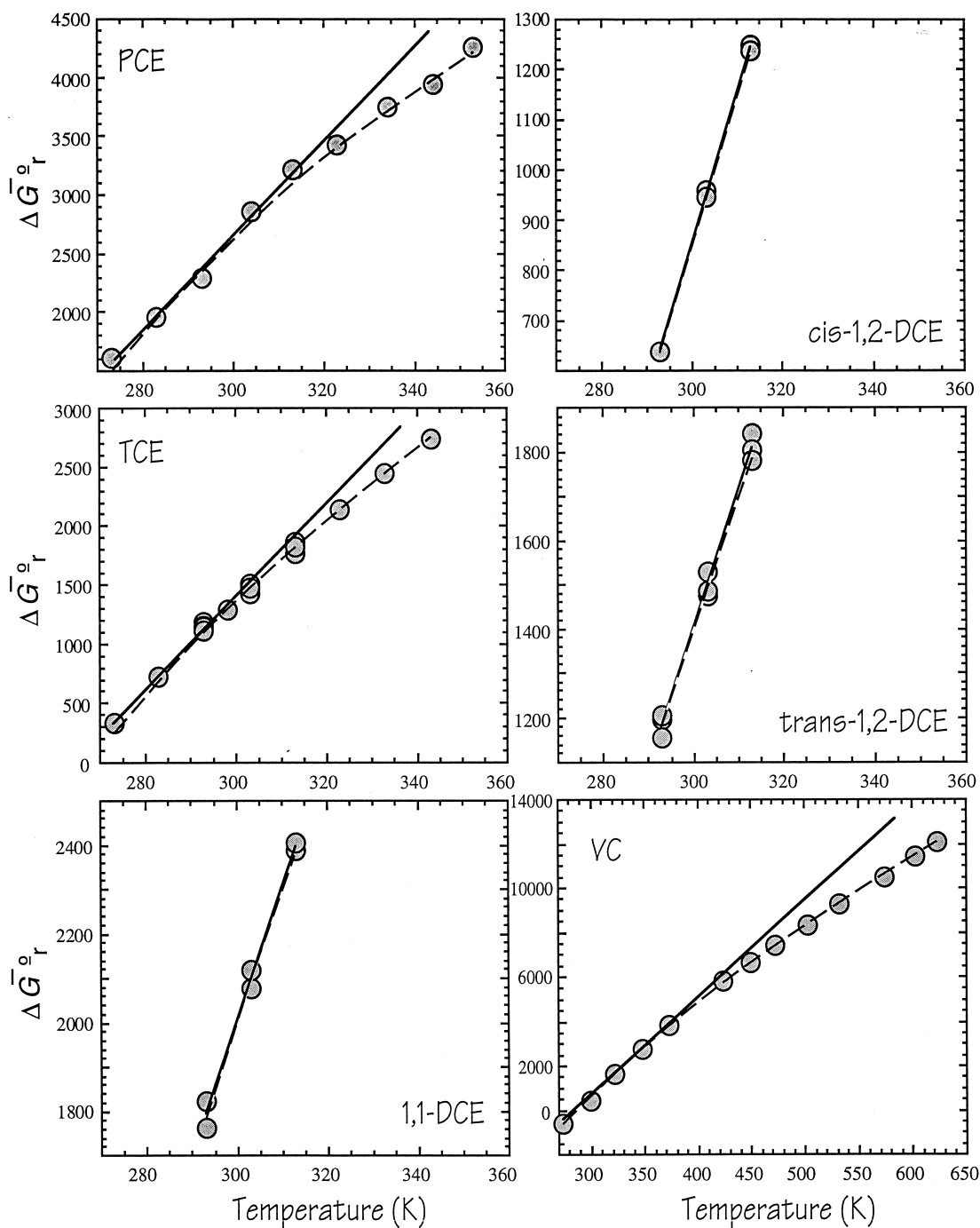


Fig. 1. Experimental Gibbs free energies (gray circles) for gas-solubility reactions ($\Delta\bar{G}_r^\circ$) involving PCE, TCE, 1,1-DCE, *cis*-1,2-DCE, *trans*-1,2-DCE, and VC as functions of temperature in Kelvins. Solid lines are linear regressions of values below 313 K for 1,1-DCE, *cis*-1,2-DCE, and *trans*-1,2-DCE, below 300 K for PCE and TCE, and below 370 K for VC. Dashed lines are regressions of values using optimized values for heat capacity.

\bar{S}° for the elements $\text{H}_{2(g)}$, $\text{Cl}_{2(g)}$, and $\text{C}_{(\text{graphite})}$ in their standard reference states were taken from Wagman et al. (1982). Values of $\Delta\bar{H}_{f, aq}^\circ$ and \bar{S}_{aq}° for $\text{PCE}_{(aq)}$, $\text{TCE}_{(aq)}$, $1,1\text{-DCE}_{(aq)}$, $\text{cis-1,2-DCE}_{(aq)}$, $\text{trans-1,2-DCE}_{(aq)}$, and $\text{VC}_{(aq)}$, calculated with Eqns 8 to 10 by using regressed values of $\Delta\bar{H}_f^\circ$ and $\Delta\bar{S}_r^\circ$, are given in Table 2.

2.7. Estimation of Standard Partial Molal Volumes of Aqueous Chloroethylene Species

Values of standard partial molal volumes (\bar{V}_{aq}°) for the aqueous chloroethylene species are unavailable in the literature, but values of \bar{V}_{aq}° are required for estimation of the thermodynamic

Table 1. Values of standard partial molal Gibbs free energy ($\Delta\bar{G}_r^\circ$), enthalpy ($\Delta\bar{H}_r^\circ$) and entropy ($\Delta\bar{S}_r^\circ$) of gas-solubility reactions involving chlorinated-ethylene species. Tabulated values are based on linear regressions of experimental gas-solubility values. R^2 represents the best-fit linear regression coefficient.

Species	$\Delta\bar{G}_r^\circ$ ^a	$\Delta\bar{H}_r^\circ$ ^a	$\Delta\bar{S}_r^\circ$ ^b	R^2
PCE	2583	-9595	40.88	0.997
TCE	1311	-10452	39.52	0.996
1,1-DCE	1946	-7039	30.15	0.996
<i>cis</i> -1,2-DCE	795	-8161	30.05	0.999
<i>trans</i> -1,2-DCE	1342	-7951	31.18	0.996
VC	475	-12951	45.11	0.999

^a Cal/mol.

^b Cal/mol/K.

properties of formation for any aqueous species at elevated pressures. We have estimated these values by making use of a linear correlation between values of the critical volume (V_{crit}), representing the molar volume of a gas at its critical point and \bar{V}_{aq}° for 45 neutrally charged aqueous species, as shown in Fig. 2. Values of V_{crit} were taken from Reid et al. (1987), and values for \bar{V}_{aq}° were taken from compilations of experimental values reported in Shock et al. (1989), Shock and Helgeson (1990), Cabani et al. (1981) and Høiland (1986). This correlation may be expressed through the linear equation

$$\bar{V}_{aq}^\circ = 6.275 + 0.293V_{crit} \quad (11)$$

where $R^2 = 0.9960$. It can be applied to a wide variety of neutral inorganic and organic species, including noble gases (Ne, Ar, Kr, Xe), diatomic nonpolar species (O_2 , H_2 , N_2), polyatomic inorganic species (NH_3 , CO_2 , H_2S , SO_2), alcohols (methanol, ethanol), aliphatic, alicyclic, aromatic organic species (e.g., CH_4 , ethylene, propane, acetone, methyl formate, diethyl sulfide, benzene, aniline, toluene), and halocarbon species (e.g., CH_3F , CH_3Cl , C_2H_5Br). Values for each species used to construct this correlation are individually labeled in Fig. 2. The correlation appears to be generally applicable to a wide variety of neutral aqueous species, and may therefore be used to estimate values of \bar{V}_{aq}° for aqueous species for which V_{crit} values are available in the literature.

In this study we have applied Eqn. 11 to estimate \bar{V}_{aq}° values for $PCE_{(aq)}$, $TCE_{(aq)}$, and $VC_{(aq)}$, for which V_{crit} values are supplied in Reid et al. (1987). Experimental values of V_{crit} for

the three DCE isomers are unavailable in the literature, therefore we have interpolated these values using a systematic correlation between V_{crit} and the number of chlorine atoms present in each compound, shown in Fig. 3. This correlation ($R^2 = 0.999$) yields a V_{crit} value for all DCE isomers of 211 cm^3/mol , which is similar to the value of 224 cm^3/mol generated by using the estimation procedure of Fedors (1979) based on group-additive structural contributions. For the sake of consistency the values of Reid et al. (1987) for PCE, TCE, and VC were used in Fig. 3 to calculate V_{crit} values for DCE isomers, and these values were used in conjunction with Eqn. 11 to estimate \bar{V}_{aq}° for all chloroethylene species.

2.8. Estimation of Standard Partial Molal Heat Capacities and Revised HKF Equation-of-State Parameters at Elevated Temperatures and Pressures

The apparent standard partial molal Gibbs free energy of formation of an aqueous species ($\Delta\bar{G}^\circ$) at a given pressure and temperature is related to the conventional standard partial molal Gibbs free energy of formation ($\Delta\bar{G}_r^\circ$) at the reference temperature (T_r) and pressure (P_r) of 298.15 K and 1 bar according to the definition:

$$\Delta\bar{G}^\circ = \Delta\bar{G}_r^\circ + (\Delta\bar{G}_{P,T}^\circ - \Delta\bar{G}_{P_r,T_r}^\circ). \quad (12)$$

The value of the parenthetical free energy term ($\bar{G}_{P,T}^\circ - \bar{G}_{P_r,T_r}^\circ$) expresses the difference between the conventional standard partial molal Gibbs free energy of formation of an aqueous species at the reference temperature and pressure and at the conditions of interest. This value may be calculated by using the standard partial molal entropy at the reference conditions (\bar{S}_{P_r,T_r}°) and integrating the standard partial molal volume (\bar{V}_{Tr}°) and heat capacity ($\bar{C}_{P_{Pr}}^\circ$) as functions of pressure and standard temperature according to the relationship:

$$\Delta\bar{G}_{P,T}^\circ - \Delta\bar{G}_{P_r,T_r}^\circ = -\bar{S}_{P_r,T_r}^\circ(T - T_r) + \int_{T_r}^T \bar{C}_{P_{Pr}}^\circ dT - T \int_{T_r}^T \bar{C}_{P_{Pr}}^\circ d \ln T + \int_{P_r}^P \bar{V}_{Tr}^\circ dP. \quad (13)$$

The estimation procedure described in Section 2.6 provides values for $\Delta\bar{G}_r^\circ$, $\Delta\bar{H}_r^\circ$, and \bar{S}° of aqueous chloroethylene species at

Table 2. Standard partial molal thermodynamic and HKF equation of state parameters for aqueous chloroethylenes at 25°C and 1 bar.

Species	$\Delta\bar{G}_{f,P_r,T_r}^\circ$ ^a	$\Delta\bar{H}_{f,P_r,T_r}^\circ$ ^a	\bar{S}° ^b	\bar{C}_p° ^b	\bar{V}° ^c	$a_1 (\times 10)$ ^d	$a_2 (\times 10^{-2})$ ^a	a_3 ^a	$a_4 (\times 10^{-4})$ ^f	c_1 ^b	$c_2 (\times 10^{-4})$ ^f	$\omega_{P_r,T_r} (\times 10^{-5})$ ^a
PCE	7483	-12995	40.70	160.0	91.1	14.1804	26.8436	-4.8012	-3.8886	98.5546	29.5574	-0.1500
TCE	6061	-11852	38.26	135.0	81.3	12.8394	23.5678	-3.5109	-3.7532	83.9031	24.4649	-0.1500
1,1-DCE	7726	-6739	38.78	95.0	68.2	11.0468	19.1914	-1.7922	-3.5723	60.4606	16.3169	-0.1500
<i>cis</i> -1,2-DCE	6620	-7712	39.23	95.0	68.2	11.0468	19.1914	-1.7922	-3.5723	60.4606	16.3169	-0.1500
<i>trans</i> -1,2-DCE	7700	-6950	38.16	95.0	68.2	11.0468	19.1914	-1.7922	-3.5723	60.4606	16.3169	-0.1500
VC	12785	-4551	18.11	45.0	55.8	9.3500	15.0507	-0.1702	-3.4011	31.1575	6.1319	-0.1500

^a cal/mol.

^b cal/mole K.

^c cm^3/mol .

^d cal/mole bar.

^e cal K/mole bar.

^f cal K/mol.

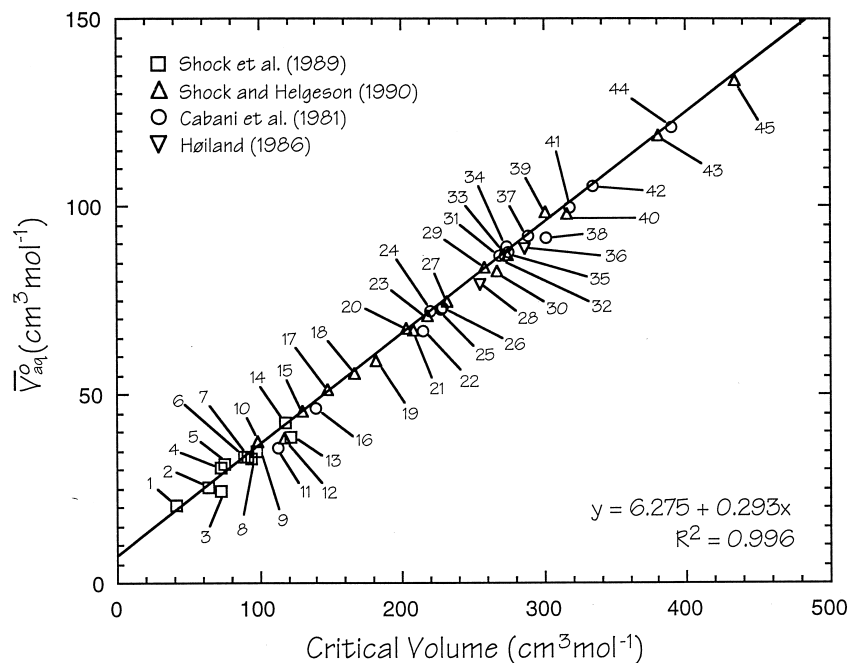


Fig. 2. Linear correlation between critical volumes and standard partial molal volumes of the aqueous species for 45 compounds. Values for each species are labelled numerically and by source on the diagram. Identification key: [1] Ne, [2] H₂, [3] NH₃, [4] O₂, [5] Ar, [6] N₂, [7] Kr, [8] CO₂, [9] H₂S, [10] CH₄, [11] CH₃F, [12] methanol, [13] SO₂, [14] Xe, [15] ethylene, [16] CH₃Cl, [17] ethane, [18] ethanol, [19] ethanamine, [20] propane, [21] acetone, [22] C₂H₅Br, [23] 1-propanol, [24] 2-propanol, [25] methyl acetate, [26] ethyl formate, [27] 1-propanamine, [28] trimethylamine, [29] benzene, [30] 2-butanone, [31] 2-butanol, [32] 1-butanol, [33] 2-methyl-1-propanol, [34] aniline, [35] 2-methyl-2-propanol, [36] ethyl acetate, [37] piperidine, [38] diethyl amine, [39] 2-pentanone, [40] toluene, [41] diethyl sulfide, [42] 1-pentanol, [43] 1-hexanol, [44] triethylamine, [45] 1-heptanol.

the reference conditions but does not yield information regarding standard partial molal heat capacity (\overline{C}_p°) for individual aqueous species or other parameters which are required to rigorously assess thermodynamic behavior at nonstandard conditions. Nonetheless, values of $\Delta\overline{G}_r^\circ$, $\Delta\overline{H}_r^\circ$, and \overline{S}° derived using experimental data from conditions near 25°C and 1 bar may be

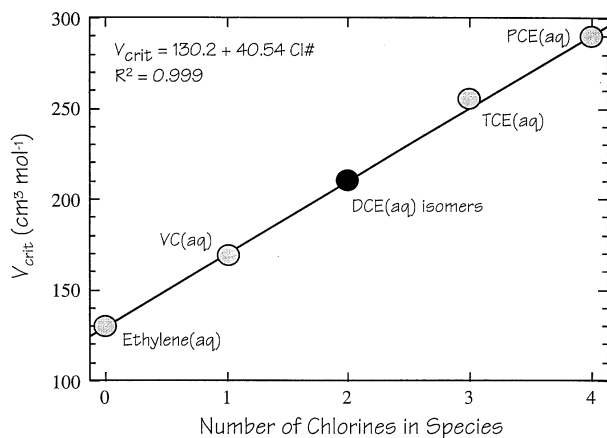


Fig. 3. Linear correlation among critical volumes of chloroethylene gases and the number of chlorines present in each compound. Values for PCE_(aq), TCE_(aq), VC_(aq), and ethylene_(aq) are depicted with gray circles; the interpolated value for all three DCE_(aq) isomers is shown as a black circle.

used to constrain parameters such as \overline{C}_p° and other identities that are necessary for calculation of properties at elevated pressures and temperatures. Following the procedures developed by Shock et al. (1989) for the regression of Gibbs free energy data, we iteratively constrained \overline{C}_p° by regression of $\Delta\overline{G}_{P,T}^\circ$ values for chloroethylene gas-solubility reactions as a function of temperature using correlations provided by Helgeson et al. (1981), Tanger and Helgeson (1988), Shock and Helgeson (1988; 1990) and Shock et al. (1989) for the revised HKF equations of state. Values of \overline{C}_p° for individual chloroethylene species were constrained to provide values for heat capacities of gas-solubility reactions that in turn yield values for $\Delta\overline{G}_r^\circ$ that provide an optimal fit to the experimental data. Resulting values for \overline{C}_p° at 298 K and 1 bar provide a much closer fit to experimental values of $\Delta\overline{G}_{P,T}^\circ$ at moderately low temperatures (~60–100°C) than does an assumption of zero heat capacity. Values of \overline{C}_p° derived in this way are tabulated in Table 2. In addition, Figure 1 depicts estimates of $\Delta\overline{G}_r^\circ$ for chloroethylene gas-solubility reactions as a function of temperature (dashed lines) generated by using optimized values for \overline{C}_p° .

Constraints on the \overline{C}_p° term alone could not account satisfactorily for the observed variation in $\Delta\overline{G}_r^\circ$ for VC gas-solubility as a function of temperature. At increasing temperatures above ~100°C estimated values of $\Delta\overline{G}_r^\circ$ for VC gas-solubility depart significantly from the experimental values as a result of the increasing influence of reduced solvation shielding at ele-

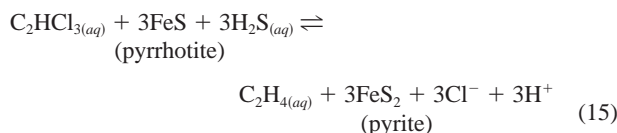
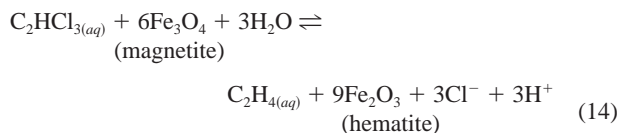
ated temperatures. In order to take account of this effect, values of the effective Born solvation coefficient for neutral species (Helgeson et al., 1981; Shock et al., 1989) were iteratively adjusted for VC until a best fit to the experimental data at all reported temperature conditions could be achieved. Because experimental values for chloroethylene species other than VC are unavailable at temperatures above $\sim 80^\circ\text{C}$, it is not possible to evaluate whether the Born term for VC is anomalous with respect to the other chloroethylene species. However, for the sake of consistency we have adopted the same value for the Born term for all chloroethylene species (-1.5×10^4 cal/mol). This value remains provisional, however, and could be more closely constrained if additional experimental data for other chloroethylenes at elevated temperatures were available.

Values of estimated thermodynamic properties and revised HKF equations-of-state parameters for aqueous chloroethene species are tabulated in Table 2. Values listed include HKF parameters a_1 , a_2 , a_3 , a_4 , c_1 , c_2 , which represent empirical fit parameters specific to the HKF treatment, and the Born solvation function, ω (e.g., Helgeson et al., 1981; Shock et al., 1989; Shock and Helgeson, 1988; 1989; 1990). These parameters, together with values for gases, minerals, and aqueous species of interest, may be used to calculate apparent standard partial molal thermodynamic properties of reactions involving the aqueous chloroethylenes under a wide range of temperature and pressure conditions.

3. STABILITIES OF AQUEOUS CHLOROETHENE SPECIES UNDER ENVIRONMENTAL CONDITIONS AND ELEVATED TEMPERATURES AND PRESSURES

3.1. Abiotic Reductive Dechlorination of Aqueous Chloroethene Species in the Earth's Crust

We may estimate the stability of aqueous chloroethene species as a function of temperature, pressure, and oxidation state in the presence of mineral phases and aqueous species that are likely to be encountered in the subsurface, using our calculated standard partial molal thermodynamic properties of the aqueous chloroethenes and published values for appropriate minerals and dissolved species. The following expressions illustrate possible reactions that may occur in the subsurface, and which can result in degradation of $\text{TCE}_{(aq)}$ to ethylene $_{(aq)}$:



Eqns. 14 and 15 depict $\text{TCE}_{(aq)}$ degradation to ethene $_{(aq)}$ concomitant with the reaction of magnetite to form hematite, and pyrrhotite to form pyrite. We depict Eqns 14 and 15 in terms of $\text{TCE}_{(aq)}$ degrading to form ethene $_{(aq)}$, although similar reactions could also be written for $\text{PCE}_{(aq)}$, any of the $\text{DCE}_{(aq)}$ isomers, or $\text{VC}_{(aq)}$.

The relative abundances of aqueous TCE and ethylene under

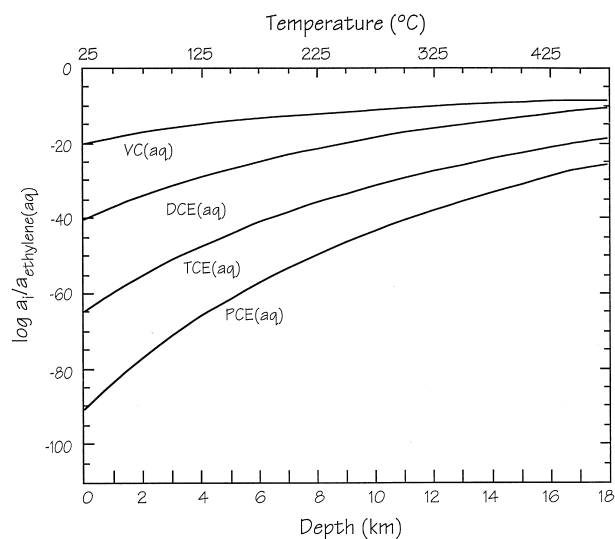


Fig. 4. Calculated logarithms of the equilibrium ratio of activities of PCE, TCE, *cis*-1,2-DCE, and VC, relative to ethylene, as a function of depth in the Earth's crust (geothermal gradient = $25^\circ\text{C}/\text{km}$), at equilibrium with magnetite and hematite according to reaction [14] described in the text. See text for details of model calculation.

conditions of interest may be evaluated using predicted values for the equilibrium constant K of a given reaction and the law of mass action, which for Eqn. 14, for example, and pure minerals for which activities equal unity, can be written as:

$$K = \frac{a_{\text{C}_2\text{H}_{4(aq)}} a_{\text{Cl}^-}^3 a_{\text{H}^+}^3}{a_{\text{C}_2\text{HCl}_{3(aq)}} a_{\text{H}_2\text{O}}^3} \quad (16)$$

Expressed in logarithmic terms and rearranged, this expression may be written as:

$$\log \left[\frac{a_{\text{C}_2\text{HCl}_{3(aq)}}}{a_{\text{C}_2\text{H}_{4(aq)}}} \right] = 3 \log a_{\text{Cl}^-} - 3\text{pH} - \log K - 3 \log a_{\text{H}_2\text{O}}, \quad (17)$$

which depicts the relative abundances of aqueous TCE and ethylene as a function of $\log K$, pH, and the activities of Cl⁻ and water. If we assign a value of -0.3 to the logarithmic activity of the chloride ion in crustal solutions, in accordance with the recommendation of Helgeson (1992), and assume that the activity of water is approximately unity, this expression reduces to a function of pH and $\log K$. We have calculated the value of the ratio of the logarithms of activities for aqueous chloroethylenes and aqueous ethylene at neutral pH for reactions analogous to Eqn. 14 and 15 as a function of depth in the Earth's crust, by using an average continental geotherm of 25°C per kilometer as shown in Fig. 4. Our calculated chloroethylene/ethylene activity ratios are not strongly sensitive to either pH or $\log a_{\text{Cl}^-}$, in comparison to the effects of the temperature dependence of $\log K$, thus geologically reasonable variations in pH or $\log a_{\text{Cl}^-}$ will not tend to alter dramatically the resulting activity ratios. $\log K$ values at elevated temperatures and pressures were calculated using the program SUPCRT92 (Johnson et al., 1992). Values of $\log K$ for reactions involving *cis*-1,2-DCE $_{(aq)}$, *trans*-1,2-DCE $_{(aq)}$, and 1,1-DCE $_{(aq)}$ are similar; therefore, only values for one DCE isomer are shown in

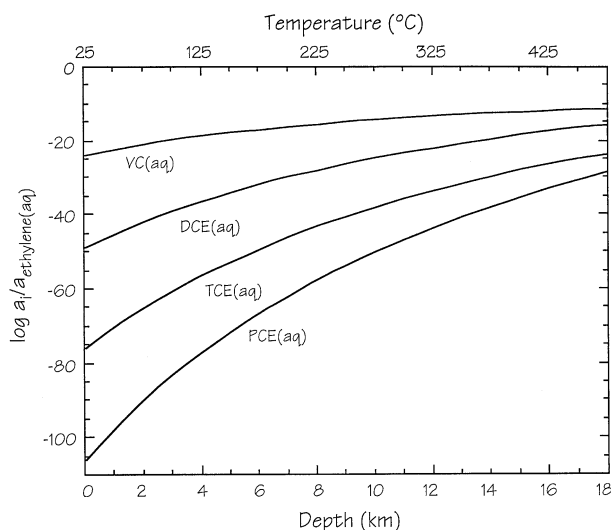


Fig. 5. Calculated logarithms of the equilibrium ratio of activities of PCE, TCE, *cis*-1,2-DCE, and VC, relative to ethylene, as a function of depth in the Earth's crust (geothermal gradient = 25°C/km), at equilibrium with pyrrhotite and pyrite according to Eqn. 15 described in the text. See text for details of model calculation.

Figures 4 and 5. Field and experimental studies have demonstrated that stepwise reductive dehalogenation of PCE or TCE to ethylene proceeds overwhelmingly through *cis*-1,2-DCE, rather than through *trans*-1,2- or 1,1-DCE (e.g., de Bruin et al., 1992). For this reason and for the sake of clarity we depict only the *cis*-isomer in Figs. 4 and 5.

The mineral assemblage hematite-magnetite acts as an important buffer of oxygen fugacity in sedimentary basins (Helgeson, 1992), and may influence the speciation of dissolved chloroethylene species by coupled reductive dehalogenation reactions similar to Eqn. 14, if such reactions are energetically favorable in subsurface environments. Energetic favorability does not itself guarantee that a reaction will proceed, as kinetic limitations may prevent or retard a favored reaction. Nonetheless, energetic favorability is a necessary condition without which a reaction will not proceed regardless of kinetic alacrity. Figure 4 illustrates calculated logarithms of equilibrium chloroethylene/ethylene activity ratios for reactions analogous to Eqn. 14 but also involving PCE_(aq), *cis*-1,2-DCE_(aq), and VC_(aq), as a function of depth, at neutral pH and log chloride ion activity equal to -0.3. Our calculations illustrate that the equilibrium activity of all chloroethylene species in crustal fluids at equilibrium with magnetite and hematite will be very low in comparison to the activity of ethylene_(aq) under all depicted conditions of temperature and pressure. At 25°C and 1 bar pressure, the activities of VC_(aq) and PCE_(aq), which bracket the range for chloroethylene species, are 20 and 91 orders of magnitude, respectively, lower than the activity of ethylene_(aq). Under surface conditions the reactions of PCE_(aq), TCE_(aq), *cis*-1,2-DCE_(aq), and VC_(aq) forming ethylene_(aq) by oxidation of magnetite to hematite are strongly favored, but decreasingly so, as depth and temperature increase. Even so, equilibrium activities of all chloroethylene species remain lower by a factor of 9, for VC_(aq), to 26, for PCE_(aq), orders of magnitude at the maximum illustrated temperature

and pressure conditions (~5 kbars, 475°C). Based on these estimates it appears that the presence of magnetite in sedimentary environments will promote the conversion of chloroethylene contaminants to ethylene_(aq) under nearly all geologically reasonable conditions. Barring kinetic inhibitions, reactions such as Eqn. 14 should proceed even in the shallow subsurface, where magnetite is abundant, although increasing temperatures in the deeper subsurface may accelerate reaction rates. The coupling of magnetite oxidation to reductive dehalogenation of chloroethylenes would thus appear to be an effective mechanism for abiotic (or microbially mediated) degradation of these contaminants, but rigorous experimental validation of this possibility is currently lacking.

In addition to magnetite and hematite, assemblages including pyrite and pyrrhotite serve as important buffers of oxygen fugacity in the subsurface. The reaction of pyrite with magnetite to form pyrrhotite and oxygen is one such f_{O_2} buffering reaction. The oxidation state of sulfur in pyrrhotite is reduced relative to sulfur in pyrite; therefore, oxidation of the former mineral to the latter must involve coupled electron transfer with another reductive reaction. Schoonen and Barnes (1991) have shown experimentally that conversion of FeS minerals, including pyrrhotite but also the intermediate phases mackinawite and greigite, to pyrite, involves coupled electron transfer to aqueous reduced-sulfur species such as thiosulfate or tetrathionate. Alternately, oxidation of FeS precursor minerals to pyrite could occur by coupled reductive dehalogenation of chloroethylenes, where these species are present in solution in the presence of FeS minerals. Pyrite is the most abundant iron-sulfide mineral in the Earth's crust; therefore, examination of possible chloroethylene dehalogenation reactions involving this mineral and its formation-precursors is geologically reasonable.

Reactions such as Eqn. 15 involve reductive dehalogenation of chloroethylene species coupled with oxidation of pyrrhotite to pyrite. We have calculated equilibrium activities of PCE_(aq), TCE_(aq), *cis*-1,2-DCE_(aq), and VC_(aq) relative to ethylene_(aq) as a function of depth and temperature, using the same geotherm used in the previous example. Activities of chloride and H⁺ also remain the same as in the previous example. The activity of H₂S_(aq) is a univariant function of the fugacity of H_{2(g)} in the presence of pyrrhotite and pyrite, and an invariant value in the presence of pyrrhotite, pyrite, and magnetite (Shock et al., 1995) under given conditions of pressure and temperature. The invariant log activity of H₂S_(aq) in the presence of pyrite, pyrrhotite and magnetite at 25°C and 1 bar is -8.05, whereas at 475°C and ~5 kbars, corresponding to the highest values of pressure and temperature along our adopted continental geotherm, for which thermodynamic properties of aqueous reactions may be calculated by using SUPCRT92 (Johnson et al., 1992), this value is -0.90. We adopt a value for the log activity of H₂S_(aq), for our calculations of chloroethylene stability as constrained by reactions such as Eqn. 15, equal to the pyrite-pyrrhotite-magnetite invariant activity of H₂S_(aq) plus one log unit, reflecting an assemblage of pyrite-pyrrhotite in which magnetite is not required. However, activity ratios are not strongly sensitive to the value of log $a_{H_2S(aq)}$ used in the calculation, in comparison with the sensitivity of values to changes in reaction log K with temperature and pressure.

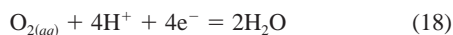
As shown in Fig. 5, estimated equilibrium logarithmic ratios of aqueous chloroethylene activity to ethylene activity deter-

mined by reactions analogous to Eqn. 15 are strongly negative throughout the range of conditions depicted. At 25°C and 1 bar, the log of the ratios of $\text{PCE}_{(aq)}$ to ethylene $_{(aq)}$ and $\text{VC}_{(aq)}$ to ethylene $_{(aq)}$ are approximately -106 and -24 , respectively. Clearly, oxidation of pyrrhotite coupled to reduction of aqueous chloroethylenes is strongly favored energetically under these conditions. At greater depth in the crust, this energetic favorability diminishes, but remains significant at 475°C and ~ 5 kbars, where log-activity ratios for $\text{PCE}_{(aq)}$ and $\text{VC}_{(aq)}$, relative to ethylene $_{(aq)}$, are estimated to be -35 and -11 , respectively.

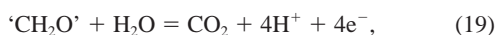
A wide variety of other abiotic equilibria involving the aqueous chloroethylene species may be depicted using the values listed in Table 2, including reductive dehalogenation equilibria involving other mineral phases or aqueous species, or for example oxidation equilibria describing chloroethylene degradation in the presence of ozone (e.g., Clancy, 1996; Beltran et al., 1997; Sunder and Hempel, 1997). An exhaustive depiction of all possible equilibria involving the chloroethylenes is beyond the scope of this work. However, it is informative to include in this discussion an additional class of reactions that can degrade chloroethylenes in the subsurface and that are potentially important throughout the biosphere; those mediated by bacteria.

3.2. Microbially Mediated Reductive Dechlorination of Aqueous Chloroethene Species

Intense interest exists in the capacity of microbial life to affect profound biogeochemical influences over the speciation, transport, and cycling of chemical species in the biosphere. One aspect of this interest centers around the ability of some microbes to degrade aqueous contaminants. Microbial degradation of organic contaminants is generally carried out through substitution of contaminant species by some microbes for compounds that are more typically used as part of a metabolic cycle. A typical metabolic cycle for an aquatic aerobic bacterium, for example, involves respirative reduction of O_2 to H_2O , according to an overall reaction such as:



where electrons and protons are produced and subsequently consumed in separate metabolic subcycles. An important proton- and electron-consuming subcycle for heterotrophic organisms is the oxidation of organic matter, releasing energy (food), i.e.,



where 'CH₂O' represents organic matter having a typical carbohydrate stoichiometry for C, H, and O of 1:2:1. An overall metabolic reaction can be written by combining Eqns. 18 and 19 to get:



which represents the overall metabolism of an aerobic heterotroph.

Anaerobic dissimilatory heterotrophy as exhibited by bacteria and archaea also makes use of overall reactions similar to Eqn. 19, but couples such reactions to the reduction of oxidants

other than O_2 . The chief oxidants employed in oxygen-poor aquatic and sedimentary environments include nitrate, oxidized transition or heavy metal ions such as Mn^{4+} and Fe^{3+} , minerals such as MnO_2 and $\text{Fe}(\text{OH})_3$, sulfate, elemental sulfur, and carbon dioxide. In a typical sediment column, these oxidants are sequentially consumed and exhausted in general order of decreasing reduction potential, as is demonstrated by chemical profiles in sedimentary pore waters (e.g., Nealson and Stahl, 1997). Potentially any reducible chemical species or mineral phase may also be used by some microbial lifeforms, or may substitute facultatively for any of the listed oxidants, as long as the overall metabolic reaction is energetically productive.

Experimental evidence demonstrates that some microbes are capable of facultatively, and in some cases obligately, using halogenated hydrocarbons as respirative oxidants under anaerobic conditions in the laboratory (e.g., de Bruin et al., 1992; Ninomiya et al., 1994; Komatsu et al., 1994; Sonier et al., 1994; Gerritse et al., 1995; Krumholz et al., 1996). These anaerobes can reductively dehalogenate aqueous chloroethylenes, yielding dissolved ethylene or ethane and chloride. Other studies have shown that some aerobic microbes can oxidize aqueous chloroethylenes through a series of co-metabolic pathways yielding CO_2 and chloride (e.g., Oldenhaus et al., 1989; Tsien et al., 1989; Duba et al., 1996). By using our estimated thermodynamic properties for aqueous chloroethylene species, we have evaluated quantitatively the energetic potential offered by these contaminant species to anaerobic microbes in the shallow and deep subsurface. However, a similar approach could also be applied to understanding the energetics of aerobic degradation pathways in oxidizing surface and ground waters.

The potential range of environmental and geochemical parameters found in natural settings effectively renders impractical an approach based on specific solute activities to calculate the energetic favorability of reactions, as used in the previous section. Instead, we may gain insight into the overall energetic utility offered by chloroethylene species, relative to more common oxidants, by directly comparing energy yields of electrochemical half-reactions on an electron-molar basis. This approach has been used successfully to demonstrate that some anaerobic microbes can degrade aqueous chlorobenzene species by preferentially exploiting reactions having higher free energy yields than alternate reactions (Beurskens et al., 1994).

Table 3 lists some of the more important reducing half-reactions used by microbial life to generate electrons used for other metabolic purposes, such as the oxidation of carbohydrates. Also listed in Table 3 are per-electron standard reduction potentials (E° values) in volts for single-chloride-loss reductive dehalogenation half-reactions involving the aqueous chloroethylenes. Each of these reactions may be coupled with a reaction such as Eqn. 19 to generate caloric (food) energy, and differences in reduction potential among these oxidants may therefore be compared directly in terms of their intrinsic energy yields. The most energetic overall reaction, for example, reduces oxygen. Lacking sufficient quantities of oxygen, respiration characterized by nitrate consumption would tend to dominate. Upon depletion of nitrate, available Mn^{4+} is consumed, followed in general succession by available Fe^{3+} , sulfate, sulfur, and CO_2 (methanogenesis or acetogenesis), respectively.

Figures 6 and 7 illustrate E° values in volts for the electrochemical half-reactions depicted in Table 3, along with E°

Table 3. Examples of reductive half-reactions commonly used by microorganisms as respiratory pathways, and reductive half-reactions affecting single-Cl dechlorination of aqueous chloroethylene species.

Reaction	E° at 0°C (volts)	E° at 100°C (volts)
$O_{2(aq)} + 4H^+ + 4e^- = 2H_2O$	1.270	1.277
$2NO_3^- + 12H^+ + 10e^- = N_2 + 6H_2O$	1.221	1.250
$MnO_{2(s)} + 4H^+ + 2e^- = Mn^{2+} + 2H_2O$	0.956	0.968
$Fe^{3+} + e^- = Fe^{2+}$	0.726	0.907
$SO_4^{2-} + 10H^+ + 8e^- = H_2S_{(aq)} + 4H_2O$	0.289	0.346
$S_{(s)} + 2H^+ + 2e^- = H_2S_{(aq)}$	0.133	0.187
$CO_{2(aq)} + 12H^+ + 12e^- = CH_{4(aq)} + 2H_2O$	0.104	0.115
$PCE_{(aq)} + H^+ + 2e^- = TCE_{(aq)} + Cl^-$	0.704	0.720
$TCE_{(aq)} + H^+ + 2e^- = 1,1-DCE_{(aq)} + Cl^-$	0.635	0.656
$TCE_{(aq)} + H^+ + 2e^- = cis-1,2-DCE_{(aq)} + Cl^-$	0.659	0.681
$TCE_{(aq)} + H^+ + 2e^- = trans-1,2-DCE_{(aq)} + Cl^-$	0.636	0.655
$1,1-DCE_{(aq)} + H^+ + 2e^- = VC_{(aq)} + Cl^-$	0.572	0.546
$cis-1,2-DCE_{(aq)} + H^+ + 2e^- = VC_{(aq)} + Cl^-$	0.549	0.521
$trans-1,2-DCE_{(aq)} + H^+ + 2e^- = VC_{(aq)} + Cl^-$	0.572	0.547
$VC_{(aq)} + H^+ + 2e^- = C_2H_{4(aq)} + Cl^-$	0.522	0.573

Each reaction shown may be coupled to a reaction oxidizing organic matter to achieve an overall metabolic reaction. Reductive potentials (E°) in volts are listed for each reaction at 0 and 100°C. Values were calculated by using SUPCRT92 (Johnson et al., 1992).

values of single-chloride-loss reductive dehalogenation half-reactions for aqueous chloroethylenes. Figure 6 illustrates E° values at approximately 0°C, representing cold bottom-water conditions in aquatic settings, whereas Fig. 7 depicts values at 100°C, representing deep sedimentary basin or hydrothermal settings. Analogous values may be calculated at higher temperatures, but the highest documented temperature at which a well-characterized microbial isolate can reproduce is 113°C (Stetter, 1995).

Our calculated values shown in Figs. 6 and 7 indicate that per-electron energy yields for respirative implementation of aqueous chloroethylenes are generally lower than that for ferric iron reduction, but significantly higher than that for sulfate reduction. This result is similar under both low temperatures and the highest temperatures at which known microbes can grow. At low and high temperatures under which known life can reproduce, single-chloride-loss reductive dehalogenation of

any chloroethylene species yields appreciably more energy per mole of electrons than does sulfate reduction.

4. DISCUSSION

Our estimates of standard partial molal thermodynamic properties for the aqueous chloroethylenes at elevated temperatures and pressures may be used to predict the equilibrium stabilities of these species under a wide range of environmental and geologic conditions. As examples of the utility of this approach, we have provided estimates of the equilibrium stabilities of $PCE_{(aq)}$, $TCE_{(aq)}$, all $DCE_{(aq)}$ isomers, and $VC_{(aq)}$, relative to ethylene_(aq), as determined by abiotic reductive dechlorination reactions involving minerals common in the upper crust. In addition, we have calculated the energetic yields of electrochemical half-reactions dechlorinating these species at elevated temperatures under which known microbial life can survive. These estimates may be used to assess the potential for

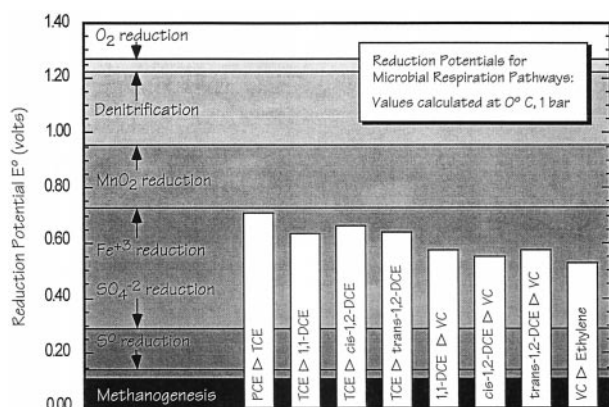


Fig. 6. Calculated reduction potentials at 0°C and 1 bar for half-reactions affecting reductive dechlorination of PCE, TCE, 1,1-DCE, *cis*-1,2-DCE, *trans*-1,2-DCE, and VC each by one chlorine number (white columns). These values are shown in relation to reduction potentials of oxidants commonly used by microbial life as respirative half-reactions (shaded background).

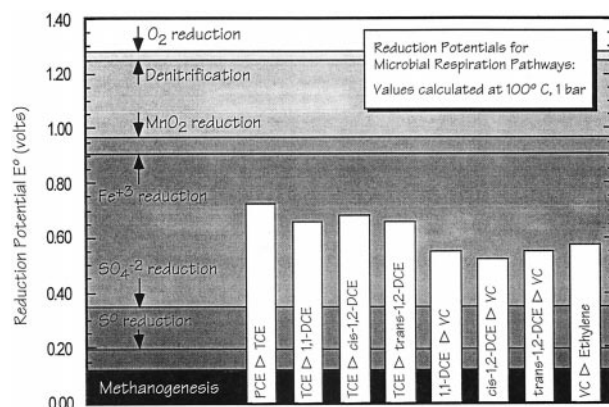


Fig. 7. Calculated reduction potentials at 100°C and 1 bar for half-reactions affecting reductive dechlorination of PCE, TCE, 1,1-DCE, *cis*-1,2-DCE, *trans*-1,2-DCE, and VC each by one chlorine number (white columns). These values are shown in relation to reduction potentials of oxidants commonly used by microbial life as respirative half-reactions (shaded background).

microbial degradation of these species under natural conditions in the subsurface.

Abiotic reactions in a homogeneous solution or at mineral surfaces are typically slow in comparison to biotically mediated reactions; however, the potential impact of abiotic halocarbon-mineral reactions in the subsurface may be significant at elevated temperatures or where residence times are long (or groundwater velocities slow). Our calculations indicate that chloroethylene reductive-dechlorination reactions involving common crustal minerals such as magnetite and pyrrhotite are favored energetically at Earth's surface, and remain energetically favorable at elevated temperatures in the subsurface. Additional computations, not shown in this contribution but reproducible with the provided thermodynamic values, demonstrate that similar reactions involving oxidation of pyrite to Fe^{2+} and sulfate or thiosulfate are also energetically favored at earth's surface conditions and at elevated temperatures in the subsurface. Pyrite is a highly effective catalyst, and the most common sulfide mineral in the earth's crust. Dehalogenation reactions involving this mineral may therefore strongly influence the persistence of halocarbon compounds in the subsurface. Estimates of the energetic favorability of chloroethylene-dechlorination reactions involving pyrrhotite and pyrite are supported qualitatively by low-temperature experimental data reported by Lipczynska-Kochany et al. (1994) for CCl_4 degradation in the presence of these minerals. Additional results reported by Kriegman-King and Reinhard (1994) demonstrate oxidation of pyrite to Fe^{2+} and sulfate coupled to abiotic degradation of CCl_4 at room temperature. Our calculations indicate that analogous reactions involving the aqueous chloroethylenes are also favored energetically under geologically reasonable conditions in the upper crust. Overall reactions that are energetically favored may occur abiotically spontaneously if not kinetically inhibited, or they may be enzymatically facilitated to obtain metabolic energy by living organisms. Thus, reactions involving magnetite, pyrrhotite, and pyrite may be facilitated by microbial life in subsurface settings where these biota are abundant.

Our results indicate that microbially mediated reductive dehalogenation of aqueous chloroethylene species will tend to be energetically favored under anaerobic conditions, and especially under conditions that are sufficiently reducing to promote sulfate reduction. At low temperatures in reducing estuarine, lacustrine, or marine habitats, or in shallow sedimentary-basin pore waters, aqueous chloroethylene reduction is expected to proceed by microbial respiration where active sulfate reduction, sulfur reduction, methanogenesis, or acetogenesis also occurs. Under conditions sufficiently reducing to favor ferric iron reduction, insufficient energy yields are associated with reductive dechlorination of aqueous chloroethylenes to promote significant microbial degradation, insofar as sufficient nitrate, oxidized Mn or ferric iron is available. These interpretations are supported by field and experimental evidence showing complete dechlorination of $\text{PCE}_{(aq)}$ and $\text{TCE}_{(aq)}$ to ethylene $_{(aq)}$ by microbial anaerobes. For example, Tanhua et al. (1996) demonstrated that dissolved halocarbon concentrations in Black Sea waters diminish as conditions grow more reducing with increasing depth. The authors found that depletion of aqueous halomethanes occurs predominantly below the onset depth of

denitrification, whereas haloethane degradation occurs primarily below the onset depth of sulfate reduction.

Sonier et al. (1994) found that sulfate-reducing cultures of anaerobic bacteria from a deep groundwater aquifer effectively degraded aqueous trichlorofluoromethane (CFC-11), although significant $\text{TCE}_{(aq)}$ degradation was not observed. However, de Bruin (1992) found that methanogenic microbial cultures from Rhine river sediment and granular sludge could rapidly degrade $\text{PCE}_{(aq)}$ to ethylene $_{(aq)}$. These results are consistent with experimental observations of Gerritse et al. (1995), Komatsu et al. (1994), and Ninomiya et al. (1994), who measured chloroethylene degradation by microbial consortia under anaerobic conditions; however, these authors did not explicitly report experimental redox conditions. Further work defining more precisely the redox conditions under which microbial dechlorination of chloroethylenes occurs under controlled conditions, and by which taxa, would greatly facilitate prediction of the remediation capabilities of bacterial populations under natural conditions. Further investigations of halocarbon degradation in redox-layered microbial communities would be particularly useful.

At higher temperatures where life is possible, such as in sedimentary basin pore waters and hydrothermal settings, bacterial degradation of chloroethylenes is also favored under strongly anaerobic conditions. Energetic yields of sequential dechlorination reactions involving aqueous chloroethylenes are estimated to be productive at high temperatures under conditions that are sufficiently reducing to favor sulfate-reduction. Under conditions favoring S^0 -reduction, methanogenesis or acetogenesis by thermophilic or hyperthermophilic bacteria and archaea, it is expected that chloroethylene degradation will be especially favored. Hyperthermophilic cultures in such settings, either natural or engineered, could therefore prove highly effective in the destruction of aqueous halocarbon contaminants. Further investigations exploring this possibility would be both informative and profitable.

5. CONCLUSIONS

Our estimated values for the standard partial molal thermodynamic properties of the aqueous chloroethylene species may be used, together with similar properties for gases, minerals, and other aqueous species, to evaluate the equilibrium stabilities of these species under a wide variety of environmental and geologic conditions, including pressures up to 5000 bars and temperatures up to 1000°C. These values provide a means for assessing quantitatively whether the aqueous chloroethylenes tend to degrade to other chemical species under conditions of environmental or biogeochemical interest. In this study we provide examples of reductive dehalogenation reactions involving minerals common in the Earth's crust, by which the aqueous chloroethylenes are favored energetically to degrade to ethylene under geologically reasonable conditions. We also illustrate that chloroethylene reductive-dehalogenation reactions are sufficiently productive energetically that these species could serve competitively as terminal electron acceptors in place of natural oxidants such as sulfate, S^0 , or CO_2 , for microbial respiration under strongly reducing conditions. These conclusions are generally supported by field and laboratory microbial studies, although at present microbial respiration of

chlorocarbons remains poorly quantified with respect to system redox states. The values presented in this work could be used to guide future geomicrobiological studies, by illustrating energetic constraints that will tend to govern chloroethylene co-metabolism under natural conditions.

Other potential applications of the values presented in this study include investigations of the speciation of chloroethylenes with respect to chloroacetic acids (Helgeson, 1992), other halogenated compounds such as halomethanes or haloethanes, dissolved or refractory organic matter (e.g., carboxylic acids, humic substances) in surface and near-surface waters, buried organic matter or hydrocarbon compounds in the deep subsurface, or synthetic reactive media used for engineered ground water remediation. These values could also be used to assess the favorability of oxidative reactions that degrade these species, as can occur during water ozonation (e.g., Clancy, 1996; Beltran et al., 1997; Sunder and Hempel, 1997) or microbial oxidative co-metabolism (e.g., Oldenhuis et al., 1989; Tsien et al., 1989; Duba et al., 1996). Furthermore, these values should prove useful in evaluating the magnitude of natural volcanic or microbial production of chloroethylenes (Stoiber et al., 1971; Isidorov, 1990) and the influence of such processes on global organochlorine cycling.

Finally, the methods used in this study to estimate the standard partial molal thermodynamic properties of aqueous chloroethylene species may also be used to evaluate the properties of other halocarbon species for which gas-solubility data exist, but for which thermodynamic properties of the aqueous species are not available. There are many halocarbon species for which there is ample environmental and geochemical interest in their properties and stability, including halogenated aliphatic and aromatic species such as ethylene dibromide, dibromochloropropane, pentachlorophenol, hexachlorobenzene, and higher molecular weight halocarbons such as dioxins, polychlorinated biphenyls (PCBs), and major compounds found in the pesticides alachlor, chlordane, DDT, dalapon, endrin, heptachlor, lindane, methoxychlor, picloram, simazine, and toxaphene. The methods depicted in this work could also be used to estimate the properties of these and other halocarbon species of interest, thereby providing a means to rigorously calculate their equilibrium stabilities over a wide range of conditions outside those in the laboratory.

Acknowledgments—This research was facilitated by funds provided by the National Research Council and the University of North Carolina at Charlotte. We thank Marc Willis, N. Lee Wolfe, and Valentine Nzen-gung for many helpful discussions concerning the behavior of halocarbons in nature and under engineered conditions. Additional thanks are due to Carla Koretsky for supportive guidance and advice.

REFERENCES

- Beltran F. J., Gonzalez M., Rivas J., and Tierno M. (1997) Elimination pathways during water ozonation of volatile organochlorine compounds. *Toxicol. Environ. Chem.* **63**, 107–118.
- Beurskens J. E. M., Dekker C. G. C., van den Heuvel H., Swart M., and de Wolf J. (1994) Dechlorination of chlorinated benzenes by an anaerobic microbial consortium that selectively mediates the thermodynamic most favorable reactions. *Environ. Sci. Technol.* **28**, 701–706.
- de Bruin W. P., Kotterman M. J. J., Posthumus M. A., Schraa G., and Zehender A. J. B. (1992) Complete biological reductive transformation of tetrachloroethene to ethane. *Appl. Environ. Microbiol.* **58**, 1996–2000.
- Cabani S., Gianni P., Mollica V., and Lepori L. (1981) Group contributions to the thermodynamic properties of non-ionic organic solutes in dilute aqueous solutions. *J. Solution Chem.* **10**, 563–595.
- Clancy P. B. (1996) Treatment of chlorinated ethenes in groundwater with ozone and hydrogen peroxide. *Environ. Progr.* **15**, 187–193.
- Duba A. G., Jackson K. J., Jovanovich M. C., Knapp R. B., and Taylor R. T. (1996) TCE remediation using *in situ*, resting-state bioaugmentation. *Environ. Sci. Technol.* **30**, 1982–1989.
- Fedors R. F. (1979) A method to estimate critical volumes. *AIChE J.* **25**, 202.
- Gerritse J., Renard V., Visser J., and Gottschal J. C. (1995) Complete degradation of tetrachloroethene by combining anaerobic dechlorinating and aerobic methanotrophic enrichment cultures. *Appl. Microbiol. Biotechnol.* **43**, 920–928.
- Gribble G. W. (1994) The natural production of chlorinated compounds. *Environ. Sci. Technol.* **28**, 310A–319A.
- Harr J. (1996) *A Civil Action*. Vintage Books.
- Harper D. B. (1985) Halomethane from halide ion—a highly efficient fungal conversion of environmental significance. *Nature* **315**, 55–57.
- Hayduk W. and Laudie H. (1973) Solubilities of gases in water and other associated solvents. *AIChE J.* **19**, 1233–1238.
- Helgeson H. C. (1992) Calculation of the thermodynamic properties and relative stabilities of aqueous acetic and chloroacetic acids, acetate and chloroacetates, and acetyl and chloroacetyl chlorides at high and low temperatures and pressures. *Appl. Geochem.* **7**, 291–308.
- Helgeson H. C., Kirkham D. H., and Flowers G. C. (1981) Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures: IV. Calculations of activity coefficients, osmotic coefficients, and apparent molal and standard and relative partial molal properties to 600°C and 5 KB. *Am. J. Sci.* **281**, 1249–1516.
- Heron G., Christensen T. H., and Enfield C. G. (1998) Henry's law constant for trichloroethylene between 10 and 95°C. *Environ. Sci. Technol.* **32**, 1433–1437.
- Høiland H. (1986) Partial molar volumes of biochemical model compounds in aqueous solutions. In: *Thermodynamics Data for Biochemistry and Biotechnology*. (ed. H. J. Hinz) pp. 1–44. Springer-Verlag.
- Horvath A. L. (1982) *Halogenated Hydrocarbons: Solubility-Miscibility with Water*. Marcel-Dekker.
- Imhoff P. T., Frizzell A., and Miller C. T. (1997) Evaluation of thermal effects on the dissolution of a nonaqueous phase liquid in porous media. *Environ. Sci. Technol.* **31**, 1615–1622.
- Isidorov V. A. (1990) *Organic Chemistry of the Earth's Atmosphere*. Springer-Verlag.
- Johnson J. W., Oelkers E. H., and Helgeson H. C. (1992) SUPCRT92: A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bar and 0 to 1000°C. *Computers and Geosciences* **18**, 899–947.
- Komatsu T., Momonoi K., Matsuo T., and Hanaki K. (1994) Biotransformation of cis-1,2-dichloroethylene to ethylene and ethane under anaerobic conditions. *Wat. Sci. Technol.* **30**, 75–84.
- Kriegman-King M. R. and Reinhard M. (1994) Transformation of carbon tetrachloride by pyrite in aqueous solution. *Environ. Sci. Technol.* **28**, 692–700.
- Krumholz L. R., Sharp R., and Fishbain S. S. (1996) A freshwater anaerobe coupling acetate oxidation to tetrachloroethylene dehalogenation. *Appl. Environ. Microbiol.* **62**, 4108–4113.
- Lipczynska-Kochany E., Harms S., Milburn R., Sprah G., and Nadarajah N. (1994) Degradation of carbon tetrachloride in the presence of iron and sulphur containing compounds. *Chemosphere* **29**, 1477–1489.
- Nealson K. H. and Stahl D. A. (1997) Microorganisms and geochemical cycles: What can we learn from layered microbial communities? *Rev. Mineral.* **35**, 5–34.
- Ninomiya K., Sakai M., Ohba E., and Kashiwagi N. (1994) Kinetic model for the biotransformation of tetrachloroethylene in groundwater. *Wat. Sci. Technol.* **30**, 13–18.
- Oldenhuis R., Vink R. L. J. M., Janssen D. B., and Witholt B. (1989)

- Degradation of chlorinated aliphatic hydrocarbons by *Methylosinus trichosporium* OB3b expressing soluble methane monooxygenase. *Appl. Environ. Microbiol.* **55**, 2819–2826.
- Reid R. C., Prausnitz J. M., and Poling B. E. (1987) *The Properties of Gases and Liquids*. McGraw-Hill.
- Schoonen M. A. A. and Barnes H. L. (1991) Reactions forming pyrite and marcasite from solution: II. Via FeS precursors below 100°C. *Geochim. et Cosmochim. Acta* **55**, 1505–1514.
- Shock E. L. and Helgeson H. C. (1988) Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Correlation algorithms for ionic species and equation of state predictions to 5 kb and 1000°C. *Geochim. et Cosmochim. Acta* **52**, 2009–2036.
- Shock E. L. and Helgeson H. C. (1990) Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Standard partial molal properties of organic species. *Geochim. et Cosmochim. Acta* **54**, 915–945.
- Shock E. L., Helgeson H. C., and Sverjensky D. A. (1989) Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Standard partial molal properties of inorganic neutral species. *Geochim. et Cosmochim. Acta* **53**, 2157–2183.
- Shock E. L., McCollom T., and Schulte M. D. (1995) Geochemical constraints on chemolithoautotrophic reactions in hydrothermal systems. *Origins Life Evolution Biosphere* **25**, 141–159.
- Shock E. L., Oelkers E. H., Johnson J. W., Sverjensky D. A., and Helgeson H. C. (1992) Calculation of the thermodynamic behavior of aqueous species at high pressures and temperatures: effective electrostatic radii, dissociation constants, and standard partial molal properties to 1000°C and 5 kb. *J. Chem. Soc. (London) Faraday Trans.* **88**, 803–826.
- Sonier D. N., Duran N. L., and Smith G. B. (1994) Dechlorination of trichlorofluoromethane (CFC-11) by sulfate-reducing bacteria from an aquifer contaminated with halogenated aliphatic compounds. *Appl. Environ. Microbiol.* **60**, 4567–4572.
- Stetter K. O. (1995) Microbial life in hyperthermal environments. *ASM News* **61**, 285–290.
- Stephenson R. M. and Malanowski S. (1987) *Handbook of the Thermodynamics of Organic Compounds: Section on Vapor-Liquid Critical Constants of Fluids*. Elsevier.
- Stoiber R. E., Leggett D. C., Jenkins T. F., Murrmann R. P., and Rose W. I. (1971) Organic compounds in volcanic gas from Santiaguito volcano, Guatemala. *Geolog. Soc. Am. Bull.* **82**, 2299–2302.
- Stull D. R., Westrum E. F., and Sinke G. C. (1969) *The Chemical Thermodynamics of Organic Compounds*. John Wiley & Sons.
- Stumm W. and Morgan J. J. (1996) *Aquatic Chemistry*. John Wiley & Sons.
- Sunder M. and Hempel D. C. (1997) Oxidation of tri- and perchloroethylene in aqueous solution with ozone and hydrogen peroxide in a tube reactor. *Wat. Res.* **31**, 33–40.
- Tanger J. C. and Helgeson H. C. (1988) Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: revised equations of state for the standard partial molal properties of ions and electrolytes. *Am. J. Sci.* **288**, 19–98.
- Tanhua T., Fogelqvist E., and Basturk O. (1996) Reduction of volatile halocarbons in anoxic seawater, results from a study in the Black Sea. *Marine Chem.* **54**, 159–170.
- Toxics Release Inventory (1995) United States Environmental Protection Agency.
- Tse G., Orbey H., and Sandler S. I. (1992) Infinite dilution activity coefficients and Henry's law coefficients of some priority water pollutants determined by a relative gas chromatographic method. *Environ. Sci. Technol.* **26**, 2017–2022.
- Tsien H. C., Brusseau G. A., Hanson R. S., and Wackett L. P. (1989) Biodegradation of trichloroethylene by *Methylosinus trichosporium* OB3b. *Applied and Environmental Microbiology* **55**, 3155–3161.
- United States Environmental Protection Agency (1993) *Drinking Water Regulations and Health Advisories*. Office of Water, U.S. Government Printing Office.
- Wagman D. D., Evans W. H., Parker V. B., Schumm R. H., Halow I., Bailey S. M., Churney K. L., and Nuttall R. L. (1982) *The NBS Tables of Chemical Thermodynamic Properties; Selected Values for Inorganic and C1 and C2 Organic Substances in SI Units. J. Phys. Chem. Ref. Data* **11**. American Chemical Society.
- World Resources Institute (1996) *World Resources 1996–97*. Oxford University Press.